

*Crystal Growth
from
High-Temperature
Solutions*

D. Elwell and H. J. Scheel

Online-Edition of the original book
with additional Chapter II and Appendices A and B



Academic Press London New York San Francisco

A Subsidiary of Harcourt Brace Jovanovich, Publishers

Part 010

Please get the complete edition from
<http://e-collection.library.ethz.ch/view/eth:4822>

2011 © D. Elwell & H. J. Scheel

7. Experimental Techniques

7.1.	Principles	279
7.1.1.	Metastable region, nucleation, seeding	279
7.1.2.	Techniques to produce supersaturation	293
7.1.3.	Preparation of solid solutions and homogeneously doped crystals	321
7.1.4.	Preparation of special modifications and of metastable phases	329
7.1.5.	Growth of compounds with defined valency states	330
7.2.	High Temperature Technology	332
7.2.1.	Furnaces	332
7.2.2.	Temperature control (including programming)	340
7.2.3.	Crucibles	356
7.2.4.	Separation of crystals from solution	372
7.2.5.	Chemicals	375
7.2.6.	Atmosphere control	379
7.2.7.	Stirring techniques	381
7.2.8.	High-pressure technology	396
7.2.9.	Typical procedures for growth of oxides and chalcogenides	399
7.3.	Special Techniques, Specific Problems	404
7.3.1.	Crystal growth from HTS at medium and high pressure	404
7.3.2.	Undesirable crystal growth from high-temperature solutions	413
7.3.3.	Unexplored techniques and areas	415
7.4.	Summary.	420
	References	421

It is mentioned several times in the book that the experience obtained from crystal growth from aqueous solutions can be applied to HTS[†] growth. The same is partially true for the experimental techniques. Therefore it is good practice for scientists and technicians entering the field of HTS growth to obtain some experience with solution growth at low temperatures where the growing crystals may be readily observed. For this reason, reference is made below to a few books and review papers which deal with experimental techniques in crystal growth from (aqueous) solutions: Brice (1973), Buckley (1951), Crystal Growth (1949), Gilman (1963), Haussühl (1964), Holden and Singer (1960), Khamskii (1969), Mullin (1972), Neuhaus (1956), Smakula (1962), Tarjan and Matrai (1972), Van Hook (1961) and Wilke (1973).

[†] HTS high-temperature solution(s).

This chapter deals first with the principles and with the main factors which have to be taken into account when large crystals of high quality are to be grown. However, the conditions for stable growth have been discussed in Chapter 6, and several aspects that are relevant to experiments have been mentioned in Chapters 3, 4 and 5.

The second part of this chapter treats high-temperature technology as far as is necessary for HTS growth. In particular the attainment and control of high temperatures, the crucible problems and stirring techniques are discussed in some detail.

In Section 7.3 a discussion is given of special techniques and of some relatively unusual aspects, including a speculative treatment of some possible techniques for future development.

7.1. Principles

7.1.1. Metastable region, nucleation, seeding

A typical example of a phase diagram used in crystal growth from HTS is shown diagrammatically in Fig. 7.1. The solvent can be an element, a compound or a combination of compounds. The solute is an element or a compound with a melting point generally higher than that of the solvent, but in principle one could consider growing crystals from eutectic systems

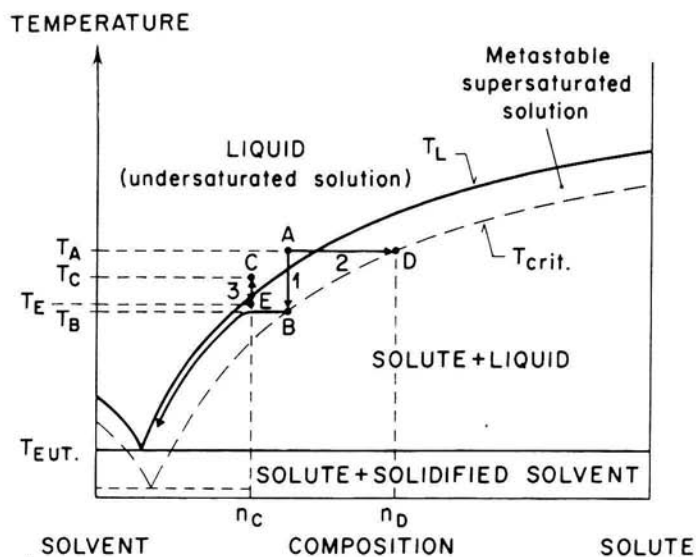


FIG. 7.1. Typical eutectic phase diagram showing the metastable Ostwald-Miers region and crystal growth by slow cooling (1), by solvent evaporation (2) and by gradient transport (3).

in which the "solvent" has a higher melting point. As described in Chapter 3 the liquidus temperature curve is given, at least approximately in the majority of cases, by the Van't Hoff equation.

A solution of composition n_A equilibrated at the temperature T_A can be cooled, in the absence of seeds and agitation, to the temperature T_B at which spontaneous nucleation occurs. In the region between the liquidus line and the dashed line intersecting B the solution is said to be undercooled or supersaturated and this region is called the *metastable* or *Ostwald-Miers* region. The metastability results because a nucleus of critical size must be formed before crystalline material is precipitated, as discussed in Section 4.2.

Metastability is a very complex phenomenon and it is still difficult to make reliable statements on the factors which critically determine the width of the metastable region. In addition, experiments are often difficult to reproduce and disagreement has often been reported between the results of workers who studied nucleation in aqueous solutions. It is, however, clear that the width of the metastable region will be greater if the build-up of high local solute concentrations can be avoided. A broad metastable region is therefore favoured by a small solution volume, a high viscosity and a low solubility. In addition the complexity of the solute and of the solution appears to have an important influence, as will be discussed later in this section. The time dependence of nucleation should also be included in any discussion of metastability (see Eqn 4.11).

The metastable Ostwald-Miers region is of paramount importance for the crystal grower since for the growth of large crystals the experimental conditions must be controlled to such an extent that no unwanted nucleation can occur. Homogeneous nucleation is rather improbable in practical crystal growth experiments and will only occur in highly super saturated solutions. Generally heterogeneous nucleation occurs on the container walls or at the surface of the solution, assuming that no undissolved particles are present.

As indicated by curve 1 of Fig. 7.1, continued slow cooling of the solution from temperature T_B is accompanied by crystal growth at much lower supersaturation because of the presence of the crystals which nucleated at B . If solvent is evaporated at constant temperature (curve 2 of Fig. 7.1) the metastable region is passed and nucleation occurs at D . Alternatively, as in 3, the solvent is transported from a hotter (saturated) to a cooler (supersaturated) region.

According to Neuhaus (1956) the width of the metastable Ostwald-Miers region in growth from aqueous solutions depends on the nature of the crystallizing substance, on the degree of agitation and on additives, as demonstrated in Figs 7.2(a) and (b). Figure 7.2(a) indicates that the width of the metastable region increases with increasing degree of "complexity"

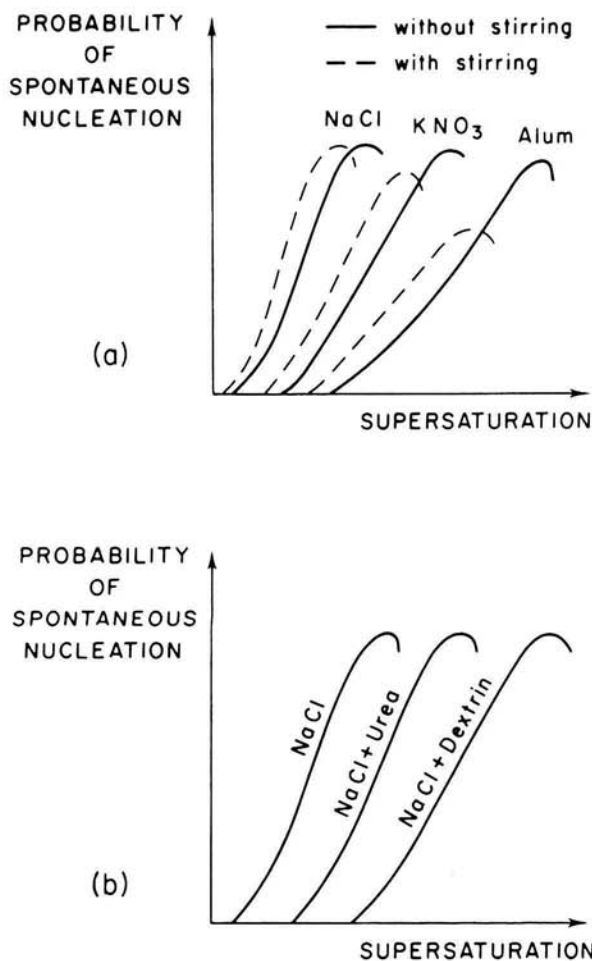


FIG. 7.2. (a) Probability of spontaneous nucleation as a function of agitation and of "complexity" of participating substance (Neuhaus, 1956). (b) Probability of spontaneous nucleation in relation to the type of additive for the example of NaCl crystallization from aqueous solution (Neuhaus, 1956).

($\text{NaCl} \rightarrow \text{KNO}_3 \rightarrow \text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), whereas stirring produces the opposite effect. The role of additives on the habit is discussed in Chapter 5. Here the role of additives in generally increasing the width of the metastable region is shown by Fig. 7.2(b). Neuhaus attributed the effect of urea to complex formation in front of the growing crystal, whereas dextrin is said to increase the width of the metastable region by increasing the viscosity.

It would be interesting to establish more quantitatively the relation between the width of the metastable region and such factors as the chemical and crystallographic "complexity" of the crystal, the species present in the solution, the viscosity and the degree of agitation.

In high-temperature solutions the width of the metastable region varies from 1 to 100°C, and very viscous systems (e.g. borate solutions) can be quenched as glasses. As discussed in Chapter 3, there seems to be a relationship between complex formation in the solution and the width of the metastable region. Qualitatively one is tempted to say that missing "complexity" of the crystals might be the cause of the difficulty in obtaining large crystals by flux growth of the simple compounds TiO_2 , ZrO_2 , BeO , whereas it is becoming easier to grow large crystals with increasing "complexity": GdVO_4 , SrTiO_3 , GdAlO_3 , $\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{Y}_3\text{Fe}_5\text{O}_{12}$, $\text{Pb}_3\text{MgNb}_2\text{O}_9$. On the other hand there are many other factors which influence nucleation phenomena, for example complex formation in front of the growing crystal.

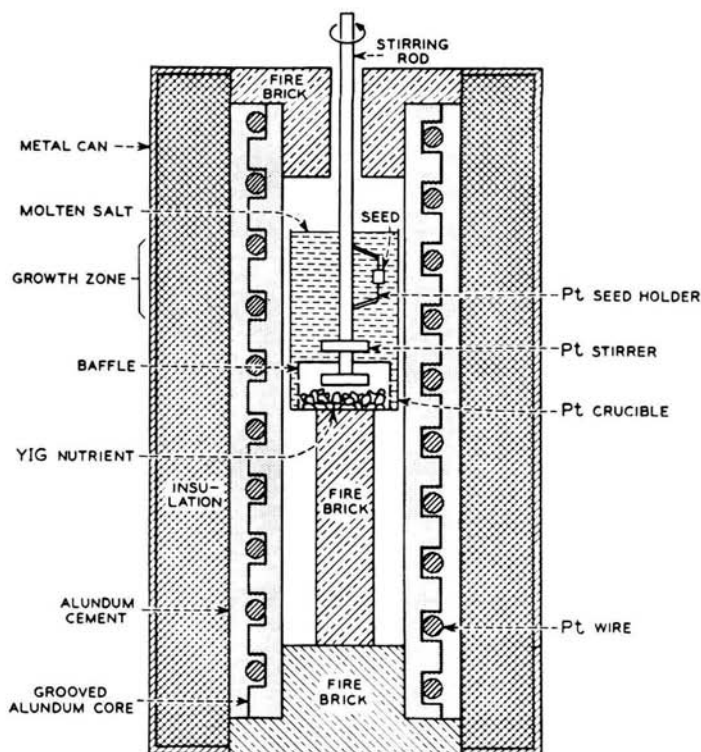


FIG. 7.3. $\text{Y}_3\text{Fe}_5\text{O}_{12}$ -crystallization on a rotating seed, with nutrient in the hotter zone (Laudise, 1963).

TABLE 7.1. Crystals Prepared by Top-seeded Solution Growth by the Slow-cooling Technique†

Crystal	Solvent	Size	Reference
KNbO ₃	K ₂ CO ₃	12–15 g	Miller (1958)
K(Nb, Ta)O ₃	K ₂ CO ₃		Triebwasser (1959)
BaTiO ₃	BaF ₂	7.5 g	Linares (1960)
BaTiO ₃	TiO ₂	20 × 10 mm	Von Hippel <i>et al.</i> (1963)
NiFe ₂ O ₄	Na ₂ Fe ₂ O ₄	1 cm ³	Kunnmann <i>et al.</i> (1963)
KTaO ₃	K ₂ CO ₃		Wemple (1964)
K(Nb, Ta)O ₃	K ₂ CO ₃	14 × 14 × 12 mm	Bonner <i>et al.</i> (1965)
K(Nb, Ta)O ₃	K ₂ CO ₃		Wilcox and Fullmer (1966)
Ba ₂ Zn ₂ Fe ₁₂ O ₂₂	Ba ₂ B ₂ O ₅	10 g	Aucoin <i>et al.</i> (1966)
KTaO ₃	K ₂ CO ₃		Senhouse <i>et al.</i> (1966)
(Ba, Pb)TiO ₃	BaB ₂ O ₄ —PbB ₂ O ₄	~15 × 10 mm	Perry (1967)
(Ba, Sr)TiO ₃	TiO ₂	~8 × 8 × 8 mm	Bethe and Welz (1971)
KTaO ₃	K ₂ CO ₃	280 g	Bonner <i>et al.</i> (1967)
K(Nb, Ta)O ₃	K ₂ CO ₃	75 × 60 × 25 mm (1300 g)	
Pb ₃ MgNb ₂ O ₉	PbO—B ₂ O ₃	~1 cm ³	Bonner and Van Uitert (1967)
GeO ₂	Na-germanate	3–10 mm	
K(Nb, Ta)O ₃	K ₂ CO ₃		Epstein (1970)
Bi ₄ Ti ₃ O ₁₂	Bi ₂ O ₃ , Bi ₂ O ₃ —GeO ₂ , Bi ₂ O ₃ —MoO ₃		
Gd ₂ (MoO ₄) ₃	MoO ₃		
KNbO ₃	K ₂ CO ₃	2 cm ³	Hurst and Linz (1971)
SrTiO ₃	TiO ₂	14 × 14 × 6 mm	Belruss <i>et al.</i> (1971)
Y ₂ Ti ₂ O ₇	TiO ₂ + Ba-borate	>1 cm ³	Belruss <i>et al.</i> (1971)
Ba ₂ MgGe ₂ O ₇	GeO ₂	>1 cm ³	Belruss <i>et al.</i> (1971)
(Ca, Sr, Ba)Y ₂ (Zn, Mg) ₂ Ge ₃ O ₁₂	Ca(Sr, Ba)O + GeO ₂	>1 cm ³	Belruss <i>et al.</i> (1971)

† For experimental details see Chapter 10.

TABLE 7.2. Crystals Prepared by Top-seeded Solution Growth by the Gradient Transport Technique†

Crystal	Solvent	Size	Reference
$Y_3Fe_5O_{12}$	$BaO \times 0.6B_2O_3$	$\sim 10 \times 10$ mm	Linares (1964)
$Y_3Fe_5O_{12}$	$BaO \times 0.6B_2O_3$	$\sim 40 \times 10$ mm	Kestigian (1967)
$Y_3Fe_5O_{12}$	$BaO \times 0.6B_2O_3$	?	Bennett (1968)
$Y_3Fe_5O_{12}$	$BaO \times 0.6B_2O_3$	$20 \times 20 \times 10$ mm	Tolksdorf (1974b)
$NiFe_2O_4$	$BaO \times 0.62B_2O_3$	10×8 mm	Smith and Elwell (1968)
$K(Nb, Ta)O_3$	K_2CO_3	~ 1 cm ³	Whipps (1972)
$(Zn, Mn)_2Ba_2$ $(Fe, Mn)_{12}O_{22}$	$BaO \times 0.5B_2O_3$	$\sim 15 \times 15 \times 4$	Tolksdorf (1973)

† For experimental details see Chapter 10.

The temperature control requirements necessary for stable and homogeneous growth (see Chapter 6 and Chapter 7.1.3) are normally much more stringent than those necessary to prevent spontaneous nucleation. This implies that if spontaneous nucleation occurs during the growth of a crystal then its quality is often bad due to formation of inclusions and striations.

The growth of large crystals is favoured by the use of seed crystals, which is common practice in crystal growth from aqueous solutions. However, in high-temperature solutions technical reasons make the use of seeds very difficult. Since the seeds cannot be observed in the (platinum) crucibles and in the opaque solutions the solubility curve has to be known very exactly and the conditions carefully adjusted in order to prevent dissolution of the seed crystals.

Growth on a rotating seed immersed in the solution has been described by several authors (see Table 7.5), and an example of an experimental arrangement is shown in Fig. 7.3. Timofeeva and Kvapil (1966) fixed seed crystals near the base of an unstirred crucible and still observed multi-nucleation. This shows that seed crystals are only of major advantage when the solution is homogenized by forced convection or when the solution volume is small as is often the case in the travelling solvent technique and in liquid phase epitaxy.

The most popular means of nucleation control is by top-seeding as can be seen from Tables 7.1 and 7.2. The arrangement used successfully at MIT for the growth of several crystals is shown in Fig. 7.4. The position of the crystal-liquid interface is important with respect to inclusion formation, dislocation density and maximum attainable growth rate. With increasing depth of the growth face (in the solution) the temperature gradient at the interface becomes smaller and the supersaturation gradient increases, the stable growth rate decreases, but also the dislocation density

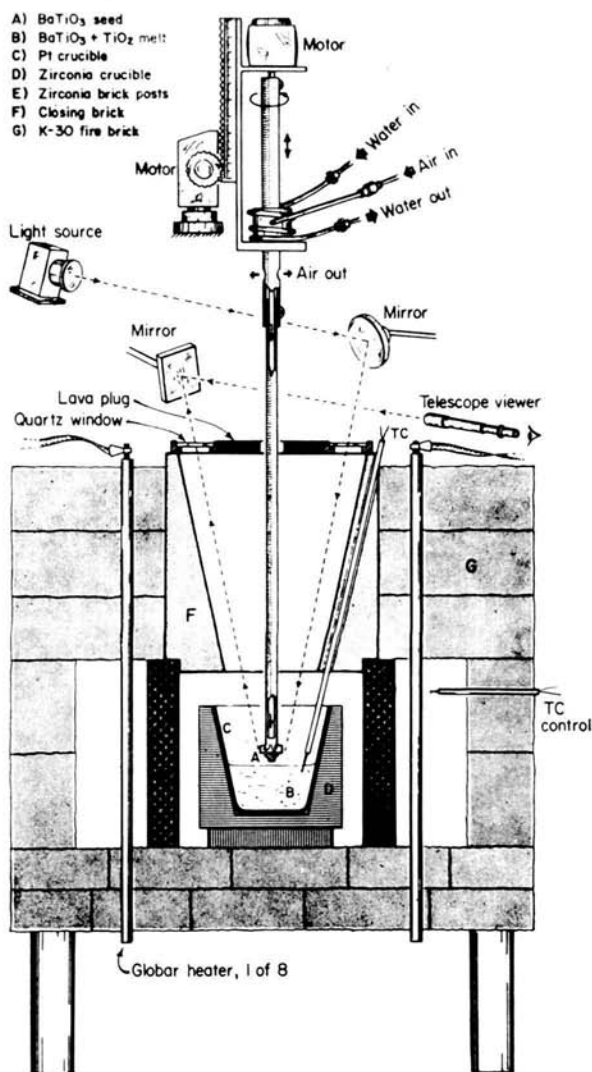


FIG. 7.4. Arrangement for crystal growth by top seeding (Von Hippel *et al.*, 1963; Belruss *et al.*, 1971).

will decrease if inclusions are not trapped. The temperature gradient also determines the degree of facetting as discussed by Wilcox (1970). The technique of growth on rotating seed crystals at the top of a solution, with or without withdrawal, has been given a variety of names (Czochralski, Kyropoulos, pulling from solution etc.), but it seems that the term *top-*

seeded solution growth (TSSG) first introduced by Linz *et al.* (1965), and described in detail by Belruss *et al.* (1971), is becoming increasingly popular and is therefore adopted in the following discussion.

The size of seeds used in HTS growth has to be a compromise between various requirements. As is discussed in Chapter 6 and may be seen from the topographs of Chapter 9, edge and spiral dislocations propagate from the seed in a direction approximately normal to the growing faces. The high-quality (nearly dislocation-free) regions between these dislocation bundles are obviously larger when small seeds are used.

Small seed crystals, on the other hand, have the disadvantage of being easily dissolved and also require an extremely low supersaturation if the maximum stable growth rate is not to be exceeded (see Section 6.6.1). Therefore one has to choose the optimum seed size in relation to the solution volume and the degree of control over the supersaturation. If large samples are available for use as seeds, it is advantageous to use seed plates of that crystallographic orientation which is optimum with respect to low impurity incorporation, high stable growth rate, and the intended application; good examples of the application of these criteria are provided by the hydrothermal growth of quartz crystals (Ballman and Laudise, 1963) and by the growth of ADP from aqueous solution (Egli and Johnson, 1963). In LPE-grown layers of magnetic garnets the orientation-dependent site preference of several ions is used to optimize the properties of the magnetic bubble domains as will be mentioned in the next chapter. As is well-known from crystal growth from aqueous solutions it is desirable to etch the seeds (to dissolve the damaged surface layer and to remove adsorbed impurities) before growth is commenced in order to obtain high quality material.

The mounting of seed crystals in flux growth of oxides normally necessitates the use of platinum wire. Since pure platinum is very soft at the temperatures used and since the wire has to be as thin as possible, it is proposed to use alloys of platinum with 1–10% rhodium or iridium. The wire thicknesses should range from 0.1 to 0.5 mm depending on the size of the seed, degree of stirring and the length of the experiment. If the seeds are immersed in the high temperature solution it is generally desirable to drill a hole into the crystal so that wire may be inserted for fixing to the seed holder. The alternative of wrapping the wire around the crystal is disadvantageous since the crystal may become loose when an outer layer is dissolved during the first stage of the experiment. Examples of seed mountings for top-seeded solution growth are shown in Figs 7.5 and 7.6. For growth from metallic solutions a seed holder may be ground from graphite, boron nitride or alumina. The seed may be conveniently held by a peg of the same material as the holder, which is inserted through a horizontal hole in the seed and the holder.

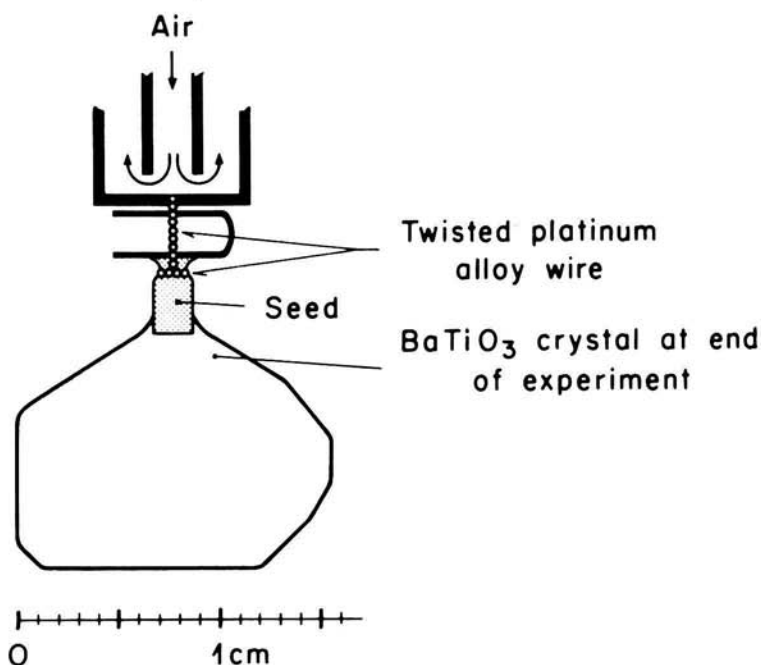


FIG. 7.5. Seed mounting for growth of BaTiO_3 by top-seeded solution growth. (Courtesy A. Linz and V. Belruss, MIT.)

The difficulties mentioned above and the high-vapour pressure of many HT solvents have prevented a wide application of seeding, especially when supersaturation is achieved by slow cooling or by solvent evaporation where a number of additional crystals are generally produced by *spontaneous nucleation*. A technique to reduce the number of nuclei after their formation is based on the variation of the surface energy of a crystal with the crystal radius. If the temperature of a supersaturated solution is held constant for a long time, the small crystallites will be dissolved and the size of the larger crystallites will increase. However, the effectiveness of this process diminishes as the crystallites attain macroscopic dimensions, and it is significant only in solutions which contain a large number of crystals.

The reduction of the number of nuclei can be enhanced by the temperature cycling technique which was proposed by Schäfer (1964) for chemical transport reactions and by Hintzmann and Müller-Vogt (1969) for high-temperature solutions. The latter authors used temperature cycling during the whole cooling cycle whereas Scheel and Elwell (1972) argued that temperature oscillation is only advantageous in the first stage

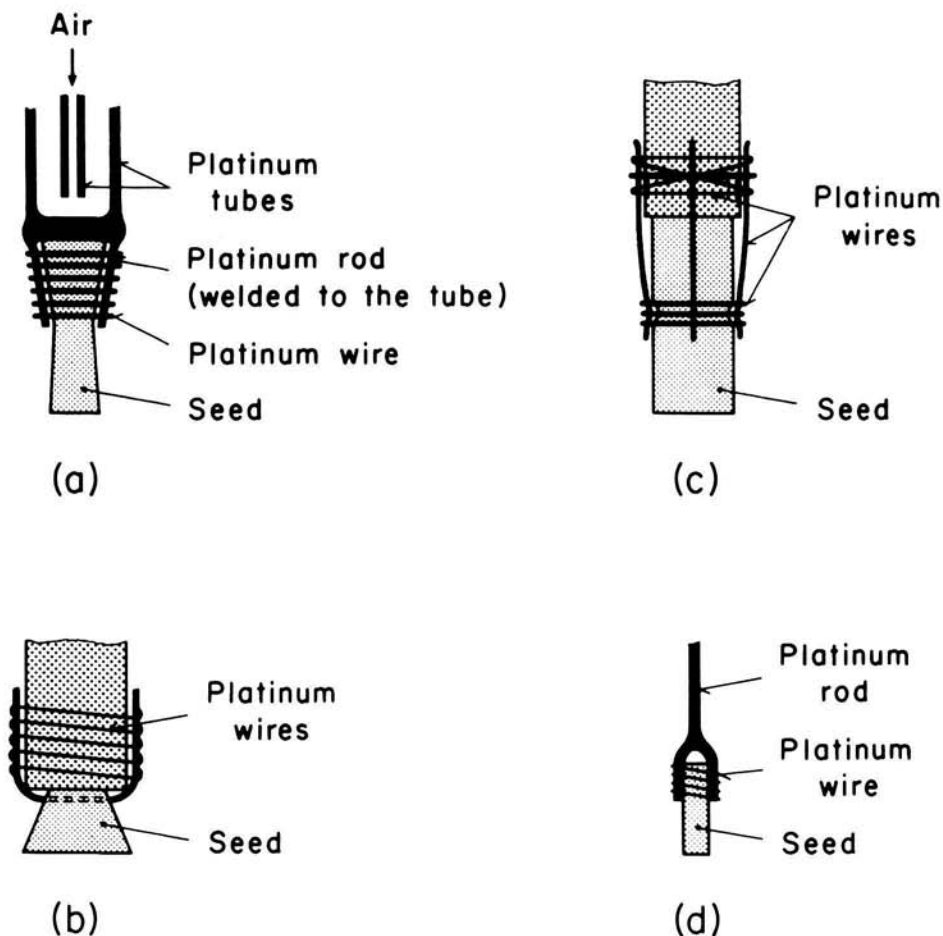


FIG. 7.6. (a)–(d) Examples of seed mounting.

of the experiment when nucleation occurs. This is demonstrated in Fig. 7.7, which shows the procedure of Scheel and Elwell. First the mixture of solute and solvent is held at the temperature A , about 50° above the liquidus temperature T_L , for about 15 hours (the "soaking period") in order to ensure complete dissolution. Then the temperature is lowered to C , a temperature significantly below T_L and T_M , the temperature of the limit of the metastable region. Most of the crystallites formed during this initial cooling are dissolved when the melt is heated to G . This procedure is repeated ($\rightarrow C' \rightarrow E \rightarrow C'' \rightarrow J$ according to the dashed line) until a tempera-

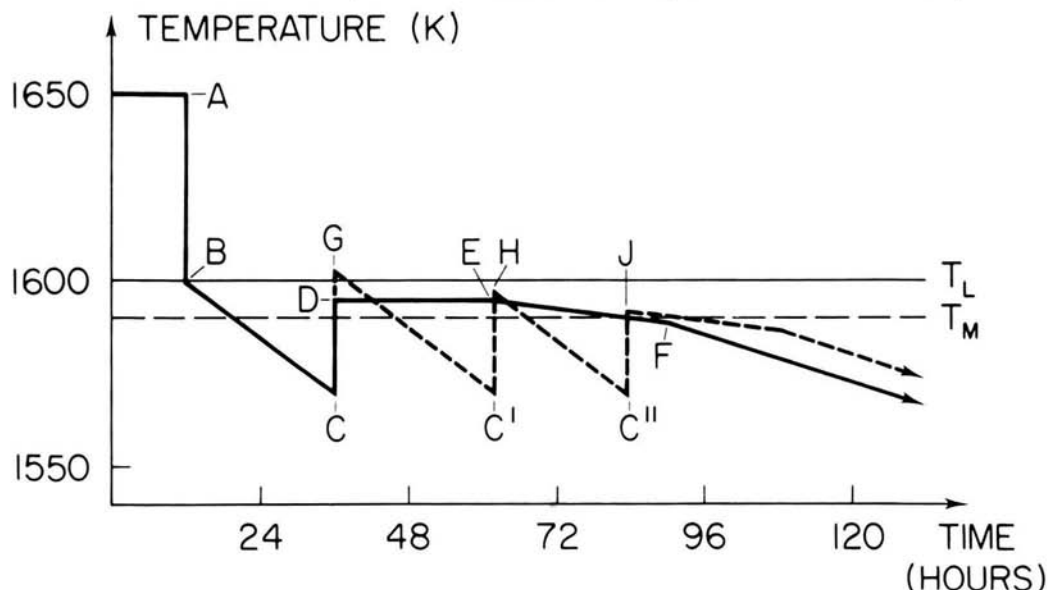


FIG. 7.7. Temperature cycling at the start of a slow cooling experiment in order to decrease the number of spontaneously nucleated crystals (Scheel and Elwell, 1972).

ture below T_L is reached such that only a few crystallites have "survived". Then the temperature programme as described in Section 6.6.1 is started from J . If the temperatures T_L and T_M are accurately known, the procedure should follow the full line ($A \rightarrow C \rightarrow D \rightarrow E \rightarrow F$) so that programmed cooling starts after the minimum period required for dissolution of the smaller crystallites.

Depending on the temperature gradients in the crucible, nucleation occurs at the surface (which is also the favoured location in the case of solvent evaporation because of high local supersaturation) or at the crucible walls. In order to provide a preferred site for nucleation *localized cooling* has been proposed in several papers and has been used in melt growth by the classical techniques of Bridgman, Kyropoulos and Czochralski.

A "cool" spot or region can be provided by an air jet (Chase and Osmer, 1967; Grodkiewicz *et al.*, 1967; Scheel, 1972), by fixing cooling fingers (heat sink, ceramic rod, heat pipe) to the crucible wall, or by placing the crucible into an appropriate temperature gradient (by suitable choice of position in the furnace with respect to the heating elements). For example nucleation at the bottom of the solution was achieved by Linares (1967) and by many other authors, but in most cases multinucleation occurred.

Kvapil (1966) and John and Kvapil (1968) used a baffle above the cooler base in order to reduce the number of nuclei as shown in Fig. 7.8. They also applied a hydraulic seal in order to prevent solvent evaporation.

However, cooling of the base is often disadvantageous in stationary crucibles: the homogenization of the solution by natural convection is minimized (see Chapter 6), and the stable growth rate is low. Therefore localized cooling of the crucible base is only effective when the solution is homogenized. With nonvolatile solutions a stirrer can be applied, and with volatile systems where the crucible has to be sealed the stirring technique of Scheel (1972) by accelerated crucible rotation (see 7.2.7) is very effective

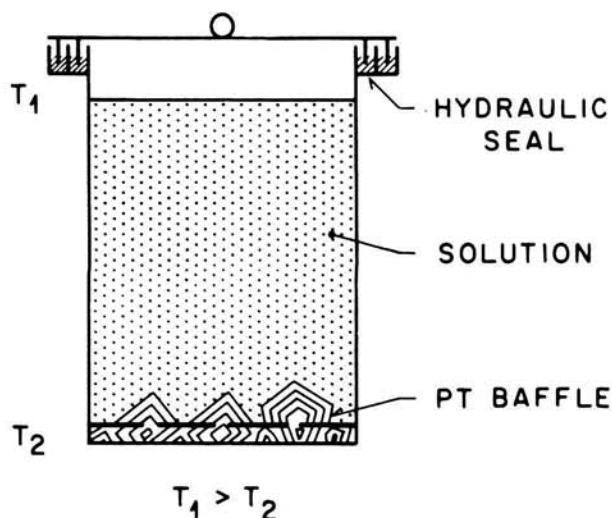


FIG. 7.8. Reduction of the number of crystals nucleated at the cooler base by a baffle. Flux evaporation is minimized by a hydraulic seal (Kvapil, 1966; John and Kvapil, 1968).

so that by proper control of the experimental conditions one or a very few crystals are spontaneously nucleated on the cooled crucible base.

However, stirring of the solution has to be smooth; with strong agitation or by shaking of the solution the width of the metastable region is made extremely small, and multinucleation will occur due to local density fluctuations and to collision of the crystallites among themselves or with the container or stirrer. An effective technique of nucleation control was applied by Bennett (1968) and by Tolksdorf (1968) and is schematically shown in Fig. 7.9(a)–(d). The crucible is contained in a high-temperature furnace. After soaking (a) the solution is cooled until either the saturation point is exactly reached or until spontaneous nucleation has occurred (b).

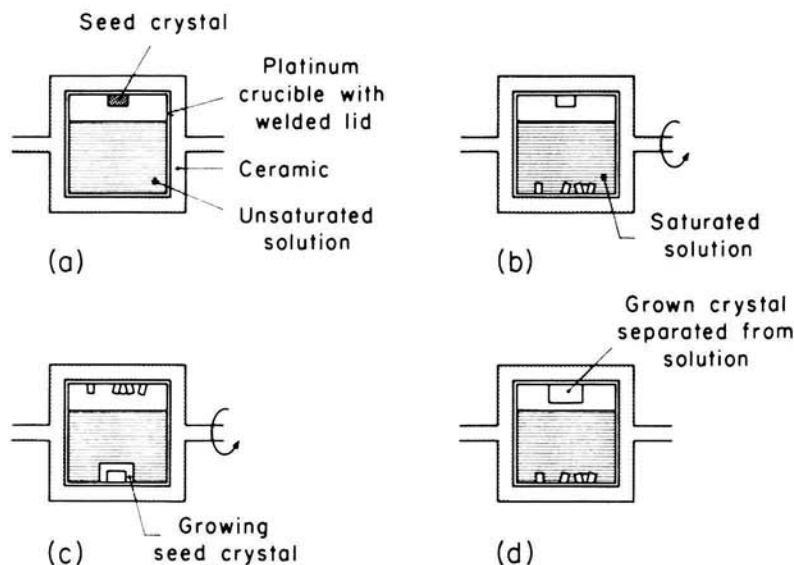


FIG. 7.9. Immersion of a seed crystal into a saturated solution. (a) Initial position at high temperature. (b) After a certain degree of cooling spontaneous nucleation occurs at the bottom, and the crucible is inverted (c) so that the saturated solution covers the crystal, which grows during continued cooling. (d) After termination of cooling the grown crystal is separated from the solution by re-inversion of the crucible into the initial position (Bennett, 1968; Tolksdorf, 1968).

The crucible is then inverted so that spontaneously nucleated crystals are separated and the seed crystal is immersed in a saturated solution and grows by continuous cooling (c). At the end of the run the crucible is inverted again, thereby separating the grown crystal from the solution (d). This technique in combination with localized cooling and with the accelerated crucible rotation technique was used by Tolksdorf and Welz (1972) to produce large inclusion-free crystals of magnetic garnets for various applications.

An alternative approach to reduce the number of crystals nucleated, which has been successfully used in a number of cases, relies upon the addition to the solution of small quantities of some material which is not incorporated into the crystal. The most popular additive is B_2O_3 which is thought to increase the width of the metastable region, probably because of the formation with the various cations of complexes corresponding to the borates which are stable at lower temperatures. The widespread use of additives such as B_2O_3 has led to the development of empirical statements of the form: "The more complex the solution, the greater the solubility and

the width of the metastable region, and the fewer the number of crystals nucleated."

Remeika (1970) reported a dramatic decrease in the number of ferrite or garnet crystals nucleated in a $\text{PbO/B}_2\text{O}_3$ solvent when 0.1–0.5% by weight of V_2O_5 was added. Similarly Scheel (see Kjems *et al.*, 1973) was able to prevent multinucleation of LaAlO_3 from a $\text{PbO—PbF}_2\text{—B}_2\text{O}_3$ flux and therefore to grow large inclusion-free crystals when 0.7 wt% V_2O_5 was added. The beneficial effect of this small V_2O_5 addition is attributed to the formation of LaVO_4 -like complexes in front of the growing crystals. If these complexes are distributed statistically among LaAlO_3 -like complexes, they will tend to retard the formation of critical LaAlO_3 nuclei and hence to reduce nucleation.

In principle the effect of addition of PbF_2 to PbO could be described in the same way since it permits the formation of complexes such as LaOF . According to this model, however, V_2O_5 will be particularly effective since it forms a larger complex.

Grodziewicz *et al.* (1967) reported a beneficial effect for the growth of large garnet crystals of adding several divalent metal oxides or SiO_2 . The effect of the latter was confirmed by Page (unpublished, reported by Brice, 1973) who found that the number of $\text{Y}_3\text{Fe}_5\text{O}_{12}$ crystals nucleated from a PbO—PbF_2 flux decreased from 50–100 when pure chemicals were used to 3 or 4 when 0.08% Si was substituted for Fe in the melt. These impurities may also act by forming complexes but additional complications arise from the tendency of iron in the crystal to exist as Fe^{2+} or Fe^{4+} ions in small concentration. One of the most remarkable examples of nucleation reduction has been reported by Robertson *et al.* (1973), who observed the nucleation of only one yttrium iron garnet crystal from a $\text{PbO—PbF}_2\text{—B}_2\text{O}_3$ flux when growth occurred in oxygen under a pressure of ten atmospheres. The reduction in this case was attributed to the lack of crystals of a second phase which often act as nuclei for garnets.

One point which is frequently neglected in connection with nucleation control in HTS growth is the quality of the containers. The use of new platinum containers with polished inner walls generally results in fewer crystals (by heterogeneous nucleation) than in crucibles which have been used frequently and which show strong recrystallization and a rough surface. Platinum crucibles can be re-used (as is necessary because of the high cost of re-fabrication) when they are carefully cleaned, reshaped and chemically or mechanically polished as is discussed in detail in Section 7.2.3. The same arguments apply to other types of container.

Thus control of nucleation in HTS growth is generally problematic and needs careful control of all chemical and experimental conditions. By homogenization of the solution and by use of appropriate seeds, large

crystals can be grown. If spontaneous nucleation has to be chosen, smooth stirring of the solution combined with localized cooling will limit the number of nucleated crystals generally to one or very few.

7.1.2. Techniques to produce supersaturation

As in crystal growth from aqueous solutions and as is obvious from Fig. 7.1, supersaturation can be obtained by *slow cooling* (1), by *solvent evaporation* (2) or by the *temperature gradient technique* (3) in which nutrient is held in a hotter region: solution saturated in the hot region is transported to a cooler region by natural or forced convection and so becomes supersaturated. Apart from these three most popular techniques there are a few special methods to obtain supersaturation such as the *reaction technique* in which solute constituents formerly separated diffuse to the region where reaction (and crystallization) proceeds. If crystal constituents are transported in the vapour phase to the liquid solution in order to precipitate the (solid) crystal, this may be termed the *VLS† mechanism*, which is well known as an important mode of whisker growth (Wagner and Ellis, 1964). The temperature gradient, reaction and VLS techniques, together with electrolytic growth will be referred to collectively as *transport techniques*. Reaction equilibria which are shifted by means other than by temperature change (included under "slow cooling"), solvent evaporation or temperature gradients include evaporation of "reaction products" and the *salting out* effect. The techniques of obtaining supersaturation will be described according to the following classification:

A. Slow cooling, B. solvent evaporation, C. transport techniques.

The supersaturation value used in an experiment is determined by the requirement that the growth rate should not exceed the maximum stable value, as discussed in Chapter 6. It is not possible at present to give a quantitative criterion for the maximum supersaturation, apart from that specified by Eqn 6.26. If the solution, stirring rate, temperature gradient etc. are optimized, the supersaturation may have a maximum value such that the growth rate obtains its ultimate stable value. Very small supersaturations are, however, pointless since the crystal will exhibit growth and dissolution fluctuations as shown for Czochralski growth by Witt and Gatos (1968) and by Kim *et al.* (1972).

In practice the relative supersaturation normally has a value in the region of 0.1–1%, as in aqueous solution growth, although the corresponding supercooling is appreciably higher at high temperatures. For an ideal solution with $n_s \propto \exp(-\phi/RT)$, the relative supersaturation is

† VLS vapour-liquid-solid.

$$\sigma = \frac{\Delta n}{n_e} = \frac{\phi \Delta T}{RT^2}.$$

Thus for $\phi = 50$ kJ/mole and $T = 1200^\circ\text{C}$, $\Delta T = 3.6^\circ\text{C}$ for $\sigma = 1\%$.

A. Slow cooling. The most common technique for producing supersaturation in flux growth is by slow cooling (see Tables 7.1 and 7.3 and Chapter 10) where generally a linear cooling rate of 0.2°C h^{-1} to 10°C h^{-1} is applied. If inclusion-free crystals larger than a few millimetres have to be grown a cooling rate of less than 1°C h^{-1} is necessary as discussed in Chapter 6.

The linear growth rate v (in cm/h) by slow cooling is related to the cooling rate (Laudise, 1963; Cobb and Wallis, 1967) according to

$$v = \frac{V}{A\rho} \left(\frac{dn_e}{dT} \right) \left(\frac{dT}{dt} \right), \quad (7.1)$$

where V is the volume of solution (cm^3), A the area of the growing crystal (cm^2) and ρ its density (g cm^{-3}), dn_e/dT the change in solubility per degree [$\text{g cm}^{-3} ^\circ\text{C}^{-1}$] and dT/dt the cooling rate in $^\circ\text{C/h}$. Obviously, Eqn 7.1 only holds when all the solute precipitated is deposited on the crystal.

The optimum cooling rate for stable growth as a function of various growth parameters is also discussed in Chapter 6. It was shown that a constant linear growth rate and therefore a cubic decrease of temperature with time will cause unstable growth. Scheel and Elwell (1972) and Pohl and Scheel (1975) have shown that the temperature regulation and the cooling rate have to be adjusted in such a way that the slope of the effective cooling curve (including any oscillations or fluctuations) never exceeds the slope of the calculated optimum cooling curve for stable growth at the corresponding temperature. The general rule is that the slower the growth rate the better and larger the crystals. However, one has to find a compromise between the slow cooling rate and the correspondingly long duration of an experiment. Also Laudise (1963) stressed the fact that cooling rates which are not at least comparable with the temperature fluctuations due to inaccurate regulation are pointless. A very slow initial cooling rate is impractical for the (normal) case where the super-solubility curve is not known with sufficient accuracy and much time is lost before nucleation starts.

The advantages of the slow cooling technique are:

1. That a closed container (sealed crucible) can be used thereby preventing evaporation of volatile solvent or solute constituents which are poisonous or corrosive and which cause uncontrolled supersaturation.
2. The technique is relatively simple for the growth of crystals up to

5–10 mm size. For larger high-quality crystals the effort on apparatus, temperature regulation and programming has to be increased.

3. The slow cooling technique is very suitable for exploratory materials research. It is usually simple to crystallize known crystals and also new phases in sizes from 2 to 5 mm, which are suitable for X-ray structure determinations and a number of physical measurements.

The slow cooling technique has several disadvantages which arise from the continuously changing growth temperature:

1. The concentration of equilibrium defects varies through the crystal (however for a typical temperature range such as 1500°K to 1200°K this is generally not critical).
2. The concentration of incorporated impurities and dopants changes according to the differences in the solubility behaviour of the solute and the dopants or impurities. Frequently this is manifested in the shifting of equilibria in the solutions as discussed in Section 3.4. For example, it is extremely difficult to produce homogeneous chromium doping in Al_2O_3 and other oxides by the slow cooling technique and the solvent evaporation or transport techniques are then preferable.
3. For the preparation of solid solutions the same arguments as above for dopants hold, only the effect on the composition is more drastic. In Section 7.1.3 the techniques to obtain homogeneous solid solutions will be discussed.
4. Frequently in slow-cooling experiments unwanted phases appear (sometimes "non-reproducibly" or depending on the crucible size: the explanation is uncontrolled evaporation of a solvent constituent as in the case of $\text{Y}_3\text{Fe}_5\text{O}_{12}$ crystals grown from $\text{PbO-PbF}_2\text{-B}_2\text{O}_3$ flux where magneto-plumbite, YFeO_3 or $\text{Y}_{20}\text{O}_{16}\text{F}_{28}$ are the unwanted phases, see Tolsdorf and Welz, 1972). Reproducibility is an absolute necessity and can in this case be achieved by sealing the crucibles by welding and by careful control of all parameters including the purity of the chemicals used.

According to the degree of nucleation control the following versions of the slow-cooling technique can be distinguished:

Spontaneous uncontrolled nucleation (Table 7.3).

Reduction in the number of crystals nucleated by an oscillatory temperature variation at the start of the experiment.

Localized cooling.

Localized cooling and ACRT stirring (see Section 7.2.7).

Bennett-Tolsdorf seeding technique (with and without ACRT).

Top-seeded solution growth.

TABLE 7.3. Examples of Crystals Grown by the Slow-cooling Technique and Spontaneous Nucleation†

Crystal	Solvent	Size (mm)	Remarks	Reference†
Al ₂ O ₃	PbO/B ₂ O ₃ ; PbF ₂	30	Plates	Nelson and Remeika (1964), White and Brightwell (1965)
BaTiO ₃	KF	34 × 24 × 0.4	Butterfly twin	Remeika (1958)
BeO	Various	10	Prisms	Newkirk and Smith (1965)
C (graphite)	Fe, Ni	30 × 0.5 × 0.5		Austerman <i>et al.</i> (1967)
Cd _{1-x} Cu _x Cr ₂ Se ₄	CdCl ₂	3-4		Tyco (1971)
CdS	Na ₂ S _x	15 × 1 × 1; 5 × 5 × 0.2	Prisms, plates	Scheel (1974)
GaFeO ₃	Bi ₂ O ₃ /BiF ₃	12 × 6 × 6		Linares (1962)
GdAlO ₃	PbO/PbF ₂ /B ₂ O ₃	35 × 30 × 25	210 g, ACRT	Scheel (1972)
Gd ₃ Fe ₅ O ₁₂	PbO/B ₂ O ₃	10		Remeika (1963)
Gd ₃ Ga ₅ O ₁₂	PbO/B ₂ O ₃	8		Remeika (1963)
In ₂ O ₃	PbO/B ₂ O ₃	10 × 10 × 1		Remeika and Spencer (1964)
LaB ₄	La	5-8		Deacon and Hiscocks (1971)
LiFe ₅ O ₈	PbO/B ₂ O ₃	20		Pointon and Robertson (1967)
Mn ₃ O ₄	PbF ₂ /PbO	10 × 10		Wanklyn (1972)
MnTe	Te	50 × 15 × 15	ACRT	Mateika (1972)
NaCrS ₂	Na ₂ S _x	20 × 20 × 0.2	Plates	Scheel (1974)
Y ₃ Al ₅ O ₁₂	PbO/PbF ₂ /B ₂ O ₃	50	Large crucible	Grodkiewicz <i>et al.</i> (1967)
Y ₃ Fe ₅ O ₁₂	PbO/PbF ₂ /B ₂ O ₃	~ 300 g	Large crucible	Nielsen (1964)
Y ₃ Fe ₅ O ₁₂	PbO/PbF ₂ /B ₂ O ₃	~ 60	Large crucible	Grodkiewicz <i>et al.</i> (1967)
Y ₃ Fe ₅ O ₁₂	PbO/PbF ₂ /B ₂ O ₃	57 g	Bennet-Tolksdorf nucleation control	Bennett (1968)
Y ₃ Fe ₅ O ₁₂	PbO/PbF ₂	~ 30 × 25 × 25	(49 g) nucleation control	Tolksdorf (1968)
Y ₃ Fe ₅ O ₁₂	PbO/PbF ₂ /B ₂ O ₃	30 × 25 × 25	Inclusion-free, ACRT	Scheel (1972)
Y ₃ Fe ₅ O ₁₂	PbO/PbF ₂	60 × 50 × 25	250 g, ACRT	Tolksdorf (1974a)
Y ₃ Fe _{3.8} Ga _{1.2} O ₁₂	PbO/PbF ₂ /B ₂ O ₃	30 × 25 × 25	Inclusion-free ACRT	Scheel (1972)
ZnO	PbF ₂	50		Nielsen and Dearborn (1960)

† For experimental details and for references see Chapter 10.

B. Evaporation of solvent. Solvent evaporation, the basis of common salt production for thousands of years, has also been frequently used in crystal growth from HTS. In this case the linear growth rate of the crystal is given by

$$\dot{v} = \frac{n_e}{\rho A} \left(\frac{dV}{dt} \right) \quad (7.2)$$

with the symbols corresponding to those of Eqn 7.1, so that dV/dt is the solvent evaporation rate.

Flux evaporation has been systematically used by Tsushima (1966), Grodkiewicz and Nitti (1966), Roy (1966), Wood and White (1968) and by Webster and White (1969). The technique has been especially used for compounds which react with the solvent at lower temperatures $\left(\text{TiO}_2 + \text{PbO} \xrightarrow{< 1200^\circ\text{C}} \text{PbTiO}_3; \text{HfO}_2 + \text{PbO} \xrightarrow{< 1200^\circ\text{C}} \text{PbHfO}_3 \right)$ or for a cation of which the valence state changes by oxidation at lower temperatures $\left(\text{Cr}^{3+} \xrightarrow{< 1100^\circ\text{C}} \text{Cr}^{6+}, \text{ see Section 3.4} \right)$. Roy (1966) stressed the

TABLE 7.4. Crystals Prepared by the Solvent Evaporation Technique†

Crystal	Solvent	Size	Reference
BaTiO ₃	BaCl ₂	—	Timofeeva and Zaleskii (1959)
BaTiO ₃	BaCl ₂	—	Arend (1960)
In ₂ O ₃	B ₂ O ₃	few mm	Roy (1966)
TiO _{2-x}	Na ₂ B ₆ O ₁₀	few mm	Roy (1966)
Fe ₂ O ₃	Na ₂ B ₆ O ₁₀	few mm	Roy (1966)
Cr ₂ O ₃	Na ₂ B ₆ O ₁₀	few mm	Roy (1966)
VO ₂	V ₂ O ₅	few mm	Roy (1966)
BaAl ₁₂ O ₁₉	PbF ₂	2 × 2 × 0.1 mm	Tsushima (1966)
Al ₂ O ₃	PbF ₂	10 × 10 × 1 mm	Tsushima (1966)
ZnAl ₂ O ₄	PbF ₂	1 × 1 × 1 mm	Tsushima (1966)
ZnMn ₂ O ₄	PbF ₂	2 × 2 × 2 mm	Tsushima (1966)
CoMn ₂ O ₄	PbF ₂	2 × 2 × 2 mm	Tsushima (1966)
LaAlO ₃	PbO + PbF ₂	3 × 3 × 0.4 mm	Tsushima (1966)
HfO ₂	PbF ₂ —B ₂ O ₃	~ 1 g	Grodiewicz and Nitti (1966)
ThO ₂	PbF ₂ —B ₂ O ₃	~ 5 mm	Grodiewicz and Nitti (1966)
TiO ₂	PbF ₂ —B ₂ O ₃	~ 2 mm	Grodiewicz and Nitti (1966)
Al ₂ O ₃ : Cr	PbF ₂ —B ₂ O ₃	57 × 2 mm	Grodiewicz and Nitti (1966)
YCrO ₃	PbF ₂ —B ₂ O ₃	7 × 4 mm	Grodiewicz and Nitti (1966)
MgO	PbF ₂	—	Webster and White (1969)
SrSO ₄	NaCl	few mm	Patel and Bhat (1971)
BaSO ₄	NaCl		
PbSO ₄	NaCl		

† For experimental details see Chapter 10.

advantages of the flux evaporation method especially for such cases where oxides of metals with a specified valence state have to be grown. The constant temperature and a carefully controlled oxygen partial pressure allow growth of oxides of lower valency states as was shown by Berkes *et al.* (1965), Roy (1966) and by Bartholomew and White (1970). Flux evaporation could also be used to grow crystals which show a low variation of solubility with temperature or a retrograde solubility behaviour. Several crystals prepared by solvent evaporation at high temperatures are listed in Table 7.4, and further examples are given in Chapter 10.

Since solvent evaporation may be carried out isothermally, this technique offers the advantages connected with growth at constant temperature:

1. Easy and often closer temperature control.
2. Constant concentration of equilibrium defects.
3. Approximately constant incorporation of solvent ions as impurities.
4. In the cases where the distribution coefficient of impurities or dopants is not extremely different from unity and if growth takes place either under the regime of pure diffusion control or under complete mixing, a homogeneous incorporation of dopants and impurities can be expected.

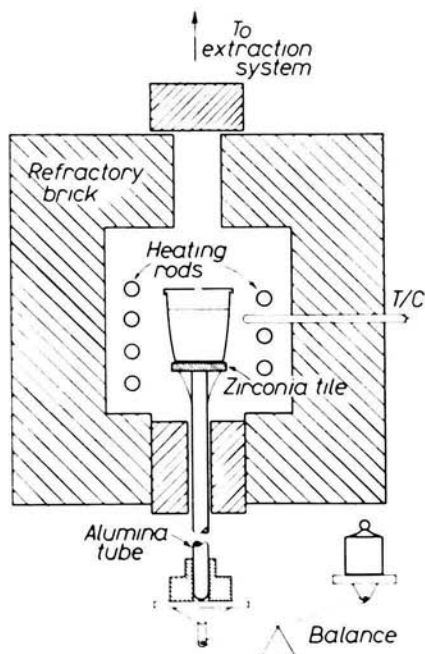


FIG. 7.10. Open system for solvent evaporation with monitoring by a balance (Wood and White, 1968).

Disadvantages of the isothermal flux evaporation technique are the difficulty of controlling the evaporation rate and thus the growth rate, and the poisonous and corrosive nature of the solvent vapours (e.g. PbF_2) if an open system such as that shown in Fig. 7.10 is used. The advantage of this system is that the balance permits a measurement of the rate of evaporation and hence of the mass deposition. The use of an air flow to remove PbF_2 vapour will, however, normally produce temperature fluctuations.

In order to prevent corrosion of furnace ceramics and heating elements by the action of the solvent vapours, closed evaporation systems have been proposed and three such designs are shown in Fig. 7.11. These systems permit control or programming of the evaporation rate through variation in the temperature T_2 at which condensation occurs.

An important feature of the flux evaporation technique is that nucleation should take place in the lower part of the crucible. The surface region of the solution has to be warmer, otherwise crystallization at the surface would diminish the free surface area of the solution and thereby decrease the rate of evaporation. Therefore, in a symmetric (to the heat source) position of the crucible, little natural thermal convection occurs.

Depending on the relative densities of solute and the solution some solutal convection can occur, the latter being favoured by a higher density of the crystal. However, any natural convection in this case of a cooler crucible base will be slow, so that growth is diffusion-controlled unless stirring is applied. This can be achieved for closed systems by the accelerated crucible rotation technique as in the apparatus shown in Fig. 7.11(c). In this apparatus, the evaporation rate will be governed by the dimensions r_1 and r_2 as well as by the temperatures T_1 and T_2 so that considerable flexibility is available to the experimenter for optimization of the growth conditions.

In principle the evaporation rate w is constant when the temperature is held constant and is given by the Arrhenius equation

$$w = w_0 \exp(-H_v/RT)$$

where w_0 is the rate constant, H_v the activation energy of vaporization, R the gas constant and T the absolute temperature. From measurement of the weight loss as a function of temperature Giess (1966) determined an activation energy of 33 kcal/mole for the evaporation of PbF_2 from a $\text{Y}_3\text{Fe}_5\text{O}_{12}$ — PbO — PbF_2 melt, whereas Perry (1967) estimated an activation energy of 62 ± 5 kcal/mole for the evaporation of BaB_2O_4 — PbB_2O_4 flux during crystallization of $(\text{Ba}, \text{Pb})\text{TiO}_3$.

In order to achieve an optimum stable growth rate during the course of crystallization a program for the evaporation according to the principles of the stable growth rate of Scheel and Elwell (1972) has to be worked out,

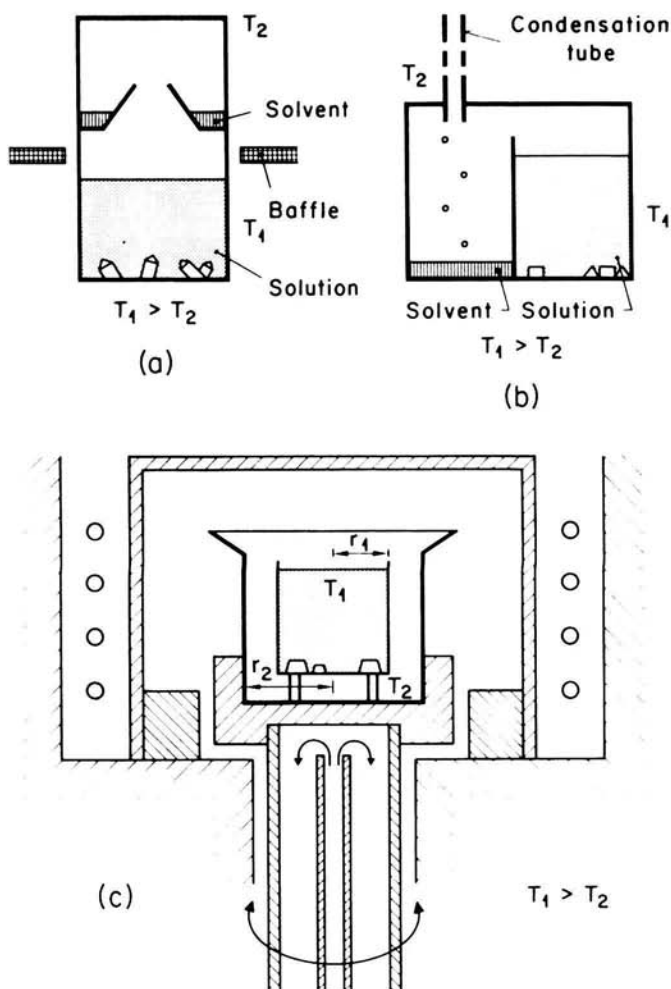


FIG. 7.11. Arrangements for flux evaporation experiments. (a) System with collection of the evaporated solvent (Hart, quoted in White, 1965). (b) Evaporation with condensation tube (Brice, 1973). (c) Flux evaporation-condensation system with ACRT stirring (Scheel, 1972).

and accordingly the rate of evaporation can be controlled by the temperature, by a gas flow to remove the solvent vapours, by baffles, by the free surface area of the solution etc.

C. Transport techniques. In principle all methods of crystal growth from solutions depend on transport of solute to the crystal, whether the supersaturation is provided by slow cooling or by solvent evaporation. The term

"transport techniques" is used here for such cases where supersaturation is achieved exclusively by transport of solute or solute constituents which were initially not dissolved in the solution and are either solid (becoming gradually dissolved and transported to the growing crystal) or in the vapour phase. The following transport techniques can be distinguished:

- (i) Transport by a temperature gradient (between nutrient and crystal) in bulk solutions.
- (ii) Travelling solvent zone crystallization.
- (iii) Diffusion of reactants (solute constituents) = flux reaction technique;
 - (a) Solid source
 - (b) Vapour phase source (VLRs)
 - (c) Shifting equilibria.
- (iv) Vapour-liquid-solid (VLS) mechanism.
- (v) Electrolytic growth in high-temperature solutions.

(i) *Transport in a temperature gradient.* The principle of the gradient transport technique is shown in Fig. 7.1 (process 3). Nutrient is held at a temperature T_c in a solution of average composition n_c . If by natural or forced convection a flow of solution occurs towards a region of average temperature T_E where a seed crystal is held, the solution becomes supersaturated and crystallization occurs at the seed surface.

For natural convection the average mass transport rate and its dependence on the properties of the solution (viscosity, thermal conductivity, thermal expansion coefficient, heat capacity) is discussed in Section 6.6.2. For a given solute-solvent system the mass transport rate and hence the supersaturation and growth rate may be varied by adjusting the temperature difference, the area and form of seed and nutrient, and the depth of the solution. Alternatively the seed may be rotated so that a column of solution is drawn up from the basal region at a rate which is given by Cochran (1934). An example of the variation in crystal growth rate with rotation rate is shown in Fig. 4.10. A theoretical treatment of thermal gradient transport has been given by Dawson *et al.* (1974). If the flow of solution is assumed to be rapid compared with diffusion through the boundary layer, and neglecting solvent evaporation, the growth rate $\dot{v}$ is given by

$$\dot{v} \left[\frac{\rho \delta}{D} + \frac{\rho \delta_N A}{D A_N} \right] + \left[\frac{\dot{v}}{F} \right]^{1/m} = \frac{n_c \phi}{RT^2} \Delta T. \quad (7.3)$$

Here the subscript N refers to the nutrient, ϕ is the heat of solution, and the interface kinetics are taken to be such that $\dot{v} = F(n_i - n_c)^m$. The parameter which is normally varied to adjust the growth rate is the temperature difference ΔT between crystal and nutrient.

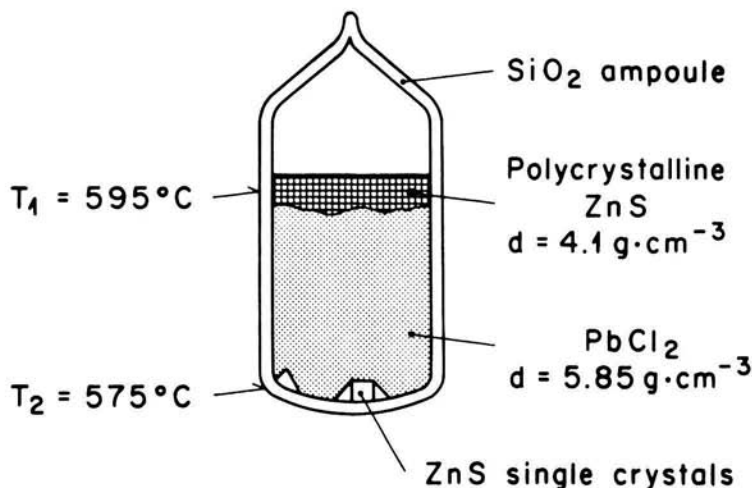


FIG. 7.12. Apparatus used for growth of zinc sulphide by solute transport (Linares, 1968).

As an example of application of crystal growth by transport in a temperature gradient, Fig. 7.12 shows the growth of zinc sulphide where polycrystalline nutrient is floating at the hotter surface and where transport occurs downwards to the cooler end of the ampoule.

Another example of achieving supersaturation with the nutrient held in a hotter unstirred zone is shown in Fig. 7.13 where GaAs nutrient material is floating in an outer annular chamber while the slowly rotated (10 rpm) GaAs crystal grows in a slightly cooler inner chamber and is slowly withdrawn. As shown in Table 7.2 a number of authors used a gradient transport technique where nutrient is held in a hotter zone and where the rotated crystal is slowly withdrawn, and a suitable arrangement is shown in Fig. 7.14. This apparatus may incorporate an annular cooling jacket for control of the interface temperature gradient.

Growth on fully immersed seed holders as shown in Fig. 7.3 is normally more difficult if the phase diagram and parameters affecting growth conditions are not accurately known. A few examples are quoted in Table 7.5.

The advantage of a constant growth temperature is obvious for the production of homogeneous solid solutions and of homogeneously doped crystals as described in Section 7.1.3, and therefore the temperature gradient technique has been frequently used. Recently Tolksdorf and Welz (1973) described a gradient transport technique where the advantages of the Tolksdorf (1968) seeding method and the ACRT stirring technique

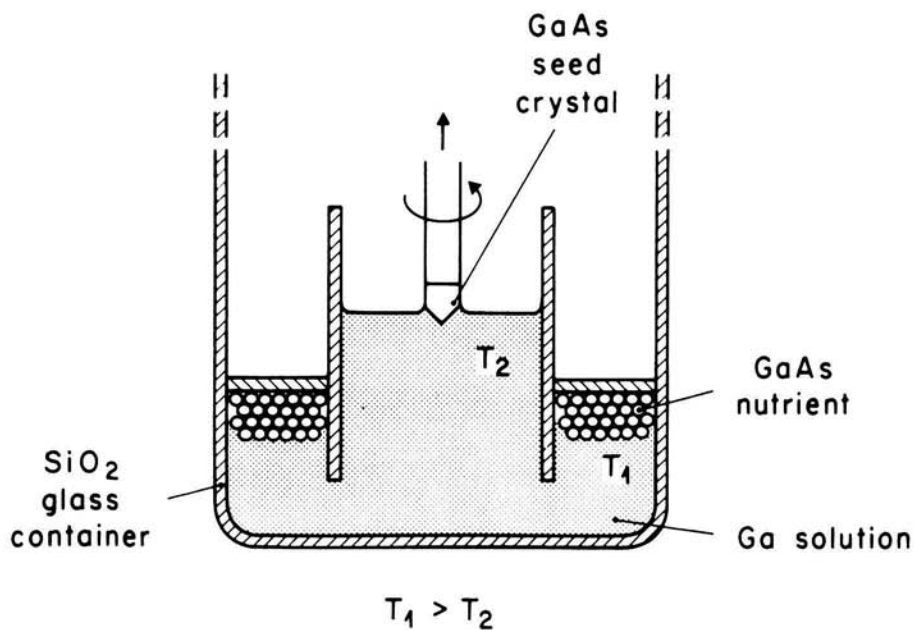


FIG. 7.13. Gradient transport technique for growth of GaAs (Lyons, 1965).

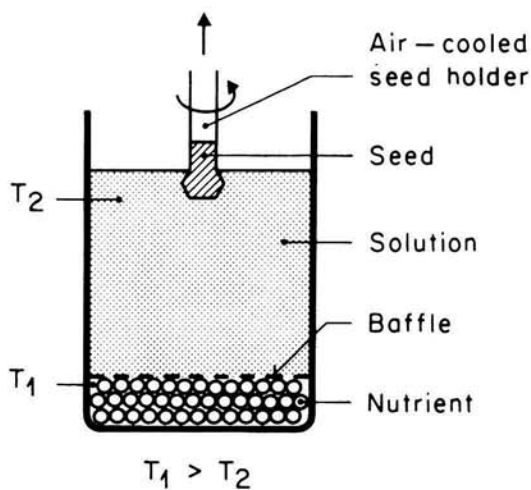


FIG. 7.14. Typical arrangement for gradient transport with top seeding.

TABLE 7.5. Crystals Prepared from Immersed Seeds by the Gradient Transport Technique†

Crystal	Solvent	Size	Reference
CoFe ₂ O ₄	Na ₂ B ₄ O ₇	10–15 mm	Reynolds and Guggenheim (1961)
Y ₃ Fe ₅ O ₁₂	BaO × 0.6B ₂ O ₃	~ 15 mm	Laudise <i>et al.</i> (1962)
ThO ₂	Li ₂ W ₂ O ₇	10 × 3 mm	Finch and Clark (1965)

† For experimental details see Chapter 10.

(Scheel, 1972) are applied to isothermal growth by temperature gradient transport. The arrangement is shown in Fig. 7.15. Large homogeneous and nearly inclusion-free crystals of solid solutions Y₃Fe_{5-x}Ga_xO₁₂ were grown. A few inclusions were trapped at the seed crystal when the air cooling was turned on in order to initiate growth, probably due to a sudden increase in the growth rate.

In growth on a rotating seed, the thickness of the solute boundary layer is, to a good approximation, independent of the diameter of the crystal. As a result, whether or not pulling is used to maintain a constant diameter, the maximum stable growth rate should not change as growth proceeds. A reduction in the growth rate will, however, be necessary if the temperature gradient at the crystal-solution interface varies as the crystal becomes larger.

(ii) *Travelling solvent zone crystallization* (TSZC). A great variety of terminology has been used to describe the technique in which a zone of solution is made to travel through a solid in a similar manner to zone melting (Pfann, 1955, 1966): thin film solution growth, travelling heater method, thin alloy zone crystallization, temperature gradient zone melting, moving solvent method, travelling solvent method, zone melting with a temperature gradient, etc. TSZC has been reviewed by Wolff and Mlavsky (1965, 1974) and by Hemmat *et al.* (1970).

The principle is shown in Fig. 7.16; (a) demonstrates the technique in which the driving force for the motion of the solution is the temperature gradient so that at the hotter side single-crystalline or dense polycrystalline feed is dissolved and then deposited at the cooler side of the solution zone. In (b) the solution zone is moved by motion of the heater, which may be a resistance heating ring or an RF coil. As the temperature profiles (c) demonstrate, both techniques are essentially equivalent. However, there are differences which determine the applicability of the two techniques, and which originate from the individual heat flow patterns as indicated in Fig. 7.16(d) and (e).

In the travelling solvent method (a) the solution moves towards an

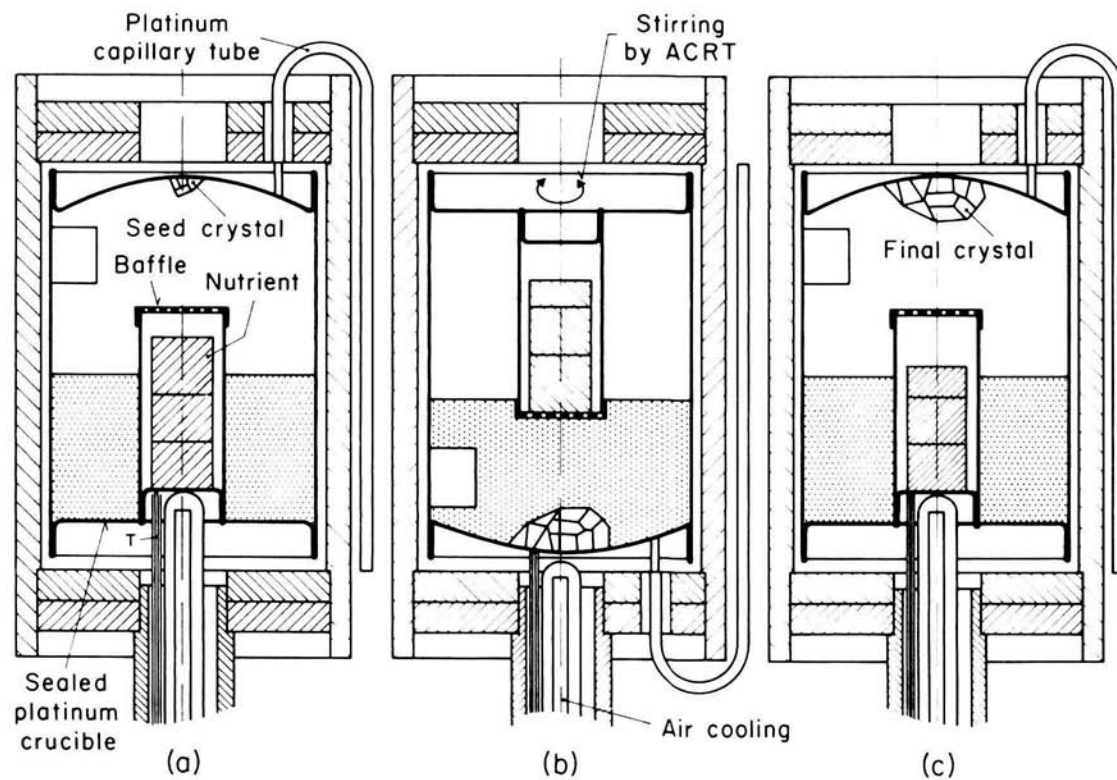


FIG. 7.15. Growth of solid solutions of $Y_3(Fe, Ga)_5O_{12}$ by gradient transport. (a) Starting position. (b) Position during crystallization. (c) Final position (after Tolksdorf and Welz, 1973).

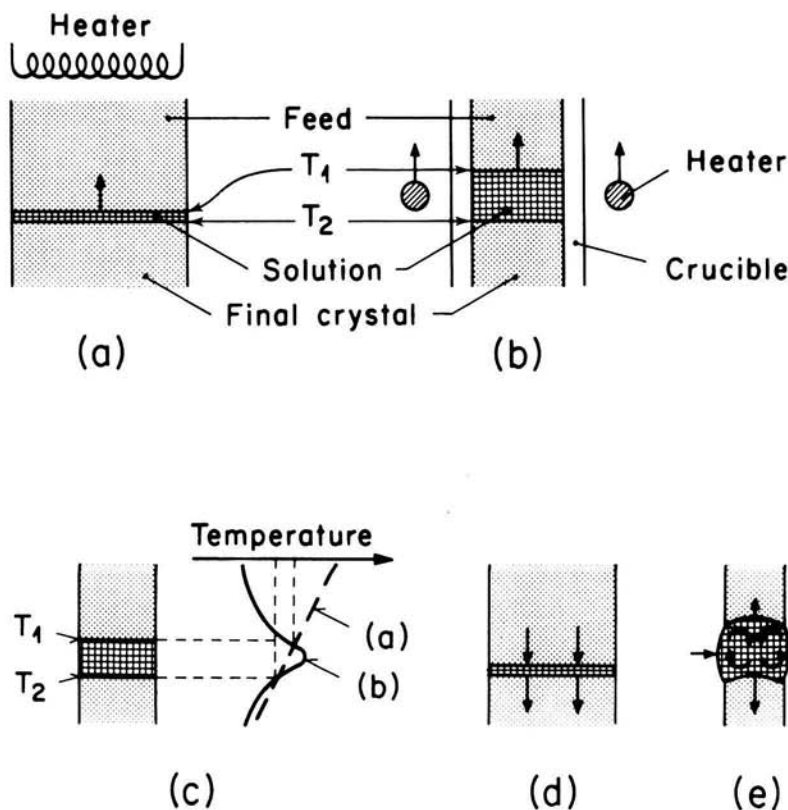


FIG. 7.16. Principle of travelling solvent zone method. (a) Solution zone travelling in a temperature gradient. (b) Solution zone travelling with a heater. (c) Temperature profiles for (a) and (b). (d) Heat flow for (a). (e) Heat flow for (b).

increasingly hotter region if the temperature gradient across the ingot or, correspondingly, if the temperature of the heater is kept constant. This would lead to a varying composition in the case of solid solutions or doped crystals, and also the rate of movement of the solution zone, and hence the growth rate, would increase with time. Therefore a temperature programme is advantageous which provides a constant growth temperature T_2 and a constant dissolution temperature T_1 . According to Wolff (1965) the solution zone in the temperature gradient driven technique can be as thin as 25–100 μm and this allows the preparation of thin crystals and devices (Mlavsky and Weinstein, 1963; Griffiths and Mlavsky, 1964). In reviews on the principles of “thin alloy zone crystallization” Hurlé *et al.* (1964, 1967) have shown that for thin solution zones the supersaturation gradient is much smaller than in bulk solutions and this allows fast growth rates

without solvent inclusions. Under favourable conditions the stable growth rates can approach those used during crystallization from pure melts as discussed in Chapter 6. The migration kinetics of a solution zone in a temperature gradient have been studied by Tiller (1963), Seidensticker (1966) and by Hamaker and White (1968).

In the travelling heater method (THM) the solution zone is orders of magnitude wider so that this technique may be conveniently used to produce large crystals. This technique is especially useful for the preparation of homogeneous solid solutions and homogeneously doped crystals (see Section 7.1.3) if the temperature difference between the dissolving and the growing interfaces is kept small and when the conditions are optimized. The maximum stable growth rate, however, is much lower than in the travelling solvent method due to the thickness of the molten solution zone. Growth rates are limited to typical values for crystal growth from bulk solutions, of the order of $500 \text{ \AA s}^{-1}$ or 3 to 5 mm per day. The onset of constitutional supercooling and the maximum stable growth rates were discussed by Hemmat *et al.* (1970) and are also treated in Chapter 6.

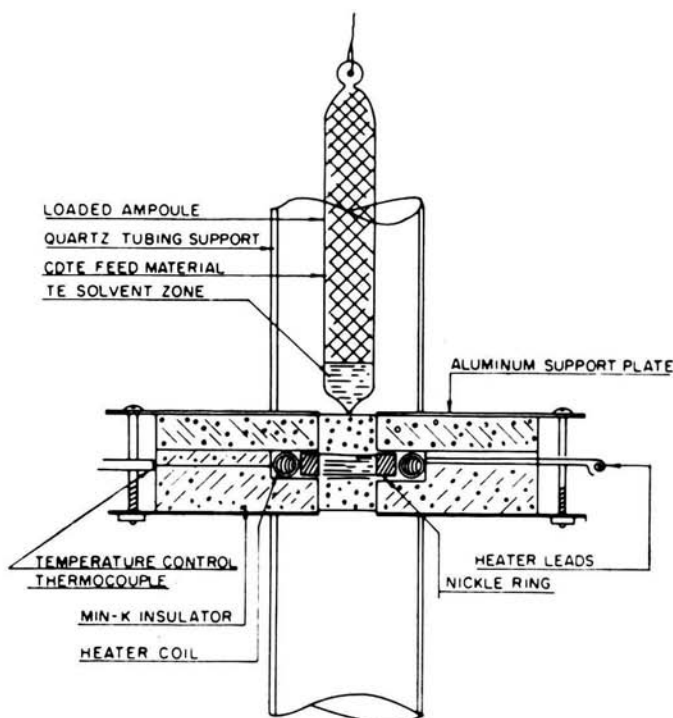


FIG. 7.17. Construction schematic of furnace for travelling heater method (Wald *et al.*, 1971).

A typical furnace used for THM growth of CdTe from Te solution is shown in Fig. 7.17 and nearly single crystals of 5 cm length were obtained by Wald *et al.* (1971) and by Bell *et al.* (1970).

Table 7.6 lists some crystals which have been grown by the travelling solvent zone method and demonstrates its wide applicability.

Modifications of the travelling heater method use a heater wire to move a solution zone along a thin crystalline layer or a heating strip which moves with the solution zone through the crystal boule. The first method was used to grow BaTiO₃ films of about 50–125 μ thickness, as shown in

TABLE 7.6. Crystals Prepared by the Travelling Solvent Zone Method

Crystal	Solvent	Method†	Crystal size	Reference
GaP	Ga	THM		Broder and Wolff (1963), Wolff <i>et al.</i> (1958), Plaskett <i>et al.</i> (1967)
GaAs	Ga	THM		Wolff <i>et al.</i> (1958)
(Ga, In)P	Ga—In	THM		Hemmat <i>et al.</i> (1970)
(Al, Ga)As	Al—Ga	THM		Hemmat <i>et al.</i> (1970)
Ga(As, P)	Ga	THM		Wolff <i>et al.</i> (1968)
Si	Au	THM		Hein (1956)
SiC	Cr	THM		Wolff <i>et al.</i> (1969)
(Zn, Hg)Te	Te	THM	4.5 cm	Wolff <i>et al.</i> (1968)
CdTe	Te	THM		Bell <i>et al.</i> (1970), Wald <i>et al.</i> (1971)
CdIn ₂ Te ₄	In ₂ Te ₃	THM		Mason and Cook (1961)
CdCr ₂ Se ₄	CdCl ₂	THM	8 × 35 mm	Hemmat <i>et al.</i> (1970)
ZnO	PbF ₂	THM	2 × 3 × 10 mm	Wolff and LaBelle (1965)
Y ₃ Fe ₅ O ₁₂	Fe ₂ O ₃	THM		Abernethy <i>et al.</i> (1961)
Y ₃ Fe ₅ O ₁₂	BaO.B ₂ O ₃	STRIP	10 × 3 mm	Tolksdorf (1974b)
(Pb, Sr)TiO ₃ (Pb, Sr) ₂ B ₂ O ₅		THM		DiBenedetto and Cronan (1968)
GaP	Ga	TSM		Weinstein and Mlavsky (1964)
GaAs	Ga	TSM		Mlavsky and Weinstein (1963)
SiC	Cr	TSM		Griffiths and Mlavsky (1964)
BaTiO ₃	BaB ₄ O ₇	STRIP		Hemmat <i>et al.</i> (1970)
CaCO ₃	Li ₂ CO ₃	STRIP	15 × 20 mm	Brissot and Belin (1971), Belin <i>et al.</i> (1972)
InAs	In	TSM		Kleinknecht (1966)
InSb	In, Pb	TSM		Hamaker and White (1968)
Ga _x In _{1-x} Sb	In, Pb	TSM		Hamaker and White (1969)
ZnSe _x Te _{1-x}		TSM		Steininger and England (1968)
CaMoO ₄	Li ₂ SO ₄	TSM	~ 1 mm	Parker and Brower (1967)

† TSM = Travelling solvent method, THM = travelling heater method, STRIP = travelling stripheater method.

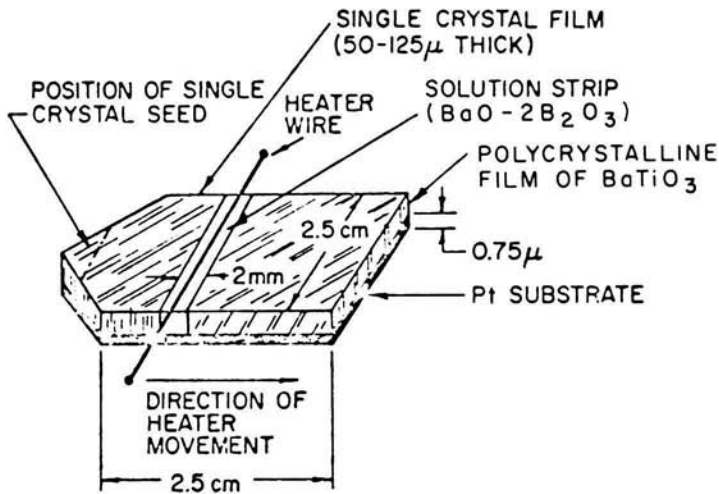


FIG. 7.18. Schematic of thin film growth by moving platinum wire heater (Hemmat *et al.*, 1970).

Fig. 7.18, by moving an infrared (focusing) line heater at a rate of 8.4 cm per day along with a strip of the BaB_2O_7 solution (Hemmat *et al.*, 1970). A travelling strip heater was first used by Brissot and Belin (1971) and by Belin *et al.* (1972) to grow large CaCO_3 crystals from a solution in Li_2CO_3 by an apparatus which is diagrammatically shown in Fig. 7.19. In this case the solution technique allows the growth at 1–2 atm. CO_2 and $700\text{--}800^\circ\text{C}$ of a compound which at its melting point of about 1340°C would have a CO_2 equilibrium pressure of about 100 atm. The linear growth rate was $600 \text{ \AA s}^{-1}$ or 5 mm per day, and the seed crystal was rotated.

Plaskett *et al.* (1967) found that in GaP crystals grown by THM in the [211] direction the twinned regions grew faster. Thus they used twinned seeds in order to obtain large inclusion-free twinned crystals from which high quality substrates for the preparation of LED† devices were cut parallel to the longitudinal twin planes.

The rate of advance of the solution, which is equal to the crystal growth rate v and to the rate of dissolution, is estimated by Wilcox (1968) to be

$$v \simeq \frac{GD\rho_c}{m(1-n_{sn})\rho_{sn}}, \quad (7.4)$$

where G is the temperature gradient in the liquid, D is the diffusion coefficient, ρ_c and ρ_{sn} the densities of the crystal and the solution, m the slope of the liquidus on the crystal-solvent phase diagram (e.g. the change

† LED = light-emitting diodes.

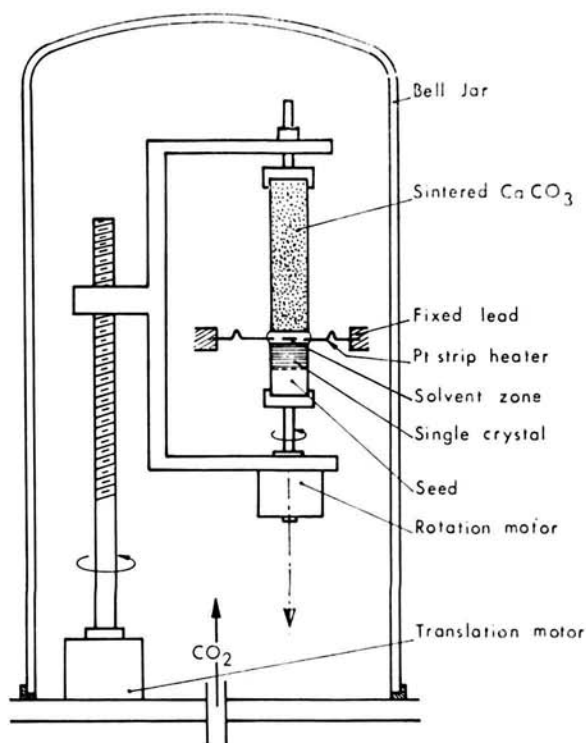


FIG. 7.19 Strip heater apparatus for growth of calcite (Brissot and Belin, 1971).

in liquidus temperature per change in weight fraction) and n_{sn} the solute concentration in the solution. This relationship is equally applicable to the movement of inclusions in a temperature gradient as discussed in Chapter 9 and shows that the solution zone travel rate increases with increasing temperature gradient, increasing solubility, increasing dependence of solubility on temperature and with increasing diffusion coefficient. The latter three properties increase with temperature, so that the temperature and the temperature gradient can be given values which allow stable growth (see discussion in Chapter 6). If the average temperature and the temperature gradient across the solution zone are kept constant, then also the maximum stable growth rate is constant because of the non-varying size of the crystal. On the other hand impurities with $k < 1$ are continuously enriched in the travelling solvent zone and may necessitate a decreasing growth rate, and also an increasing crystal perfection (decreasing number of dislocations) acts in the same direction. Equation 7.4 is approximate since it neglects the effect of interface kinetics, and applies only if the transport occurs only by diffusion.

An important aspect of the travelling solvent zone method is its purification effect. Although purification is a general effect of crystal growth from solutions (as long as growth is stable) and has been used in preparative chemistry for more than 700 years (recrystallization from solutions) the purification in TSZM is specially pronounced when the relatively small amount of solvent is considered. Even if impurities for which $k > 1$ are present in the solvent, the uptake of such impurities from the solution is clearly much lower than in growth from bulk solutions.

(iii) *Diffusion of reactants (= flux reaction technique)*. In this section those techniques are discussed which differ from those in Sections i, ii and iv in that certain of the crystal constituents are present in the solution while other constituents diffuse from a solid source or enter the solution from the vapour phase. These techniques should not be confused with reactions between starting materials which may occur in the solution prior to the production of supersaturation. For example, mixtures of Y_2O_3 and Fe_2O_3 crystallize from $PbO-B_2O_3$, PbF_2 or $BaO \cdot 0.6B_2O_3$ solvents as $YFeO_3$, $Y_3Fe_5O_{12}$, $PbFe_{12}O_{19}$, Fe_2O_3 , YBO_3 or YOF depending on the relative concentrations of starting materials but not on the degree of (or absence of!) prior solid state reaction. As another example, $BaWO_4$ crystallizes from a homogenized solution whether the starting mixture is $Na_2WO_4 + BaCl_2$ or $BaWO_4 + NaCl$. Despite the fact that reactions take place in both the above examples it would be rather inconvenient to classify all such experiments under the term "reaction technique" or "indirect flux method".

In the following we shall restrict the term "reaction technique" to those examples where by a reaction between constituents (formerly separated) supersaturation is achieved and precipitation occurs, or where by oxidation or reduction during the experiment supersaturation is continuously produced. The "reaction" is taking place during the crystal growth process, generally by transport (on a macroscopic scale) of the reactants to the crystallization region. Several examples of this "reaction technique" were reported in the last century and are listed in Table 2.1.

(a) *Solid source*. To this category belong the cases where crucible constituents become constituents of the crystal or serve as reduction or oxidation media. Reactions with crucible materials are frequently undesirable and many examples were reported in the 19th century. As a recent example lead feldspar solid solutions $PbAl_2Si_2O_8-KAlSi_3O_8$ crystallized in prisms up to 15 mm length on a sillimanite-type ceramic lid on which PbO and PbF_2 from a flux growth experiment condensed (Scheel, 1971).

In the thirties emerald was produced by IG Farben (Espig, 1960) by a flux reaction technique as shown diagrammatically in Fig. 7.20(a). Pieces of silica float on a solution containing beryllia and alumina in the correct

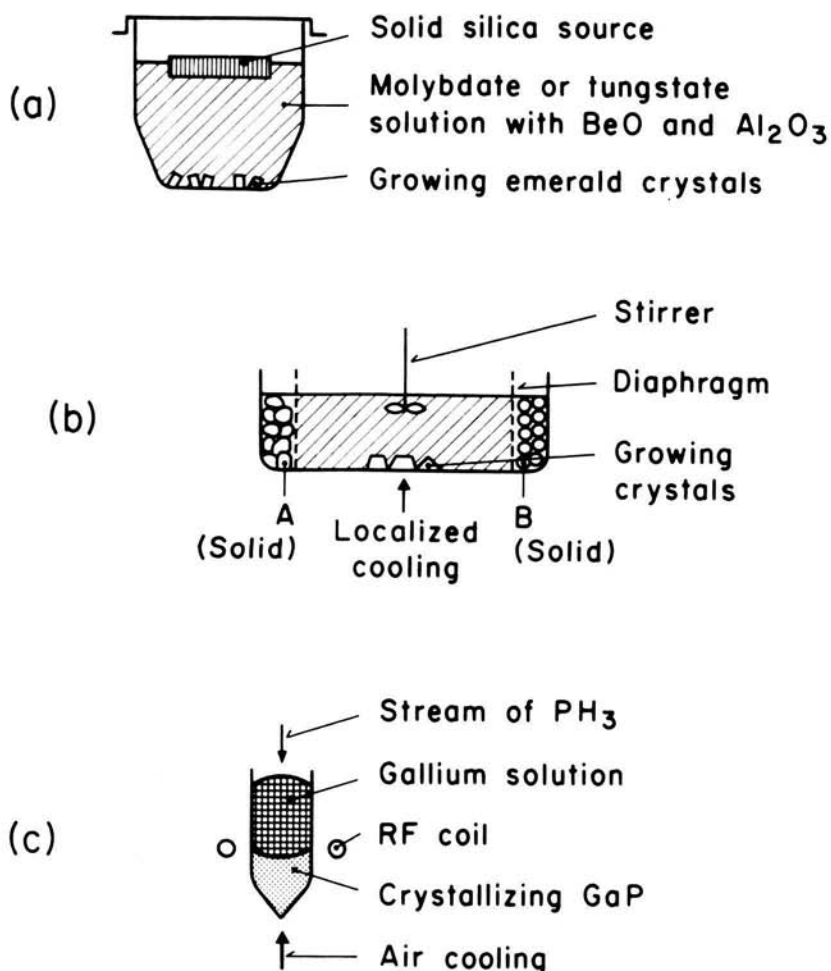


FIG. 7.20. Examples of the flux reaction technique. (a) Growth of emerald by the method of Espig (IG Farben) with silica as the solid source (after Wilke, 1956). (b) System of two reactants separated from the growth region by diaphragms. (c) Crystallization of gallium phosphide from gallium solution with PH_3 vapour as phosphorous source.

proportions and by dissolution and diffusion the reaction product emerald ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}:\text{Cr}$) is precipitated. A more sophisticated arrangement is shown in Fig. 7.20(b), where the reactants *A* and *B* are separated from the growth regions by diaphragms. Preferentially the site of nucleation is

provided by localized cooling, or a seed crystal can be applied when the solution is saturated.

Examples of the use of solids which slowly dissolve and produce reduction reactions have been published by McWhan and Remeika (1970) and by Foguel and Grajower (1971). The former used slowly dissolving VN in order to grow V_2O_3 from $KF + V_2O_5$ melts in platinum crucibles, whereas Foguel and Grajower reduced V_2O_5 — KF melts with the graphite crucible and grew high purity V_2O_3 crystals up to 6.5 mm length and 2 mm diameter.

(b) *Vapour phase source* (VLRS). As discussed in Chapter 2, among the earliest crystals grown from high-temperature solutions were tungsten bronzes prepared by Wöhler (1823) from sodium tungstate melts which were reduced by hydrogen to produce Na_xWO_3 . Since that time many crystals have been prepared by the *vapour-liquid-reaction-solid* (VLRS) technique, and in the following only a few examples will be given. Transparent crystals of $BaFe_{12}O_{19}$, $SrFe_{12}O_{19}$, Fe_2O_3 and $LiFe_5O_8$ have been prepared from $BaCl_2$ or BaF_2 , $SiCl_2$, $NaCl$ and $LiCl$ melts, respectively, containing Fe_2O_3 , which were reacted with oxygen at 1250° by Brixner (1959). Similar experiments on growth by reaction with oxygen or water yielded crystals of $CaMn_2O_4$, $Ca_2Nb_2O_7$, $CaFe_2O_4$, $Ca_3Al_{10}O_{18}$, $CaCrO_4$, Ca_2SiO_4 , Ca_2PO_4Cl , $Ba_5(VO_4)_3Cl$, $Ba_5(MnO_4)_3Cl$, $BaCrO_4$, $BaSb_2O_6$, $BaFe_{12}O_{19}$, $BaWO_4$, BaB_2O_4 , $BaSi_2O_5$, $BaPbO_3$ and $BaTi_3O_7$ (Brixner and Babcock, 1968), Sr_2VO_4Cl and Sr_2VO_4Br (Brixner and Bouchard, 1970), Ca_2PO_4Cl , Ca_2VO_4Cl , $Sr_5(PO_4)_3Cl$, Sr_2VO_4Cl , $Ba_5(PO_4)_3Cl$ and $Ba_5(VO_4)_3Cl$ (Brixner and Weiher, 1970).

Semiconductors such as the III–V compounds may also be prepared from solutions in the Group III metals, with the Group V element supplied via the vapour phase, as in the experiment of Plaskett (1969) and of Poiblaud and Jacob (1973). The principle is shown in Fig. 7.20(c), the growth of gallium phosphide being promoted by the relative motion between the ampoule and the RF coil. A similar technique was developed by Kaneko *et al.* (1973, 1974) for production of GaP crystals from gallium solution. The supply of reactant or dopant gases is also frequently used in liquid phase epitaxy as mentioned in Chapter 8.

Decomposition resulting in a volatile crystal component occasionally has been used to grow bulk crystals or crystalline layers from high-temperature solutions. As an example, DeVries (1966) was able to control the decomposition of molten CrO_3 at medium oxygen pressures in order to grow thin layers of CrO_2 epitaxially on various substrates. Another example is the crystallization of the highly refractory uranium monosulphide (M.P. $2460^\circ C$) by decomposition of uranium disulphide (M.P. 1560°) at 1700 – 1900° in tungsten crucibles, as reported by Van Lierde and Bressers (1966).

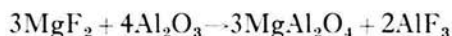
Complex systems have been used by Von Philipsborn (1967, 1969) and by Von Neida and Shick (1969) and Shick and Von Neida (1971) to grow a variety of chalcogenide spinels by VLRS technique. Von Philipsborn (1971) reviewed crystal growth of chalcogenide spinels of which it is difficult to obtain crystals larger than 5 mm. Another example of the VLRS mechanism is the growth of NiO whiskers from molten nickel (Ahmad and Capsimalis, 1967).

An interesting modification of the VLRS mechanism has been proposed by Wagner (1968) and named SLV growth: by a reaction $B + 2HX \rightarrow BX_2 + H_2$ volatile BX_2 is removed from the solution of A in B so that A crystallizes.

(c) *Technique of shifting chemical equilibria.* According to the law of mass action (which in its ideal form only holds for dilute solutions) of Guldberg and Waage (1867) solution equilibria are shifted when a volatile component is vaporizing. This shift in equilibrium may be used to crystallize compounds which otherwise would not precipitate. This source of supersaturation was already known in the 19th century, and Morozewicz (1899) expressed the temperature-dependent relationship



Dugger (1966, 1967) reported on a "new hydrolysis technique" which, however, must be a shifting equilibrium technique when one analyses the experimental conditions. Large amounts of water which would be required to grow $MgAl_2O_4$ crystals by hydrolysis could not be present in a molybdenum crucible containing BaF_2 , MgF_2 and Al_2O_3 , which was heated at $900^\circ C$ in vacuum and then heated up to $1650^\circ C$ for three hours in a helium atmosphere. Thus hydrolysis cannot have taken place. It is much more probable that according to the equation



aluminium fluoride with a boiling point of $1537^\circ C$ was evaporated and the chemical equilibrium shifted to cause the precipitation of $MgAl_2O_4$.

This mechanism of shifting chemical equilibrium should be applied more often to grow other crystals of highly refractory compounds. On the other hand the growth temperature is relatively high which is disadvantageous both from the experimental point of view and because of the higher concentration of defects.

Another technique of shifting chemical equilibria which apparently has not been used in flux growth is based on the so-called "salting-out effect" where a more soluble compound dissolves and so precipitates the required phase. The isothermal solution mixing technique of Woodall (1971), which

was used to grow multiple-layer films (see Section 8.4.4), is a further example of growth by shifting equilibria. As illustrated in Fig. 8.13, solutions of Ga/Al/As of different composition may be mixed isothermally to produce a supersaturated composition from which a $\text{Ga}_{1-x}\text{Al}_x\text{As}$ solid solution precipitates.

(iv) *Vapour-liquid-solid (VLS) mechanism.* In general the VLS growth mechanism is one by which the solute is transported in the vapour phase prior to dissolution in the solvent and subsequent crystallization. It therefore differs from other transport techniques only in that the solute is initially transported as a vapour rather than by dissolution of nutrient material. Although this technique has been applied to the growth of bulk crystals and films, its initial application was in the growth of whiskers and the main emphasis in VLS growth has remained in this area.

The use of the VLS mechanism was first reported by Wagner and Ellis (1964, 1965) who produced whiskers of silicon up to 0.2 mm in diameter on dots of gold which were deposited on a silicon crystal. At temperatures above the eutectic, the gold dissolves the substrate and preferentially removes the relatively imperfect regions. The liquid can absorb material from the vapour readily so that the surface droplet becomes supersaturated and crystalline material is deposited. As growth proceeds, the liquid droplet remains at the end of the filament which may grow at a rate of about $1\text{ }\mu\text{m/min}$. A solidified droplet may be seen at the end of the CaB_6 whisker (Rea and Kostiner, 1971) which is shown in Fig. 7.21. The whiskers are of high quality and are often free from dislocations. The uniformity may also be very good although thickening may occur by direct deposition from the vapour at steps on the lateral faces.

A crystalline substrate is not essential for whisker growth since supersaturation will still occur due to absorption from the vapour. As dissolution from the vapour continues, crystals will nucleate and will tend to grow as needles. In the experiments of Frosch (1967) needles were grown on the wall of the container where wet hydrogen was passed over adjacent crucibles containing GaP and Ga, respectively. The characteristic solvent droplet (in this case gallium) was found at the end of most needles. Schönherr (1971), however, disputes the effectiveness of the VLS mechanism in the growth of GaP whiskers by transport in wet hydrogen since growth was observed to cease when a whisker became covered with a Ga droplet.

Wagner (1967) has discussed the perfection of silicon whiskers grown by VLS and demonstrated that the branching and kinking, which is frequently observed, results from lateral driving forces. Temperature gradients along the substrate surface are particularly effective in producing such phenomena. Occasionally whiskers of very complex shape have been



Fig. 7.21. VLS growth demonstrated by the solidified droplet at the end of CaB_6 whiskers (Rea and Kostiner, 1971).

produced by the VLS mechanism, for example the continuous coils and spirals of ZnS and GaAs observed by Addamiano (1971).

Quite a wide variety of materials have now been grown by the VLS technique, either deliberately or by accident. Examples are given in Table 7.7. In addition, some interesting experiments were reported by Givargizov and Sheftal (1971) in which composite whiskers were grown, for example of silicon and lanthanum hexaboride in alternate sections.

The methods used to transport the vapour depend on the material crystallized and correspond in general to those used for chemical transport reactions and vapour phase epitaxy. Silicon, for example, may be transported by direct sublimation which has the advantage that impurities from the carrier gas are avoided. A transporting gas such as HCl or $\text{H}_2/\text{H}_2\text{O}$ is normally preferred particularly for such materials as GaAs and GaP . The carrier gas should have a very low solubility in the solvent or, if this solubility is appreciable, should be rejected from the growing crystal. Doping of the whiskers during growth may be effected by admixtures to the vapour phase.

Few quantitative studies of whisker growth have been presented, a notable exception being that of Bootsma and Gassen (1971) who studied

TABLE 7.7. Materials Grown by the VLS Method

Material	Solvent	Form	Size	Reference
C (diamond)	Ni, Fe, Mn	Whiskers	$130 \times 50 \mu\text{m}$	Derjaguin <i>et al.</i> (1968)
CaB_6	?	Whiskers	$100 \times 20 \mu\text{m}$	Rea and Kostiner (1971)
GaAs	Au, Pd, Pt	Whiskers	—	Barns and Ellis (1965)
GaP	Ga	Whiskers	—	Holonyak <i>et al.</i> (1965)
GaP	Ga	Bulk crystals	$20 \times 1\text{--}2 \text{ mm}$	Ellis <i>et al.</i> (1968)
NiBr_2	Cu, Co, Mn, Fe	Whiskers	—	Sickafus and Barker (1967)
$\text{Pb}_{1-x}\text{Sn}_x\text{Te}$		Bulk crystals	$60 \times 9 \text{ mm}$	Mateika (1971)
Se	Tl	Whiskers	—	Keezer and Wood (1966)
Si	Au	Whiskers	$200 \mu\text{m}$ dia	Wagner and Ellis (1964)
Si	Au	Film	$15 \mu\text{m}$ thick	Filby and Nielsen (1966)
SiC	Ni	Film	$20 \mu\text{m}$ thick	Berman and Comer (1969)
SiC	Si etc.	Whiskers	—	Berman and Ryan (1971)

the growth of silicon and germanium whiskers using silane (SiCl_4) and germane (GeCl_4) decomposition, respectively. These authors found evidence to support the validity of the VLS mechanism and concluded that the decomposition at the vapour-liquid interface is rate determining rather than the solid-liquid interface mechanism.

VLS may also be used for the growth of bulk crystals but again few examples are available. Ellis *et al.* (1968) investigated the growth of GaP crystals in gallium metal with transport by wet hydrogen from a GaP source. Needle-shaped crystals up to 2 cm in length and 1–2 mm in cross-section were grown in an hour but many crystals exhibited twinning, branching or even curvature. Tiller (1968) proposed the use of VLS for the growth of a number of compound semiconductors in the convection-free cell which is shown in Fig. 6.19.

The largest crystals grown to date by the VLS method are probably those of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ solid solutions reported by Mateika (1971). Crystals up to 60 mm in length and 9 mm diameter have been prepared by a specific drop technique but it should be mentioned that the liquid in this case is not a solution but a melt of the same composition as the growing crystal.

For the growth of epitaxial layers, transport of solute constituents including dopants in the vapour phase may be convenient and the technology of vapour transport, particularly of semiconductors, is well established. The use of a thin layer of solution rather than a bulk liquid is discussed in Section 6.3 where reference is made to the potential value of this arrangement for fast stable growth. If the problem of the stability of a

thin surface layer can be solved, this arrangement could well become an important mode of application of the VLS technique.

Activity in whisker growth by VLS appears to have declined since 1970–71 but the versatility of the VLS technique makes it a useful tool which may be used to tackle otherwise difficult materials problems.

(v) *Electrolytic growth.* The use of electrolysis in the growth of crystals from high-temperature solution is analogous to its use for electro-deposition of metals except that in the latter case precautions are normally taken to avoid the formation of large crystals. The crystals grown by electrolysis have, however, not normally been of metals but of transition metal oxides such as MoO_3 . The essential characteristic of electrolytic growth is that oxidation or reduction occurs at the electrodes and many applications of interest yield crystals in which the valence of a constituent element differs from that of its ions in the solution.

Typical experimental arrangements for electrolytic crystal growth, based on the designs of Kunnmann and Ferretti (1964) and of Rogers *et al.* (1966) are shown in Fig. 7.22(a) and (b). In the latter arrangement a central cathode carries a seed crystal (crystallization alternatively proceeds on the wire itself) which is inserted into an inner cell. The crucible wall is used as an anode so that the separation of the cathode and anode compartments prevents re-oxidation of the crystal by the gas evolved at the walls. The inner cell is mounted on a ceramic support which also provides thermal insulation and growth normally proceeds isothermally at low current densities, typically around 10 mA/cm^2 . Holes in the cell partition permit the flow of ions in the solution but prevent the flow into the growth region of crystallites of undissolved nutrient material which may be present in the outer cell. A similar cell to that shown in Fig. 7.22(b) is described by Perloff and Wold (1967), who used an alumina crucible. The cell actually shown was used in attempts to grow Fe_3O_4 crystals from a solution of Fe_2O_3 in $\text{BaO}/0.62\text{B}_2\text{O}_3$.

According to the review of Kunnmann (1971), electrolytic crystallization may be performed in three ways—direct electrochemical decomposition of the solvent, electrochemical decomposition of a solute in an inert solvent, or by the use of electrochemical transport phenomena. The latter alternative could in principle be applied to any material which may be dissolved and subsequently recrystallized electrochemically but no examples of its use are known to the authors. The distinction between the first and second techniques is not always clear but many experiments may be considered in the first category. As an example, MoO_3 has been crystallized up to $7 \times 3 \times 2 \text{ mm}$ in size by reduction of $\text{K}_2\text{O}/\text{MoO}_3$ and $\text{Na}_2\text{O}/\text{MoO}_3$ melts at about 600°C (Wold *et al.*, 1964; Perloff and Wold, 1967). The process involves a reaction of the form

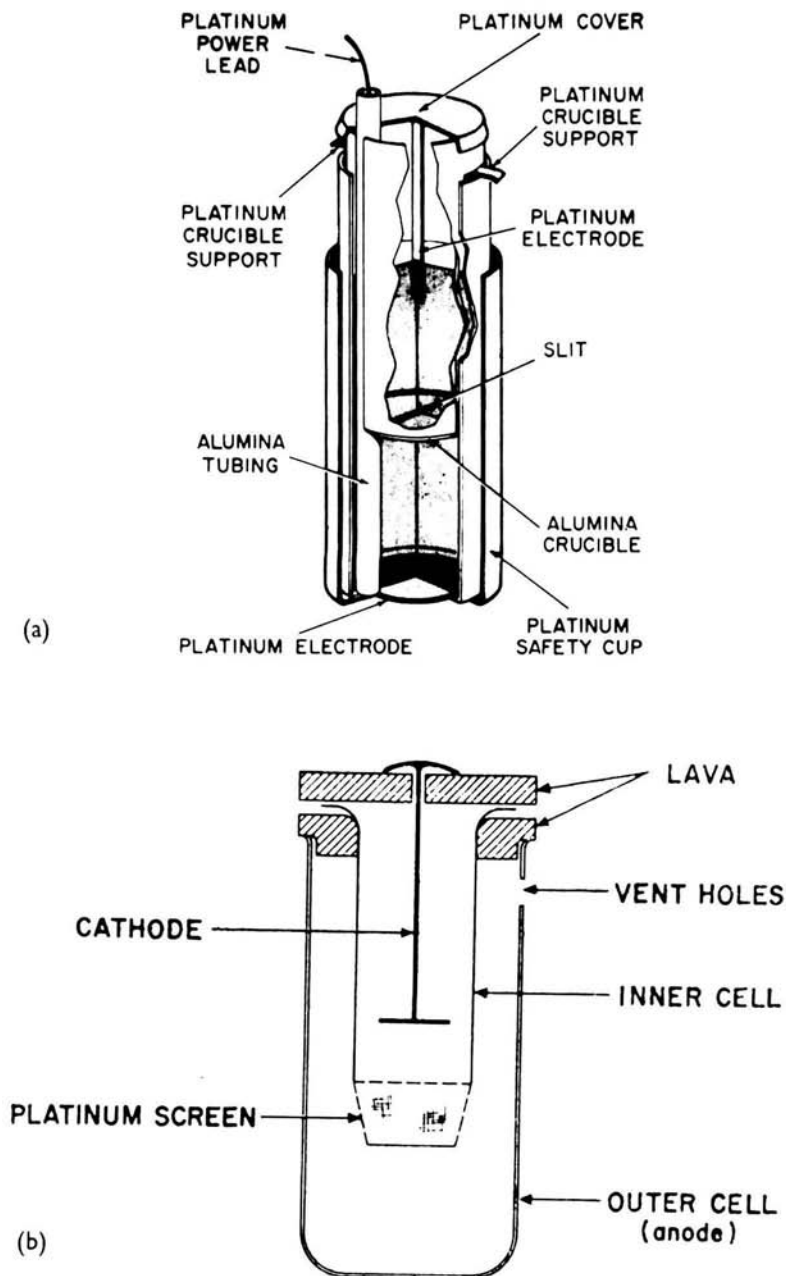
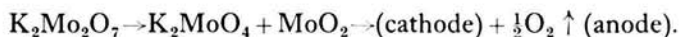
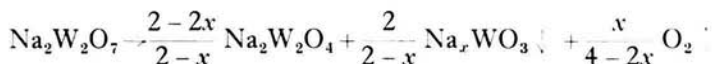


FIG. 7.22. (a) Cell for crystal growth by electrolysis of fluxed melts (Kunnmann and Ferretti, 1964). (b) Platinum double cell for electrolysis (Rogers *et al.*, 1966).



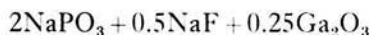
The so-called sodium tungsten bronzes, which are highly conducting oxides of composition Na_xWO_3 , may be similarly prepared by reduction of sodium tungstate fluxes:



Reactions of this type suffer from the disadvantage that the composition of the liquid, and therefore possibly of the crystal, changes continuously as growth proceeds.

The most successful attempt to grow crystals by electrolytic decomposition from an "inert" flux was probably the crystallization of $\text{Co}_{1+x}\text{V}_{2-x}\text{O}_4$ spinels from sodium tungstate fluxes by Rogers *et al.* (1966). The description of the dissolution and crystallization process in terms of Lewis acid-base theory is given in Section 3.7.1. The general idea is that the basicity of $\text{Na}_2\text{W}_2\text{O}_7/y\text{Na}_2\text{WO}_4$ solvents increases directly with the value of y ; if the solute can be considered as a solid solution A_2B_{1-z} of components A and B which differ in their basicity, then the value of z of the crystallizing phase will be determined by the value of y of the solvent. In the growth of $\text{Co}_{1+x}\text{V}_{2-x}\text{O}_4$ spinels, electrolytic reduction of V^{5+} to V^{4+} and V^{3+} is required and the value of x was found to depend upon the solvent composition in agreement with the principles outlined above.

Cuomo and Gambino (1970) have proposed the use of electrolysis for crystal growth and epitaxial deposition of compound semiconductors. They demonstrated that, for example, gallium phosphide could be deposited on a silicon substrate from a melt of composition



at 800°C. A current of 50 mA/cm² was employed and a 100 μm layer was deposited in twenty hours.

In principle a great variety of borides, carbides, germanides, etc. may be prepared by electrolytic reduction of melts containing the corresponding oxidized form—borate, carbonate, germanate, etc.

Many preparations of such compounds from halide solutions were reported by Andrieux and co-workers (Andrieux, 1929; Andrieux and Weiss, 1948; Andrieux and Marion, 1953). These syntheses are normally performed at very high current densities and may therefore yield metastable phases. Kunnmann (1971) has reported attempts to reproduce the experiments at low current densities and finds that these are successful in over half the examples considered. Although preparations of this kind are the subject of a not inconsiderable number of patent applications, further

study appears necessary before the reproducible growth of crystals of good size and quality can be achieved.

7.1.3. Preparation of solid solutions and homogeneously doped crystals

Many of the materials of interest for devices or for academic studies are solid solutions or contain dopants which are added in order to produce a desired change in some property. The ability to vary the composition of a crystal is clearly an extremely powerful tool for the materials scientist and the concept has been developed of molecular engineering—tailoring a material to meet a specific set of properties by the addition of controlled quantities of dopants to some suitable host-crystal. The difference between a solid solution and a doped crystal is mainly one of degree, although the term “solid solution” is restricted to members of an isostructural series whereas dopants may differ in structure and even in valence from the host. However, the chromic oxide which is added to alumina to produce the characteristic red colour of ruby would normally be referred to as a dopant, whereas a compound $\text{Al}_{1.8}\text{Cr}_{0.2}\text{O}_3$ would be termed a solid solution between Al_2O_3 and Cr_2O_3 . In the preparation of solid solution crystals it is of great importance that the properties should not vary significantly throughout the material, which implies that the composition should be uniform.

There are two types of concentration variation which normally concern the experiments: the relatively long range variation due to a change in the solution composition or growth temperature or growth rate as the crystal grows, and short range variations due to transients within the solution. Time-dependent effects have been treated by Slichter and Burton (1958) who consider the changes in concentration due to a step-function change in the melt concentration and to sinusoidal variations in the growth rate. The latter fluctuations normally lead to the periodic variations in composition termed *striations* (see Section 9.2.4). In crystals pulled from the melt the dopant concentration frequently exhibits a radial variation due to flow effects not associated with crystal rotation, such as thermal convection or crucible rotation (Carruthers, 1967). The major cause of striated dopant distributions in melt growth and probably in solution growth is oscillatory variation of the temperature (Hurle, 1966, 1967; Hurle *et al.*, 1968). The relation between striations and composition in solid solutions is well illustrated by Fig. 7.23, in which the Ta/Nb ratio in crystals of nominal composition $\text{KTa}_{0.64}\text{Nb}_{0.36}\text{O}_3$ is compared with the optical absorption (Whiffin, 1973). In the diagram, contrast between the bands is maximized by arrangement of crossed polars, and the Ta/Nb ratio is determined by electron microprobe.

Striations may be eliminated if temperature oscillations can be suppressed, as is discussed in Section 9.2.4. The use of artificially induced

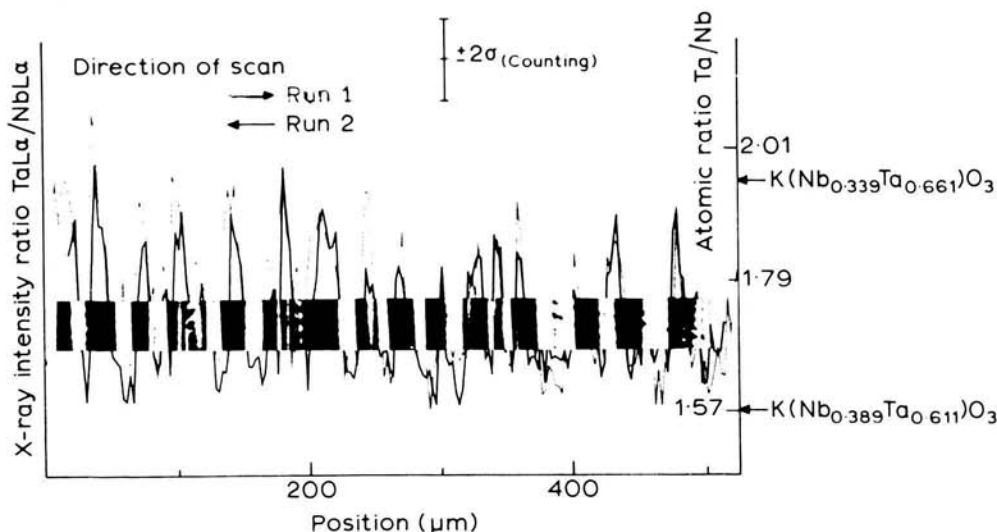


FIG. 7.23. Striations in a $K(\text{Ta}, \text{Nb})\text{O}_3$ crystal indicated by electron microprobe measurements and an overlaid transmission photograph of the crystal taken in polarized light (Whiffin, 1973).

striations as a means of determining the instantaneous growth rate as suggested by Witt and Gatos (1969) is a potentially valuable tool for the investigation of segregation in crystals grown from high-temperature solution. The interesting technique of Mateika (1971) of producing large homogeneous crystals of solid solutions from the melt with a vapour source has been mentioned in Section 7.1.2 (C.iv). The problem of avoiding relatively long range variations in flux growth will be treated in this section.

Distribution coefficient. The incorporation of an impurity into a crystal may be characterized by a *distribution coefficient* k which is defined as the ratio of the concentration of the dopant in the solid to that in the liquid. It is possible to define three distribution coefficients:

- the equilibrium coefficient $k_0 = n_s/n_{sn} (\tau = 0)$
- the interface coefficient $k^* = n_s/n_{sn} (z = 0)$
- the effective coefficient $k = n_s/n_{sn} (\tau \neq 0)$

where n_{sn} is the concentration of the dopant in the solution and n_s that in the solid.

The value of k_0 may be determined from the phase diagram. Thurmond and Struthers (1957) have given an expression of the form

$$\ln k_0 = \frac{\Delta H_F' - \Delta H_M'}{RT_M} - \frac{\Delta H_F'}{RT_m'} - \frac{\Delta H_F' - \Delta N_M'}{\Delta H_F} \ln(1 - X), \quad (7.5)$$

where ΔH_F is the enthalpy of fusion of the solvent of melting point T_m , $\Delta H_F'$ and $\Delta H_M'$ the enthalpy of fusion and mixing respectively of the solute, which melts at temperature T_M' , and X the fractional concentration of solute. Values of k_0 for a wide variety of crystals and dopants have been tabulated by Kröger (1964) and by Brice (1973).

Kamenetskaya (1967, 1968) has calculated the change in composition of solid-solution crystals nucleating in a two-component liquid by considering the changes in free energy. This theory may be used to estimate the variation in the concentration of solvent molecules present substitutionally in the crystal but does not refer to the more usual situation in solution growth where the solvent is rejected by the crystal.

In general the effective value of k will differ from k_0 and a relatively simple relation which has been widely applied was derived by Burton, Prim and Slichter (1953), namely

$$k = \frac{k_0}{k_0 + (1 - k_0) \exp(-\tau \delta / D)} \quad (7.6)$$

According to this equation, k will tend to k_0 at low values of τ (and δ) and to unity at high values of growth rate. In practice τ often varies inversely as δ , for example as the crystal rotation rate is changed, so that k will vary mainly through its dependence on k_0 and D unless growth occurs mainly under kinetically limited conditions where this inverse dependence does not apply.

Equation 7.6 is derived by solving the time-independent differential equation for solute flow in the usual boundary layer approximation. Earlier treatments of the segregation of dopants have been given by Hayes and Chipman (1939) and by Wagner (1950), the latter considering the effects of natural convection in addition to convection by the rotating crystal. A review of segregation including reference to its importance in purification has been given by Pfann (1966).

The Burton-Prim-Slichter equation is valid only so long as $k^* \simeq k_0$. If this condition is not met, a correction may be applied by considering the solute concentration in an adsorbed surface layer. Trainor and Bartlett (1961) considered the build-up of impurities due to the propagation of steps across the surface at a rate τ_{st} and arrived at a relation

$$k^* = k_0 [1 - \tau_{st} / \{\beta D_i (1 - k_0) \tau_s / \tau_i\}]^{-1}, \quad (7.7)$$

in which D_i is the surface diffusion coefficient of the impurity, τ_s / τ_i the ratio of sticking times of solvent and impurity on the surface and β a function which depends on the growth rate and the rate of impact of impurity atoms.

An alternative approach to the same problem has been used by Kröger (1964). By combining Eqn (7.6) with a theory due to Hall (1952, 1953), he arrives at an expression

$$k = \frac{k_0 + (k_{ads} - k_0) \exp(-v_{deads}/v)}{1 - \{1 - \exp(-v\delta/D)\} \{1 - k_0 - (k_{ads} - k_0) \exp(-v_{deads}/v)\}} \quad (7.8)$$

where v_{deads} is the rate of transfer of impurity atoms from the surface layer to the solution and k_{ads} is the distribution coefficient for adsorption into this layer. Equation (7.8) reduces to the Burton-Prim-Slichter equation if $k_{ads} = k_0$ and, while it is clearly of wider applicability, its value is reduced by the difficulty of predicting values of k_{ads} and v_{deads} .

Examples of distribution coefficient measurement. Measurements of the distribution coefficient in solution growth should be treated with caution since in some cases the dopant may be present in minute inclusions rather than substitutionally in the crystal lattice. This is particularly the case when the dopant is a constituent of the solvent, and some examples where high values of distribution coefficient may have such an origin are discussed in Chapter 9. If the dopant has a valence which differs from that of the host lattice, the distribution coefficient will depend strongly on the presence of charge compensating ions. The theory of coupled substitution of ions of unlike valence has been considered by Millett *et al.* (1967), who determined the distribution coefficients of lithium and chromium in zinc tungstate pulled from the melt, using radioactive chromium (see Section 3.6.2).

Rare earth ions in $Y_3Al_5O_{12}$: Rare-earth doping of yttrium aluminium garnet is of practical importance in connection with the application of these materials as lasers. Monchamp *et al.* (1967) found a regular dependence of the distribution coefficient on the size of the ionic radius of the rare-earth ion. The value of the distribution coefficient was found to vary with increasing rare-earth ionic radius from 1.9 for Tm to 0.25 for Pr for growth from a PbF_2/B_2O_3 flux. An alternative and closely related plot was given by Van Uitert *et al.* (1970) who plotted the distribution coefficient of Y^{3+} in $(Y, R)_3Al_5O_{12}$ (R = rare earth) solid solutions and showed that the logarithm of this coefficient varies linearly with the Espinosa ionic radii of the R^{3+} (Fig. 7.24). Also shown in Fig. 7.24 is the distribution coefficient of Pb in orthoferrites grown from PbO/B_2O_3 fluxes.

The distribution coefficient of rare-earth ions in garnets depends on the crystal facet into which substitution occurs, as was demonstrated by Wolfe *et al.* (1971).

Gallium in $Y_3Fe_5O_{12}$: The saturation magnetization of yttrium iron garnet is too high for several applications, for example in microwave devices and for bubble domain memories. Gallium substitution is

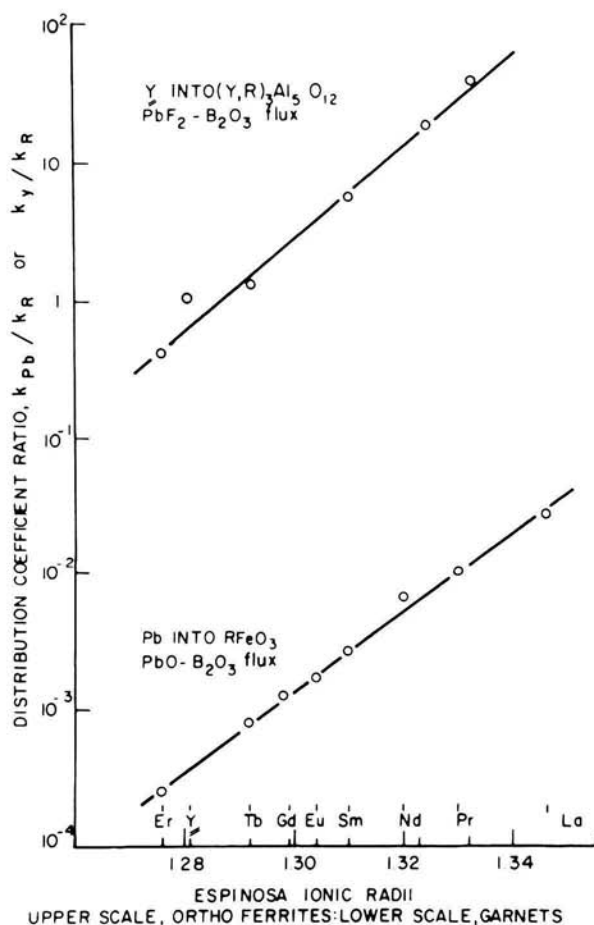


Fig. 7.24. Distribution coefficient ratios k_Y/k_R and k_{Pb}/k_R versus radii of rare-earth ions R, for Y entering the garnet (upper line) and for Pb entering rare-earth orthoferrites (lower line) (after Van Uitert *et al.*, 1970).

frequently employed as a means of reducing the magnetization and uniformity is often very important. The distribution coefficient of Ga in $Y_3Fe_5O_{12}$ grown from PbO/PbF_2 solvent was measured by Nielsen *et al.* (1967). These authors defined a coefficient in terms of the fractional concentration of gallium, that is

$$k' = \frac{\frac{\text{moles Ga}_2\text{O}_3}{\text{moles Ga}_2\text{O}_3 + \text{moles Fe}_2\text{O}_3} \text{ in crystal}}{\frac{\text{moles Ga}_2\text{O}_3}{\text{moles Ga}_2\text{O}_3 + \text{moles Fe}_2\text{O}_3} \text{ in solution}}.$$

The value of k' was found to be in the region of 2.0 and to vary only slowly with temperature and with the absolute Ga concentration. A large change was found to result from the preferential evaporation of PbF_2 from imperfectly sealed crucibles and the resulting variation in magnetization throughout the crystal is plotted in Fig. 9.6(a). When sealed crucibles were used a much more uniform gallium distribution was observed, since the temperature variation in k' compensates for the change in gallium concentration in the solution as growth proceeds.

Makram *et al.* (1968) also reported the preparation of solid solutions of $\text{Y}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ by slow cooling from lead salt solvents. In their experiments a high pressure of oxygen was used to suppress solvent evaporation. The value of k' was found to be about 1.7. Large inclusion-free and homogeneous crystals of the same solid solution were also grown by Scheel (1972) using accelerated crucible rotation and sealed crucibles.

Distribution coefficients for Ga have also been measured in magnetic garnet films grown by liquid phase epitaxy. Giess *et al.* (1972) found values of 1.94–1.74 for a linear growth rate of $0.98\text{--}5.18 \times 10^{-6} \text{ cm s}^{-1}$ at 980° for solid solutions $\text{Y}_{2.4}\text{Eu}_{0.6}\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ grown from $\text{PbO--B}_2\text{O}_3$. These values are in good agreement with the 1.96–1.76 reported by Blank *et al.* (1973) between 1065° and 918°C . Blank and Nielsen also measured the distribution coefficient in $\text{Y}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ solid solutions and noted that their values of 2.26–2.09 between 1077° and 879°C were within 10% of the values found in bulk crystals. Data for gallium distribution coefficient as a function of temperature for $\text{Y}_{2.7}\text{Gd}_{0.3}\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ films are reported by Janssen *et al.* (1973) who used a radio-isotope labelling technique. These values range from $k' = 2.0$ at 1000°C to $k' = 1.4$ at 780°C and are therefore in general agreement with the data of other groups.

In general, however, distribution coefficients in films grown by LPE will depend upon the mismatch between the film and the substrate. This dependence is illustrated clearly for Pb and Bi incorporation into garnet films by Robertson *et al.* (1975). Robertson *et al.* (1974b) have also noted that the Pb concentration may be much higher in the initial stages of growth than in subsequent growth of the film and this variation should be taken into account when any results of distribution coefficients in epitaxially grown films are quoted.

Experimental methods. Of the methods available for the preparation of homogeneous solid solutions, the most widely used are the gradient transport techniques. These have the advantage that growth occurs isothermally and, even if the distribution coefficient differs appreciably from unity, there will be equilibrium between the growth and dissolution rates of the various constituents provided that growth does not occur too

rapidly. The success of the gradient transport method in the preparation of solid solutions of composition $\text{Y}_3\text{Fe}_{5-x-y}\text{Ga}_x\text{Al}_y\text{O}_{12}$ by Linares (1965) is discussed in Section 9.2.4 (see Fig. 9.14). Other examples of the application of gradient transport to grow homogeneous solid solutions are $\text{InAs}_{1-x}\text{Sb}_x$ (Stringfellow and Greene, 1971—see Section 8.4.1) and $\text{Y}_{3-x}\text{Nd}_x\text{Al}_{5-y}\text{Cr}_y\text{O}_{12}$ (Timofeeva *et al.*, 1969). In the latter case the improved homogeneity compared with crystals grown by slow cooling was confirmed by electron probe microanalysis.

Tolksdorf and Welz (1972) have developed apparatus in which the gradient transport method is used in combination with seeding by the Bennett-Tolksdorf technique (Section 7.1.1) and with stirring by Scheel's accelerated crucible rotation (Section 7.2.7). In the initial stage shown in Fig. 7.15(a), the solution is saturated, and spontaneous nucleation might occur. The crucible is then inverted as in Fig. 7.15(b) with the temperature maintained constant but with a "cool finger" brought into contact with the region immediately below the seed crystal. The nutrient material is supported on a perforated baffle and is in contact with the solution so that dissolution may occur, and the transport of solute across an adverse temperature gradient is enhanced by accelerated crucible rotation. The homogenizing effect of the stirring action is particularly valuable in this case. After growth has occurred for the required period, typically a few days, the crucible is reinverted and the solution runs off the crystal as in Fig. 7.15(c).

In such experiments, where solid solution crystals are grown on a seed which is an end member of the series (e.g. $\text{Y}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ on $\text{Y}_3\text{Fe}_5\text{O}_{12}$) defects can arise because of the lattice mismatch between the seed and the crystal. A solution to this problem was suggested by Chicotka (1971) which can be applied to certain cases such as the growth of $\text{Ga}_{1-x}\text{In}_x\text{P}$ crystals on a GaP seed. If crystallization occurs initially at a relatively high temperature, the composition of the phase deposited is close to that of GaP. The temperature is then lowered with the solution in contact with nutrient material, and the crystal composition becomes progressively richer in indium as growth occurs by slow cooling. When the temperature has been lowered to that corresponding to the terminal composition, cooling is stopped and subsequent growth occurs by gradient transport. In this way the composition of the crystal is changed gradually and an abrupt change in lattice parameter is avoided.

The travelling solvent zone method (Section 7.1.2. CII) may similarly be used to prepare homogeneous crystals, provided that growth conditions are isothermal. DiBenedetto and Cronan (1968) were able to prepare very homogeneous crystals of $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ by the slow passage of a $\text{PbO/SrO/B}_2\text{O}_3$ solvent zone through the source material. The solvent

composition was found to be critical for the growth of homogeneous crystals.

If polythermal methods are used the resulting crystals will normally be inhomogeneous and any exceptions to this rule require rather unusual conditions. In attempting to grow $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ crystals from PbO solution, Manzel (1967) determined the separate solubilities of NiFe_2O_4 and ZnFe_2O_4 and selected a temperature range over which the slope of the solubility curves was the same for both components. This condition will not, however, always result in homogeneity since the competing ions may have very different probabilities of incorporation into the crystal lattice.

Since according to Eqn 7.6 the interface distribution coefficient will depend upon the growth rate and the thickness of the boundary layer, it is possible in principle to prepare homogeneous solid solutions by programming growth in such a way that kinetic effects are used to compensate for the temperature dependence of the equilibrium distribution coefficient. This programming may be effected by changing the cooling rate, and hence the growth rate, or by a variation in the degree of stirring which will affect the boundary layer thickness. This type of procedure has not yet been attempted, so far as the authors are aware.

Homogeneous solid solutions may also be prepared by many of the reaction techniques described in Section 7.1.2C. Such reactions normally occur at constant temperature and the composition of the crystal grown will mainly depend upon the rate of arrival at the interface of the reactants. Since the transport rate of the various reactants may be varied independently in, for example, growth by the method illustrated in Fig. 7.20(b), the composition may be maintained constant once a steady state has been established.

Luzhnaya (1968) discusses several examples of the preparation of solid solutions from metallic solvents. The majority of the compounds listed are solid solutions of the III-V semiconductors, such as $\text{GaSb}_{1-x}\text{P}_x$. Stambaugh *et al.* (1961) utilized programming of the vapour pressure above the melt to prepare solid solutions of $\text{Ga}_{1-x}\text{Al}_x\text{As}$ and $\text{Ga}_{1-x}\text{In}_x\text{P}$. This method relies on the introduction into the melt of the more volatile metallic species by transport in the vapour phase. The crystals grown in these experiments were not homogeneous but the use of the VLS mechanism does provide an alternative means of achieving homogeneity if the vapour pressure is suitably adjusted. This method was in fact used by Rodot *et al.* (1968) who supplied phosphorous and arsenic from separately heated ampoules to prepare homogeneous crystals of $\text{GaAs}_{1-x}\text{P}_x$ from gallium solution.

Several examples of characterization of solid solution crystals are discussed in Chapter 9 where methods of studying homogeneity are treated.

7.1.4. Preparation of special modifications and of metastable phases

In general those phases crystallize from high-temperature solutions which are thermodynamically stable. In the following a few examples will be given of the growth of special modifications stabilized by trace impurities and of the growth of metastable phases. Mineralogists are familiar with the fact that rutile is the only stable modification of pure TiO_2 and that anatase and brookite are modifications which are stabilized by trace impurities. Similarly tridymite is a form of SiO_2 which is stabilized by alkali ions and which is not a modification of pure silica as was shown by Flörke (1955).

Similarly four modifications of sodium disilicate have been prepared by Hoffmann and Scheel (1969) from $\text{Na}_2\text{Si}_2\text{O}_5$ glass on a variety of metal oxide pellets, the metal oxides having either a chemical or an epitaxial effect on the crystallization of the various $\text{Na}_2\text{Si}_2\text{O}_5$ modifications. As an example of the effect of impurities on the crystallization behaviour of alloys the compound Al_3Er may be mentioned which crystallizes in the cubic AuCu_3 type unless traces of silicon (less than 10^{-2} wt%) are present in which case a rhombohedral form of Al_3Er crystallizes (Meyer, 1970). Thus if a modification cannot be crystallized in its stability region, the influence of epitaxy and trace impurities is worth investigating. The effect of solvents on the crystallization of carbon as diamond or graphite is discussed in Section 3.7.3.

Metastable phases occasionally grow in the stability field of an other phase when its nucleation and growth is facilitated, for instance by providing seed crystals. Thus Roy and White (1968) claim to have grown cm-size quartz-type GeO_2 crystals on substrates of natural quartz from high-pressure solutions, and propose the use of high-pressure solution growth technique at relatively low temperatures for growth of metastable phases.

It was shown by Scheel (1968) that in cases where a system is far from equilibrium metastable phases can be grown. In the example given, crystals of up to 2 mm length of the metastable β -quartz phase of the composition $\text{MgAl}_2\text{Si}_3\text{O}_{10}$ were grown from a glass of that composition in the presence of a small amount of lithium tungstate flux in the temperature range $600^\circ\text{--}800^\circ$ whereas higher temperatures or long heating resulted in crystallization of the thermodynamically stable cordierite phase. According to Ostwald's step rule the less metastable quartz-phase crystallizes from a metastable glass quenched from high temperatures (and having still the high-temperature structure) until finally the stable cordierite phase is formed. The crystallization of metastable phases from glasses is a common phenomenon, and accordingly one would expect that metastable phases could also be crystallized from viscous high-temperature solutions, when

the system is far from equilibrium. Similarly from systems which allow high supersaturation of the stable phase, crystals from another phase (which might be thermodynamically unstable) might form if seeds of the required phase or a substrate which allows epitaxial overgrowth are provided. As discussed in Section 3.8.5. and by Blank and Nielsen (1972) a rare-earth garnet $\text{PbO}-\text{B}_2\text{O}_3$ solution can be saturated with respect to rare-earth orthoferrite and supersaturated with respect to garnet, simultaneously, thus explaining the growth of phases in a metastable field.

The importance of seeds for the growth (reproduction) of the various polytypes of silicon carbide has been demonstrated by Knippenberg and Verspui (1966) although in this case the degree of "metastability" as deducible from differences in free energy is expected to be very small for the SiC polytypes (Knippenberg, 1963).

7.1.5. Growth of compounds with defined valence states

The great majority of HTS growth experiments yield materials in which the ions are in "normal" valence states, so that the atmospheric conditions need not be closely specified. So, for example, most crystal growth from molten salt solutions occurs in an air ambient and crystallization from metallic solutions takes place under hydrogen or an inert gas. Many examples are known, however, where materials having ions in relatively unusual valence states have been prepared from HTS or where special conditions have been used in order to produce material of high stoichiometry. The techniques which are available for such preparations may be broadly divided into three groups: (i) electrolytic growth, (ii) the use of a solvent of controlled oxidizing or reducing power, (iii) the use of controlled atmospheres.

Crystal growth by electrolysis is discussed in Section 7.1.2 where the examples are discussed of MoO_2 and the sodium tungsten bronzes. Further examples of transition metal oxides with ions in reduced valence states are given in the table of Chapter 10, and it is likely that further applications of this technique will be made, for example to produce materials of higher than normal valence state, or to grow crystals of magnetic oxides with controllable concentrations of Fe^{2+} or Fe^{4+} .

Reference is also made in Sections 7.1.2 and 3.4.1 to examples where the oxidation state of transition metals may be influenced by the basicity of the solvent. In general, additional factors such as the solubility will have a major influence on the choice of a solvent, and atmosphere control provides a simpler means by which the valence state may be varied.

The use of atmosphere control in the crystallization of phases unstable in air at the growth temperature is discussed in some detail in Section 3.4.1. In that section the Magneli phases $\text{Ti}_n\text{O}_{2n-1}$, europium chalcogenides,

vanadium dioxide VO_2 and chromium-containing oxides are quoted as examples of materials which can be crystallized from high-temperature solution when the atmosphere is adjusted to the equilibrium range for the required phase.

Many other examples of materials, especially oxides, are known in which an atmosphere other than air is used in order to improve stoichiometry. Oxides containing iron are often difficult to prepare as single crystals with the iron in a single valence state, and considerable effort has been devoted to the preparation particularly of the ferrite spinels with negligible concentrations of Fe^{2+} . The equilibrium partial pressure of oxygen above these materials may be extremely high at temperatures near the melting point, and Ferretti *et al.* (1962) found that an oxygen pressure of nearly 120 atmospheres was required to prepare crystals of CoFe_2O_4 free from Fe^{2+} ions from a highly concentrated solution in NaFeO_2 at 1590°C . Such pressures require rather expensive autoclaves and the use of more easily realizable pressures at lower temperatures has been advocated by Makram and co-workers. Makram and Krishnan (1967) used an oxygen pressure of 15 atm. for the growth of garnet crystals from PbF_2/PbO by slow cooling from 1300 – 900°C . The application of a gas pressure can cause major changes in the nucleation and growth characteristics, particularly from the volatile lead solvents, so that the properties of the crystals grown may be changed by factors other than those associated with the variation in stoichiometry. Some complexities of yttrium iron garnet crystal growth under pressure have been discussed by Robertson and Neate (1972) and by Robertson *et al.* (1973). The work of the latter authors is of particular interest since the reproducible crystallization of only one crystal per crucible is reported under oxygen pressures in excess of ten atmospheres, as discussed in Section 7.1.1. Makram *et al.* (1968) reported that the gallium distribution in solid solutions of composition $\text{Y}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ was homogeneous when crystals were grown by slow cooling under an oxygen pressure of 15 atm.; they attributed this homogeneity to the absence of inclusions and voids in their crystal so that strained regions with locally high concentrations of Ga were avoided. However, the results of Nielsen *et al.* (1967) and Scheel (to be published) show that good homogeneity of the $\text{Y}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ crystals is achieved by prevention of PbF_2 evaporation and seems to be relatively unrelated to the mechanism suggested by Makram and co-workers.

The growth of nickel ferrite NiFe_2O_4 under oxygen pressure has been reported by Makram (1966) and by Robertson *et al.* (1969). In the latter experiments borate solvents were used and the application of oxygen pressures of only two atmospheres was found to increase markedly the concentration of flux inclusions.

7.2. High Temperature Technology

7.2.1. Furnaces

The discussion here of furnace design is necessarily brief, and detailed descriptions of laboratory and industrial furnaces may be found in various handbooks of physics and engineering and in the books of Campbell (1959), Smakula (1962), Wilke (1963, 1973), Otto (1958) and Brice (1973).

Of the various types of heating only resistance and induction heating are used, while heating by flames, plasmas, lasers, image techniques and by electrons has not found significant application in crystal growth from high-temperature solutions. Reactions between heating elements, insulating materials, crucibles, thermocouples, etc. are important in the design and use of high-temperature furnaces, and these aspects will be discussed in Section 7.2.3.

Resistance furnaces for flux growth are generally used up to 1600°C, while at higher temperatures induction heating by R.F. generators is preferred. However, the range of *resistance heating* can be extended by use of molybdenum, tungsten or graphite heating elements in neutral or hydrogen atmospheres or in vacuum, whereas in oxidizing atmospheres rhodium (up to 1800°C), zirconia or thoria may be used. The two latter have the disadvantages that they require pre-heating and that they need high power and are sensitive to thermal shock and to steep thermal gradients. Table 7.8 summarizes the properties of a few popular heating elements, of which Kanthal† A1, silicon carbide (Globar, Crusilite, Crystolon, Silit) and molybdenum disilicide (Kanthal, Super Mosilit) are most frequently used in flux growth.

Furnaces with Kanthal A1 and similar heating elements are readily available in many shapes, and also various types of heating elements and Kanthal A1 wire are available. It should be noted that metal-based heating elements such as Kanthal A1 become brittle after the first firing. The lifetime is long if corrosion is prevented and if the temperature does not exceed 1150°C for extended periods in the case of Kanthal A1.

Silicon carbide heating elements in the form of rods, tubes or spiral tubes are suitable for the construction of simple furnaces according to individual requirements. As thermal insulation a half brick (about 4½ inches) around the hot space is sufficient when a layer of 1 to 2 cm of ceramic wool or similar insulating material is placed between the bricks and the outer wall of, for example, asbestos. It is possible to connect the heating elements directly to the thyristors, but the latter should be adjustable according to the ageing of the SiC elements. (Usually compensation is provided for 100 to 500% increase of resistance, which tends to occur after one month

† Registered trademark by Bulten-Kanthal AB, Sweden.

TABLE 7.8. Properties of Heating Elements Most Frequently Used in Flux Growth

Heating element	Max. working temperatures ($^{\circ}\text{C}$)†	Atmosphere
Kanthal A1	1375 $^{\circ}$ (w), 1150 $^{\circ}$ (y)	air
Silicon carbide	1550 $^{\circ}$ (w), 1350 $^{\circ}$ (m), 1200 $^{\circ}$ (y)	(dry) air
Kanthal-Super ST	1700 $^{\circ}$ (w), 1600 $^{\circ}$ (m), 1500 $^{\circ}$ (y)	air‡
Kanthal-Super N	1700 $^{\circ}$ (w), 1600 $^{\circ}$ (m), 1500 $^{\circ}$ (y)	air‡
Kanthal-Super 33	1800 $^{\circ}$ (w), 1700 $^{\circ}$ (m), 1600 $^{\circ}$ (y)	air‡
Platinum	1550 $^{\circ}$ (m)	air
Rhodium	1800 $^{\circ}$ (w)	air
ThO ₂ (with La ₂ O ₃ or CeO ₂)	2000 $^{\circ}$ (w)	air
ZrO ₂ (stabilized)	2400 $^{\circ}$	air
Molybdenum	1800 (w), 2400	Vacuum or H ₂
Tantalum	2600 (w)	Argon or H ₂
Tungsten	2600 $^{\circ}$ (w)	Vacuum
	3000 $^{\circ}$ (w)	Argon
Graphite	2600 $^{\circ}$ (w)	Inert gas

† For estimated or experienced durations of the order of weeks (w), months (m) or a year (y). As discussed in the text the lifetime may vary significantly.

‡ In non-oxidizing atmospheres the maximum working temperature is reduced by 100 to 350 $^{\circ}$.

to four months use.) SiC heating elements are advantageous when the duration of typical (1300 $^{\circ}\text{C}$) experiments does not exceed one or two weeks and when the furnace requires frequent cooling to room temperature although it is better to keep the furnace always above 750 $^{\circ}$ even when not in use. Elmer (1953) and Bovee (1953) have discussed the properties of SiC heating elements and their lifetime. Of the latter it must be said that it depends very much on the conditions (load, ambient atmosphere and temperature, continuous or intermittent use) and on the fabrication with Globar, Crusilite and Crystolon being known for reliability. A stagnant oxidizing atmosphere is best for a long lifetime, and if corrosive vapours are produced in flux growth experiments it is preferable to blow air gently along the heating elements. Because of the so-called "silicon carbide pest" SiC elements should never be used below 750 $^{\circ}\text{C}$, otherwise the protective SiO₂ film will crack and fast oxidation will occur. The relationship between surface load and surface temperature of the SiC heating elements and the furnace temperature is shown in Fig. 7.25; for comparison the permissible surface load of Kanthal A1 wire heating elements at 1000 $^{\circ}\text{C}$ is 4 W/cm² and at 1250 $^{\circ}\text{C}$ 1.7 W/cm².

Molybdenum disilicide heating elements have significant advantages over SiC such as a longer lifetime, higher maximum working temperature and absence of ageing effect. Disadvantages are the higher price and low resistance, and MoSi₂ elements have to be handled with great care, so that

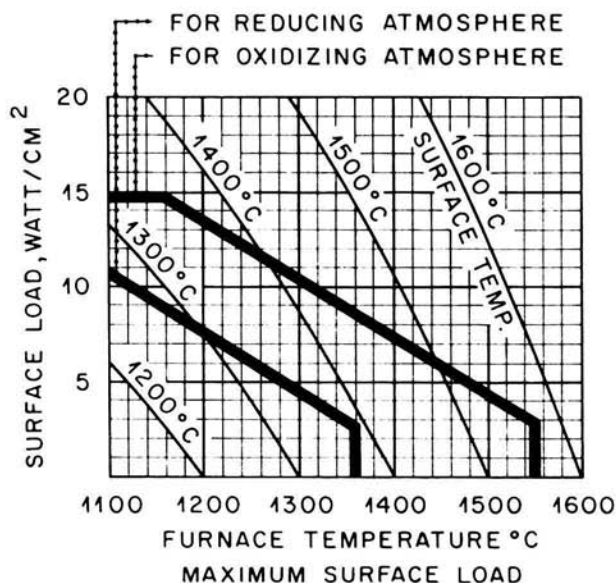


Fig. 7.25. Relation between element surface temperature, furnace temperature and surface load of silicon carbide heating elements. The maximum recommended surface load for oxidizing and reducing atmospheres is indicated by the strong lines.

furnace construction should be left to specialists unless the manufacturer's instructions† are followed very carefully.

The lifetime of Kanthal Super N elements exceeds two years when the following precautions are taken (Scheel, unpublished):

- The furnace is never cooled below 800°C.
- Dry air is gently flown into the heating element compartment continuously.
- Corrosive vapours cannot reach the elements.
- The temperature does not exceed 1500°C, and the surface load should not exceed a value of 15–20 watts per cm² (see Fig. 7.26).
- If used below 1450°C, the furnace should be heated to 1450°–1500°C for one to two days every six months in order to anneal the elements for strain removal.
- The temperature of the heating elements is regulated by continuous control.
- Vibrations are prevented by placing the furnace on an anti-vibration mount.

† Bulten-Kanthal AB, Hallstahammar, Sweden.

- (h) The U-shaped heating elements should hang freely from the top of the furnace.
- (i) The hot zone of the element should not reach into the ceramic insulation.
- (j) The terminals should be kept cool by having a free distance between the roof and the contact of 4–5 cm.

The surface load of Kanthal Super elements and their temperature and current are plotted against the furnace temperature in Fig. 7.26. The shaded area shows the optimum conditions. The resistance increases

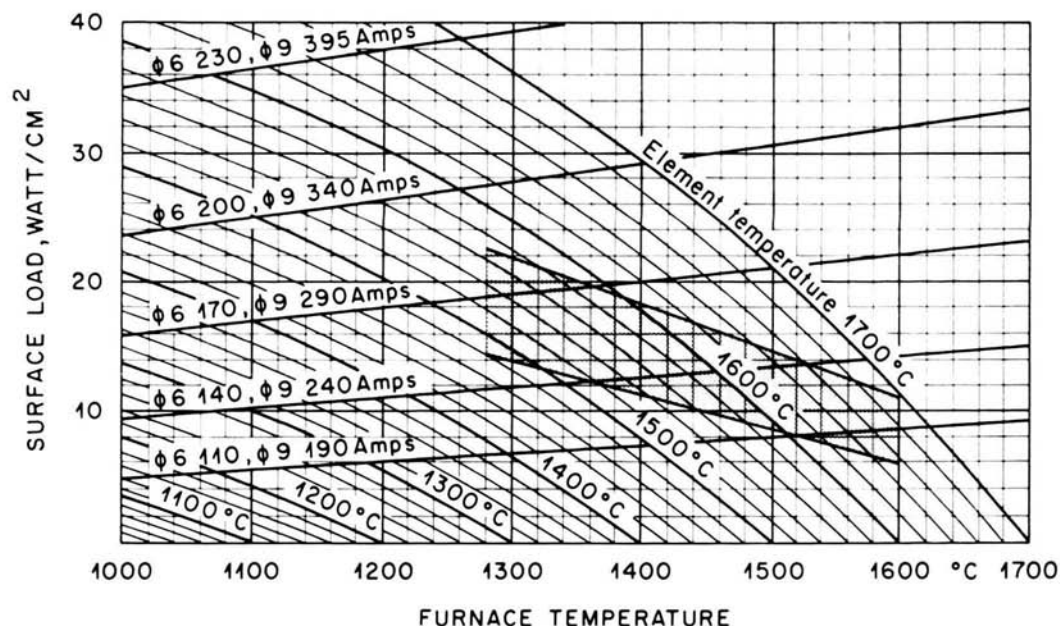


FIG. 7.26. Surface load, temperatures and current of kanthal super heating elements (of 6 and 9 mm diameter) versus furnace temperature.

steeply with temperature as shown in Fig. 7.27, where for comparison the resistance *versus* temperature change of SiC, graphite and Kanthal A1 are also shown.

The oxidation behaviour of MoSi_2 heating elements has been studied by various groups. Fitzer (1956) was the first to describe an anomalous oxidation behaviour at temperatures below 800° and called it "silicide pest". On severe oxidation the "pest" oxide consisting of crystalline MoO_3 and amorphous SiO_2 particles is formed and the heating element

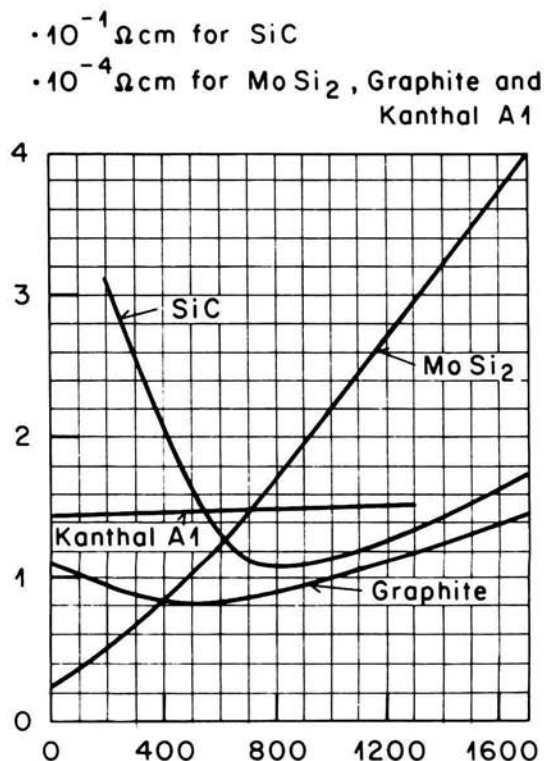
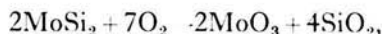
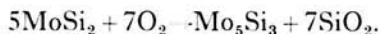


FIG. 7.27. Electrical resistivity of various heating element materials.

disintegrates. Above 800°C a protective SiO₂ layer can form according to



and the molybdenum oxide evaporates (Bartlett *et al.*, 1965). As was shown by Wirkus and Wilder (1966), another oxidation reaction occurs above 1200°C and just beneath the protective SiO₂ layer. This reaction may be described by



Thus typical MoSi₂ heating elements consist of interior bulk MoSi₂, a thin Mo₅Si₃ and an outer glassy or semicrystalline SiO₂ layer. The overall oxidation of the MoSi₂ elements is controlled by oxygen diffusion through the SiO₂ layer. Generally MoSi₂ heating elements have a protective oxide layer when delivered, and it is proposed to keep this intact by a slow flow of dry air along the heating elements.

TABLE 7.9 Properties of Firebricks and Insulating Ceramics

Name	Composition	Max. working temperature	Melting point	Density of compound	Density of brick ceramic	Thermal conductivity compound	Thermal conductivity ceramic†	Lin. expansion coefficient	Thermal shock resistance	Atmosph.	Remarks
Silica	SiO ₂	1100°	1710°	2.30	~1.5	0.012	0.003	0.5 × 10 ⁻⁶ /°C	good	oxid.	Corroded by fluorides
Sillimanite	Al ₂ O ₃ × SiO ₂	1500°		3.25	~2.3	0.008	0.003		medium	oxid.	Corroded by fluorides
Mullite	3Al ₂ O ₃ × SiO ₂	1650°	1920°	3.16	~2.0	0.009	0.007	5.3	medium	oxid.	Corroded by fluorides
Alumina	Al ₂ O ₃	1800°	2020°	3.97	~2.8	0.014	0.005	9.0 (8.6, 9.5)	poor	any	
Spinel	MgAl ₂ O ₄	1850°	2135°	3.60	~2.2	0.013	0.005	8.8	poor	oxid.	
Zircon	ZrSiO ₄	1700°	2420°	4.56	~3.3	0.008	0.005	4.2 (3.4, 5.6)	good	oxid.	Corroded by fluorides
Zirconia	ZrO ₂ ‡	2300°	2700°	5.60	~4.4	0.005	0.002	10.0	poor	oxid.	
Beryllia	BeO	2300°	2570°	3.01	~2.8	0.046	0.02	8.9	good	oxid.	Extremely poisonous dust and vapours
Magnesia	MgO	2400°	2800°	3.58	~2.5	0.016	0.006	14	medium	oxid.	
Thoria	ThO ₂	2400°	3050°	9.86	~6.3	0.007	0.005	9.7	poor	any	Radioactive
Urania	UO ₂	2200°	2800°	10.96		0.02		10		oxid.	Radioactive
Yttria	Y ₂ O ₃	2000°	2410°	5.01				9.3		any	
Graphite	C	3000°	> 3600°	2.25	~1.9	0.16		2-5	good	} reducing or vacuum oxid.	
Boron nitride	BN (hexag.)	2000°	3000° (dec.)	2.25	~1.9	0.04-0.12	0.03-0.07	0.05-10 (~2)	good		
Silicon carbide	SiC	1600°	2830° (dec.)	3.22	~2.6	0.10	0.02	4.4	good		Corroded by fluorides
Silicon nitride	Si ₃ N ₄	1500°	1900° (dec.)	3.44	~2.0	0.045		3.2 (2.47)	good	neutral	Corroded by fluorides
Silica glass wool	SiO ₂	1000°	1710°	2.30		0.012	~0.001		good	oxid.	Corroded by fluorides
Ceramic wool		1200°	~1700°	3.20		0.008	~0.001		good	oxid.	Corroded by fluorides
Zirconia wool	ZrO ₂ ‡	2300°	2550°	5.60		0.005	~0.0005		good	oxid.	

† At 1000°C, in cal/cm°C sec.

‡ Stabilized with CaO or Y₂O₃.

Thermal insulation in resistance furnaces is generally achieved by firebricks of which the most common with their properties are listed in Table 7.9. Dense bricks can carry loads and are resistant to abrasion while the lighter (porous) bricks are better insulators. The maximum working temperature of firebricks based on mullite and sillimanite increases with the alumina content. The space containing the crucibles is preferably separated from the heating elements by dense ceramic tubes or plates. If platinum crucibles are used, care must be taken that they cannot come into contact with silicon carbide ceramic because platinum alloys with SiC at high temperatures; also borides, nitrides and metals should not contact platinum. Only dense alumina-rich firebricks or pure alumina, spinel, magnesia or zirconia ceramics are recommended as supports for platinum crucibles.

Corrosion by flux vapours shortens the lifetime of the firebricks, especially if porous bricks face the chamber containing the crucibles. The resistance to corrosion is increased if such firebricks are coated with an alumina-rich high-temperature cement. Also zirconia or SiC wall plates may be used in order to decrease the number of repairs necessary. Another application of insulating bricks and ceramics is to fill the furnace chamber as much as practical in order to reduce temperature fluctuations by air convection and to increase the thermal capacity of the whole furnace.

Induction heating is generally used when the required temperature exceeds about 1600°C. At such high temperatures difficulties arise with heating elements and their atmosphere requirements and with dense ceramics, especially when the duration of experiments is of the order of weeks or months as in many growth experiments from high-temperature solutions. For work in neutral or reducing atmospheres graphite, molybdenum, tungsten and tantalum heating elements may be used, and excessive loss of heat is prevented by the use of metallic radiation shields, generally contained in water-cooled metal containers. For oxidizing atmospheres and temperatures exceeding 1700°C stabilized zirconia or thoria tubes may be used as heating elements; however, these oxides have to be preheated to about 1600°C in order to make them sufficiently conductive.

The most reliable and practical way of heating to about 2000°C in any atmosphere for crystal growth from high-temperature solutions is by induction heating, and this source of heat has been reviewed by May (1950), Stansel (1949), Brunst (1957) and Simpson (1960). The frequency of generators is about 450 kHz, and it should be noted that typical RF generators have an output of about 50% of their power consumption. For most applications generators of 15 to 30 kW RF power are appropriate, and care should be taken in obtaining sufficient coupling between the RF coil and the conducting crucible or melt. Also the wall thickness of metal

crucibles should be uniform, and the crucibles as well as insulation or radiation shields should be centred carefully in the coil.

According to Duncan *et al.* (1971) the penetration depth of the RF heating is given by

$$d = \frac{3750 \times \rho^{1/2}}{(f \times \mu)^{1/2}} \text{ cm,}$$

[with ρ the resistivity in ohm-cm of the heated material, μ the relative permeability of the heated material ($= 1$ for non-magnetic materials), f the induction heating frequency (Hz) and d the skin depth of the material being heated, at which the current density reaches $1/e \sim 37\%$ of the value at the surface]. The value of d is about seven times greater for 10 kHz than for 500 kHz (2.8 mm and 0.4 mm for platinum, respectively). Thus these authors propose the use of 10 kHz RF heating in order to overcome the common problems of hot spots and catastrophic failures, especially when crucibles are used near their melting points. Also 10 kHz motor-generators are said to be insensitive to line voltage fluctuations and to be very reliable.

Special heat sources might be used for specific experiments. Thus for transparent solutions the crystal growth process may be observed if furnaces with transparent regions are used. For temperatures up to 1100°C quartz-glass tube furnaces with a slit in the insulation or reflectors have been used, and Lord and Moss (1970) described a furnace with water cooling between two concentric glass tubes. A furnace consisting of an inner quartz-glass tube with the heating wire wound around it and an outer concentric quartz-glass tube with a thin gold layer evaporated on it was first described by Rabenau (1963/1964) and later in detail by Reed (1973). An approximately 200–500 Å thick gold layer shows high reflectivity for the infrared but is partially transparent to visible light. Another example of transparent furnaces was reported by Wood and Van Pelt (1972) who used tin-oxide coated silica-glass tubes as transparent heating elements. A spray coating system was used to achieve a uniform coating, and such furnaces have been used up to 700°C.

Localized heating as necessary for temperature-gradient transport and travelling solution zone techniques has been discussed in Section 7.1.2. Heat pipes may be useful for localized heating as well as for localized cooling as indicated by Steininger and Reed (1972) but except for a brief mention in a paper of Steininger and Strauss (1972) heat pipes have not yet found wide application in crystal growth from high-temperature solutions. With heat pipes temperatures approaching 2000°C may be obtained, and the lifetime of the heat pipe using lithium as fluid and TZM alloy as pipe material is said to be above one year (Harbaugh and Eastman, 1970) at a temperature of 1500°C. Temperature stabilization needs special precautions

and is best achieved by pressure control of open heat-pipe systems according to Vidal and Haller (1971).

7.2.2. Temperature control (including programming)

Temperature evaluation. Of the variety of temperature measurement and control techniques only a few are generally used because of their reliability, accuracy and convenience, and these are indicated in Fig. 7.28, together with their common ranges of measurement and control. Thermometers based on thermal expansion of liquids (and gases) and of solids (bimetal thermometers) are very common and may be used up to relatively modest temperatures (500°C) but are not applicable or reliable at higher temperatures. Thus, in this section only resistance thermometry, thermoelectric thermometry and optical pyrometry will be discussed. The measurement and control of temperature have been reviewed in

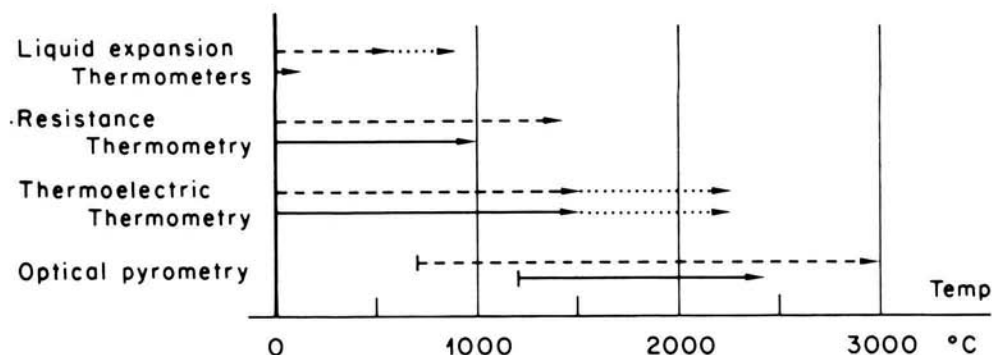


FIG. 7.28. Temperature ranges for measurement (broken lines) and reliable control (solid lines) for various common temperature evaluation techniques.

"Temperature" (1941, 1955, 1962), by Baker *et al.* (1953, 1961), Kostkowski (1960), Rubin and by Best (1967).

How precisely and accurately† can a temperature be measured? This question has been discussed, in addition to above references, by Dike (1958), Roeser and Lonberger (1958), Stimson (1961) and by Gray and Finch (1971).

According to the International Practical Temperature Scale of 1968 (IPTS-68, 1969) the temperature is established by interpolating between the points 100°C (boiling point of water), 419.58°C (freezing point of zinc), 961.93°C (freezing point of silver) and 1064.43°C (freezing point of gold).

† Precision is qualitatively the inverse of the (mean) deviation from a given temperature, whereas accuracy is the inverse of the (mean) deviation from a point on the (absolute) International Practical Temperature Scale of 1968.

In various laboratories the freezing points of antimony (630.5°C), aluminium (660.1°C) and copper (1083°C) are used for calibration, but extreme care is necessary with respect to purity (corrosion of container, influence of gases) in all direct calibration work.

Chemicals of high purity needed for calibration according to IPTS-68 may be obtained either from a national institution of standardization or from the National Bureau of Standards, Washington, D.C., U.S.A. However, it is more convenient to obtain calibrated thermocouples, resistance thermometers or pyrometers from commercial suppliers or from the above institutions. The accuracy of temperature measurement at the gold point (1064.43°C) using calibrated Pt-PtRh 10% thermocouples may be as good as 0.2°C , and using non-calibrated commercial thermocouples the accuracy is generally better than 2.5°C .

A standard thermocouple properly used has a precision of 0.1°C around the gold point, that means that the standard deviation is 0.1° about the mean of that laboratory. At the National Bureau of Standards Pt-PtRh 10% thermocouples are annealed for one hour at 1450°C before calibration.

For temperatures exceeding the melting point of gold the melting points of palladium (1552°C) and platinum (1769°C) have been proposed as standards. For temperatures up to 1300°C the platinum *versus* platinum 10% rhodium thermocouples are reliable to within 0.25% if used in a clean oxidizing atmosphere and if extended periods above 1300°C are avoided. The International Temperature Scale above the gold point is defined in terms of the Planck radiation equation and the ratio of the spectral radiance, in the visible region, of a black body at the temperature to be measured to the spectral radiance of a black body at the gold point. However, with a black body and using a calibrated optical pyrometer (with disappearing filament) the standard deviations from IPTS-68 at the gold point and at 2000°C may be as low as 0.6° and 3° , respectively. Generally in practice it is found difficult to obtain a precision of better than 6°C using an optical pyrometer.

The first part of the following section deals with temperature sensors whereas the second part briefly treats techniques for the control and programming of the temperature of furnaces.

Resistance thermometry. This topic has been reviewed in the general references mentioned previously and by Berry (1966) while Daneman and Mergner (1967) discussed the equipment necessary for measuring exact resistance ratios. Resistance thermometry is based on the change of resistance of materials with temperature, and the resistance change is measured with resistance bridges or potentiometers.

The resistance of pure metals increases with temperature whereas semi-

conducting materials (e.g. germanium, oxides) show a logarithmic decrease in resistance with increasing temperature which is used in the so-called *thermistors*.

Resistance thermometers allow very precise measurements of temperature as long as the resistance of the metal is not changed by recrystallization, oxidation, impurities or evaporation. Thus nickel and copper are generally used only up to 200°C, platinum up to 1000°C, and tungsten, molybdenum and tantalum (in a protective atmosphere) up to 1200°C, whereas thermistors are used up to 300°C and with special compositions (though not reliably) up to 1600°C. The platinum resistance thermometer may be calibrated if prepared from ultra-pure platinum and if mounted in a helium-filled jacket. In Fig. 7.29 the dependence on temperature of the resistance of various materials is shown.

Resistance thermometry allows the measurement of temperatures up to 1000° with a precision not achieved by other techniques (McLaren, 1957). However, the limited temperature range and lifetime have prevented its wide use in crystal growth from high-temperature solutions. An exception is the range of controllers marketed by CNS Instruments, which use

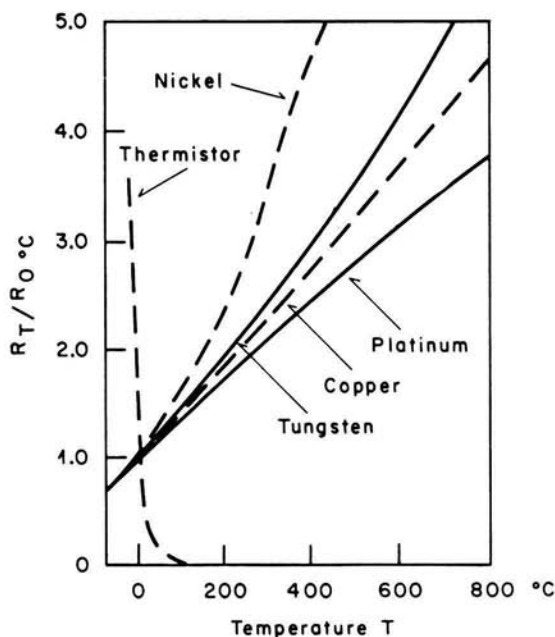


FIG. 7.29. Resistance ratios for temperatures T to the temperature of 0°C for various metals and a typical thermistor.

platinum resistance thermometers for temperature control up to 1400°C, but for temperature regulation over extended periods the resistance thermometer should not be used at temperatures higher than about 1000° because of the change of resistance due to evaporation and recrystallization of the platinum.

Thermoelectric thermometry. The most common temperature measurement and control techniques are based on thermocouples. Since the thermoelectric power of a variety of metal and alloy combinations is known, the temperature of one junction can be determined provided the other junction has a known temperature, preferably the ice point (0°C). The thermoelectric power of a variety of thermocouples has been listed as a function of temperature by Shenker *et al.* (1955) and is shown for high and low temperatures, respectively, in Fig. 7.30(a) and (b). Table 7.10 lists the sensitivities at various temperatures, the maximum temperatures of use, the necessary atmospheric conditions and the stability of a variety of thermocouples.

At temperatures up to 600° the similar thermocouples copper-constantan and iron-constantan are commonly used, whereas for temperatures up to 900°C the chromel-alumel thermocouple is popular. Pallador† and Platinel‡ (Pt, Pd, Ir, Au alloys) are thermocouples with a high sensitivity, comparable with chromel-alumel, and which can be used up to 1200 and 1300°C. Platinum *versus* platinum rhodium 10% is the most frequently used thermocouple for the range 500° to 1400°C, although other thermocouples based on noble metals are now available which are more stable at higher temperatures and have similar sensitivity above 1000°C. As an example the platinum 94% rhodium 6% *versus* platinum 70% rhodium 30% is listed which has the advantage of having a negligibly small sensitivity around room temperature. Scheel and West (1973) use thermopiles made from several PtRh6% *versus* PtRh30% couples as sensing elements for furnace control. Such thermopiles have the advantage of very high sensitivity so that changes in e.m.f. due to variation in the furnace temperature are very large in comparison with noise or changes due to variation in the ambient temperature. The latter effects normally result in fluctuations at the input to a furnace controller of about $\pm 3 \mu\text{V}$ which corresponds to the change in output from a Pt *versus* PtRh10% thermocouple due to a change in the furnace temperature of $\pm 0.3^\circ\text{C}$. A sensing device of high sensitivity to variations in the furnace temperature but insensitive to cold junction temperature changes is therefore necessary if stabilization to say $\pm 0.05^\circ\text{C}$ is to be achieved. The PtRh6% *versus*

† Trademark of Johnson Matthey Ltd.

‡ Trademark of Engelhard Industries.

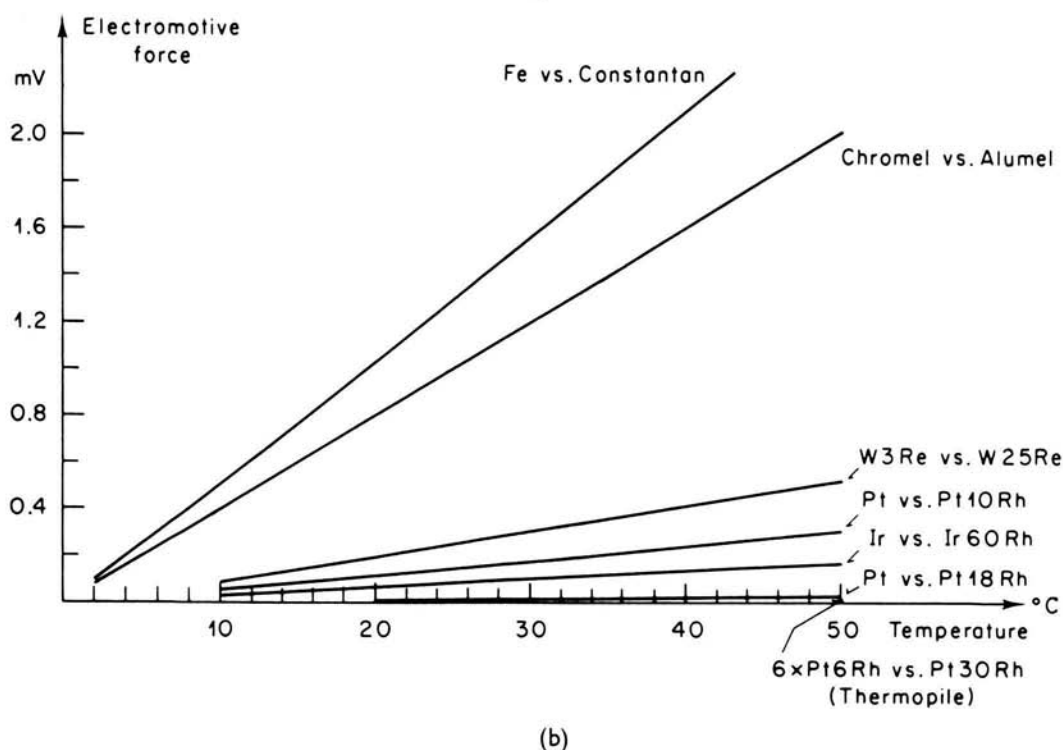
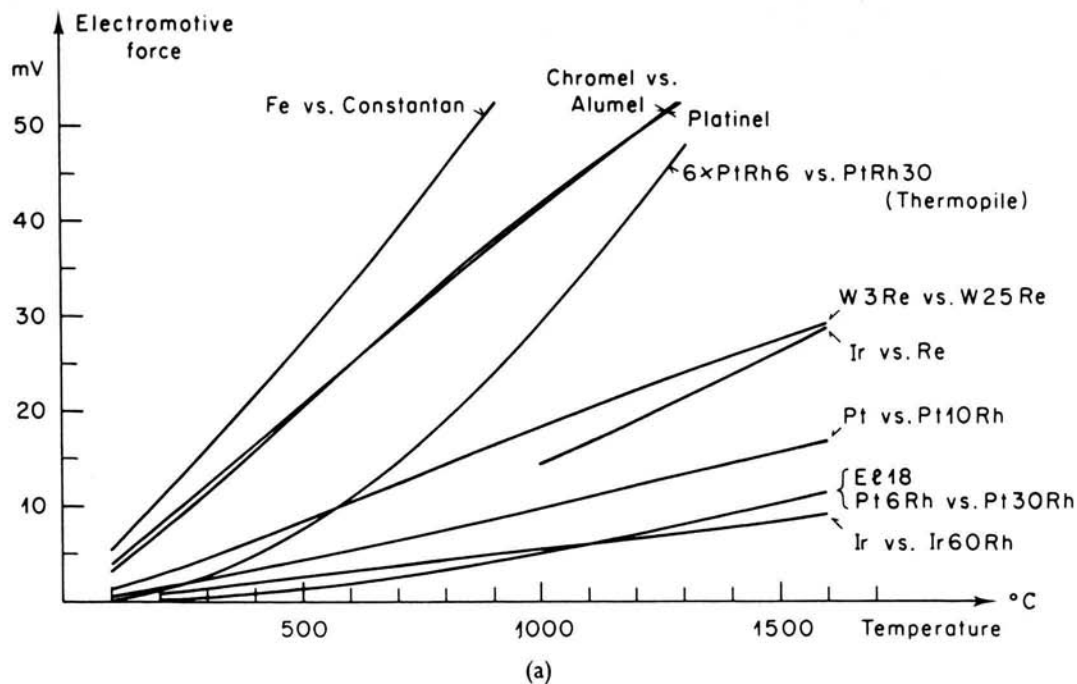


FIG. 7.30. (a) Electromotive forces (for high temperatures) of various common thermocouples and of the PtRh6-PtRh30 thermopile proposed by Scheel and West (1973). (b) Electromotive forces of various common thermocouples for the temperature range 0° to 50°C.

TABLE 7.10. Properties of Various Thermocouples

Thermocouple	Sensitivity: $\mu\text{V}/^\circ\text{C}$ at			Max. temp. of use		Atmosphere	Estimated temperature shift at		
	25°C	800°C	1200°C	intermittent	continuous		temp.	10 hours	1000 hours
Iron-Constantan	51	64		800°C	650°C	reducing inert, or oxidizing	650°		2.5
Chromel-Alumel	40	40	36	1260°C	1100°C	oxidizing or neutral	1000° 1200°	0.5 $^\circ$ 2.0 $^\circ$	5.0 fails
Pd-Pt85Ir15	19	37	45	1500°C		inert or oxidizing†	1200°	0.5 $^\circ$	5.0
Platinel	32	41	39	1300°C	1150°C	oxidizing, inert or reducing	1200°		3.0
Pt-Pt90Rh10	6	10.9	12.0	1700°C	1450°C	oxidizing	1200° 1500°	0.2 $^\circ$ 1.0 $^\circ$	2.0
Pt94Rh6-Pt70Rh30	~ 0.07	7.55	10.5	1800°C	1500°C	oxidizing	1700°	4.0 $^\circ$	
Thermopile of 6PtRh6-PtRh30 thermocouples	~ 0.4	45.3	63	1800°C	1600°C	oxidizing			
Pt80Rh20-Pt60Rh40				1830°C	1600°C	oxidizing	1800°	6.0 $^\circ$	
	25°C	1600°C	2000°C						
Ir-Rh60Ir40	3	5.8	6.2	2000°C	1800°C	inert or slightly oxidizing	2100°	10.0 $^\circ$	
W-Ir		25	26.3	2100°C	2000°C	inert or vacuum	2100°	10.0 $^\circ$	
Re-Ir				2100°C	2000°C	inert or vacuum			
W97Re3- W75Re25	10	17	14	2400°C	2200°C	inert or reducing			
W-Re	~ 5	12	6.5	2400°C	2200°C	or vacuum inert or reducing			
						or vacuum			
SiC-C		~ 300	~ 300	~ 2700°C		vacuum			Fragile, not reliable
B ₄ C-C		~ 330	~ 330	~ 2400°C		vacuum			Fragile, not reliable

† Pd is oxidized slowly in air between 700° and 900°C, iridium above 900°C.

PtRh30% thermocouples have the additional advantage of a long lifetime at temperatures up to 1600°C.

For temperatures exceeding 1800°C thermocouples based on tungsten or rhenium are used, but the brittleness, the instability and the stringent requirements on atmosphere lead many researchers to prefer optical pyrometry where possible. The fragile nature of the carbon-based thermocouples prevent their popularity although their sensitivity is extremely high.

Some remarks on the thermocouples based on platinum alloys are appropriate as these are in common use in crystal growth from high-temperature solutions, and several of the points also hold for other thermocouple materials. Many aspects, including chemical and physical properties and stability, are discussed by Caldwell (1962) and by Vines (1941). The general features of thermoelectric temperature measurement have been discussed by Finch (1966).

The most stringent requirements are those of purity, which should be better than 99.99% of the individual metal or alloy, and of homogeneity. Any physical and chemical inhomogeneities produce spurious effects by acting as thermocouples themselves. A clean oxidizing atmosphere (e.g. air) is necessary, and traces of hydrogen, carbon monoxide, hydrocarbons, sulphur (or other chalcogenide), pnictides (except N₂) or metal-containing vapour corrode the platinum-based thermocouples or may have an effect on its thermoelectric characteristics. The oxidizing atmosphere also keeps all trace impurities oxidized so minimizing their influence. In addition, the insulating ceramic tubes should be of high purity and should not contain silica (SiO₂, mullite, sillimanite) since SiO₂ has a detrimental effect in reducing atmospheres or at high temperatures, and metals, carbides, borides etc. cannot be used in contact with platinum-based thermocouples because of alloying. Also the ceramic sheath tubes made of high-purity alumina should be impervious in order to prevent volatile flux components (e.g. PbF₂) from coming into contact with the thermocouple. The high temperature limit for a variety of thermocouples as given in Table 7.10 may be lowered by the material which it contacts (insulating or sheath tubes), and this aspect is discussed in Section 7.2.3.

The optimum diameter for thermocouples based on platinum is 0.5 mm but thinner wires of 0.1–0.2 mm may be preferred for a fast response, and thicker wires are used under harsh conditions because of their mechanical and thermal stability. Volatility is an important factor for noble metal thermocouples (and resistance thermometers) at high temperatures. For instance, the loss of platinum in vacuum is 7×10^{-20} g cm⁻² s⁻¹ at 727°C, 5×10^{-11} at 1227°C and 10^{-6} at 1727°C (Vines, 1941). According to Crookes (1912) platinum is twice as volatile as rhodium in air at 1300°C, one-third as volatile as palladium, and one-thirtieth as volatile as iridium, and these

differences in volatility are partially explained by the relative ease of formation of volatile oxides.

Recrystallization is another cause of limited lifetime. Alternating cooling and heating, by its expansion effects, may cause failure of a recrystallized thermocouple junction. In order to achieve precise and reliable thermocouple output the thermocouples should be regularly replaced after a period of hours or months depending on the couple material and the conditions of use.

For exact temperature recording and control a reference junction held at a precisely controlled reference temperature is required, or the thermocouple may be connected to copper held at exactly 0°C (see Figs. 7.31a and b). A controlled 0°C junction based on Peltier cooling is convenient and the triple point cell of water with a temperature of $+0.0099^{\circ} \pm 0.0001^{\circ}\text{C}$ may be used if the duration of experiments is not too long (both reference systems are commercially available). Reference baths at other temperatures than 0°C have the disadvantage that the e.m.f. is not zero (or nearly zero).

Extension wires prepared from alloys with similar thermoelectric characteristics are frequently used because of their lower price and higher mechanical stability. In this way a thermocouple is extended to the reference temperature or the measuring or control unit. However, the accuracy decreases with the use of extension wires, and care must be taken that all connections of the pair of thermocouple wires or any extension wires are isothermal.

The small thermocouple signals necessitate careful shielding and grounding, otherwise stray voltages may be introduced by direct coupling or by capacitive coupling. If the thermocouple line is close to motors, transformers or power-circuits it can only be fully shielded by magnetic shielding. Non-magnetic shielding can be penetrated by magnetic fields of not too high frequency. Twisting of the thermocouples minimizes such magnetic interactions. Also a coaxial arrangement of the thermocouple line has many advantages. Grounding should be effected according to Fig. 7.31(c) or (d).

In certain cases the use of a thermopile might be necessary in which a number n of thermocouples are connected in series and produce n times the e.m.f. of a single thermocouple and thus a larger signal. If an average temperature signal is required then several thermocouples of equal resistance are connected in parallel. A special arrangement for rotating thermocouples using electrically isolated ballbearings as coupling elements in a thermocouple circuit has been described by Robertson and Scholl (1971). Such an arrangement may be advantageous as an alternative to a commutator for growth on a rotating seed or by the accelerated crucible rotation technique (see Section 7.2.7).

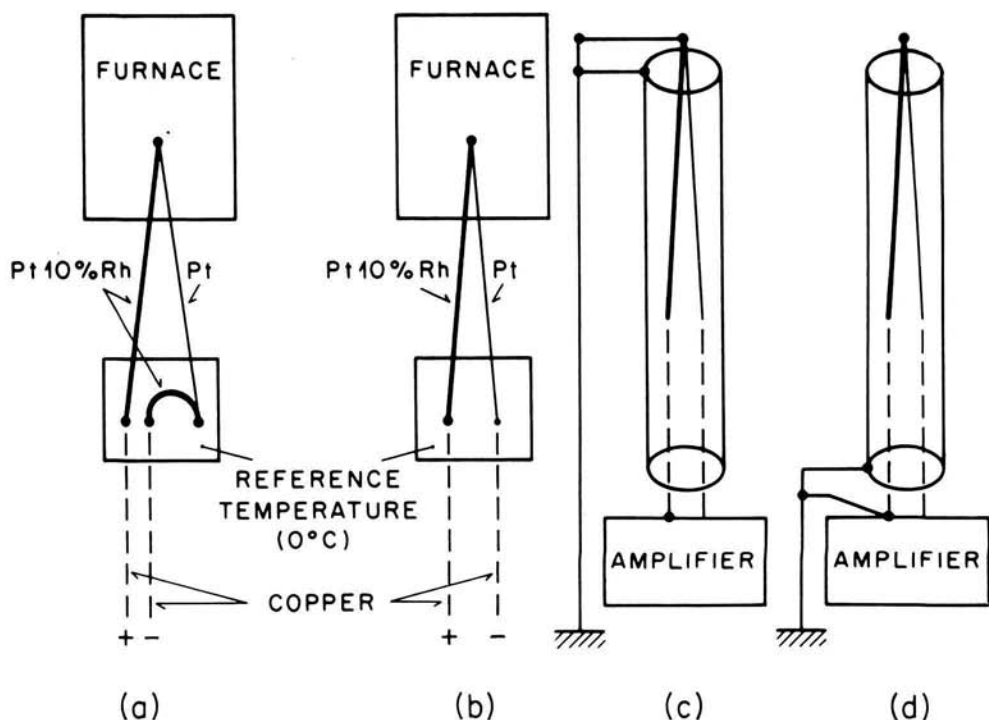


FIG. 7.31. (a)–(d) Thermocouple arrangements and methods of shielding.

Temperature measurement by *optical pyrometry* is used when thermoelectric techniques are not reliable, for example at high temperatures and in corrosive gas atmospheres, or in induction heating. However, vapours and material condensed on the observation windows might have a dramatic effect on the reliability of optical techniques. Optical thermometry has been described in "Temperature" (1941, 1955, 1962), by Harrison (1960), Dike *et al.* (1966), Euler and Ludwig (1960), Kostkowski and Lee (1962) and by Poland *et al.* (1961).

Many optical pyrometers (e.g. the disappearing filament) indicate the brightness temperature, so the spectral emissivity of the radiating source (the region of which the temperature has to be measured) as well as reflectance and absorption of the windows and lenses between object and pyrometer may lead to deviations from the true temperature. Thus the indicated temperature can be more than 10% lower than the actual temperature. Ideally the whole arrangement should be calibrated using fixed points. Emissivity is the emittance of a material having an optically

smooth surface and a thickness sufficient to be opaque, and emittance is the ratio of the energy radiated by a surface (per unit area and unit time) to the energy which would be radiated by a black body at the same temperature. Applying Wien's law, the true temperature T is related to the brightness temperature T_B by

$$\frac{1}{T_B} - \frac{1}{T} = -(\lambda/C_2) \log_e \epsilon_\lambda,$$

where C_2 is the second radiation constant (1.438 cm degree) and ϵ_λ the emittance at wavelength λ . Typical values of spectral emittance are given in Table 7.11 and a few temperature corrections for various emittances and temperatures are listed in Table 7.12. Quartz-glass windows and lenses necessitate corrections of the order of 5 to 30°C. In applying temperature corrections it must be kept in mind that the surface structure of the observed hot body (e.g. crucible) has a significant effect on the emittance. The problem of the emissivity may be reduced by the use of a *two-colour* pyrometer which compares the radiation at two different wavelengths as suitable filters are introduced alternately into the radiation ("Temperature" 1962, p. 419). The output voltage from the detection system may be calibrated in terms of the source temperature.

Radiation pyrometers or photoelectric pyrometers can, in addition to indicating, also record and control the temperature and are used for example in silicon production by Czochralski-pulling.

TABLE 7.11. Spectral Emittances ϵ for Various Materials

Material	ϵ	Material	ϵ
Graphite	0.76	Al ₂ O ₃	0.30
Graphite, powder	0.95	BeO	0.31–0.35
Gold, solid	0.04–0.16	Fe ₂ O ₃	0.63–0.98
Gold, liquid	0.07–0.22	Fe ₂ O ₃ , liquid	0.53
Iron, solid	0.35–0.37	steel, oxidized	0.75–0.90
Iron, liquid	0.37	MgO	0.70
Molybdenum, solid	0.37–0.43	ThO ₂ , solid	0.50–0.57
Platinum, solid	0.30–0.38	ThO ₂ , liquid	0.69
Platinum, liquid	0.38	TiO ₂ , solid and liquid	0.51, 0.52
Tantalum	0.50	Y ₂ O ₃	0.60
Tungsten	0.39–0.46	ZrO ₂	0.40

TABLE 7.12. Temperature Corrections for Various Emittances ϵ and Temperatures, Calculated for the Effective Wavelength $\lambda = 0.655 \mu$

ϵ	800°C	1000°	1200°	1400°	1600°	1800°	2000°	2200°C
0.1	136	196	269	355	457	575	710	864
0.2	91	131	178	233	297	371	453	546
0.3	67	95	129	169	214	265	323	387
0.4	50	71	96	125	158	196	238	284
0.5	38	53	72	93	117	145	175	209
0.6	27	39	52	68	85	105	127	151
0.7	19	27	36	47	59	72	87	103
0.8	12	17	22	29	36	45	54	64
0.9	6	8	10	13	17	21	25	30

In order to overcome the problem of absorption by vapours and windows a *light pipe* has been proposed. A sapphire single crystal is fixed near to or at the object (crucible), and the radiation transmitted by this light pipe out of the hot region is sensed by appropriate thermocouples or radiation sensitive devices.

An infrared television system has been successfully applied to Czochralski growth of refractory oxides and of copper crystals by O'Kane *et al.* (1972) and by Gärtner *et al.* (1972). Process control using a computer allowed exact control of the crystal diameter, and similar equipment could be helpful or necessary for the growth of "difficult" crystals by the top-seeded solution growth technique.

Temperature control. The signals obtained from the various temperature sensors are generally amplified and used to control the power input to the furnace. In the following we shall restrict the discussion to thermocouple sensors and resistance heating, the arrangement most typically used in crystal growth from high-temperature solutions. The regulation of RF generators has been discussed in Section 7.2.1. Mechanical temperature regulators and on-off control do not fulfil the requirements of crystal growers and have been progressively replaced by electronic controllers and by proportional or continuous (or stepless) temperature control to which the following discussion will therefore be restricted.

In a regulation system as shown diagrammatically in Fig. 7.32 pure proportional control of the furnace temperature is defined by

$$P - P_0 = K_P(W - X),$$

where P_0 is a chosen mean value of the input power. If $P - P_0$ and $W - X$ are expressed in the same units then K_P is a dimensionless constant which

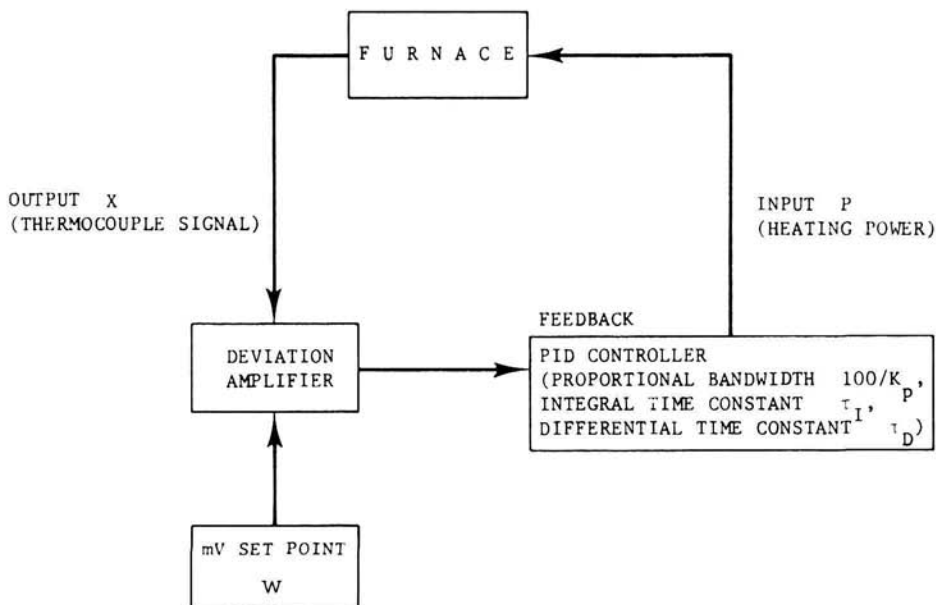


Fig. 7.32. Temperature regulation circuit (diagrammatic).

is a measure of the amplification of the feedback signal $W - X$. The reciprocal value $100/K_P$, expressed in percent is called the proportional band width. A purely proportional-controlled system is stable only if the output indicates any changes in the input (heating power) immediately and proportionally. In normal systems this is never the case, and the time constant is a measure of the delay time caused by the heat capacity of the furnace and of the sensing thermocouples. With pure proportional control the steady-state temperature deviates from the set point, and the degree of deviation changes irregularly within the limits of the proportional band. The difference $W - X$ decreases with large K_P , but either the stability of the system or the instrument itself limits the maximum K_P .

In order to achieve a stable temperature without a setting error in real systems with a response time lag the so-called three-term controllers or *PID controllers* should be used. These contain in addition to the adjustable proportional band (*P-term*) the integral (*I*) and the differential (*D*) terms. The idealized *I-term* depends on the integral of the feedback signal so that the power delivered to the furnace includes a term

$$P_I(t) = \frac{1}{\tau_I} \int_0^t (W - X) dt,$$

where $(W - X)$ is again expressed in the same units as P and $1/\tau_I$ is the

adjustable proportionality factor of the I -term, τ_I being called the integral time. Thus the integral term produces an increase in the heating power which is linear with time. Integral control (also named reset control) has the effect of shifting the proportional band in such a way that the deviation of the actual temperature from the set point is minimized (which is achieved neither by P - nor by $P + D$ -control).

Idealized differential control or derivative (or rate) control depends on the differential of the feedback signal so that, at time t , the output of the controller has a component

$$P_D(t) = \tau_D \frac{d}{dt} (W - X).$$

The addition of differential control reduces the tendency towards oscillation when the proportional band is narrowed (i.e. K_P made large). If the chosen derivative time τ_D is too large, a small change of the actual temperature will drive the controller to its limits of zero and maximum power, so that the system tends towards on-off control with a long time constant.

The general equation for a three-term controller is

$$P(t) - P_0 = K_P(W - X) + \frac{1}{\tau_I} \int_0^t (W - X) dt + \tau_D \frac{d(W - X)}{dt}.$$

Although it would be possible to calculate the optimum proportional bandwidth, integral time and derivative time such a calculation would be very complicated considering the many factors which have to be taken into account (furnace design, characteristics of heating elements, power supply, thermocouples, etc.) and which are generally not known.

In practice the P , I and D terms are set by "experience" or by measuring the time constant of the system. A practical procedure to optimize the parameters of PID controllers has been described by Ziegler and Nichols (1942). Firstly, the I and D terms are adjusted in order to obtain pure proportional control by setting the integral time as large as possible and the differential time as small as possible. By increasing the amplification K_P to a value $K_P(\text{crit.})$ where undamped oscillations are just achieved the period $\tau(\text{crit.})$ of these oscillations can be determined. Then the parameters of a PID controller are set as follows:

$$\begin{aligned} K_P &= 0.6 K_P(\text{crit.}) \\ \tau_I &= 0.5 \tau(\text{crit.}) \\ \tau_D &= 0.12 \tau(\text{crit.}). \end{aligned}$$

If the dynamic behaviour (amplification factor F_A , time constant τ_c , dead

time τ_d) of the control system is known then the parameters are set according to Oppelt (1964):

$$K_P = 1.2 \frac{\tau_c}{\tau_d} \frac{1}{F_A}$$

$$\tau_I = 2 \tau_d$$

$$\tau_D = 0.42 \tau_d$$

(see also Smith and Murrill, 1966).

The effect of the various control techniques for a typical furnace system is demonstrated in Fig. 7.33. As shown with examples 1 and 2 the sensing thermocouple should be near to the heating element and the same applies in *PID* control, since the dead time is thus decreased. In addition to an optimum setting of the *PID* terms, a stabilized power supply is necessary for highest precision of the temperature control, as proved by examples 8 and 9 where the temperature is shown to be unaffected by a change in the line voltage.

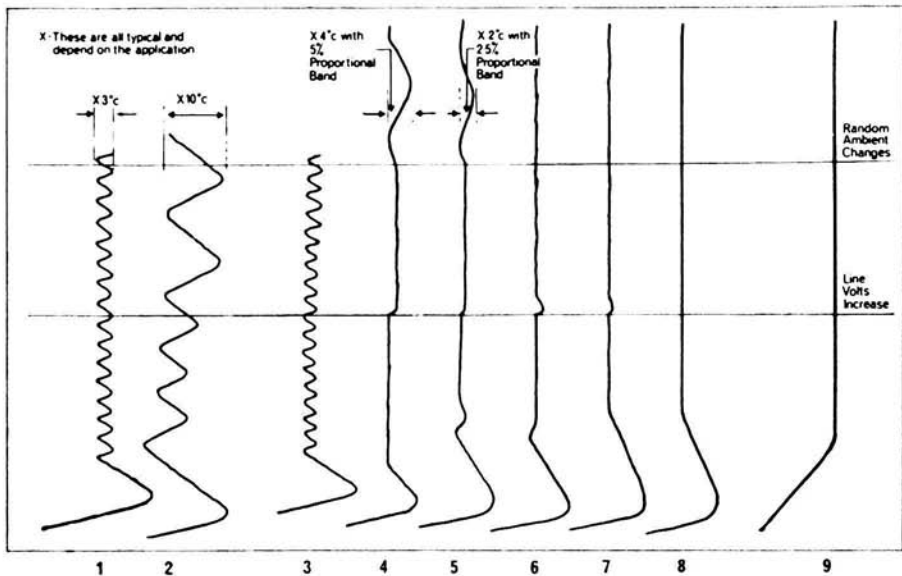
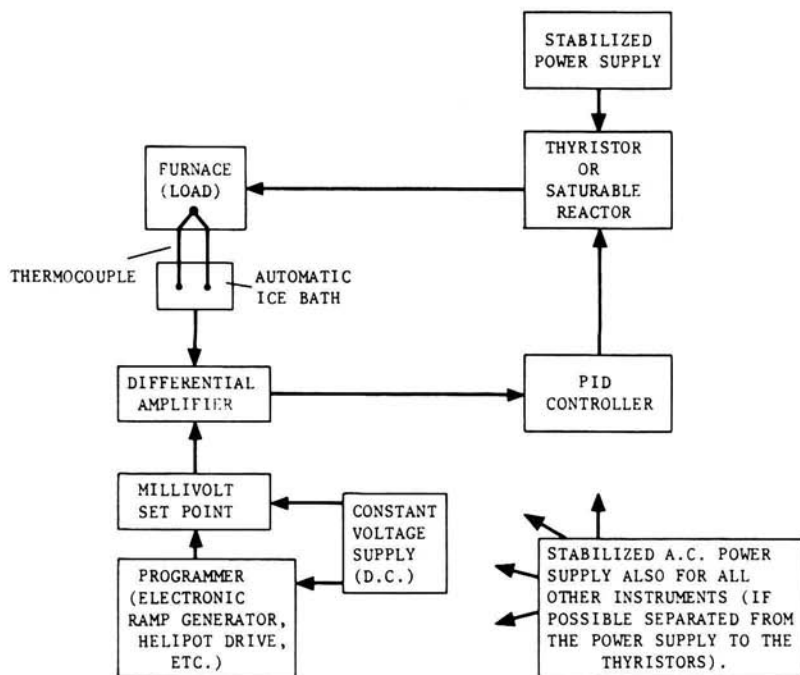


FIG. 7.33. Typical control records, recorded from the control thermocouple, using various control methods. Thermocouple $\frac{1}{2}$ inch from heater in all cases except 2 (Courtesy Eurotherm Ltd.). (1) On-off control. (2) On-off control. Thermocouple $1\frac{1}{2}$ in from heater. (3) Proportional control. Proportional band too narrow. (4) Proportional control. Proportional band wide. (5) Proportional control. Proportional band optimum. (6) Proportional + integral control. (7) Proportional + integral + derivative control. (8) Proportional + integral + derivative with power stabilization. (9) Proportional + integral + derivative with power stabilization with derivative start up.

By using a high-quality commercial *PID* controller and an arrangement similar to that shown in Fig. 7.34(a), by careful installation of the sensing thermocouple and of the signal lines, very precise control of furnace temperatures may be achieved, of the order of 0.1 to 0.5°C at temperatures around 1200°C using a normal Pt/Pt-10Rh thermocouple. The arrangement of Fig. 7.34(a) is a typical example.



(a)



(b)



(c)

FIG. 7.34. (a) Example of furnace-sensor-controller arrangement for precise temperature regulation. (b) Continuous control by phase angle firing. (c) Continuous control by fast cycling.

The signal from the *PID* controller may regulate a saturable reactor or a thyristor which is itself connected to the heating elements directly (resistive load) or via a variac or transformer (inductive load). Saturable reactors (or magnetic amplifiers) are very reliable and not sensitive to mechanical, electrical or thermal disturbances whereas the thyristor (also called silicon-controlled rectifier S.C.R.) is faster, cheaper and more sensitive. In thyristors the power control is achieved either by *phase angle firing* or by *fast cycling*, the principles of which are schematically shown in Fig. 7.34(b) and (c). Phase angle firing obviously distorts the mains waveform and with large installations this might be serious. It can also cause radio interference, and for these reasons phase angle firing should not be used in research laboratories except where precautions are taken. Rapid cycling if synchronized with the mains does not distort the mains waveform, and there is no radiated interference. However, in both cases, specific difficulties may arise and should be discussed with specialists.

Temperature programming. According to Fig. 7.34(a) programming is achieved by changing the millivolt set point. The simplest way to do this is to change the resistance in the mV circuit by means of a motor-driven potentiometer (Helipot) or similar device. The precision is frequently not sufficient, and potentiometers are sensitive to dust and vapours thus necessitating frequent cleaning. Motors with changeable gears[†] attached to helipots provide a wide range of cooling rates which are, depending on the type of thermocouple, more or less linear. As was pointed out by Scheel and Elwell (1972), by Pohl and Scheel (1975), and in Section 6.6, the cooling rate should frequently be below 1°C per hour and the temperature regulation better than 0.1°C for flux growth of oxides by the slow-cooling technique, and these goals necessitate the application of fully electronic programmers[‡] or of computer-assisted process control. Also the commercially available instruments with rotating cams or drums, in which the programmed value of the temperature is sensed mechanically or optically, are generally not sufficiently precise. Laudise (1963) pointed out that the precision of the temperature control should be commensurate with the slow cooling rates used, and Scheel and Elwell (1972) expressed the necessity of a continuous (stepless) cooling curve if crystals of high quality are to be grown. Further details of temperature programming in the slow-cooling technique are discussed in Sections 6.6 and 7.1.2.

[†] For instance of Halstrup, 7815 Kirchzarten, W-Germany.

[‡] For example, Eurotherm Ltd. (Worthing, Sussex, England) offers electronic programmers in which capacitors are slowly discharged by field-effect transistors and thus generate an electronic ramp.

7.2.3. Crucibles

Most experiments in crystal growth from high-temperature solutions are carried out in containers, either in crucibles or in ampoules. Thus crystal growers are faced with the choice of a practical crucible material which should be resistant to corrosion by the solvent, solute and the atmosphere at the high growth temperatures. Further requirements are a high mechanical strength, ease of shaping and of cleaning, good thermal shock resistance, reasonably long lifetime (little recrystallization) and a low price.

There are two materials which fulfil most of the above requirements, namely graphite and silica glass (also called quartz glass). These two materials have many unique properties and find wide applications, graphite for several metals which have a low tendency towards carbide formation and for such compounds which are stable against reduction, especially for the preparation of semiconductor crystals and of semiconductor layers by liquid phase epitaxy. Silica-glass crucibles, boats and ampoules may also be used for the preparation of semiconductors and for those metallic melts which do not cause reduction. Obviously SiO_2 glass cannot be used to contain solvents for oxides and for oxide melts, and its upper limit of temperature is around 1100°C (1000° for extended use). For growth of most oxides and oxide compounds, platinum is the only choice because of its resistance to corrosion, and it has to be used despite its high price and softness. Thus the various aspects of the use and handling of platinum crucibles will be discussed in some detail.

As a rule suitable crucible materials are those which have a type of bonding different from that of solvent and solute provided that no decomposition reaction occurs. The difference in the chemical bond type generally leads to a sufficiently small solubility of the crucible material in the solvent, especially when this material has a relatively high melting point. Examples of the bonding difference rule are the use of platinum crucibles for ionic melts, of (ionic) oxide and of covalent graphite and nitride crucibles for metallic melts, and further examples are given in Table 7.13 which lists the most common crucible materials with their properties and their applications. Table 7.14 summarizes the corrosion resistance of various crucible materials against a variety of molten metals for 300° and 600°C , respectively, and several properties of a variety of crucible materials have already been listed in Table 7.9 (see Section 7.2.1). In Table 7.15 examples of crucibles for a variety of melts and solutions, together with the temperature range, are given [see also Janz (1967)].

A well-known rule in solid-state reactions is that the reaction between two compounds of similar bond type starts at temperatures of $0.3\text{--}0.4 T_F$ for metals, of $0.6 T_F$ for ionic compounds and $0.8\text{--}0.9 T_F$ for silicates.

T_F is the mean absolute melting point of the two components. According to these values, compounds may be melted in crucibles of the same bond type if the above values are not exceeded, that is, if the melting point of the solvent or solution is much lower than that of the crucible. For example, sodium chloride may be melted in alumina crucibles, and several low melting point metals may be contained in refractory metal crucibles. However, many refractory metal crucibles (except noble metals) cannot be used for ionic compounds since they are oxidized by the latter.

Table 7.16 gives the temperatures at which reactions between refractory materials start, so that mechanical contacts between two different materials (for instance crucible and support) should be held at significantly lower temperatures than those given in the table. Further information on the usefulness of crucible materials and of their reactions may be obtained from the appropriate phase diagrams (see Sections 3.7–3.9).

Much information on refractory materials, on high-temperature oxides, refractory metals, carbides, nitrides and on the corresponding phase diagrams has been collected in a book series edited by Margrave (1965–), in *High Temperature Technology* (1960), by Campbell (1959) and by Kingery (1959).

Composite materials, glass-ceramics and cermets find several applications in high-temperature technology due to the often unique properties originating from the combination of two or more components. However, in flux growth corrosion is generally the greatest problem, and so crucible materials are chosen mainly to minimize this problem. However, coatings of more corrosion-resistant materials on containers made of materials with high mechanical strength (and frequently lower price) may be useful for several applications in crystal growth. For instance, oxides (Al_2O_3 , ZrO_2) are flame- or plasma-sprayed on to refractory metals and vice versa. Frequently one may observe that resistance to corrosion increases with higher purity of the crucible material.

Corrosion is related to the wetting angle of the melt. The larger the difference in the type of bonding between crucible and melt, the smaller the wetting and the corrosion normally observed. Although it has been proposed to determine covalency or more generally the bonding character from the measured wetting angle and thus to select optimum crucible materials, such determinations of wetting angles are not conclusive. The contact angles frequently depend strongly on the atmosphere, on the surface finish of the solid phase, on adsorbed gas and impurity layers and sometimes even on surface reaction products. However, some useful conclusions may be obtained if a series of experiments are performed as by Champion *et al.* (1973) on the wetting of refractory materials by molten intermetallic compounds.

TABLE 7.13. Crucible Materials, Properties and Applications†

Crucible material	Melting point (°C)	Used for	Max. temp. of use (°C)	Atmosphere	Remarks
Nickel	1453	(R.E.)F ₃ , ZrF ₄ , halides	900	oxygen-free	stable in air up to ~ 900°C
Niobium	2415		~ 1100 ~ 2000	reducing, neutral reducing, neutral, vacuum	Na + K 800° Na + K 600°
Molybdenum	2610		1900	reducing, neutral, vacuum	Ti ₂ O ₃ 1820–1920° (not: TiO reacts)
		Al ₂ O ₃	2050	reducing, neutral, vacuum	Hg 600°, Na + K 700°
Tantalum	3000		2400	reducing, neutral, vacuum	Na + K 600°
		La	1700	reducing, neutral, vacuum	
Rhenium	3180		2380	reducing, neutral, vacuum	
Tungsten	3410		2500	reducing, neutral, vacuum	Eu(+ EuO) 2150°, Hg, Na 600°
		Al ₂ O ₃ , La ₂ O ₂ S	2050	reducing, neutral, vacuum	
Silver	961	KOH	550		
		halides	> 750		
Gold	1063	vanadates	~ 1000		
		Na ₂ CO ₃ , etc.	900		Au–Pd alloys are stronger and resistant to higher temperature

† Thermal shock resistance and other properties; see Table 7.9.

Platinum	1772	silicates, earth alkali borates, LaF ₃	~ 1500	oxidizing	
		PbO, PbF ₂ , Bi ₂ O ₃ , PbO—B ₂ O ₃ , V ₂ O ₅ , molybdates, tungstates	1300	oxidizing	
		NaCl	1000		
Rhodium	1960				
Iridium	2442	stable oxide compounds	2200	neutral	
Graphite	~ 3700 (subl.)	metals, alloys	~ 1000–2000	neutral, reducing	stable in air up to 500°C
		fluorides			Hg 350°
Glassy carbon		alkali halides, sulphides	1000		silicon 2000 (2200° for SiC)
Boron nitride	3000 (dec.)	similar to graphite	approx. 2000	neutral, reducing	stable in air up to 700°C
		Ga (+ GaP)	> 1050		
Aluminium nitride	~ 2200 (dec.)	cryolithe, metals, alloys	1000–1600	neutral, reducing	stable in air up to 700°C
Silicon nitride	1900 (dec.)	metals, alloys	1500	neutral, reducing	
Silicon carbide	2830 (dec.)	metals, alloys	1500	neutral, reducing (see Section 7.2.1)	stable in air up to 1600°
Tantalum carbide	3875	metals, alloys	approx. 3000		
Oxide glasses (Pyrex, Duran, Vycor, Suppremax, etc.)	800–1200	halides (except fluorides) metals, alloys, sulphides, etc.	500		Na + K 300°, Hg 350°
Silica glass	1710	halides (except fluorides)	900	oxygen-free	
		metals, alloys	1100	oxygen-free	
		sulphides, selenides, tellurides		oxygen-free	
		silicon	1500	oxygen-free	Te + (Zn, Hg) Te 650°
Mullite, Sillimanite	1850	metals, alloys	~ 1400	oxygen-free	Hg 350°
		alkali polysulphides	~ 1000	oxygen-free	

TABLE 7.13 cont.†

Crucible material	Melting point (°C)	Used for	Max. temp. of use (°C)	Atmosphere	Remarks
Alumina	2020	metals, alloys sulphides, selenides halides (except fluorides) Ga (+ GaP) alkali polysulphides	1800 1000 1150 1000	oxygen-free halogen or neutral oxygen-free oxygen-free oxygen-free	Na + K 500° Na ₂ CO ₃ 900° vapours and dust very poisonous! Na + K 600°
Spinel	2135	metals, alloys			
Zircon	2420	metals, alloys			
	2715				
Zirconia	2550	metals, alloys			
Beryllia	2570	metals, alloys			
Calcia	2600	metals, alloys			
Magnesia	2800	metals, alloys			Na + K 200° radioactive
Thoria	3050	metals, alloys			
Fluorite	1360	Bi ₂ O ₃ fluorides, metals	1100 ~ 1150		attacked by HCl, chlorides

† Thermal shock resistance and other properties; see Table 7.9.

TABLE 7.14. Resistance of Crucible Materials to Attack by Liquid Metals at 300° and 600°C (Kelman *et al.*, 1950).
The Corrosion Resistance is Good (+ +), Fair (+) or Bad (-)

		Li	Na, K	Hg	Pb	Bi	Cd	Tl	In	Ga	Al	Sn	Zn
Pyrex Glass	600°	-	-	-	-	-	-	-	-	-	-	-	-
	300°	-	++	++	++	++	++	++	++	++	-	++	-
Silica Glass	600°	-	-	-	++	++	++	++	++	++	-	++	-
	300°	-	++	++	++	++	++	++	++	++	-	++	-
Porcelain	600	-	-	-	++	-	-	-	-	-	-	-	-
	300	-	-	++	++	-	-	-	-	-	-	-	-
MgO (porous)	600	-	+	-	-	-	-	-	-	-	-	-	-
	300	-	++	-	-	-	-	-	-	-	-	-	-
Al ₂ O ₃ , BeO (dense)	600	-	+	-	++	-	-	-	-	++	++	-	-
	300	-	++	++	++	-	-	-	-	++	++	-	-
Graphite	600	-	-	-	-	++	-	-	-	++	++	-	++
	300	-	-	++	++	++	-	-	-	++	++	-	++
Cr—Ni Austen. Steel	600	+	++	-	-	-	-	++	++	-	-	+	-
	300	++	++	-	++	-	-	++	++	+	-	+	-
Nickel	600	-	++	-	-	-	-	-	-	-	-	-	-
	300	+	++	-	-	-	-	-	-	-	-	-	-
Ag, Au, Pt	600	-	-	-	-	-	-	-	-	-	-	-	-
	300	-	-	- (Pt +)	-	-	-	-	-	-	-	-	-
Molybdenum	600	-	++	++	++	++	-	-	-	-	-	-	-
	300	++	++	++	++	++	-	-	-	++	-	-	-
Tantalum	600	-	++	-	++	-	-	-	-	+	-	-	-
	300	-	++	++	++	-	-	-	-	++	-	-	-
Tungsten	600	-	++	++	-	-	-	-	-	++	-	-	-
	300	-	++	++	-	-	-	-	-	++	-	-	-

TABLE 7.15. Crucible Materials Used for Various Melts and Solutions, and the Maximum Temperatures Applied

Melt or solution	Crucible	Temp. (°C)	Reference
Pb	Nb, Ta	950	
	BeO, SiO ₂	1000	
	C	550	
	Porcelain	850	
	Pyrex	350	
Bi	Mo, C	1000	
	Nb	450	
	SiO ₂	900	
Bi—Pb—Sn Eutectic	W	500	
	Pyrex	300	
Ga	W, Re	800	
	Ta, ZrO ₂ , Pyrex	500	
	Nb, Mo	400	
	C	>800	
	BeO	>1000	
	Al ₂ O ₃	1150	
Al	SiO ₂	1160	if oxygen-free atm.
	Al ₂ O ₃ , BeO	1000	
	C	1200 (1700)	
	ThO ₂ , ZrO ₂	>1000	
	C, Al ₂ O ₃ , SiC	900	
Zn	C	1300	
Sb	C	1300	
Ti	Y ₂ O ₃	~1700	Helferich and Zanis (1973)
La + LaB ₄	Ta	1200–1700	Deacon and Hiscocks (1971)
Eu + EuO	W	2150	Shafer <i>et al.</i> (1972)
US ₂ + US	W	1700–1900	Van Lierde and Bressers (1966)
Ti ₂ O ₃	Mo	1820–1920	Reed <i>et al.</i> (1967)
Alkali halides	Supremax glass	750	Janz (1967)
Bi ₂ O ₃	ThO ₂	1100 (4h)	Tiche and Spear (1972)
KOH + BeO	Ag	550	Levin <i>et al.</i> (1952)
KF + V ₂ O ₅ + V ₂ O ₃	Pt	950	McWhan and Remeika (1970)
V ₂ O ₅	Pt	max. 700	Kennedy <i>et al.</i> (1967)
PbO + PbF ₂ + Oxides	Pt	1300	Various authors
PbO + B ₂ O ₃ + Oxides	Pt	1300	Various authors
PbO + V ₂ O ₅ + Oxides	Pt	1350	Various authors
BaO × 0.6B ₂ O ₃ + Oxides	Pt	1400	Various authors
KF + BaTiO ₃	Pt	1200	Various authors
Na ₂ CO ₃ + BaTiO ₃	Ni	1200	Reducing atm., Kawabe and Sawada (1957)

TABLE 7.16 Temperatures of first noticeable reaction (upper right part) and the maximum working temperatures (lower left part) in °C.

	SiO ₂	Al ₂ O ₃ + 2SiO ₂	Al ₂ O ₃	B ₂ O ₃	MgO	ZnO	TiO ₂	MgAl ₂ O ₄	ZrSiO ₄	Ta ₂ O ₅	CaF ₂	BN	SiC	AlN	Si ₃ N ₄	C	Mo	W	Ni	Al	V	Nb	Zr	Ti	Pt	Atmosph. check	
SiO ₂	1700 1250															1400 N	1500 N	1600 N			800 H ₂				750 NR	ON (R) + *	
Al ₂ O ₃ + 2SiO ₂	1850 1800	1100																							750 NR	ON (R) m	
Al ₂ O ₃	2015 1900	1200	1200		1800	1800	1700	1800		1700						1800 L	2000	2000	2100	1800 L	1800 L	1100	1600	1600	1500 (V) 1550 (O)	ONR m	
B ₂ O ₃	2550 2000 V 2350	1000	1100	1200	1800	1900	2100	1800		1600						2100	1900	2100	1800 L			1100	1600	1600	1550	ONR + *	
MgO	2800 1600 (V) 2400 (O)	1000	1100	1200	1600	1500	2200	1800		1500						1800	1800	2000	1800 L			1800	1800	1400	1650 (ON)	O	
ZnO	2677 2100 V 2400	1000	1200	1600	1600	1800	2200	1800								1800	2150	2100	1800 L			1800	1800	1600	1150	NR m	
TiO ₂	3400 2300 V 2800	1000	1200	1500	1800	1900		1800								1950	2200	2200	1800 L			1800	1800	1600	1150	NR m	
MgAl ₂ O ₄	2100 1950	1200	1300	1400	1600	1800																			~1600	NR m	
ZrSiO ₄	2420 1870	1100	~1000	~1000	1200																				~1600	NR +	
Ta ₂ O ₅	1150	1100	1200	~1400	1200																				~1600	NR +	
CaF ₂	1150	800	800	~1000																					~1600	NR +	
BN	2600 (O) 1700 N	1400	1400	1400	1400																				~1600	NR +	
SiC		1100																							~1600	NR +	
AlN	2000																								~1600	NR +	
Si ₃ N ₄	1500	1400																							~1600	NR +	
C	2300 V 1000 N (1800)	1000	(1800)	(2300)	(1800)	1800	1950										1300	1500	1300						~1600	NR +	
Mo	2100 V	1400 N	(2000)	(1900)	(1800)	2150	2200										1600	2300	1300						~1600	NR +	
W	2400 V	1600 N	(2100)	(2100)	(2000)	2100	2300										1700	2300							~1600	NR +	
Ta		1500 N	(2000)	(2000)	(1800)	2100	2300																		~1600	NR +	
Ni	1200 (NR) 1000 (O)									1700															~1600	NR +	
Pt	2000 (R) 1700 (O)	700	700	1300	500	1600	1100	1100	1600	800	1500 (O)														~1600	NR +	
PROPOSED MAXIMUM WORKING TEMPERATURES																											
Atmosphere	ONV	ON	ONV	ON	ON	ON	ON	ON	ON	ON	N	NRO	NRO	NRO	NRO	RNV	RNV	RNV	RNV	NV	RNV	RNV	RNV	RNV	O		

PROPOSED MAXIMUM WORKING TEMPERATURES

Atmosphere	ONV	ON	ONV	ON	ON	ON	NO	NO	NO	O	N	NR	NR	NR	NR	RNV	RNV	RNV	RNV	NV	RNV	RNV	RNV	RNV	O
------------	-----	----	-----	----	----	----	----	----	----	---	---	----	----	----	----	-----	-----	-----	-----	----	-----	-----	-----	-----	---

~ Estimated values; N Neutral atmosphere; R Reducing; L Liquid; O Oxidizing atmosphere; V Vacuum.

Thermodynamic data may give some general indication of the stabilities of crucible materials and their reactions with high-temperature melts, but results to better than the order of magnitude must not be expected because of the limited reliability of much thermodynamic data, of the influence of the grain size, impurities and dislocations of the crucible material, as well as of the detailed chemistry of the solution and the gas atmosphere. The data for stabilities of the crucible materials given in Tables 7.13 to 7.16 must be regarded as approximate. As an example of the estimation of interface reactions using thermodynamic data, the paper of Armstrong *et al.* (1962) may be mentioned. These authors claimed that at fairly high temperatures strong reactions with silica occur for those metals of which the oxides form low-melting eutectics with silica.

In the following paragraphs two classes of crucible materials will be discussed in detail because they are the most frequently used in flux growth, namely (A) ceramic crucibles, and (B) noble metal crucibles. The general aspects of the size of crucibles are discussed in Section B.

A. Ceramic crucibles.

Silica: Silica glass is highly corrosion-resistant and is easy to form to any desired shape. It is transparent and has a low thermal expansion coefficient, so that it is resistant to thermal shock. The resistance of silica against corrosion can be increased by deposition of a thin carbon layer obtained by decomposition of acetone or ethanol at 500 to 700°C in an atmosphere low in oxygen or by deposition of an alumina layer about 500 Å thick as reported by Widmer (1971). Silica glass crystallizes slowly around 1000°C (especially where traces of alkali, like NaCl from sweat, are present) and more quickly above 1100°, and the crystallization products, tridymite and cristobalite, undergo destructive phase transitions between 100 and 400°C so that recrystallized silica frequently breaks or explodes in this temperature range. At temperatures above 1100° softening takes place, but silica glass can be used for Czochralski growth of silicon at 1540° when its shape is maintained by an external graphite container. Chemically silica is stable against carbon, many metals, sulphides, selenides and halides up to 1000°C, but it is attacked by fluorine-containing vapours and liquids, basic melts (with formation of silicates), many oxides, hydroxides, phosphates, alkali and alkaline earth metals, aluminium and boiling phosphoric acid. Lead, tin and cadmium corrode silica only if the ampoule contains traces of oxides. For experiments in oxygen- and water-free atmospheres the hydroxide layers adsorbed at the surface must be removed by etching with HF—HNO₃ mixtures, immediately followed by short rinsing with metal-free distilled water and subsequent heating at 1000°C for two hours in vacuum. For use at temperatures below 750°C silica glass may be re-

placed by Vycor† or Suppremax†, below 500°C by Pyrex† or Duran† glass.

Oxide ceramics: Of the pure oxide ceramics, alumina finds the widest application in crystal growth from high-temperature solutions, but the more expensive zircon ZrSiO_4 , zirconia ZrO_2 and thoria ThO_2 are generally more resistant against corrosion. For example, thoria is not measurably attacked by bismuth oxide at 1100° and thus can be used for growth of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and similar compounds (Tiche and Spear, 1972). For many applications (melts of metals, sulphides and halides except fluorides) the relatively inexpensive porcelain (mullite, sillimanite), or ceramics based on magnesium silicates, pyrophyllite and Lavite† which can be shaped before the first firing are adequate. For example, glazed porcelain crucibles have been repeatedly used for potassium pyrosulphate melts between 700 and 900°C in order to clean platinum crucibles. According to Jaeger and Krasemann (1952), who investigated the stability of alumina against various agents, borax melts polish the surface of alumina ceramics. However, silicates are not useful in reducing atmospheres at high temperatures. Most ceramic crucibles are sensitive to acids and are either dissolved (BeO , MgO , CaO), or show cracking when reheated after cleaning with acid. In many aspects new types of ceramics which have nearly 100% density and are translucent or even transparent (Al_2O_3 , Yttralox† = 90% Y_2O_3 , 10% ThO_2) have many advantages (corrosion resistance, vacuum-tight, high maximum working temperature) but are disadvantageous with respect to thermal shock resistance. For special applications single crystalline alumina crucibles and tubes produced by flame fusion or edge-defined film-fed growth might be useful.

Ceramic containers and tubes may be sealed if required either by a high-temperature cement or by welding with a flame or plasma. In principle cheap ceramic containers covered with a thin platinum layer might be used as a replacement for the very expensive platinum crucibles, or corrosion-resistant layers (e.g. of Al_2O_3 or ZrO_2) may be evaporated or plasma-sprayed on to porous and thus shock-resistant crucibles, but such combinations have not yet found wide applications.

Base metals and non-oxide ceramics: Of the base metals nickel, stainless steel, molybdenum, tungsten and tantalum are most frequently used as crucibles, but at temperatures above about 500° oxygen- and water-free atmospheres are required. At such low oxygen pressures as 10^{-3} atm and at high temperatures up to 10 atom % oxygen is dissolved in niobium and tantalum whereas in molybdenum and tungsten the oxygen solubility is smaller by orders of magnitude. At higher oxygen concentrations the metals are completely oxidized. The oxidation behaviour and other properties of

† Trademarks.

refractory metals have been described by Jaffee in *High Temperature Technology* (1960), and the oxidation of Nb and Ta is discussed by Fromm and Jehn (1972). Molybdenum and tungsten crucibles are suitable for containing melts of pure molten alumina, but are attacked by ruby melts.

In crystal growth from high-temperature solutions Mo, W and Ta crucibles are probably most widely used for growth of chalcogenides of the lower valency states from the corresponding metal melts (e.g. EuS, EuSe, EuTe from Eu) as well as for growth of other refractory compounds (WC, LaB₆) from metallic solutions.

Sawada *et al.* (1951) and Kawabe and Sawada (1957) used nickel crucibles for the growth of BaTiO₃ from Na₂CO₃ solution in a reducing atmosphere and found no attack of the crucible. In air or even in nitrogen, nickel is attacked by carbonate melts. Hauptman *et al.* (1973) used iron crucibles for growth of Fe₂TiO₄ from BaO—B₂O₃ solutions in a nitrogen atmosphere and Garrard *et al.* (1974), Ni and Mo for growth of fluorides.

Of the non-metal non-oxide refractories graphite is probably the oldest and most popular, and the development of pyrolytic graphite and of glassy carbon has extended the usefulness of carbon crucibles. A characteristic of graphite is that its strength increases with temperature and so is higher than many other refractories (BeO, MgO, ZrO₂, W) above 2000°C. Because of its corrosion resistance, its excellent thermal shock resistance and its relatively low price, graphite is the first choice as crucible material for metals (except those which form carbides), fluorides, and sulphides. Its disadvantages are its reducing action and that it has to be protected from oxidation above about 500°C. The III–V analogue of carbon, boron nitride, shows a slightly better oxidation resistance and a very high electrical resistivity of about 10⁷ Ω cm at 1000°C. BN is resistant to molten nonferrous metals and many salts, and its oxidation in air starts only above about 900°C.

Another III–V analogue is the nitride AlN, and AlN ceramics containing small amounts of silicon carbide decompose above 2200°C and are very resistant towards molten metals. They are not wetted by molten steel and do not react with cryolite melts at 1040°C. In air AlN is oxidized above about 700°C.

Silicon carbide is the most important of the refractory carbides. It has a hardness 9 on the Mohs scale, a high thermal conductivity and low thermal expansion coefficient and is thus very resistant towards thermal shock. Another advantage of SiC is its oxidation resistance up to about 1550°C (with the exception of the range below 750°C where "silicon carbide pest" occurs and where the protective SiO₂ layer cannot form so that SiC is oxidized).

Little attention has been given to refractory borides, silicides and

sulphides and their application to flux growth although they are expected to exhibit a good corrosion resistance against metals and fused salts, and a reasonable stability because of their high melting points, generally between 2000 and 3000°C. For example, zirconium boride ZrB_2 has a melting point of 3040°C, is oxidation-resistant up to 1000° and is not wetted by many molten non-ferrous metals such as Zn, Al, Pb, Cu, Sn and brass.

B. Noble metal crucibles. In crystal growth of oxide compounds and of some fluorides from high-temperature solutions the most common crucible materials are noble metals, and from this group of metals platinum has found by far the widest application. Since platinum has a relatively high price, the initial cost as well as refabrication costs form a significant (if not the largest) portion of the costs of flux growth of oxides. The prices of platinum (and of iridium) fluctuate enormously, as may be seen from Fig. 7.35. In this connection it should be noted that several companies and syndicates ask prices which are 50% and more higher than the free market (U.S.) price. The free market price tends to be a sensitive indicator of demand and supply trends. The bulk of platinum is costed at the fixed producer price, and both prices vary widely. A price of 120 dollars per

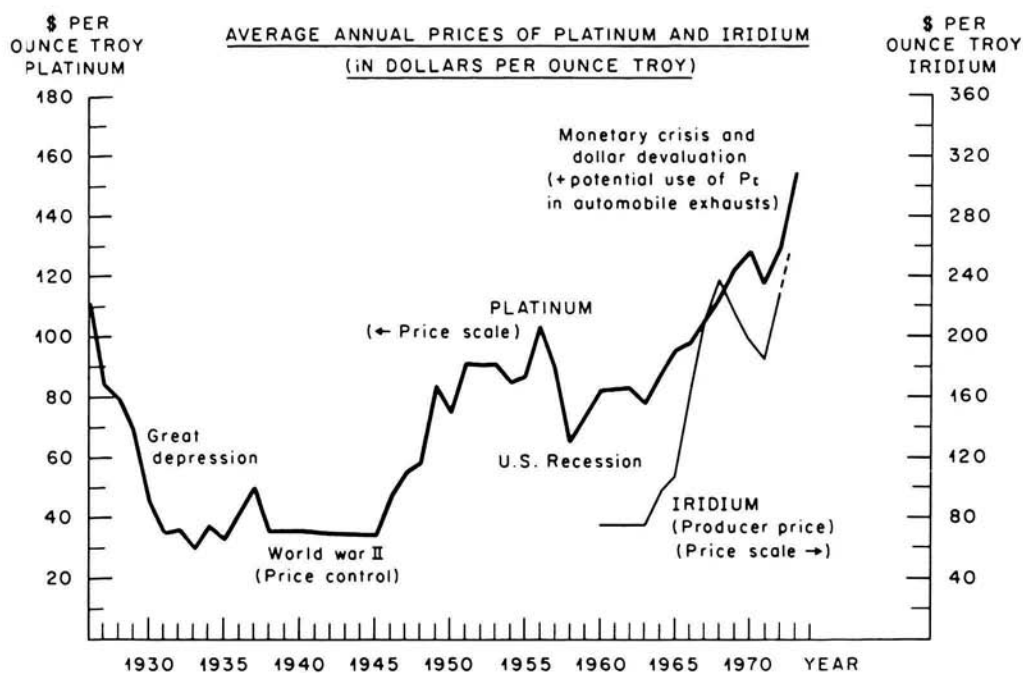


FIG. 7.35. Price fluctuations of platinum and iridium.

ounce platinum may be used as a guideline for the free market price, and 50 dollars per ounce for the producer price. In 1971/1972 there was a shortfall in the free market price of about 40 dollars per ounce until the U.S. government decided not to postpone the Clean Air Act of 1970. The steep increase in the platinum price caused by the potential demand for platinum in automobile exhausts was accelerated by the monetary crisis of 1972/1973. The platinum price may drop significantly if the crisis is settled, if an alternative to platinum in exhausts is adopted or if Russia offers abnormally large quantities of platinum to the Western market as happened at the end of the fifties.

Platinum crucibles for flux growth may be obtained from various sources, either in standard shapes or to special order. Frequently it may be faster and more convenient to order round platinum sheets and have them shaped by a local noble metal spinning shop. A variety of crucible forms used in several laboratories are shown in Fig. 7.36; (a) shows a standard crucible with lid which is commercially available in several sizes; (b) a modification of the crucible rim and lid of Kvapil (1966) and John and Kvapil (1968), which allows sealing by a liquid; (c) a special crucible form used by Scheel (1972) and Scheel and Schulz-DuBois (1971) which is mechanically stable and to which a flat round lid can be welded. After the experiment, crucible and lid are separated by cutting the welded rim, and can be re-used about five times; (d) shows a modification of the lid with a hole of 0.4 mm diameter (Elwell and Morris, unpublished) which is loosely covered by a platinum sheet and which can be sealed after heating up and expansion of the enclosed air by pressing on this sheet from above; (e) the crucible arrangement of Tolksdorf (1968) made from a large diameter platinum tube and with a lid sealed to it having a platinum capillary to release pressure; and (f) shows a diagram of the large crucibles used at Bell Laboratories and at Airtron for pilot plant flux growth. Slightly conical crucibles are advantageous for removing solidified flux and for reshaping which should be done on plastic formers with a plastic or leather hammer. Preferred wall thicknesses are from 0.5 to 1 mm for a crucible volume of 30 to 1000 cm³, 0.3 mm being the practical minimum. A greater wall thickness increases not only the lifetime of the crucible, but also allows the destruction by beating with a slightly convex hammer of grains formed by recrystallization.

The crucible size is discussed here because it has a dramatic and often restricting effect when expensive noble metals have to be used as crucible materials. According to Block (1930), Goethe had already recognized that increasing the crucible size tends to increase the crystal size, and during the past century crucible sizes up to 50 l were used as discussed in Chapter 2. In recent years platinum crucibles of 4 l and even 8 l were used by various

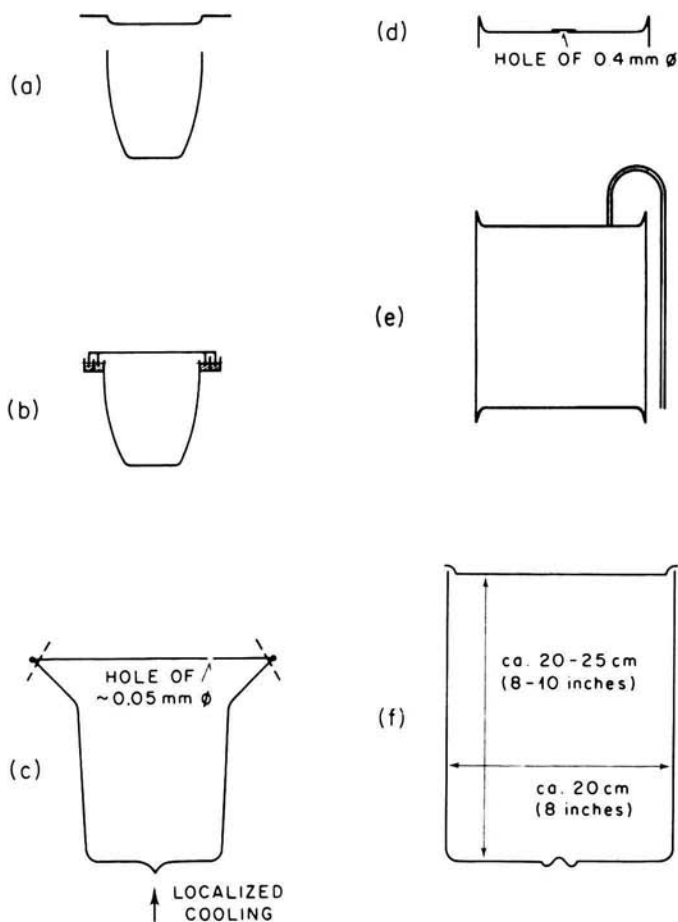


FIG. 7.36. Examples of crucible shapes used in flux growth (not to scale).

companies for the growth of garnets and ruby. However, large crucibles are not always advantageous for a number of reasons.

In Section 6.6.1 the experimental requirements for stable growth are discussed, and for large crucibles extremely low cooling rates for the first weeks or months are required if one or a very few inclusion-free crystals are to be grown. If multinucleation is tolerated or if seed crystals of sufficient area are available "normal" cooling rates (between 0.1°h^{-1} and 1°C h^{-1}) and duration of experiments can be applied. The effect of the crucible size is demonstrated in Fig. 6.16, which also shows the importance of high solution flow rates at the crystal surfaces in order to achieve stable growth. The larger the crucible the more stirring is necessary in order to

prevent convection pockets and thus uncontrolled nucleation, as discussed in more detail in Section 7.2.7. As a general rule stirring is worthwhile for crucibles larger than 100 cm³ and is necessary for crucibles larger than about 500 cm³. Another requirement with large crucibles is that temperature control and programming have to be very precise, and it is estimated that temperature oscillations larger than 0.1°C with periods larger than about one second might have harmful effects on the quality of the grown crystals.

Another obvious disadvantage of large crucibles is their price and the requirements on the size of the furnace and controller, and the total cost of systems based on crucibles more than 1 litre in size is often prohibitive.

An advantage of large crucibles is the low ratio of wetted crucible surface to the volume of solution which determines crucible corrosion and incorporation of crucible material into the growing crystals. The incorporation of, for example, platinum can be significant depending on experimental parameters as was demonstrated by Bradt and Ansell (1967). These authors found 0.1 wt% Pt in BaTiO₃ crystals grown from KF when a soaking time of four hours was applied, whereas without soaking only 0.065 wt% Pt was found.

Another advantage is obviously the quantity of crystals which can be grown simultaneously, and large crucibles are required when large-scale production of crystals is applied. Grodkiewicz *et al.* (1967) obtained a yield of 2.8 kg YIG from 81 crucibles although about 2/3 of the volume of the YIG crystals contained inclusions. This fraction of included crystals might be reduced if stirring, seed crystals and precise temperature control are applied, as discussed above.

On comparing the advantages and disadvantages of large crucibles the conclusion is reached that an optimum crucible size exists as a compromise. As a rule, crucible sizes of 25–100 cm³ are suggested for crystals of a few mm size, but for crystals larger than 1 cm³ the crucible size should increase by about 100 cm³ per cm³ crystal.

Occasionally an influence of crucible size on the crystallizing phase has been reported and explained by Flicstein and Schieber (1973). If a composition lies near the boundary of stability fields of different phases, then the difference in the evaporation rate in crucibles of different sizes might shift the PbO—PbF₂ ratio (in this case) and thus lead to different phases.

In order to produce the smallest possible surface and thus to minimize corrosion and nucleation sites the crucibles should be mechanically and chemically polished. The latter is performed for example with a potassium pyrosulphate melt at 700 to 800°C (however, Rh-containing crucibles are

attacked by pyrosulphate) for one to four hours, and any reshaping and hammering should be followed by chemical polishing.

A short preheating of Pt crucibles to about 1200°C before use prevents excessive welding of new platinum pieces when in contact. Special care in the use and handling of platinum crucibles is necessary in order to prevent crucible failures during the growth experiments (and too frequent reshaping). Platinum crucibles should only be used for ionic melts (fluorides, oxides, silicates) but never for elements and for compounds with strong covalent or metallic bonding. Thus metals, phosphorus, arsenic, antimony, bismuth, silicon, boron and sulphur should never be heated in Pt crucibles. Especially carbon, carbides or organic compounds should not contact hot Pt containers and reducing atmospheres should be prevented under all circumstances. For example, traces of organic compounds or of hydrogen may reduce the heavy-metal compounds like Bi_2O_3 , PbO and PbF_2 and may lead to destruction of the crucible. In order to maintain oxidizing conditions an oxidizing agent like PbO_2 (Garton and Wanklyn, 1967) is frequently added, or a buffer like V_2O_5 which is more easily reduced to V_2O_3 than PbO to Pb . Also a reducing atmosphere can be prevented by slowly blowing air into the furnace chamber. As supports stable oxide ceramics should be used since silica and silicates are easily reduced above 1000° to 1200°C, and the resulting SiO (or Si formed by disproportionation of SiO) forms with Pt low-melting eutectics. Thus, only alumina or other stable oxides should be used in conjunction with platinum.

Cleaning of platinum crucibles to remove adhering flux or oxides is done by careful tapping with a plastic hammer, and/or by dissolution with the appropriate hot acid or alkali solution, or by dissolution with a flux. Nitric acid or hydrochloric acid may be used separately, but a mixture of these two acids (aqua regia) will form free chlorine and dissolve platinum (iridium-rich platinum alloys are rather resistant to aqua regia). Adhering oxide crystals, if not easily removed mechanically may be dissolved in melts of potassium pyrosulphate at 700–800°C (SO_3 vapour is formed), in Na_2CO_3 — K_2CO_3 melts around 900°, in borax at about 1200°, or in KF or PbF_2 melts at 1200°C. Silicates are easily removed with concentrated hydrofluoric acid. After leaching these melts and after any hammering or reshaping the platinum crucibles should be treated with hot nitric acid for one hour, and after rinsing with sufficient distilled water the crucible should be dried by heat (not with a towel) and kept dust-free until use.

Generally pure platinum is used for growth of oxide compounds from their solutions in molten salts. Alloys of platinum frequently have advantages or are even required for special applications. Thus for growth of SrTiO_3 and BaTiO_3 from melts containing excess TiO_2 , Pt–Ir or Pt–Rh alloys are used because of their higher melting points, and for still higher

temperatures iridium might be used. According to Nielsen (1974) iridium crucibles might be used for PbO-free PbF_2 solutions in inert or slightly reducing atmosphere since Ir is not attacked by Pb up to 1600°C.

The disadvantages of Rh and Ir (and Pt-Ir alloys) is that they are more easily corroded than pure platinum by the normal Pb- or Bi- containing solvents and at low temperatures. For example Cloete *et al.* (1969) found in MgAl_2O_4 crystals no platinum, but traces of iridium which was probably present as an impurity in the platinum crucible used, and rhodium is frequently found in crystals grown from Pt crucibles. Small rhodium addition (0.5–1%) to the platinum increases its mechanical strength and decreases the tendency to recrystallization. Pt-Au and Pt-Au-Rh alloys are very little wetted by borate and silicate melts, but on the other hand Au and Rh are easily extracted from platinum containers. Iridium evaporation (as IrO_2) might be minimized by rhodium plating.

In summary, for all applications special crucible materials, shapes and sizes may be found which, with the appropriate experimental conditions, might contribute significantly to the size and quality of the flux-grown crystals. Aspects of handling noble metal crucibles are given in booklets and catalogues of the producer companies and in the reviews and papers of Brice and Whiffin (1973), Cockayne (1968), Darling *et al.* (1970), Robertson (1969), Robertson *et al.* (1974a) and Van Uitert (1970). The development of cheaper crucibles would probably extend the application of the flux method.

7.2.4. Separation of crystals from solution

In general crystallization from high-temperature solution is terminated with the solution at a temperature above the eutectic point, and the crystals produced may be separated from the excess solution either at this "final" temperature or following relatively rapid cooling to room temperature. The former alternative is generally preferable when this is convenient, as in top-seeded growth where the crystal may normally be raised out of the solution by a motorized drive mechanism.

When the crystals are grown by spontaneous nucleation, cooling of the crucibles to room temperature prior to removal of the crystals is fairly widely practised because of its relative simplicity. The excess solution is then normally dissolved in some aqueous reagent, a process sometimes referred to as "leaching". The leaching process relies on the differential solubility in this reagent of the crystal and the high-temperature solvent and it is clearly important for easy removal of the crystals that a suitable reagent should be available. Aqueous solvents for the more popular high-temperature solvents are listed in Table 3.13.

The great disadvantage of removing the excess solution at or around room temperature is that the rate of dissolution may be extremely low. A

month or even longer may be required to remove, for example, bismuth borates from a crucible of only 100 ml capacity and means of avoiding such delays are clearly desirable. Warming the container used for leaching will promote dissolution and the resulting saving in time can be dramatic especially if leaching is performed at a temperature close to the boiling point of the aqueous reagent. As an example, Elwell and Morris (unpublished) have found that excess $\text{PbO/PbF}_2/\text{B}_2\text{O}_3$ may be dissolved within 1–2 days when the crucible is maintained in fairly dilute nitric acid close to its boiling point. Boiling chips must be added to the acid and the temperature of the acid bath maintained constant by a hot plate or oilbath. The most rapid leaching rates require that the acid be replenished at frequent intervals which depend on the volume of the container used.

Cooling of the crucible and crystals to room temperature suffers from the additional disadvantage that strain may be introduced in the crystals because of the contraction of the solution as it solidifies. This is especially the case when relatively soft crystals like sulphides are grown from molten salts. However, even if crystals are removed while the solution is molten, thermal strains will be present and the crystals should be annealed if freedom from strain is important.

Removal of the excess solution above some critical temperature may be essential if the system is such that re-dissolution of the crystals would occur on further cooling. Even in systems where no such dissolution would occur, the saving in time which is achieved with hot pouring has led to its increasing use. The simplest means of pouring off the excess solution is to remove the crucible from the furnace with tongs and to decant the liquid after removing the crucible lid. This method is possible only when the lid fits loosely onto the crucible, since it is desirable that the crucible should be returned to the furnace as rapidly as possible in order to minimize thermal shock to the crystals; especially when crystals larger than about 1 cm^3 are grown cracking may occur on any sudden temperature changes.

An alternative procedure has been suggested by Grodkiewicz *et al.* (1967) who puncture the base of the crucible from below with a steel spike, without removing the crystal from the furnace. The drainage hole may be re-welded so that the crucible can be used several times before refabrication is necessary.

The seeding technique of Bennett (1968) and Tolsdorf (1968), described in Section 7.1.1, provides a particularly convenient means of removing the crystal from the residual solution by inversion of the crucible. Crucible inversion is applicable to sealed crucibles and may be used for unseeded growth if some mechanism is provided within the furnace. This mechanism may be extremely simple, for example, a wire attached to the base of the crucible which is pulled vertically upwards, provided that the crucible is

mounted on a suitable pivot (J. M. Robertson, private communication). A device which may be used for simultaneous hot pouring by inversion of a number of crucibles is shown in Fig. 7.37(a) and (b). The crucibles are mounted in a cemented firebrick block which has the primary advantage of providing a high thermal capacity during growth. At the termination of growth, a clamp mounted on a relatively massive trolley is brought into contact with the block, which may then be removed from the furnace, inverted and returned to the furnace very rapidly with little thermal shock to the crucibles. The crucible lids are crimped tightly to minimize evaporation during growth, but provide imperfect seals so that the excess solution drains away into the surrounding powder and firebrick, which is replaced after every experiment.

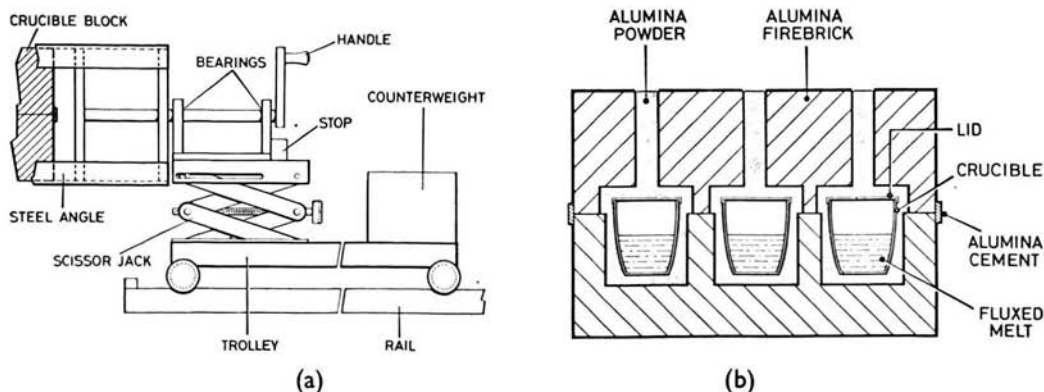


FIG. 7.37. Device for simultaneous hot pouring of several crucibles. (a) Mechanical setup. (b) Ceramic block with crucibles (Smith and Wanklyn, 1974).

Completely sealed crucibles permit a greater degree of reproducibility in the crystal growth conditions but inversion and subsequent solidification of the residual solution presents problems in the removal of the lid and of access to the crystals. Scheel (unpublished), using the sealed crucible design shown in Fig. 7.36(c), has found it more convenient to pour off the solution from the crucible by puncturing holes in the lid with a small steel spike after rapid removal of the crucibles from the furnace. The crucible is quickly replaced into a furnace which is then slowly cooled to room temperature. The small thermal shock introduced by this procedure is more than offset by the ease of access to the crystals after cooling to room temperature.

An isothermal technique to remove excess solution has been used by Kawabe and Sawada (1957) who, after growth of BaTiO_3 from Na_2CO_3 solution at 900°C , sucked up the still liquid flux through a nickel pipe by a rotary pump, and then cooled the furnace with the crucible to room

temperature. In a similar manner for sealed crucibles, pressure from outside could be used to pump the excess solution out of the crucible.

7.2.5. Chemicals

The importance of attention to chemicals cannot be overemphasized and many problems of lack of reproducibility in crystallization from high temperature solution may be related to differences in the starting materials. Most experimenters prefer to buy pure chemicals from specialist suppliers rather than undertake their own purifications but it is well known that different batches of chemicals may vary in their impurity content and in the assay of the substance in question.

In general the chemicals which are supplied can be classified into four broad categories—laboratory or reagent grade with a purity normally quoted in the region of 99%, “analytic grade”—about 99.9%, “spectroscopic grade”—up to 99.999%, and ultra-high purity grades of certain chemicals, supposedly with even higher purities, may be available according to the nature of the material required. The increasing availability of high purity chemicals has been of great value in crystal growth and has been a contributory factor in the preparation of relatively perfect crystals. The experimenter should, however, be aware of the dangers of unquestioning reliance on the manufacturer's analysis. Even where the material is accompanied by the typical result of spectrographic analysis quoting impurity levels in the ppm range, it should be realized that the manufacturer does not guarantee the assay of the material. So, for example, the material may contain volatile impurities such as organic matter, carbon dioxide or water vapour. Moreover, the stoichiometry may differ very considerably from the nominal composition.

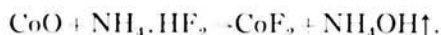
As examples of the types of problem encountered by the authors, a sample of high purity Al_2O_3 from a well-known manufacturer with a stated molecular weight of 101.9 was found by X-ray diffraction to consist mainly of hydrates. Similarly a batch of nickel oxide “NiO” from a different supplier contained about 30% by weight of metallic nickel.

Departures from ideal compositions can increase with storage, particularly once a container has been opened, and particular care is necessary with hygroscopic materials such as B_2O_3 , La_2O_3 , many halides and even the γ -modification of alumina, especially in powder form. Materials in powder form are particularly liable to attack from the atmosphere on account of their large specific surface area. In several cases it might be necessary to handle such hygroscopic substances or other reactive materials (e.g. metals) in dry-boxes or at least under a dry stream of nitrogen. It is desirable to record in a laboratory notebook the batch number of any new delivery of chemicals, and the dates on which it was received and opened.

Checks of new batches of chemicals by X-ray powder diffraction, and possibly also by chemical analysis, are desirable, and the use of a thermobalance is valuable for detection of departures from stoichiometry of oxides or of the presence of free or bound water. Chemicals should also be checked for the presence of foreign bodies such as hair or other fibres, or pieces of furnace constructional material which may have entered the sample during manufacture. It is obvious that all containers and tools which come in contact with the chemicals or the growth solution must be absolutely dry and clean. The presence of any contaminant will, of course, lead to errors in weighing out the constituents of a growth experiment, and to impurity contamination which in most cases has a bad and sometimes a catastrophic effect as for instance traces of silicon in flux growth of BeO (Austerman, 1965). The positive influence of some impurities on growth has been discussed in Chapter 3, and the effect of impurities on the habit in Chapter 5.

For specialized preparations or when the highest purity is required the availability of facilities for purification is essential. The techniques of synthesis of high-purity substances and of chemical purification have been reviewed by Kröger (1964), by Wilke (1973) and by Jonassen and Weissberger (1963–1968). The synthesis of inorganic compounds in general is the topic of books of Angelici (1969), Brauer (1960/1962), Hecht (1951), Jolly (1970) and Lux (1970) and of the series *Inorganic Syntheses* (Vols 1, 1939–13, 1972). Purification can be done by *sublimation* or *distillation*, by *heating*, possibly in a vacuum, to evaporate volatile impurities and burn off organic contaminants, and by *recrystallization*. For metals, electrolysis may also be used to separate the metal from its salts and from other metal impurities. These methods all rely on the preferential distribution of impurities between different phases, so that the principles follow the discussion of distribution coefficients outlined in Section 7.1.4. The most important technique for the preparation of high purity materials for crystal growth is *zone refining*, which employs repeated crystallization from the melt with the impurities concentrated into a thin molten zone which traverses the material. Zone refining or zone melting is the subject of books by Pfann (1966) and Schildknecht (1966), both of whom quote examples of the application of this technique to oxides, salts and metals in addition to the semiconductors and organic materials for which the technique was developed.

Additional purification methods may be used to purify certain materials, in particular by the addition of reagents which react with impurities to form volatile species. As an example, Wanklyn (1969) removed traces of oxides and hydroxide ions from fluorides by heating with ammonium bifluoride $\text{NH}_4\cdot\text{HF}_2$ to form volatile ammonium compounds, as by the reaction



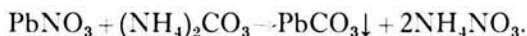
The purification of salts is considered by Corbett and Duke (1963) who consider particularly problems of the removal of hydrolysis products. The desirability of purification prior to fusion is mentioned to facilitate the removal of impurities which become more strongly bound in the liquid phase.

Several articles on the purification of semiconductors and of the materials used as dopants are contained in the book of Brooks and Kennedy (1962). The scope of this collection includes the purification of chromium and rare earth metals in addition to semiconducting elements and compounds.

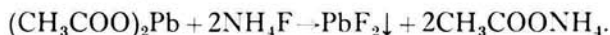
In view of the extensive literature on semiconductor materials, we consider in more detail here some examples of preparation and purification studies of other materials of particular interest.

Boric oxide. The presence of water in B_2O_3 is a well-known problem both in the use of borate fluxes and in the application of this material as an encapsulant in Czochralski growth (Mullin *et al.*, 1965). Chang and Wilcox (1971) found that reagent grade boric oxide contains about 3 wt% of water. Most of this water is removed on heating in a vacuum oven at 260–270°C, but the small traces which remain can be harmful to crystal growth. The removal of moisture from molten B_2O_3 is slow because of its high viscosity but Chang and Wilcox found that drying is accelerated if dry nitrogen is bubbled through the melt. On cooling to room temperature the moisture absorbed by vitreous B_2O_3 was found to be restricted to the surface and could be substantially removed by a vacuum without further heating.

Lead oxide and fluoride. Lead oxide and fluoride are probably the most widely used fluxes and their purification is therefore of particular interest. Schieber (1967) reported that the highest purity PbO could be prepared by precipitating lead carbonate from a solution of lead nitrate by adding ammonium carbonate:



Lead oxide is produced from the carbonate by heating to 400°C in a clean atmosphere. The preparation of pure lead fluoride is also considered by the same author who proposes that the purest material may be prepared by precipitation on mixing lead acetate and ammonium fluoride solutions:



Kwestroo and Huizing (1965) also used lead acetate in solution in order to prepare high purity lead oxide by precipitation with ammonia. But it

should be said here that PbO and PbF₂ of high purity are now commercially available so that in general purification of these important solvents is not necessary. If for special applications ultrapure PbO or PbF₂ should be required it is suggested to obtain them by zone melting in pure platinum boats or tubes.

A few examples of synthesis and purification of specific solvents and chemicals used in crystal growth from HTS have been reported: BaCl₂, SrCl₂ (Fong and Yocom, 1964); LiF (Eckstein *et al.*, 1960; Kiyama and Minomura, 1953; Weaver *et al.*, 1963; Thoma *et al.*, 1967); NaCl (Raksani and Voszka, 1969; Lebl and Trnka, 1965); KCl (Capelletti *et al.*, 1968, 1969; Kanzaki and Kido, 1960/1962; Lebl and Trnka, 1965; Butler *et al.*, 1966); Na₂WO₄ (Cockayne and Gates, 1967); V₂O₅ (Jankelevic *et al.*, 1967).

Rare-earth metals present particular problems because of their extremely high reactivity. High purity oxides are commercially available and can be used as the starting material for the elements and hence for other compounds. Alternatively the relatively impure metals available from commercial suppliers may be used as starting material, as in the method of Busch *et al.* (1971). These authors noted by mass spectrometry that metals claimed to be 99.9% pure actually contain a few wt% of non-metallic impurities, mostly dissolved gases. In their method the dissolved gases are partly desorbed and partly precipitated as non-volatile components by heating the metal to its melting point, followed by distillation. The distillation is carried out in a molybdenum vessel in a sealed UHV system at 3×10^{-7} Torr. Apart from H, C, O, Ca and Ba, impurity levels (including Mo) were less than 1 ppm. Also Habermann *et al.* (1965) purified the rare-earth metals, namely by reduction of the fluorides followed by distillation. In general, contamination from the crucible is expected to be high and the "cold crucible" of Hukin (1971) was developed to provide a clean container for rare-earth metals. Alternative methods for purification of rare-earth metals are described in the article by Love and Kleber in the collection of Brooks and Kennedy (1962).

The importance of using pure chemicals so that contamination of the crystals is minimized is shown up in a striking fashion by several physical measurements. Sproull (1962) has shown that the thermal conductivity at low temperatures is particularly sensitive to impurities and differences of two orders of magnitude are observed when pure sodium chloride is compared with commercial grade crystals.

Suppliers of chemicals of high purity or of a special pure grade for crystal growth are: Associated Lead Manufacturers Export Company Ltd., London (PbO, PbF₂); The British Drug Houses Ltd., Laboratory Chemicals Division, Poole, England ("Optran"); Eagle-Picher Company, Chemical Division, Cincinnati, Ohio, USA; Koch-Light Laboratories

Ltd., Colnbrook, Bucks, England; Materials Research Corporation, Orangeburg, N.Y.; E. Merck AG, Darmstadt, W-Germany ("Suprapur", "Optipur"); New Metals and Chemicals Ltd., Poole, England; Johnson Matthey Chemicals Ltd., London E.C.1. ("Specpure", "Puratronic", "Spectroflux"); Research Chemical Corporation, Phoenix, Arizona; Molybdenum Corporation of America, 6 Corporate Park Drive, White Plains, N.Y.; MCP Electronics Ltd., Alperton, Wembley, Middlesex, England; Schweizerische Aluminium AG, Neuhausen, Switzerland (Gallium and its compounds); Levy West Laboratories Ltd., Harlow, Essex, England (niobates, tantalates).

7.2.6. Atmosphere control

The importance of atmosphere control has been discussed at several points within this book, particularly in Section 7.1.5 in connection with the preparation of phases having ions in unusual valence states. In general the required phase must be grown in an atmosphere in which it is stable, although in practice some modification of the equilibrium condition may be effected according to the solvent in which the crystal grows. The practical problems of atmosphere control may be considered as threefold: purification of the gases if impurities are likely to enter the crystal or to affect growth; pressure control of a single pure gas phase, and partial pressure control of an active component in a mixture of gases. The vital questions of leak prevention and detection are beyond the scope of this book.

Commercial gases generally are impure, typical impurity concentrations in high-purity oxygen being 0.1% water, and in argon being 20–100 ppm oxygen. The removal of harmful impurities from the atmosphere is of particular importance in high-temperature solution growth in view of the long times required for an experiment and of the crucible lifetime, for example. A variety of methods is available for gas purification, based both on physical and chemical properties. The most commonly used technique is by chemical reaction by flowing the gas over or through a reagent which will react with the impurity but not with the principal constituent. As an example, the concentration of oxygen in nitrogen or argon may be considerably reduced by flow over copper turnings at about 600°C. Other examples of interest to crystal growers are the catalytic removal of oxygen from hydrogen or hydrogen-containing mixtures by using Pt or Pd contacts with removal of the resulting water by freezing or drying agents, and the removal of O₂, N₂, CO and CO₂ from He or Ar by passing the gas over titanium powder at 850°C. Very low oxygen concentrations in inert gases were obtained by Steinmetz *et al.* (1964) by flowing the gas through aluminium amalgam. The oxygen reacts very readily with the aluminium

to form Al_2O_3 , which floats on the amalgam, and oxygen partial pressures of 10^{-27} atm may be achieved.

A common practice is the drying of gases, and the efficiency of drying agents increases from CaCl_2 , CaSO_4 , H_2SO_4 , KOH , $\text{Mg}(\text{ClO}_4)_2$, BaO to P_2O_5 , and especially P_2O_5 distributed in silicagel is a practical drying agent. On the other hand controlled humidities can be produced by bubbling the respective gas through large volumes of specified aqueous solutions as listed in Lange's Handbook of Chemistry (1967).

The principal alternative to chemical methods utilizes differences in the boiling or freezing points of gases, and, for example, water vapour and carbon dioxide may be effectively removed from oxygen at not too high pressures by flow through a reservoir containing liquid air or a similar refrigerant. Hydrogen, which is commonly used as atmosphere in crystal growth from metallic solutions, may be purified by diffusion through solid palladium since its diffusion coefficient is much higher than that of the heavier gases. Methods of purification of gases have been reviewed by Müller and Gnauck (1965) and by Lux (1970).

The total pressure of the gas may be regulated by a device which is based on the operation of a relay by a pressure sensor for the required range. As an example, a device capable of regulating pressures up to 1 atmosphere was described by Oxley and Stockton (1966). Generally pressure regulators for operation both above and below atmospheric pressure are obtained from commercial sources. The use of high vacua is generally to be avoided in HTS growth in view of the volatility of most solvents, and a static or flowing inert atmosphere is normally preferred for syntheses at low oxygen pressures.

Controlled oxygen partial pressures in the range below about 10^{-1} atm may be most readily achieved using gas mixtures such as H_2/CO_2 , CO/CO_2 or $\text{H}_2/\text{H}_2\text{O}$. Data for the variation of oxygen partial pressure with relative concentration and temperature may be obtained from Fig. 3.4. Similarly sulphur partial pressures for mixtures of H_2S with H_2 are available from Fig. 3.5. A fairly detailed account of the importance of partial pressure in material syntheses is available in the book by Reed (1972). Alternative systems for the provision of controlled atmospheres are discussed by Kröger (1964), who treats in great detail crystal imperfections and their relation to the atmosphere.

An unusual example of the use of special atmospheres in crystal growth from high-temperature solution is the preparation of MgO and LaAlO_3 crystals doped with ^{17}O by Garton *et al.* (1972). The high cost of this isotope requires experiments on a small scale and crucibles of 10 ml capacity were used. The isotope-enriched oxygen gas was introduced into an evacuated, sealed platinum tube at room temperature with the tube

contained inside a brass cylinder, the pressure within which was adjusted so as to avoid pressure differences which might fracture or distort the platinum tube. The concentration of ^{17}O in the crystals grown was about 10%, a similar value to that in the source powder.

7.2.7. Stirring techniques

Stirring was introduced into the field of crystallization by Wulff (1884) and has become routine in crystal growth from aqueous solutions, both for growth of single crystals and for mass crystallization. Stirring is also applied in other crystal growth techniques (e.g. Czochralski growth, zone melting) whereas in crystal growth from high-temperature solutions it has not yet found widespread application mainly because of experimental problems.

A. Effects of stirring. The main effects of stirring can be divided into two categories, namely the effects due to homogenization of the solution and those due to a high solution flow rate at the growing crystal faces.

A solution homogeneous with respect to solute and impurity concentration and to temperature may result from various stirring techniques. For example, if a stirrer (with seed crystal) is inserted in the solution and rotated in a stationary container, mixing and homogenization occurs between the regions of solution moving with the stirrer and the regions adhering to the container walls. This homogenized solution contains no thermal or solutal convection cells which frequently lead to uncontrolled nucleation. Thus the whole solution is influenced by the presence of any crystal, the supersaturation is not likely to exceed the critical value for nucleation so that spontaneous nucleation can be avoided. Another effect of homogenization is that the growing crystal always sees a homogeneous diffusion field, and thus inhomogeneities in crystals such as striations are prevented or at least reduced to a minimum level. Forced convection, that is a high solution flow rate along crucible walls and crystals decreases the Ostwald-Miers range of metastability, and spontaneous nucleation might occur, especially in highly concentrated and viscous solutions.[†] Therefore, stirring should be not too vigorous and should be adjusted according to the concentration and to the viscosity in order to avoid spontaneous nucleation. The narrowing of the metastability region leads to a requirement of precise temperature control, which in flux growth we estimate should be to better than $\pm 0.1^\circ\text{C}$.

[†] As an example, in the growth of iodic acid from very concentrated and viscous aqueous solutions, stirring is disadvantageous according to S. Haussühl (private communication). However, Daval (1974) grows large HIO_3 crystals of high quality from stirred solution.

Forced convection also leads to a decrease in supersaturation, the latter being influenced by the habit of the crystals present, by nucleation at the surface and by the degree of stirring. In general, this decrease in supersaturation corresponds approximately to the narrowing of the metastability range, so that no enhanced spontaneous nucleation is observed, at least at modest stirring rates.

A high solution flow rate along the growing crystal faces has several advantages which have been demonstrated by Scheel and Elwell (1972, 1973) and mentioned in Section 6.6.2. Stirring decreases the diffusion boundary layer and reduces the supersaturation inhomogeneity across the crystal thus allowing a faster maximum stable growth rate than that without stirring. Because of the faster stable growth rates made possible by stirring, the duration of experiments may be decreased (see Fig. 6.16). Stirring is necessary if crystals larger than about 1 cm^3 are to be grown economically. The importance of stirring is underlined by the X-ray topograph of Vergnoux *et al.* (1971) which shows growth instability at the event of interruption of stirring, see Fig. 7.38.

The decrease in the boundary layer thickness has an effect on the growth mechanism and on the surface structure of the crystals grown. Surfaces of

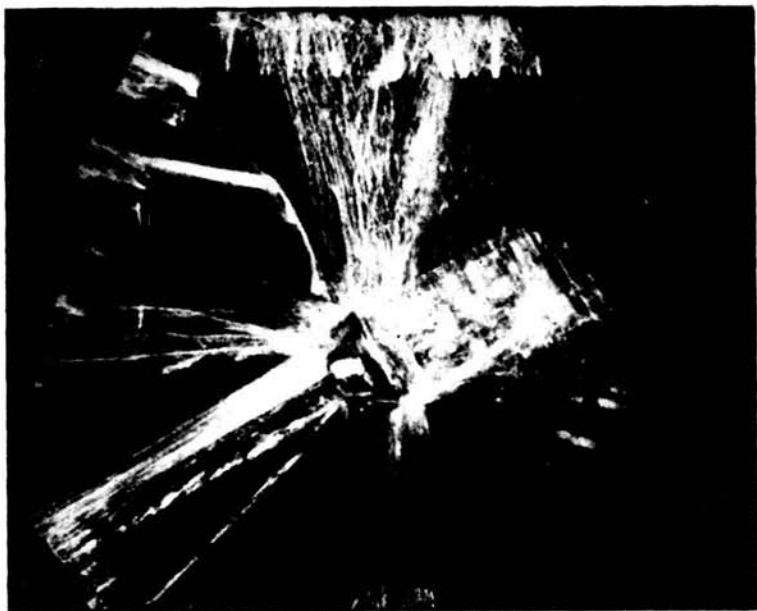


FIG. 7.38. X-ray topograph of a strontium formate crystal showing development of dislocations, probably at inclusions, at the event of interruption of stirring (Vergnoux *et al.*, 1971).

crystals grown from stirred solutions under not too high supersaturation are very flat compared to crystals grown from unstirred solutions. This led Scheel and Schulz-DuBois (1972) to propose stirring in liquid phase epitaxy, for instance by rotation of the substrate(s) in the solution, and Blank and Nielsen (1972) as well as Giess *et al.* (1972) and Ghez and Giess (1973) confirmed by experiment the advantage of stirring. Stirring in LPE has become increasingly widely applied (Vilms and Garrett, 1972; Scheel, 1973).

Through the decreased boundary layer stirring influences the incorporation of impurities or solvent ions as discussed in Section 7.1.3. Accordingly the stirring rate should not be varied too much during an experiment if inhomogeneous incorporation of impurities is to be avoided.

B. Natural convection. In unstirred solutions bulk material transport by natural convection occurs in most growth experiments due to temperature differences (thermal convection) and due to density differences arising from variations in solute concentration (solutal convection). Since natural convection has been discussed in some more detail in Section 6.6.2, here only a few general remarks will be made.

The average convection flow rate for typical high-temperature solutions lies between about 0.01 and 0.1 cm s⁻¹ (see Fig. 6.16) and thus is about two orders of magnitude smaller than typical flow rates in stirred aqueous solutions. Problems arise when the convection streams are irregular or when they form convection cells or pockets because in these cases spontaneous nucleation might occur, competing with growth of the crystals already present. Time-dependent convection also leads to striations or even unstable growth. Consequently a steady convection flow should be produced, for instance by heating one crucible wall and cooling the other, or in general by achieving temperature profiles and crucible shapes which favour a steady convection flow. As an alternative, convection may be minimized as in the convection-free cell of Tiller shown in Fig. 6.19, but experimental difficulties may arise when this cell is applied in crystal growth from high-temperature solutions. It is obvious from the discussion of stirring in Section A, that if possible smooth and continuous stirring should be applied and that the hydrodynamics in crystal growth from solutions should be dominated by adjustable forced convection.

C. Seed crystals on stirrers. Seed crystals on stirrers are used in crystal growth from aqueous solutions both in small-scale and in large-scale production of monocrystals, thus the advantages of homogeneous solutions and of high solution flow rates can be utilized. However, experimental parameters such as the rotation rate, the position of the seed between the

rotation axis and the container walls, the orientation and the fixing of the seed crystals must all be carefully adjusted. Since a small quantity of the solution rotates with the seed crystals and since a sufficient solution flow rate is needed along all faces in order to prevent inclusion veils the rotation should be reversed at least once a minute (Holden, 1949).

On the other hand, Sip and Vanicek (1962) pointed out that abrupt termination and reversal of rotation affect the crystal very unfavourably, and sudden acceleration of the solution might even cause spontaneous nucleation. Therefore Sip and Vanicek proposed that changes in the rotation rate of the seed holder should occur smoothly and that any reversals should be preceded by a pause. As an alternative to attaching the seed crystal to a rotating (or reciprocating) holder it could be fixed to the container, and the solution moved by an independent stirrer.

Seed crystals immersed in solution are not often used in crystal growth from high-temperature solutions. Laudise *et al.* (1962) applied seeds in an arrangement as shown in Fig. 7.3 in order to grow yttrium iron garnet crystals from $\text{BaO} \cdot 0.61\text{B}_2\text{O}_3$ solutions. A crucible of 7.6 cm diameter was used, and the seed holder was rotated at 200 r.p.m. with the direction of rotation reversed every 30 seconds. The dissolution of the feed material was the rate-determining step, as was discussed in detail by Laudise (1963), at least for rotation rates faster than about 50 r.p.m. One would expect that for abrupt changes in the rotation rates as above, uncontrolled nucleation would occur, and this in fact was observed. It seems that stirring is also applied in the commercial synthesis of emeralds but details of the process cannot be found in literature nor obtained from the emerald producers. There is no doubt that in any large-scale commercial crystal synthesis stirring will be applied, and the experience obtained in the growth of crystals from aqueous solutions may be applied in crystal growth from high-temperature solutions. The use of seed crystals on stirrers is generally only proposed when a number of large crystals of the same family have to be grown, in view of the effort required to determine the optimum conditions.

D. Top-seeded solution growth (TSSG). This topic has already been discussed with respect to nucleation control in Section 7.1.1, therefore the discussion of TSSG here will be restricted to its hydrodynamic aspects. The principle of TSSG is demonstrated in Fig. 7.39(a) (the whole apparatus is shown in Fig. 7.4). A seed crystal is cooled by an air stream flowing through the seed holder. The solid-liquid interface is below the liquid level so that this method differs from the Czochralski technique where in general the interface is above the melt level. Since in TSSG the crystal dips into the solution, the temperature gradient at the interface is

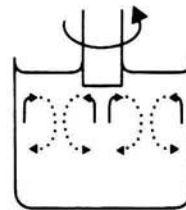
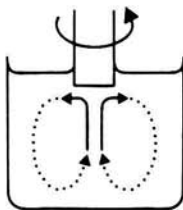
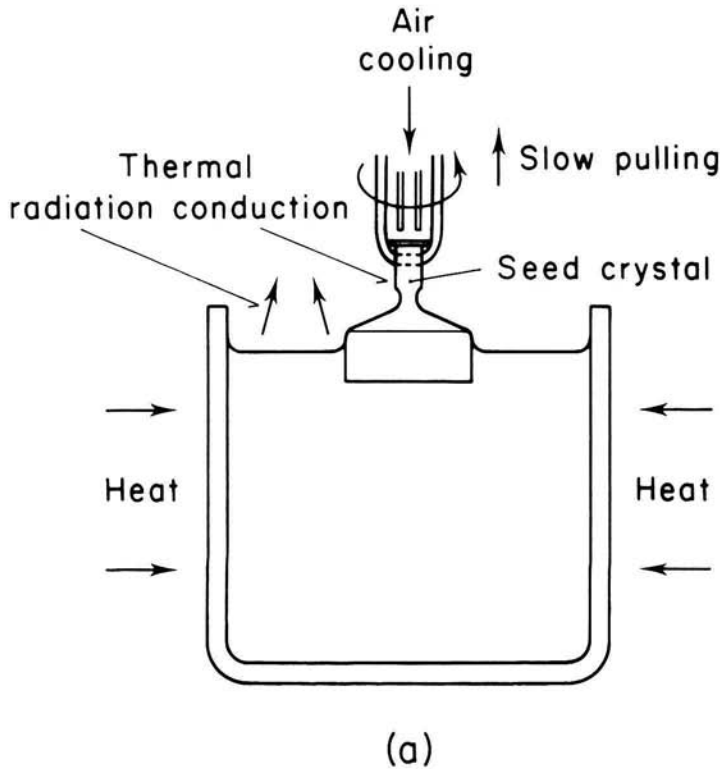


FIG. 7.39. Heat flow (a) and hydrodynamics (b) and (c) of top-seeded solution growth.

less steep than in Czochralski growth, and this encourages the facetting which is normally observed on TSSG-grown crystals.

Due to the similarity of the Czochralski and TSSG techniques the hydrodynamics and the stirring effects are expected to be similar. The effects of seed rotation on Czochralski-grown silicon crystals have been

studied by Goss and Adlington (1959), and Robertson (1966) has shown that a large crystal diameter (more than 10 mm) and high crystal rotation rates of more than about 50 r.p.m. are required to produce the upward flow (towards the crystal) as indicated in the examples of Fig. 7.39(b), (c). Cochran (1934) has analysed the flow to a rotating disc (of infinite diameter), and Burton, Prim and Slichter (1953) based their derivation of the boundary layer thickness on Cochran's analysis. An advantage of an axial rotating seed is that the solute flow is, to a first approximation, independent of the crystal radius. Greenspan (1968) extended Ekman's study of the "hydrodynamics" of hurricanes to any fluid medium and demonstrated the existence of the so-called Ekman layer flow. This is a radial flow within a narrow horizontal layer which occurs when there is a difference in rotation rates between the fluid medium and a solid boundary that is approximately perpendicular to the rotation axis (Schulz-DuBois, 1972); see also the discussion in Section 7.2.7E. Carruthers and Nassau (1968) have identified a number of flow patterns as shown in Fig. 7.40 by simulation experiments in which the relative rotation rates of crystals and crucible were varied over a wide range.

In addition to the large variety of flow patterns indicated above thermal convection may lead to temperature oscillations in the melt with the result that it is extremely difficult to grow striation-free crystals by the Czochralski and TSSG techniques. In discussing turbulent-free convection in Czochralski crystal growth Wilcox and Fullmer (1965) agree with Malkus (1954) that fluid baffling is relatively ineffective in reducing turbulent free convection, and propose shielding or an afterheater for this purpose. In contrast Whiffin and Brice (1971) propose, in addition to afterheaters, the use of baffles in order to damp thermal oscillations, as in the convection-free cell of Tiller (1968).

It seems reasonable that a stationary baffle 5 to 15 mm below the rotating crystal will minimize thermal convection not only because of the smaller effective volume of the melt and the reduced (vertical) Rayleigh number (Whiffin and Brice, 1971) but also because of its stirring effect. Also Cockayne *et al.* (1969) proposed shallow melt depths to reduce temperature fluctuations in the melt and pointed out the influence of convection in the gas above the melt.

Although many of the principles discussed above for Czochralski growth will be valid for TSSG, deviations are expected because of the difference of the height of the interface, the different temperature profile and the faceting of many crystals grown by TSSG.

E. Accelerated crucible rotation technique (ACRT). One of the problems of crystal growth from high-temperature solutions using volatile solvents

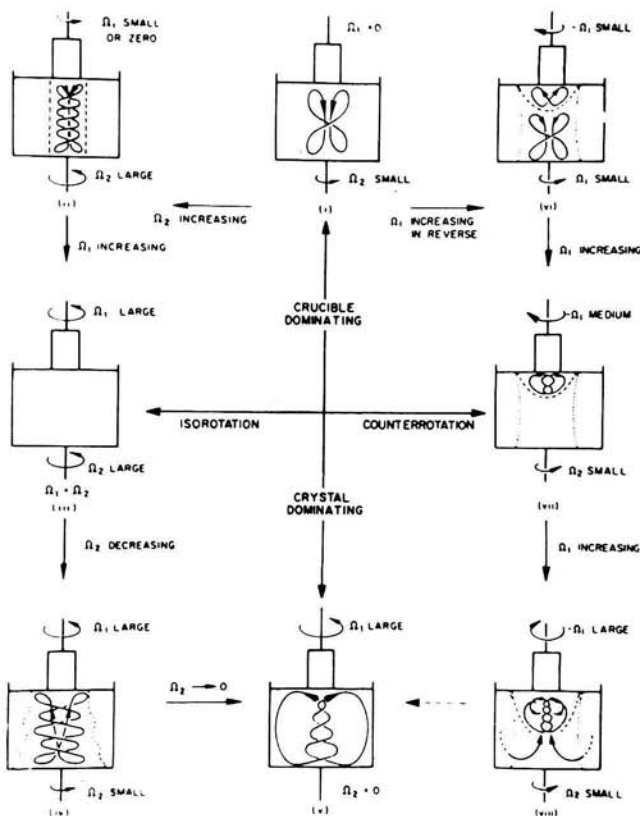


FIG. 7.40. Variation of flow patterns with the relative directions and magnitudes of crystal and crucible rotation (Carruthers and Nassau, 1968).

like PbO and PbF_2 is that the crucible should be sealed in order to prevent solvent evaporation. The high temperatures and the restriction on crucible materials prevent the application of conventional stirring techniques. According to J. W. Nielsen (1974) alternate rotation and counterrotation of crucibles with high-temperature solutions were used by Remeika and Van Uitert at Bell Laboratories and by Lepore at Airtron for initial stirring to promote dissolution of the solute; continuation of this agitation during growth did not allow control of nucleation so that this procedure was abandoned, as by Nelson and Remeika (1964) who used rotation reversal only in the initial stage in order to enhance dissolution of the components but not during crystal growth. However, Scheel demonstrated that a beneficial stirring effect in flux growth could be achieved by periodic acceleration and deceleration of the crucible rotation and by alternating the sense of

rotation. This accelerated crucible rotation technique (ACRT) permitted firstly, in a sealed crucible, the restriction of nucleation by localized cooling to one to three crystals and secondly the growth of large inclusion-free crystals (Scheel and Schulz-DuBois, 1971; Scheel, 1972).

There are two typical flow mechanisms which occur during the acceleration and deceleration of container, namely the spiral shearing distortion and the Ekman-layer flow, although on strong deceleration a transient Couette flow might occur.

The *spiral shearing distortion* for an infinite tube (thus neglecting the effect of the crucible base) has been analysed by Schulz-DuBois (1972). This type of flow is conveniently considered by reference to a uniformly rotating cylinder containing two immiscible liquids shown as black and white in the cross-section of Fig. 7.41(a). If the rotation of the tube is

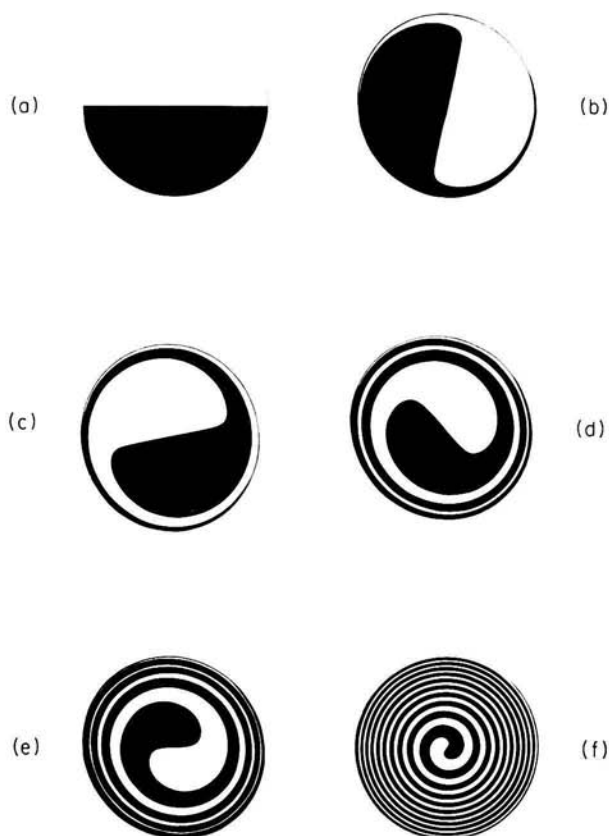


FIG. 7.41. Successive spiral shearing distortion of two liquids in a rotating tube when the rotation is suddenly stopped (after Schulz-DuBois, 1972).

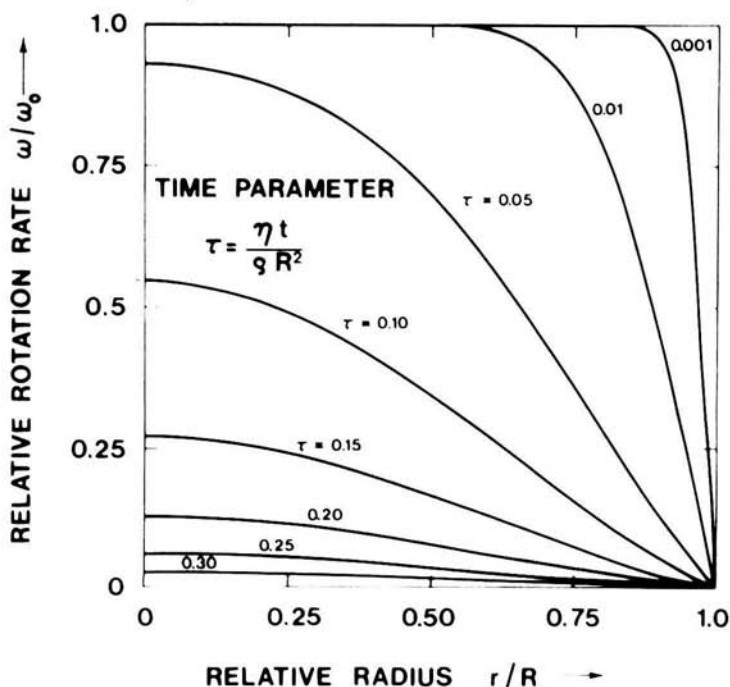


FIG. 7.42. Decrease of relative rotation rate versus relative radius in spiral shearing distortion (Schulz-DuBois, 1972).

suddenly stopped, the rotation rate of the liquid near the wall decreases rapidly due to friction, while the central region of the liquid decelerates much more slowly because of its inertia. Thus shearing occurs between the various ring-like liquid regions, and a spiral develops through successive changes in rotation as demonstrated in Figs 7.41(a)–(f). The decrease of the relative rotation rate ω/ω_0 versus the relative radius r/R is shown in Fig. 7.42, ω_0 being the initial rotation rate. After a time $t = 0.1(E\omega_0)^{-1} = 0.1\rho R^2/\eta$, the rotation rate at the centre is reduced to about $0.5\omega_0$. For crystal growth by ACRT, especially in tall narrow containers where spiral flow may be the dominant one, the acceleration and deceleration periods should be of this order since for greater periods the changes in the velocity field become increasingly slower. In the above discussion E is the Ekman number $= \eta/\rho\omega_0 R^2$ with η the viscosity and ρ the density of the solution. For a typical melt with a kinematic viscosity $\eta/\rho = 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ and a crucible of diameter $2R = 10 \text{ cm}$ the time t has a value of 250 s. However, shorter time intervals are required for the periods of continuous acceleration and deceleration to achieve an optimum and yet smooth stirring effect and for increasing the Ekman flow.

If the liquid is allowed to come to rest after the sudden halt in the rotation, it will have rotated relative to the container by the shear angle

$$\phi(r) = \rho\omega_0(R^2 - r^2)/8\eta = (1 - r^2/R^2)/8E \quad (7.9)$$

with r being the distance from the axis. From this equation the number N of spiral arms is derived as

$$N = \omega_0 \rho R^2 / 16\pi\eta = (16\pi E)^{-1} \quad (7.10)$$

and the width Δr of the spiral arms is

$$\Delta r = 4\pi\eta / \rho\omega_0 r = 4\pi ER^2 / r. \quad (7.11)$$

In order to achieve efficient mixing, Δr should be between 0.1 and 1 mm, then homogenization by thermal conduction and by diffusion occurs in less than 10^{-1} seconds. The spiral shearing mechanism as well as the Ekman-layer flow can be clearly recognized in simulation experiments described by Scheel (1972).

A flow mechanism which is of comparable importance to the spiral shearing is the so-called *Ekman-layer flow*. According to Greenspan (1968) Ekman described the rapid flow of air in a relatively thin layer near the surface of the earth in rotating wind systems such as hurricanes. The rapid suction of air occurs in this "Ekman-layer" because there the pressure difference between the high outside the hurricane and the low in the centre is not balanced by centrifugal forces as demonstrated in Figs 7.43(a), (b). A similar Ekman-layer flow occurs in a crucible when the rotation is decelerated. The opposite flow occurs as the crucible is accelerated, due to a thin layer at the crucible bottom of which the liquid is accelerated first and thrown outwards due to centrifugal forces. The Ekman-layer flow for acceleration and deceleration is shown in Figs 7.43(c) and (d) and may be demonstrated with a cup of tea containing tea leaves (Scheel, 1972). The tea leaves at the bottom flow radially outwards, when the tea is stirred, and back towards the centre when the stirring is interrupted.

According to Greenspan (1968) and to Hide and Titman (1967) the thickness d of the Ekman layer may be approximated by

$$d = RE^{1/2} = (\eta / \rho\omega_0)^{1/2}, \quad (7.12)$$

which is about 0.5 mm for the numerical example given above. The maximum radial velocity in the Ekman layer is

$$v_{\max} = \omega_0 R \quad (7.13)$$

and easily exceeds 10 cm s^{-1} for the example. Ekman components of the flow velocities in the bulk of the liquid are considerably smaller, about

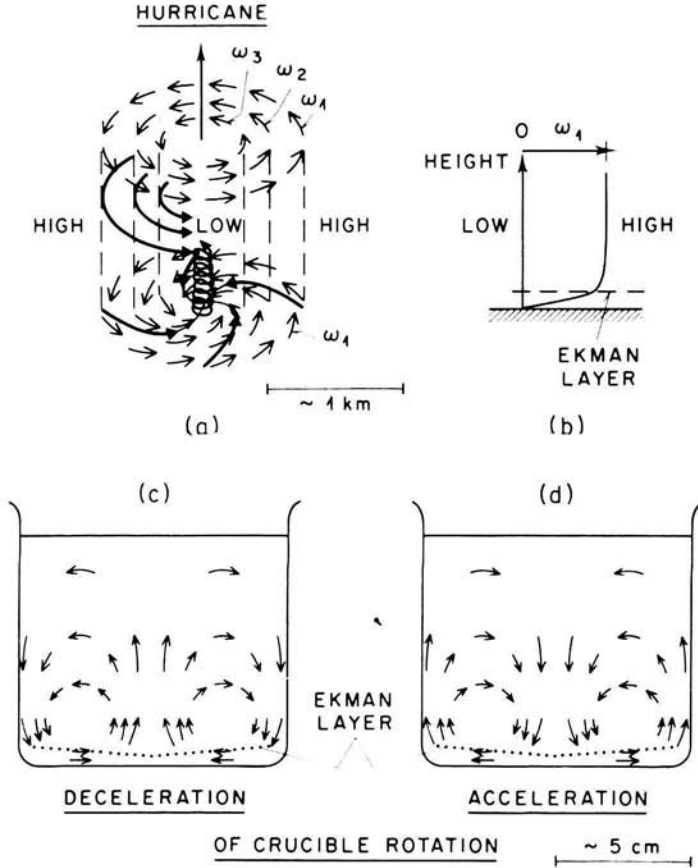


Fig. 7.43. Ekman-layer flow in a hurricane (a), (b) and in a crucible of which rotation is decelerated and accelerated (c), (d).

0.2 cm s^{-1} . Ekman layer flow in a container occurs only during acceleration and deceleration and ceases as soon as uniform rotation is achieved, approximately after the time

$$t = E^{-1/2} \omega_0^{-1} = R(\rho/\eta\omega_0)^{1/2}, \quad (7.14)$$

which for above example corresponds to about 20 s (Schulz-DuBois, 1972). If the whole liquid is accelerated from zero to ω_0 then it has passed once entirely through the Ekman-layer where it experiences acceleration, and thus the Ekman-layer flow is a valuable supplement to the circumferential mixing effect of the spiral shearing.

The high Ekman flow rate given by Eqn 7.13 occurs not only at the crucible base but also on crystals growing there and on any crystal (or

baffle) face which is approximately perpendicular to the rotation axis. Thus it also occurs in the top-seeded solution growth (and Czochralski) technique below the rotating crystal if it has a sufficient diameter and rotation rate as discussed in Section 7.2.7D.

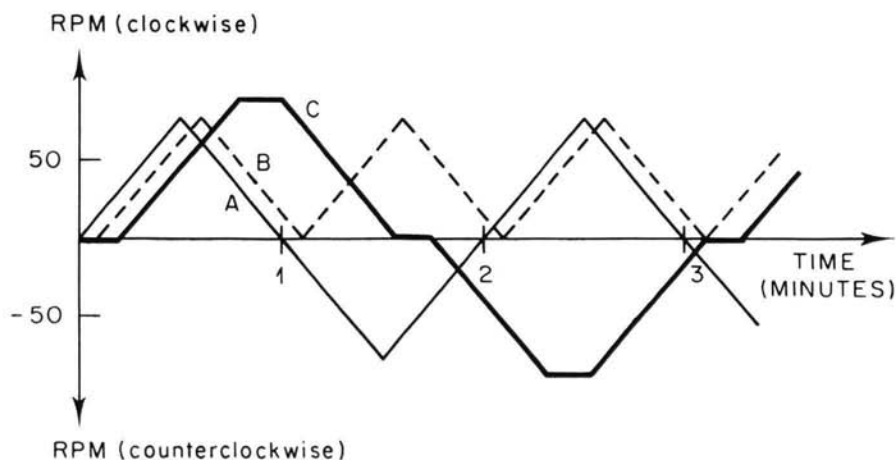
Another mechanism of flow near the walls of a rotating cylinder of large diameter is possible when its rotation is decelerated rapidly. This modified, transient type of Couette flow (Chandrasekhar, 1961) occurs in convection cells resulting from interior regions of fluid with higher rotation rates which are driven towards the walls by centrifugal forces during the transient of strong deceleration. It is unlikely that the typical conditions used in ACRT are sufficient to establish the transient Couette flow in the region near the container walls.

The stirring action of ACRT can be adjusted by the rates of acceleration and deceleration, and by the differences of the rotation rates (Scheel, 1972). Typical examples of ACRT cycles are shown in Fig. 7.44(a). The reversal of the sense of rotation as in A is advantageous for homogenizing the interior parts of the liquid which have not come to rest and which otherwise would rotate continuously and thus be affected relatively little by the ACRT mechanism. In order to achieve a smooth change when altering from acceleration to deceleration or the sense of rotation, short periods of constant (or zero) rotation rate might be used as indicated in example C. A slow ACRT stirring action is suggested in the case of relatively concentrated and viscous solutions in order to prevent spontaneous nucleation, but in very viscous systems ACRT would not be of advantage.

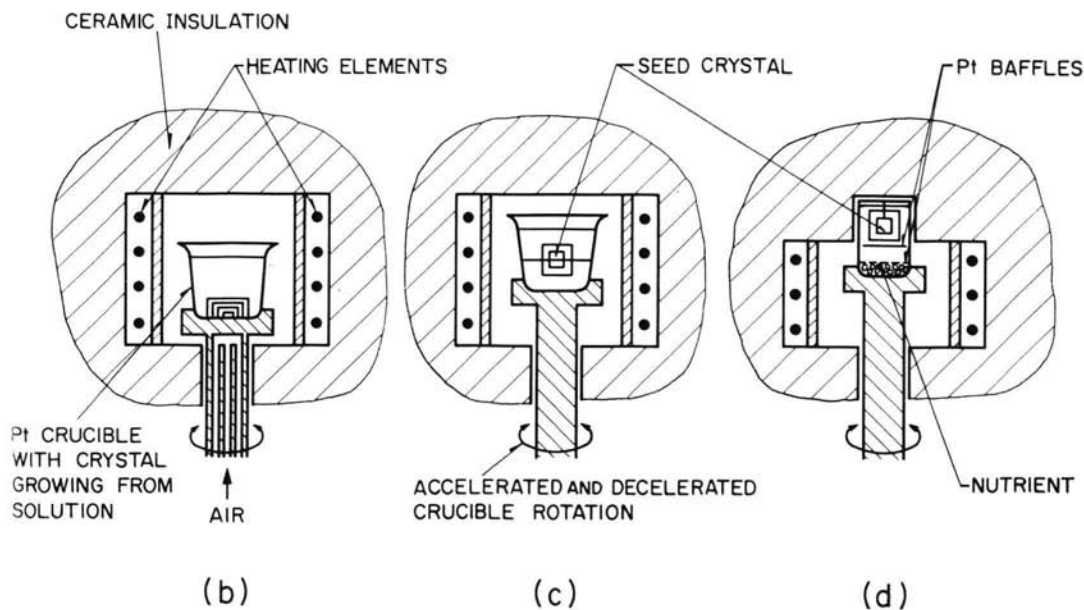
In Fig. 7.44(b)–(d) examples of experimental arrangements for flux growth by ACRT are shown, namely for nucleation control by localized cooling (b), for the application of a seed crystal in the slow-cooling technique (c) and for the gradient-transport technique with a seed (d). Similarly, Tolsdorf and Welz (1972) used ACRT in combination with the Bennett–Tolsdorf nucleation control (Section 7.1.1). The crucible is positioned on a rotatable pedestal which is connected to a motor by a belt. The rotation cycle of the motor according to Fig. 7.44(a) is obtained, for example, by electromechanical means (motor-driven cam on a motor-speed controlling potentiometer) or by commercially available electronic units with ramp generators.†

ACRT was first applied to the growth of gadolinium aluminate, and the first experiment resulted in a GdAlO_3 crystal of 210 g weight shown in Fig. 7.45(a), (b). Only this one crystal nucleated in a 500 cm³ crucible and represented 67% of the starting material. In successive experiments more large GdAlO_3 crystals and large inclusion-free crystals of magnetic garnets have been grown from relatively small crucibles (Scheel and

† Eurotherm Produkte AG, Glattbrugg, Switzerland.



(a)

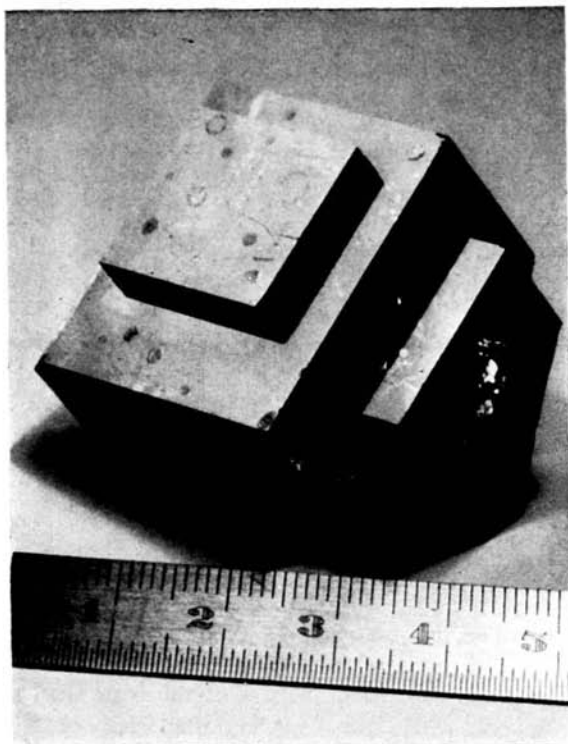


(b)

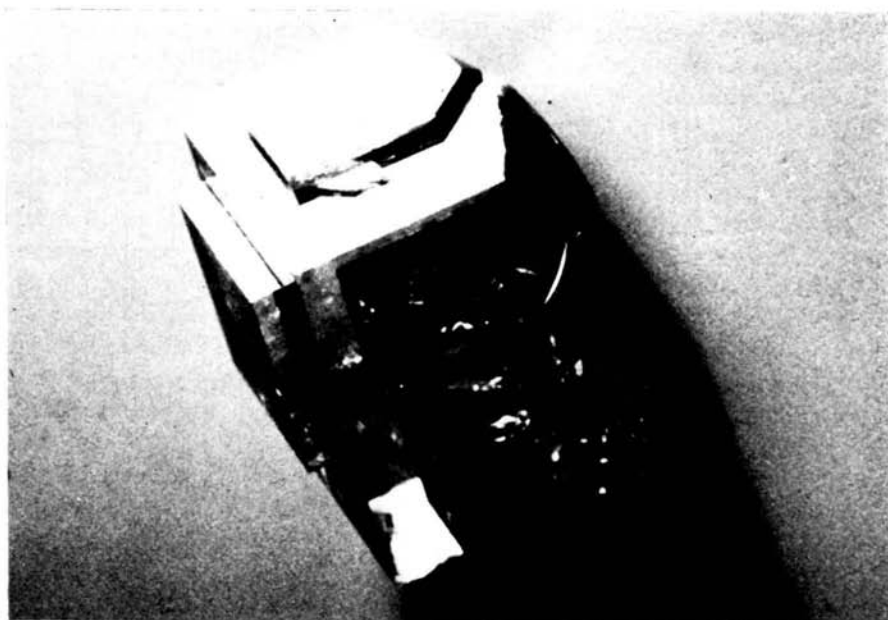
(c)

(d)

FIG. 7.44. (a) Examples of cycles of accelerated and decelerated crucible rotation. Experimental setup for ACRT with localized cooling (b), with a seed crystal (c), with seed crystal and gradient transport (d) (Scheel, 1972).



(a)



(b)

FIG. 7.45. Example of a large crystal grown by ACRT. (a) Gadolinium aluminate of 210 g weight grown in a 500 cm^3 crucible. (b) Same crystal with light reflected inside the crystal at a natural face (Scheel, 1972).

Schulz-DuBois, 1971; Scheel 1972), and experiments in other laboratories have confirmed the value of ACRT-stirring to achieve nucleation control and inclusion-free crystals (Tolksdorf and Welz, 1972; Mateika, 1972). Recently nucleation control and growth of large crystals with the help of ACRT have been achieved by Puttbach at Airtron (Nielsen, 1974) and for growth of 80 g YVO_4 crystals at Allied Chemical Corporation (Vichr, 1973).

It is not easy to predict the effect of ACRT when crystals of needle or platy shapes are to be grown but preliminary experiments of Aidelberg *et al.* (1974) indicate a beneficial effect of ACRT in the growth of magnetoplumbite plates.

Striations might occur in systems with large changes in the boundary layer thickness, and obviously changes in the boundary layer thickness do occur in ACRT. But the popular periodic rotation reversal of the seed crystal holder in crystal growth from aqueous and high-temperature solutions also leads to changes in the boundary layer thickness, and to the authors' knowledge no striations due to these hydrodynamic changes have been proven. Only Damen and Robertson (1972) have claimed to have observed striations due to ACRT. However, the periodicity of striations expected from the experimental conditions used is an order of magnitude less than the resolution of X-ray topography. Further studies are required to clarify this question.

Experiences in various laboratories show that ACRT is a powerful stirring technique applicable to laboratory and pilot plant crystal production, and it is obvious that ACRT could be useful in other crystal growth methods, such as the hydrothermal, chemical vapour transport and Bridgman-Stockbarger techniques where stirring is to be achieved in closed containers as well as in Czochralski growth (Scheel, 1972).

An alternative stirring technique has been proposed by Gunn (1971) and consists of circulating the solution around the inside of a container by moving the centre of the container in a horizontal circular path, without rotating the container at all. This technique is frequently used in rinsing out a beaker with water and is applied by chemists during titration as an alternative to magnetic stirring. The circulatory action may be adjusted by varying the angular speed of the centre of the crucible and of the crucible itself; crucible rotation in the same direction as the circular motion of the crucible centre decreases the fluid circulation while counterrotation would enhance it. In contrast to ACRT this action produces a constant solution flow (if it is not interrupted), but it is technically more complicated to apply in crystal growth from HTS.

F. Additional stirring techniques. A variety of stirring mechanisms have been conceived but have not been widely applied in crystal growth from

high-temperature solutions. Kirgintsev and Avvakumov (1965) investigated the stirring efficiency of the various stirring techniques shown in Fig. 7.46 by measuring the distribution of calcium nitrate impurity in solidifying potassium nitrate. Rotation of a stirrer at high speed and rotation of a partially filled horizontal tube have been found most effective. Bubbling gas through the liquid is less effective and vibration of a stirrer at 50 Hz showed no stirring effect at all. It is interesting to note that Wulff used a seed crystal and a rotating horizontal cylinder in 1901. Magnetic stirring is limited to temperatures of about 500°C and is thus not of interest for

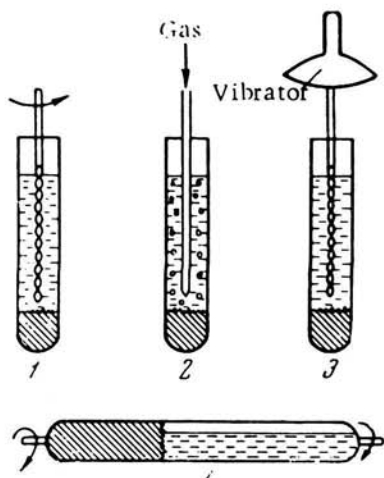


FIG. 7.46. Various stirring techniques studied by Kirgintsev and Avvakumov (1965).

HTS growth. The same is true for R.F. stirring at about 10 kHz which is not easily applied to high-temperature solutions in platinum crucibles, and if R.F. is applied for heating also, then problems arise in obtaining the required precision of temperature regulation.

7.2.8. High pressure technology

The growth of crystals at pressures in the kilobar region requires a technology completely different from that for synthesis under modest gas pressures as described in Section 7.1.5. High pressures are generated by the action of a hydraulic ram operating on a piston, or by a combination of several such rams or pistons, and it is now possible to maintain pressures of 200 kbar at temperatures of 2000°C or above. The techniques used in high pressure technology have been reviewed by Bridgman (1952), Bundy (1962), Munro (1963) and Rooymans (1972), the latter with emphasis on

chemical syntheses. A bibliography of high pressure techniques is given in the book of Paul and Warschauer (1963).

The simplest arrangement for crystallization under high pressure is that where the sample is located between a piston and a fixed closure within a cylindrical jacket. The maximum pressure that can be attained in this arrangement depends on the bursting pressure of the containing cylinder, which will be around 20 kbar for steel and 60 kbar for tungsten carbide. For higher pressures it is necessary to provide support for the cylinder or to pre-stress the inner wall so that this inner surface is in tension only at pressures in the working range. Composite cylinders are frequently used, and an outer jacket may be shrunk onto the outer surface in order to provide the compression.

In the opposed anvil arrangement, the containing cylinder is eliminated and the specimen is held in a small central region between two anvils which are tapered away from this region at about 10° . This arrangement distributes the stress immediately below the anvil surface over a much larger quantity of material, a device which Bridgman termed the "principle of massive support". The main disadvantage of this arrangement for crystal growth is that the specimen volume is necessarily very small, typically 0.2 mm in thickness and 5 mm in diameter.

Another limitation associated with the thin sample is that thermal conduction to the anvils is relatively high and the associated loss of strength reduces the maximum pressure available at high specimen temperatures. A layer of insulation may be inserted into a recess in the anvil and the pressure limitation is then set by the closeness of approach of the opposing anvils, which is primarily governed by the behaviour of the ring of pyrophyllite which behaves as a fluid under pressure and so forms a gasket enclosing the specimen. A longer compression stroke, and hence a larger specimen volume, is possible when curved anvils are used and optimization of the anvil profiles at the General Electric laboratories led to the "belt" design which is now widely used, for example, in crystallization of diamond and of which the high-pressure region is shown in Fig. 7.47.

This arrangement doubles the axial length of the specimen chamber but the "belt" which governs the movement of the gasket material as the pressure is applied must withstand the bursting pressure of the sample and therefore requires a strong binding ring. The sample is contained in a cylinder with a seal at each end, and the gaskets are normally of pyrophyllite with metal laminations and extrude as the pressure is applied.

Relatively large specimen volumes are also possible with multiple-piston arrangements of which the most popular is the tetrahedral-anvil apparatus (Hall, 1958). Four anvils, each having a triangular end surface, are located at the ends of four rams and enclose a tetrahedron of pyrophyllite

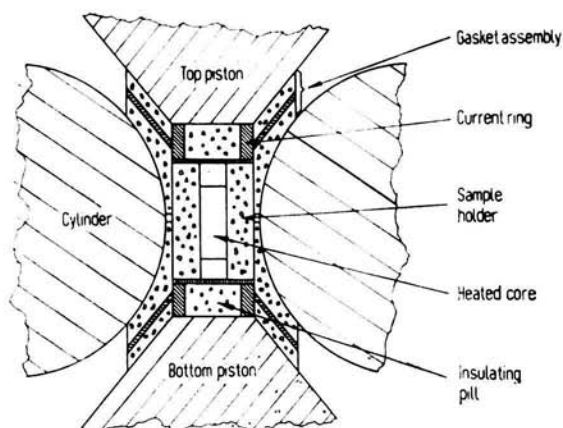


FIG. 7.47. High-pressure region in the belt apparatus used for diamond synthesis (Wentorf, 1966).

some 10% larger in edge dimensions than the anvil faces. The pyrophyllite acts as a pressure-transmitting medium and is bored out to contain the sample and heating element. Normally pressure is applied only to one ram (with the other three mounted in a support ring) which must move in such a way that non-uniform stresses are avoided. Apparatus with six rams acting on a pyrophyllite cube has also been used.

Arrangements for the production of high temperatures combined with high pressures have been reviewed by Strong (1962). External heating of the whole apparatus is possible at pressures below 10 kbar and temperatures less than 600°C. For higher temperatures, the decrease with temperature in the strength of the chamber materials requires that the specimen region only be heated while the anvils and surrounding chamber are kept cool. The main problem is then that of insulation of the specimen together with the prevention of reaction between the pressure transmitting medium and the specimen container, thermocouple and heater coil. Heating is normally effected by passing a current through the specimen or, more usually, through a tube or coil surrounding it. The low resistance of the heating element requires high currents, typically 500–1500 A at 1–3 V. The volume and friction changes caused by increase in temperature tend to reduce the pressure, and compensation for such reductions is difficult because of the absence of a suitable sensing element which may be located close to the specimen.

The measurement of high pressures presents quite severe experimental problems especially at higher values where free-piston and strain gauges are inappropriate. The change in resistivity of manganin wire has been

extensively used for pressure measurements but these are inaccurate when pyrophyllite or a similar material is used to transmit pressure, since these media are not perfectly hydrostatic. Calibration of the apparatus using tabulated transformations, such as that of Bi III-V at 77 kbar, is then necessary. The measurement of high pressure has been discussed, for example, by Munro (1963).

Temperature measurement at high pressure is complicated by the effect of pressure on the e.m.f. of the thermocouple. Corrections for Pt/Pt-10% Rh, Pt/Pt-13% Rh, chromel-alumel and iron-constantan thermocouples have been tabulated by Hanneman and Strong (1965). The correction for a Pt/Pt-10% Rh couple at 1300°C and 50 kbar exceeds 50°C. Independent measurements, with some deviations, have been reported by Peters and Ryan (1966) and sources of error in thermocouple measurements are discussed by Hanneman and Strong (1966). In general the measured e.m.f. will vary according to the pressure variation along the thermocouple wire, so that the apparent temperature will change with the design of the cell unless careful precautions are taken.

One problem in crystal growth at high pressures still to be solved in order to obtain large crystals of high quality is stirring. According to the discussion in Chapter 6 and Section 7.2.7 on the effect of stirring on the maximum stable growth rate the duration of experiments (for diamonds of 1 carat, about a week) could be shortened or the crystal size increased if forced convection could be applied. Stirring is particularly required in high pressure systems where natural transport phenomena are retarded by the densification.

7.2.9. Typical procedures for growth of oxides and chalcogenides

In this section detailed instructions are given for the preparation of some representative materials from high-temperature solutions. These "recipes" are intended for beginners in the field as illustrations of the practical procedures which are used. The complexity and the estimated price for apparatus and chemicals increase from the first to the last example; for instance the cost of apparatus and crucibles is about 200 dollars for the first experiment and up to 100 times more for the last experiment while the price of chemicals will vary from 5 dollars to several hundred dollars, depending upon the purity used.

A. Sodium chromium sulphide, NaCrS₂. 4.5 g coarse chromium powder is placed on the bottom of an unglazed ceramic crucible of about 6 cm diameter, and covered with 10 g sulphur and 60 g Na₂S × 9H₂O. The crucible is closed by a 2 mm thick disc of ceramic wool, which just fits into the crucible, and covered with a ceramic lid. It is placed in the simple

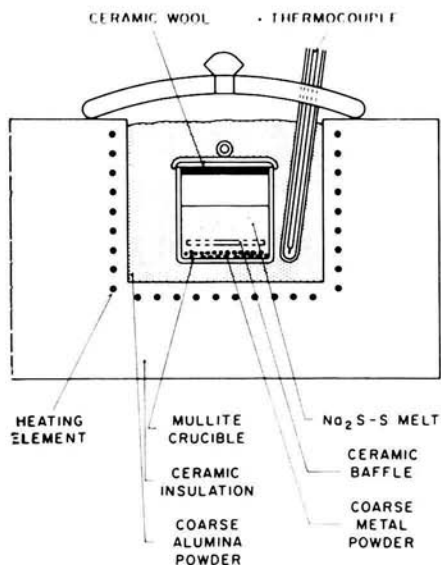


FIG. 7.48. Arrangement of crucible in muffle furnace for crystallization of metal sulphides from alkali polysulphide melts (Scheel, 1974).

muffle furnace shown in Fig. 7.48. The space below, on the sides and above the crucible is filled with coarse alumina powder in order to reduce the oxidation of melt by air. During heating to $1000 \pm 30^\circ\text{C}$ (in about three hours) excess sulphur evaporates and removes residual oxygen and water by reaction to SO_2 and H_2S , respectively, and this requires that the furnace is placed in a hood with good ventilation. The temperature is set by a variable transformer, and is reduced by about 25°C per hour by means of a motor-driven variac. At 300°C the power is shut off, and after cooling to room temperature the sodium polysulphide solvent is dissolved in water leaving hexagonal plates of NaCrS_2 up to 1 mm thickness and 2 cm diameter. The aqueous solution of polysulphide is poisonous and should be neutralized by an aqueous ZnCl_2 solution or should be reacted with KMnO_4 solution.

This simple sodium polysulphide process can be used for several other binary and more complex metal sulphides (Scheel, 1974), such as NaInS_2 , KCrS_2 , KFeS_2 , CdS , ZnS , PbS , FeS_2 , CoS_2 , NiS_2 , MoS_2 , Cu_3VS_4 , CuS , $\alpha\text{-MnS}$, HgS etc., with modified temperature programmes. In order to control nucleation and to achieve stable growth it is necessary to prevent evaporation of sulphur and to apply slower cooling rates. In the simple arrangement shown in Fig. 7.48 a ceramic baffle has been found to reduce the rate of reaction and transport and so to yield larger crystals.

B. Barium titanate, BaTiO₃. 37 g BaTiO₃ and 90 g anhydrous KF are weighed into a 100 cm³ platinum crucible which is covered by a platinum lid and placed into a horizontally loaded resistance furnace at 1100°C. This temperature is held for 8 hours after which the temperature is lowered by 15° h⁻¹ to 900°C. The crucible is then removed from the furnace and the liquid portion poured off (in a well ventilated room). The crucible is then returned rapidly to the furnace and cooled to room temperature; the crystals are freed from the remaining solidified KF by immersing the crucible in hot distilled water. Typical "butterfly" twins, as described in Section 5.5.2, of up to 1 cm size are obtained (Remeika, 1954; Remeika *et al.*, 1966). Undissolved BaTiO₃ is required for genesis of the butterfly twins, and the cooling rate has to be adjusted to prevent excessive spontaneous nucleation and to preserve the platy habit. The poisonous flouride vapours require the use of a ventilated hood during growth. A modification of this Remeika process to grow BaTiO₃ was published by Bradt and Ansell (1967).

C. Spinel, MgAl₂O₄. 80.6 g MgO, 204 g Al₂O₃, 1500 g PbF₂ and 10 g B₂O₃ are premelted in a 500 cm³ platinum crucible at 900°C, then a further 600 g PbF₂ is added. The crucible is sealed by a platinum lid which has at its centre a hole of 6 to 9 mm diameter which determines the evaporation rate of the solvent. The crucible is then placed on a zirconia ceramic plate into a silicon carbide muffle furnace which is heated to 1200°C ± <0.5° in 8 hours, and kept at that temperature for two weeks which is sufficient time to evaporate most of the solvent. After cooling to room temperature the crystals are removed mechanically and residual flux is removed by hot dilute nitric acid. Typically octahedra of 1 to 2 cm size may be obtained (Wood and White, 1968). It should be noted that the evaporated PbF₂ is poisonous and heavily corrodes furnace ceramics and heating elements.

D. Gadolinium aluminate, GdAlO₃. 264 g Gd₂O₃, 120 g Al₂O₃, 840 g PbO, 440 g PbF₂, 48 g B₂O₃ and 12 g PbO₂ are premelted in a new 500 cm³ platinum crucible (previously cleaned and chemically polished with a potassium pyrosulphate melt) of a shape shown in Fig. 7.36(c), then 400 g PbF₂ is added. The platinum lid with a hole of about 0.1 mm is sealed to the crucible by argon-arc welding. The crucible is placed into a Superkanthal muffle furnace and is centred on a ceramic holder which is mounted on a rotatable ceramic tube as shown in Fig. 7.44(b). The temperature of the furnace room is brought to 1290°C and is maintained for 15 hours during which time the accelerated crucible rotation technique (ACRT)[†] is applied using the cycle of Fig. 7.44(a): C with a maximum

[†] Furnace and ACRT mechanism are available from Käsermann & Sperisen, Biel/Switzerland and from Eurotherm Schweiz, Glattbrugg ZH, Switzerland.

rotation rate (in both directions) of 90 r.p.m. Localized cooling at the centre of the crucible bottom is now provided by a constant air stream, and the furnace temperature is reduced by 1° per hour to 1200°C , with a maximum ACRT rotation rate of 70 r.p.m. The temperature is raised to 1270°C and held at this temperature overnight, then the temperature is lowered by 0.3°C per hour to 1150°C and then by 0.5°C per hour to 900°C . During the whole cooling time the ACRT action is applied with a maximum rotation rate of 70 r.p.m. and a period of about two minutes. At 900°C the ACRT mechanism is stopped, the crucible is taken out of the furnace, and the excess solution is poured off after two holes have been punched into the lid. Then the hot crucible is quickly placed into a kanthal furnace at 850°C in order to prevent cracking of the (generally) one to three large crystals formed (see Fig. 7.45a, b) and this furnace is then slowly cooled to room temperature. After cutting the crucible rim the residual flux is dissolved in hot dilute nitric acid, and the crystals are mechanically moved from the crucible.

High precision and stability are required of the temperature controller and programmer and the application of the PtRh6/PtRh30 thermopile of Scheel and West (1973) helps to achieve large crystals. Also the air flow for localized cooling has to be well regulated, otherwise nucleation control and continuous stable growth (except for a short dendritic growth period at the beginning) may not be obtained (Scheel and Schulz-DuBois, 1971; Scheel, 1972; Scheel and Elwell, 1972, 1973).

E. Yttrium iron garnet, $\text{Y}_3\text{Fe}_5\text{O}_{12}$ (YIG). A composition in mole % of 36.3PbO, 27.0PbF₂, 5.4B₂O₃, 20.78Fe₂O₃ and 10.42Y₂O₃ and of approximately 1 kg weight is premelted in a crucible shown in Fig. 7.36(e). A lid containing a narrow S-shaped platinum tube for pressure release is welded to the crucible which must be sealed by welding. A seed crystal is fixed to the centre of the lid. The crucible is mounted into a ceramic arrangement which can be inverted as described by Bennett (1968) and by Tolksdorf (1968) and which additionally can be rotated around a vertical axis in order to achieve stirring by ACRT after the horizontal axial holders have been withdrawn, as discussed by Tolksdorf and Welz (1972). The initial arrangement is shown in Fig. 7.9(a). After heating overnight at a temperature of about 1250°C the crucible base is locally cooled by an air flow of about 160 l per hour and the temperature is reduced to 1180°C . Then the temperature is slowly reduced by 1°C per hour to 1100°C at which temperature the solution is saturated and spontaneous nucleation occurs (Fig. 7.9b). The crucible is smoothly turned into the position of Fig. 7.9(c) so that the seed crystal is immersed in the saturated solution. The temperature is now reduced at the same rate to 950°C with the cooling

air flow maintained on the region now in contact with the seed crystal. The solution is separated from the grown crystals (typically 3 cm in size) by inverting the crucible again into the position of Fig. 7.9(d), and the furnace is cooled to room temperature at 50°C per hour.

During the cooling from 1100° to 950°C, stirring is achieved by the accelerated crucible rotation technique described in detail in the previous example. In addition to the production of YIG crystals this process might be useful when crystals of the same material have to be grown repeatedly to a size larger than 1 cm³ in pilot plant production. The advantages are the Bennett-Tolksdorf nucleation control, the ACRT stirring of Scheel (1972) and the possibility of using the high temperature solution several times, thus saving chemicals.

F. Nickel ferrite, NiFe₂O₄. Well-mixed powders of 179.4 g BaCO₃ and 43.2 g dry B₂O₃ (to give BaO × 0.62B₂O₃ solvent) are placed in a weighed platinum crucible of 7 cm diameter and 7 cm height which is fitted with a lid and slowly heated to 1000–1100°. An automatic temperature program with a heating and cooling cycle of 24 hours is useful. Several fusions may be required before enough solvent has been added to produce a melt depth of about 3 cm.

After cooling to room temperature the crucible is weighed in order to obtain the mass of borate solvent. NiO and Fe₂O₃ are added in 1:1 molar proportions such that these oxides form 30% of the total weight of solution. This concentration provides several grams of NiFe₂O₄ to act as nutrient. The crucible without a lid is placed into the crystal growth furnace in a region such that the base is hotter than the melt surface. A furnace having a horizontal division and with the two sections heated independently is preferable.

The seed crystal of [111] orientation is tied firmly onto a platinum seed holder which can be cooled, rotated and withdrawn at adjustable rates (see for example the apparatus of Belruss *et al.* (1971), but also a commercial Czochralski puller with a modified seed holder would suffice).

The crucible is heated to 1320°C for a day with the seed just above the melt, then cooled to about 1250°C with the temperature difference ΔT across the solution adjusted to 10°C; direct control of this difference by opposed thermocouples is preferable (one advantage of gradient transport is that the exact growth temperature need not be accurately set and the liquidus temperature not accurately known).

The seed crystal is inserted just below the surface of the melt and rotated at 60 r.p.m. Cooling of the seed is desirable by water or air through the seed holder, typically by 5–10 l/min of air. The crystal is observed intermittently, preferably in reflected light. If it grows outward relatively

quickly it is raised at about 2 mm/day. The growth speed is regulated by increasing or decreasing ΔT . After a few days the crystal is slowly withdrawn from the solution and cooled over several hours in the furnace or by gradual removal to a cooler region (Smith and Elwell, 1968; see also Linares, 1964; Kestigian, 1967; Whiffin, 1973).

The above six recipes have been tested on several occasions, and the first two procedures are suggested for experimental courses in crystal growth. A collection of crystal growth procedures checked in independent laboratories, similar to "Organic Syntheses" and "Inorganic Syntheses", would be very helpful for many crystal growers and especially for occasional crystal growers such as physicists who require crystals of one or a few materials for research purposes. Such a compilation of "recipes" would prevent much duplication of work in the field of crystal growth.

7.3. Special Techniques, Specific Problems

7.3.1. Crystal growth from HTS at medium and high pressure

The study of high pressure phases and phase transformations has grown rapidly with the development of high pressure apparatus, particularly due to the pioneering work of Bridgman. However, the main effort has been devoted to transformations in the solid state, although an appreciable amount of research has also been carried out on hydrothermal synthesis of minerals at medium pressures and temperatures (500–3000 atm, 200–800°C). The latter work has resulted in the large scale synthesis of quartz and recently of zircon but, as was mentioned in Chapter 1, crystal growth by the hydrothermal method is beyond the scope of this book.

Relatively little crystal growth at medium or high pressure has been effected in non-aqueous solvents, with the notable exception of diamond, which is now produced very widely. The reasons for the neglect of HTS growth under pressure are mainly that:

- (a) The experimental effort required is extremely great, and increases very rapidly with the pressure p , and correspondingly with temperature T and solution volume V .
- (b) The difficulty of finding solvents in which the solute has an appreciable solubility, but for which corrosion-resistant containers exist, increases with p and T .
- (c) The difficulty in controlling the growth parameters to the degree necessary for the synthesis of good quality crystals increases with p and T . At the very high pressures used for diamond synthesis, stirring is still impossible.

In this Section the growth of diamond crystals will be briefly discussed and a few examples will then be given of other crystals which have been grown from HTS at high pressure.

A. Crystallization of diamond. Several tons of diamond are now produced per year for a variety of applications, especially for use as an abrasive. The bulk of the diamond is in the size range from 1 to $100\text{ }\mu\text{m}$ and the price of synthetic diamond grit is comparable with that of the natural mineral.

Although the synthesis of diamond has attracted the attention of scientists since the last century, a reproducible synthesis was reported only in 1955. The use of metallic solutions at 50–60 kbar and 1400–1600°C is now practised in several centres and has remained the only commercial process, in spite of studies of alternative techniques such as growth from the pure melt (Bundy, 1963), at about 4000 K and 140 kbar, and by metastable epitaxial deposition from the vapour phase at atmospheric pressure (Angus *et al.*, 1968).

The apparatus used for the solution growth experiments of diamond is of the "belt" type (Hall, 1960), the high pressure region of which is shown in Fig. 7.47. Potential solvents have been discussed by Wakatsuki (1966) and especially by Wentorf (1966). Non-metallic solvents such as Cu_2O , CuCl , AgCl , ZnS , CdO , FeS and silicate melts containing OH^- ions were found to produce only graphite, whereas several transition metals such as Fe, Ni, Co, Cr or Mn or alloys of refractory transition metals with Cu produce diamond under the same conditions of temperature and pressure. This observation was attributed by Wentorf to the low solubility (<1%) of carbon in the former group compared with that in the metallic solutions. In addition the nature of the dissolved carbon could play a vital role since Wentorf (1966) showed that carbon has a positive charge in metal solutions, a negative charge in CaC_2 or Li_2C_2 and is neutral in the compound solvents.

The phase diagrams Fe–C, Ni–C and Fe–Ni–C at 57 kbar have been determined by Strong and Hanneman (1967) and Strong and Chrenko (1971) and are shown in Fig. 7.49(a)–(c). In the Fe–C system, crystallization of diamond is restricted to the region between the diamond-graphite equilibrium at 1830 K and the melting point of Fe_3C at 1688 K. The Ni–C eutectic lies at a lower carbon concentration and at a higher temperature than in the Fe–C system. The ternary Fe–Ni–C system has several advantages over the binary systems since the diamond-solution liquidus extends over a wider range of temperature as shown in the 1400°C section. A similar advantage has been reported for the Fe–Al–C system (Strong and Chrenko, 1971). It is interesting that solvents which form compounds with

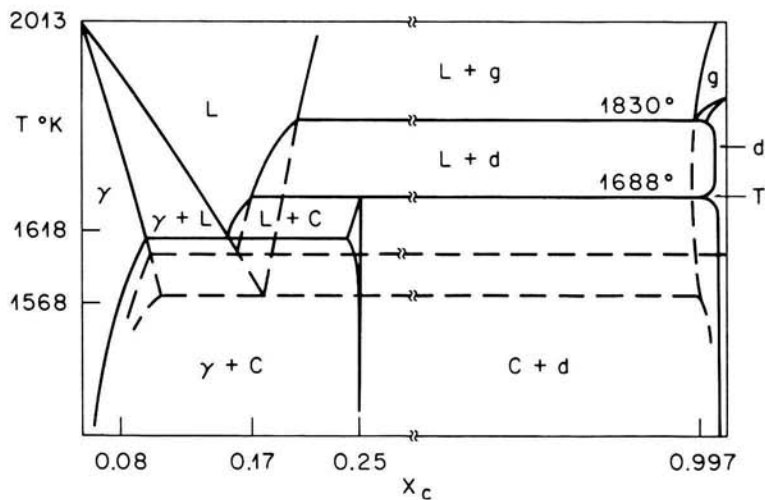


FIG. 7.49 (a)

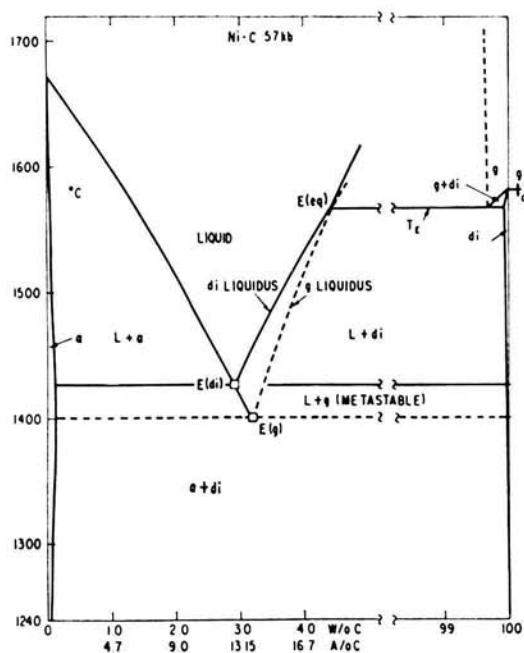


FIG. 7.49 (b)

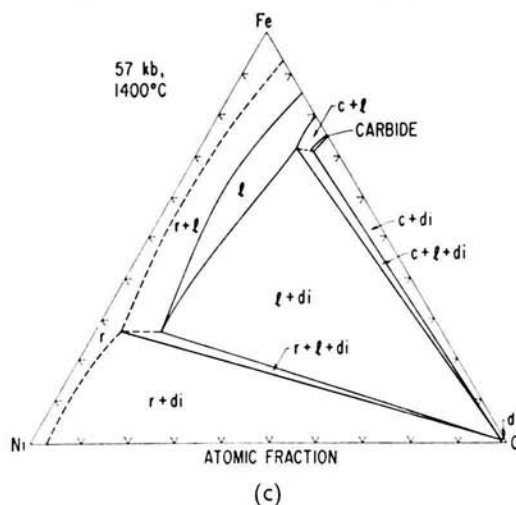


FIG. 7.49. Phase diagrams at 57 kbar applied to diamond synthesis. (a) Iron-carbon with X_c the fraction of carbon. (b) Nickel-carbon and (c) iron-nickel-carbon (Strong and Hanneman, 1967; Strong and Chrenko 1971).

the solute at lower temperatures (e.g. Fe_3C , Ni_3C) are the most suitable for diamond growth, which supports the principles discussed in Chapter 3.

Use of the phase diagrams has facilitated the growth of gem-quality diamonds up to 5 mm in diameter (0.2 g) by Wentorf (1971). A gradient transport technique was used, as shown in Fig. 7.50, at a constant pressure in the range 55–60 kbar with diamond nutrient at a temperature of about 1450°C and diamond seed crystals at about 1420°C. The use of seeds is essential since kinetic factors otherwise favour graphite crystallization, and

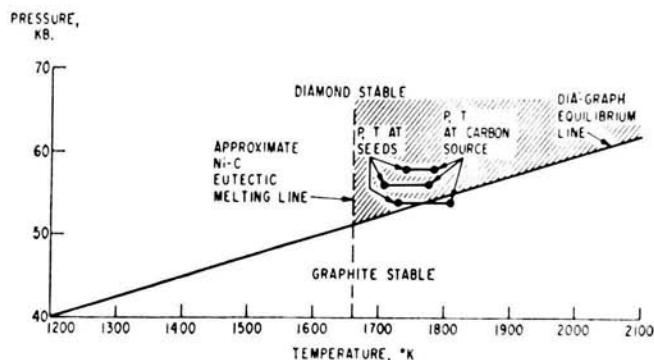


FIG. 7.50. Portion of the pressure-temperature phase diagram of carbon (Wentorf, 1971).

it was found advantageous for the growth of large crystals to locate crystals at the lower end of the pressure cell. Diamond crystallites formed by spontaneous nucleation then tend to rise towards the hotter region and are re-dissolved. With a temperature gradient of about $100^{\circ}\text{C cm}^{-1}$ the flow of solute to the seed crystals was estimated to be of the order of $10^{-4} \text{ g cm}^{-2} \text{ s}^{-1}$. If this flow is too rapid unstable growth will occur and graphite may nucleate and grow as large flakes. The maximum stable growth rate was found to be

$$\tau = \frac{1}{2Yb},$$

where Y is the average crystal diameter in mm and b has a value of 2.5 hr mm^{-2} . Thus the time required to grow a 5 mm diameter crystal is in the region of a week, which is similar to that required for a typical experiment at normal pressure (see Section 6.4).

The growth mechanism is reported to be by spreading of layers nucleated at corners and edges of the crystal (Wentorf, 1971) or at growth spirals of which a typical one published by Strong and Hanneman (1967) is shown in Fig. 7.51. Further observations on surface features and morphology have been reported by Bovenkerk (1961). The habit was observed to depend on the concentration of nitrogen in the solvent; melts containing nitrogen favour the development of $\{100\}$ and $\{111\}$ with minor $\{110\}$ and $\{113\}$, while in N-free solutions the $\{110\}$ and $\{113\}$ faces, and sometimes $\{117\}$, frequently have slower growth rates than the cube and octahedron faces. The dependence of the habit of diamond crystals on the growth temperature and pressure has been discussed by Litvin *et al.* (1968) and by Bezrukov *et al.* (1969). Naturally faceted synthetic diamonds of gem quality and weighing about 0.2 g (1 carat) are shown in Fig. 7.52. The nitrogen impurity reduces the overall growth rate by a factor of about $1/3$.

The nitrogen content tends to produce a yellow colouration and a resistivity greater than $10^{12} \Omega \text{ cm}$, while boron doping leads to a blue colour and a low resistivity of $10\text{--}10^6 \Omega \text{ cm}$. It was recently established (Collins, 1972) that boron rather than aluminium is responsible for the blue colour of natural as well as synthetic diamonds (Chrenko, 1971). Most natural and synthetic diamonds show facet-related incorporation of impurities as discussed in the review of diamond crystal growth by Strong and Wentorf (1972). Although the results of diamond crystal growth are spectacular, the cost of the larger crystals is much higher than that of natural gems. The genesis of the very large naturally occurring diamonds of high quality, such as the Cullinan with a weight of 3616 carats, is still unexplained.



FIG. 7.51. Growth spiral on a (100) face of diamond grown in nickel (Strong and Hanneman, 1967).

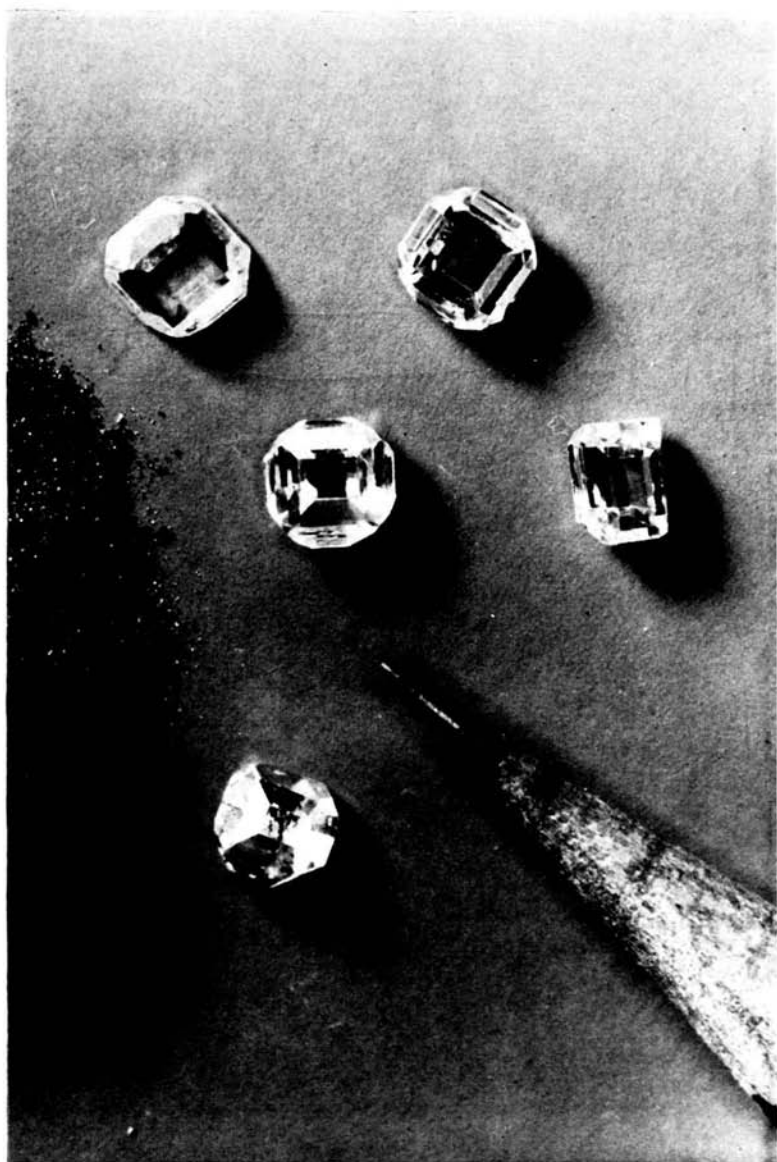


FIG. 7.52. Synthetic diamond crystals of gem quality with natural $\{100\}$ and $\{111\}$ faces (Courtesy R. H. Wentorf, General Electric Comp.).

B. Other crystals grown at medium and high pressures. The preparation of high pressure phases is of interest to chemists and mineralogists and also offers the materials scientist the opportunity to obtain particularly novel compounds or phases. In addition to the hardest materials diamond and borazon (cubic boron nitride), interesting superconducting compounds have been synthesized as an example of the variety of compounds and modifications the properties of which are related to their highly condensed structure. The crystal chemical aspects of high pressure phases have been reviewed by Neuhaus (1964), Kleber and Wilke (1969), Klement and Jayaraman (1967), Goodenough *et al.* (1972), Rooymans (1972) and by Joubert and Chenavas (1975).

In several high pressure transformations it has been shown that the addition of small amounts of "catalysts", "mineralizers" or "fluxes" has the effect of lowering the transition pressure and temperature or of enhancing the rate of reaction. The transformation of graphite to diamond discussed above will occur only in the presence of the metal solvent and, as a further example, the transformation of quartz into coesite, which occurs without "catalysts" at about 90 kbar and 2000°C, will proceed at 20–35 kbar and at 500 to 750°C with the addition of H_2O , H_3BO_3 or $(\text{NH}_4)_2\text{HPO}_4$. In reality the additions act as high temperature solvents and thus increase the mobility of the crystal constituents.

The growth of crystals of the high pressure phases is highly desirable for structural studies and for determining the physical properties, but it has been achieved only in relatively few cases. Examples are given below.

Cubic boron nitride ("Borazon", BN): Cubic BN is the III-V analogue of diamond and seems to have a slightly higher hardness than diamond, and also has the advantage of a higher resistance to oxidation. The first successful crystallization of cubic BN was reported by Wentorf (1957, 1961, 1962). He used Li, other alkali and alkaline earth metals and nitrides, Sb, Sn and Pb as solvents at pressures of 45–64 kbar and temperatures of 1500–1900°C and postulated the formation of a $\text{Li}_3\text{N} \times 3\text{BN}$ —complex acting as solvent. Depending on the growth conditions and on the impurity content small white, yellow or black crystals were prepared. DeVries and Fleischer (1972) determined phase equilibria pertinent to the growth of cubic BN, and Bezrukov *et al.* (1968) and Matecha and Kvapil (1970) studied the perfection and the growth phenomena of high pressure-grown diamond and borazon crystals.

Boron phosphide BP: Boron phosphide decomposes under atmospheric pressure at 1200°C, which is well below its melting point. It has been crystallized by slow cooling from solution in nickel or iron (Stone, 1959) and from solution in black phosphorus at temperatures of 1200–1300°C and a pressure of 15 kbar by Niemyski *et al.* (1967). The growth process

appeared to be by isothermal transport of BP in solution with boron located at the base of the graphite container acting as nutrient. Baranov *et al.* (1967) used Cu_3P as solvent and grew crystals up to $4 \times 3 \times 2$ mm in size over a period of one month.

Cobalt diphosphide CoP_2 has been crystallized from germanium at temperatures between 800° and 1200°C at 65 kbar by Donohue (1972). The same author crystallized MnCoP_4 from excess phosphorus at 1200°C and 65 kbar.

Crystallization of compounds of high oxidation states at high oxygen pressures: The synthesis of garnets and ferrites free from divalent iron at a few atmospheres oxygen pressure has been mentioned in Section 7.1.5. Although considerable research has been done on "dry" and on hydrothermal systems (see for instance Roy, 1965) high pressure crystal growth to obtain crystals of high valency states does not yet seem to have been given much attention, with the exception of CrO_2 .

Ferromagnetic CrO_2 is at atmospheric pressure only stable up to 300°C , but at pressures of 40 kbar the stability field extends to about 1400°C according to DeVries (1967) and Fukunaga and Saito (1968). DeVries (1966) grew CrO_2 layers from CrO_3 by liquid phase epitaxy at high pressure, and Chamberland (1967) grew crystals of CrO_2 up to 0.4 mm size from various fluxes at 60–65 kbar and 500 – 1000°C , the best flux being Na_2CrO_4 .

Crystallization of compounds with high coordination numbers at high pressures: Quite a number of compounds are likely to form denser modifications at high pressures, and the high pressure synthesis of several new compounds has been reported. But here again the limited volume available in high pressure apparatus and the experimental difficulties have prevented a wide activity in this most interesting field. Examples of successful crystal growth experiments are given in the following.

Lithium metaborate LiBO_2 has at normal p - T conditions a monoclinic chain structure. Marezio and Remeika (1965) reported a tetragonal high pressure phase (γ - LiBO_2) with a zinc blende-like structure and were able to grow crystals of this compound from LiCl flux at 15 kbar and 950°C (1966). The solution was held for one hour's growth time in a small tantalum container in a furnace assembly described by Kennedy *et al.* (1962). The solvent was dissolved in methanol, and small colourless crystals were obtained. With a LiCl -rich solution another phase was synthesized which was face-centred cubic with a lattice constant of $12.13 \text{ \AA}$ and which could be a lithium chloroborate of boracite type although no chemical analysis was made.

In order to study α - Ga_2O_3 as a possible laser host for chromium analogous to the isostructural corundum, crystals of this high pressure modifi-

cation of Ga_2O_3 have been grown by Remeika and Marezio (1966) although Foster and Stumf (1951) succeeded in the preparation of metastable α - Ga_2O_3 at normal pressure. In a similar experimental arrangement as mentioned for the LiBO_2 synthesis Remeika and Marezio used NaOH as solvent, and 44 kbar and 1000°C were applied during one hour. After extraction of the small colourless crystals two kinds of growth habit resembling the hexagonal plates and the rhombohedra of α - Al_2O_3 were observed. Chromium doping resulted in small green rhombohedra of which the difference in colour compared to red ruby was considered to be caused by a difference in crystal field splitting due to the significant size difference between the Al^{3+} and Ga^{3+} ions.

During studies on the effect of high pressures on rare-earth garnets it was found that some of them decomposed to the rare-earth aluminates of perovskite type and the sesquioxides of corundum type (Marezio *et al.* 1966a). Using this reaction in the presence of a NaOH flux at 70 kbar and 1000°C YGaO_3 and YbGaO_3 could be crystallized in one hour as small transparent crystallites (Marezio *et al.* 1966b). Recently Dernier and Maines (1971) reported on the high pressure synthesis and crystal data of the rare earth orthoaluminates.

Further examples of crystal growth at high temperatures and high pressures have been listed by Rooymans (1972), Goodenough *et al.* (1972) and by Joubert and Chenavas (1974).

7.3.2. Undesirable crystal growth from high temperature solutions

In a number of processes involving high temperature solutions there is undesired crystallization. In metallurgy and in the ceramic and cement industries the development of large crystals or the crystallization of undesired phases might degrade the mechanical and thermal properties of the product, and devitrification in the glass industry makes the products worthless, unless devitrification is achieved intentionally as in the fabrication of Pyroceram[†]-type ceramics.

A common problem in nuclear-reactor technology occurs in the cooling circuits (when low-melting metals and alloys such as sodium or sodium-potassium are used as coolants) as well as in the recently developed liquid uranium-bismuth alloy fuelled homogeneous reactor. A solid-liquid interaction (corrosion) occurs in the hot region in the reactor, and crystallization of the dissolved container material or of its compounds with the liquid metal occurs in the cooler region (Weeks and Gurinsky, 1958).

Another example of unwanted crystallization is the crystal growth of whiskers by the VLS mechanism which occurs occasionally in electric installations when the appropriate conditions are accidentally fulfilled.

[†] Trademark of Corning Glass Works, Corning, N.Y.

However, it is not intended to give a broad survey of the topic of this section. The above examples merely illustrate where unwanted crystal growth processes might occur and how important it might be in certain cases to prevent or to control them. In the following discussion a few examples of undesired effects observed in the practice of flux growth are briefly mentioned.

Unwanted crystal growth obviously occurs when the experiment results either in very small crystal or in crystals of an undesired phase. The former problem has been discussed in Sections 3.4.3, 3.6.2., 7.1.1 and

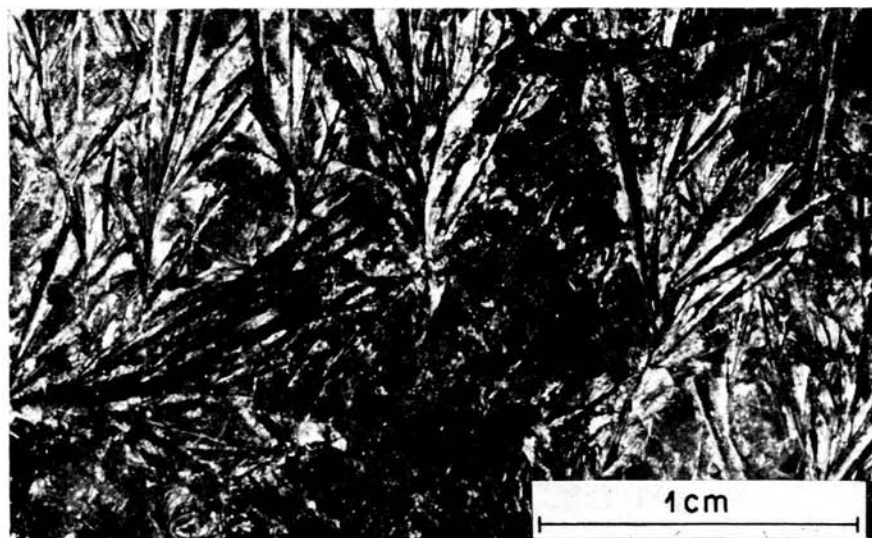


FIG. 7.53. Accidentally formed crystals of lead feldspar (Scheel, 1971).

7.2.7, the latter is a matter of the stability fields as discussed in Section 3.8.5. Another example of unexpected flux growth occurred during the preparation of ZnAl_2O_4 crystals from $\text{PbO-PbF}_2\text{-B}_2\text{O}_3$ solvent: the platinum crucibles covered with a lid (but not sealed) were placed into mullite-type ceramic crucibles with ceramic lids. After the slow-cooling experiment and removal from the furnace the underside of the ceramic lid showed elongated crystals which were identified as solid solutions of the feldspars KAlSi_3O_8 and $\text{PbAl}_2\text{Si}_2\text{O}_8$, the first synthesized Pb-containing feldspar crystals (Scheel, 1971), see Fig. 7.53. Wanklyn and Hauptman (1974) reported that silicate crystals grew in solutions for example of $\text{Er}_2\text{O}_3/\text{MoO}_3$ in PbO/PbF_2 when growth occurred in a sillimanite muffle furnace.

Crystals of up to 5 mm of platinum and of several platinum-lead

compounds have been observed in flux growth experiments with corrosive lead- and fluorine-containing melts, especially when the conditions were slightly reducing. In general these crystals are not wanted, especially when they intergrow with the required crystals. Therefore a slightly oxidizing atmosphere or a redox buffer in the melt, such as V_2O_5 , are used to minimize flux growth of Pt-containing crystals.

Most experimentalists will have observed examples of unwanted crystal growth from high-temperature solutions. Identification of the crystalline phase, for instance by X-ray powder diffraction, is worthwhile, as in some cases interesting or novel materials may have crystallized. On the other hand an investigation of the crystallized phases may indicate the parameters to be modified in order to prevent the unwanted crystallization.

7.3.3. Unexplored techniques and areas

Nearly all areas of crystal growth from high-temperature solutions are not well understood, thus the whole field might still be said to be "unexplored". However, in the following discussion only examples of those (experimental) topics will be briefly discussed which are or might become of general interest.

A. New materials. A number of materials with interesting properties for research and with potential applications exist which have not yet been grown reproducibly as crystals of sufficient size and quality by crystal growth from melt or from vapour. Several of these could probably be grown from high-temperature solutions, for example $BeO^\dagger$, $BiFeO_3$, $SbSI$, SiC and TaC . An interesting example of the success of a large effort is the growth of colourless diamond crystals of gem quality and up to 1 carat size as discussed in Section 7.3.1.

Novel materials with interesting properties may still await discovery, because of all possible compounds A_xB_y of elements A and B only approximately 50% are known, and of the compounds $A_xB_yC_z$ the estimate of Lydtin (1972) is that 1% are known, and of quaternary compounds ABCD a small fraction of a percent is known. Thus many compounds are still to be discovered, for instance by investigation of the corresponding phase diagrams or by isomorphous replacement in known structure types. In addition solid solutions might be prepared to optimize the required properties. A class of compounds which has not yet found wide interest is that containing elements in unusual valency states, partially because of experimental difficulties of preparation. Also extreme conditions (pressure, temperature) could produce interesting new materials.

[†] The reproducible growth of large BeO crystals has recently been reported by S. B. Austerman (private communication).

B. New solvent systems. As in the case of new materials, there are likely to be novel solvent systems for old and new materials which have advantages over the solvents now in use. The approach is to achieve optimum characteristics with respect to solubility and corrosivity, viscosity, metastable region, stable growth, and purity of the crystals grown from them. In developing new solvents the aspects of compound and complex formation as discussed in Chapter 3 might be useful. With increasing knowledge of solutions and of thermodynamic properties of the components the choice of solvents might be made on theoretical grounds.

It is suggested to use the "hydroflux" method for growth of various oxide compounds, hydroflux being a combination of the hydrothermal and the flux techniques. In natural crystallization water is known to be an excellent modifier of solution properties and accordingly one would expect its beneficial influence on certain solvent systems at the medium pressures required. An approach in this direction is the use of highly concentrated salt solutions, of about 50 mole %, in hydrothermal crystal growth.

C. High temperatures, high pressures. Extreme conditions such as very high temperatures and high pressures are difficult to achieve, especially in the volumes required to grow sufficiently large crystals from high-temperature solutions. With the exception of diamond and boron nitride, not much work has been done either at temperatures above 1500°C or at pressures exceeding a few atmospheres. Examples where high temperatures have been required to grow extremely refractory crystals are the growth of SiC, WC and the europium chalcogenides. Recently crystals of LaB₆, which is incongruently melting at around 1800°C, have been prepared by Deacon and Hiscocks (1971) by slow cooling from 1700°C and are reproduced in Fig. 7.54. Although the experimental difficulties increase enormously with temperature and especially with pressure, significant new results are to be expected from studies in this area.

D. Electrolysis; an electric field as a driving force for supersaturation. Crystal growth by electrolysis in molten salts seems a promising area (see Section 7.1.2), especially for the growth of refractory compounds like borides and pnictides and of compounds with defined (lower) valency states. However, the literature indicates that many compounds have been prepared by high-temperature electrolysis, partially on a production scale, but relatively little systematic work has been done on the application of electrolysis to the growth of large high-quality crystals.

Another application of electric fields across ionic solutions might be considered, namely as an easily controlled driving force for supersaturation, even in the absence of electrolytic reduction or oxidation. The growth rate may be controlled by varying the electric current through the

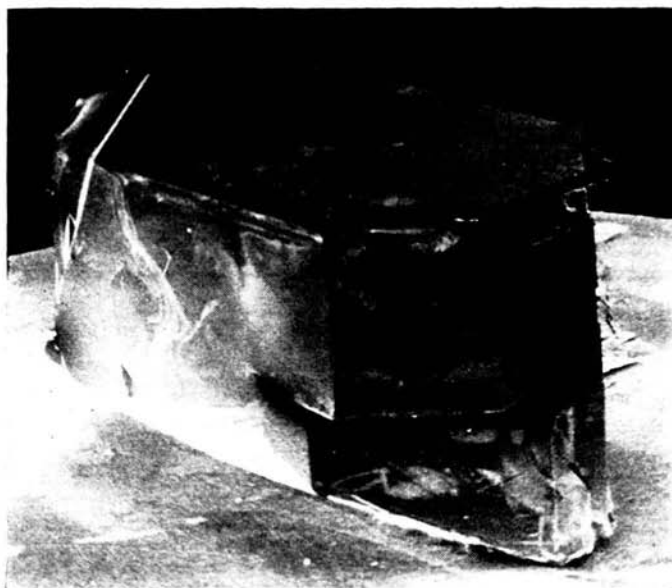


FIG. 7.54. Lanthanum tetraboride crystal of 5.5 mm length grown from lanthanum solution by cooling from 1700° to 1200° (Deacon and Hiscocks, 1971).

solution in an isothermal melt in a uniform temperature zone as was demonstrated by Elwell (unpublished) for the growth of Fe_2O_3 from $\text{BaO/B}_2\text{O}_3$. It is possible that an electrical driving force may lead to enhanced stability of growth compared with a thermal driving force. An additional use of an electrical driving force is in the provision of time markers for growth rate determinations, as in the experiments of Lichtensteiger *et al.* (1971).

E. Growth of special crystal shapes. This topic has been extensively discussed in Chapter 5. Special crystal habits are of advantage for certain applications and physical measurements. For example the BaTiO_3 butterfly twins consisting of two thin single-crystalline platelets, as grown by Remeika (1954), were important for a variety of measurements and contributed significantly to the development of ferroelectrics. In the case of BaTiO_3 the twin-plane reentrant edge (TPRE) growth on undissolved crystallites was responsible for the formation of platelets of barium titanate which otherwise grows as cubes or similar compact shapes. Other examples of TPRE growth of platelets are alumina Al_2O_3 (Wallace and White, 1967) and beryllia BeO (Austerman, 1964). It is probable that under appropriate conditions many more compounds could be grown as plates by a twin

mechanism, and a number of examples of semiconductors grown by TPPE were given by Faust and John (1964).

Crystalline fibres or whiskers of various materials (SiC , Al_2O_3) are applied as components of high-strength materials. Until now most whiskers have been produced from the gas phase via a liquid droplet by the VLS mechanism but they could also be crystallized from bulk high-temperature solutions. For example, crystalline fibres of TiO_2 , ZrO_2 and ZrSiO_4 have been prepared from borate melts (Russell *et al.*, 1962), and Morgan and Scheffler (1965) showed how these fibres could be separated from the solution.

On the other hand there are a variety of crystals which grow in inconvenient shapes like needles or plates and which are required as equidimensional bulk crystals, such as TiO_2 , YVO_4 , BeO , SbSI and SiC . There is as yet no simple general solution to this problem. The approach until now has been to modify the solvent, growth temperature and supersaturation, but it might be preferable to control the flow pattern with respect to crystal orientation in order to influence the crystal habit.

F. Liquid phase epitaxy. This topic is discussed in Chapter 8, and here it will be briefly mentioned that LPE is a still unexplored field. One of the reasons is that since the first report on LPE by Nelson (1963) this technique has been little studied as such since most LPE work has been concentrated on fabrication of specific devices. A comparison of LPE and chemical vapour epitaxy has recently been published by Minden (1973), and the first proposal for LPE as a commercial process has been made by Bergh *et al.* (1973). However, it is a long way from growth on a single substrate to the batch process proposed by Scheel and Schulz-DuBois (see Section 8.4.2) and to a continuous flow process as discussed in Section 8.6.

G. Growth of large crystals. The parameters which are important for growth of large crystals have been discussed in this chapter, and crystals of several cm in diameter and weighing several hundred grams have been obtained of various compounds. However, only two materials are grown commercially as large crystals from HTS, namely magnetic garnets and emerald, the former as inclusion-free crystals 2–5 cm in size or with inclusion-free regions of 1–2 cm thickness. It is expected that large crystals could be grown if required by application of the technology which corresponds to commercial crystal growth from aqueous solutions. Seed crystals could be fixed on rotated seed holders or into rotated solutions, and the precise temperature control and programming as discussed in Chapter 6 and in Section 7.2.2 are required. For volatile solutions accelerated crucible rotation is the alternative stirring technique. It was shown

throughout the book that it is now possible to grow large crystals of high purity and perfection, although the effort to achieve this goal varies for different materials.

H. Mass crystallization. The large-scale production of small crystals may be divided into two fields. In the first a large excess of solute, of material to be crystallized, is present with only a small amount of solvent whereas in the second field the mass of small crystals is precipitated from previously homogeneous solutions.

An example of the first field is the industrial crystallization of diamond to be used as abrasive: only small amounts of metals or alloys (Fe, Ni, Cr) as solvents are present, and accordingly the term "catalyst" has been frequently used for the metal solvent. In the high-pressure cell, under the temperature and pressure conditions required for diamond synthesis (see Sections 7.2.8 and 7.3.1), graphite or a carbon-containing compound recrystallizes through the thin solvent layer to form diamond.

A similar mechanism, crystal formation or recrystallization through a thin solution layer, occurs in many processes where materials are prepared at high temperatures. Examples are the fabrication of porcelain and cement or the recrystallization of cadmium sulphide phosphors at high temperatures by the addition of a small amount of a salt, usually sodium chloride. Generally the term "mineralizer" is used for the solvent which might remain as a component of the product as in the case of porcelain and cement or which might be subsequently dissolved, as is the NaCl after recrystallization of cadmium sulphide.

Solid state reactions used for synthesis of materials may not always be reactions in the solid state (by diffusion): the formation and crystallization of the new compounds frequently occurs in a liquid layer. This liquid might be a eutectic of the components and impurities which accelerates the rate of reaction significantly. On the other hand, small amounts of a suitable solvent might be deliberately added to the components of the required compound, as in the preparation of CdTe, GaP and other chalcogenides and pnictides at relatively low temperatures by the addition of the corresponding metal iodide (Kwestroo *et al.*, 1969; Kwestroo, 1972). Other examples are the preparation of metallic silicides and germanides by an amalgam method (Mayer *et al.*, 1967), of rare-earth nitrides by the amalgam method by Busch *et al.* (1970), of oxide compounds by the addition of salts (Wilke *et al.*, 1965; Wickham, 1970; Petzold *et al.*, 1971), of several sulphides by the addition of alkali polysulphides (Scheel, 1974), and of carbides by the addition of a metal bath (often 70 wt% Fe, 30 wt% Ni, called "menstruum") as described by Windisch and Nowotny (1972).

Other examples of industrial applications of mass crystallization from

high-temperature solutions are the fabrication of Al_2O_3 and SiC whiskers by the VLS mechanism, and the electrolytic preparation of refractory materials (metals, borides, carbides, etc.) from molten salt solutions. In these cases the precipitation of the crystals or layers occurs from homogeneous solutions, the electric field being the driving force for supersaturation. Examples of mass crystallization from high-temperature solutions with solvent evaporation or with slow cooling as driving forces for supersaturation are not known to the authors although there are methods for the preparation of interesting materials which seem easier and better than conventional technology. As an example, tons of CdS phosphor and photoconductor are fabricated by a complicated many-step process (Weisbeck, 1964) and could be crystallized from alkali polysulphide melts (Scheel, 1974) with metallic cadmium or a Cd compound as starting material.

7.4. Summary

In this section no attempt is made to summarize the whole chapter but attention is drawn to a few major points.

The experimental techniques which appear to offer most promise for the growth of large, relatively perfect crystals are slow cooling in sealed crucibles stirred by the accelerated crucible rotation technique, top-seeded solution growth, and the travelling solvent zone method. The two latter methods are restricted to solvents of low volatility and this restricts their applicability. For growth in sealed crucibles, solvents in the system $\text{PbF}_2/\text{PbO}/\text{B}_2\text{O}_3$ have been particularly successful for refractory oxides which still form the most important class of materials crystallized from high-temperature solution.

Improvements in crystal size and quality can often be obtained by the use of seeds, and the introduction of the Bennett-Tolksdorf seeding technique is a valuable innovation. The use of temperature cycling and localized cooling to restrict nucleation are particularly worthwhile since the introduction of stirring by the accelerated crucible rotation technique.

Quantitative models are now available for growth by most of the techniques mentioned and the main criteria for the design of apparatus have been established. The necessity to maintain the growth rate below the maximum stable value has been stressed. Temperature stabilization is of particular importance in any experimental method.

Although this chapter has been concerned with the growth of bulk crystals, one prediction which can be made with confidence is that the emphasis will move in the direction of crystal growth of thin layers by liquid phase epitaxy.

References

- Abernethy, L. L., Ramsey, T. H. and Ross, J. W. (1961) *J. Appl. Phys.* **32**, 376 S.
- Addamiano, A. (1971) *J. Crystal Growth* **11**, 351.
- Ahmad, I. and Capsimalis, G. P. (1967) In "Crystal Growth" (H. S. Peiser, ed.) Pergamon, Oxford.
- Aidelberg, J., Flicstein, J. and Schieber, M. (1974) *J. Crystal Growth* **21**, 195.
- Andrieux, J. L. (1929) Research on the Electrolysis of Metal Oxides dissolved in Anhydrous Boric Oxide and Borate Fluxes, Thesis, Paris.
- Andrieux, J. L. and Marion, S. (1953) *Compt. Rend.* **236**, 805.
- Andrieux, J. L. and Weiss, G. (1948) *Bull. Soc. Chim.* 596.
- Angelici, R. J. (1969) "Synthesis and Technique in Inorganic Chemistry" Saunders, Philadelphia.
- Angus, J. C., Will, H. A. and Stanko, W. S. (1968) *J. Appl. Phys.* **39**, 2915.
- Arend, H. (1960) *Czech. J. Phys. B* **10**, 971.
- Armstrong, W. M., Chaklader, A. C. D. and DeCleene, M. L. A. (1962) *J. Am. Ceram. Soc.* **45**, 407.
- Aucoin, T. R., Savage, R. O. and Tauber, A. (1966) *J. Appl. Phys.* **37**, 2908.
- Austerman, S. B. (1964) *J. Nucl. Mat.* **14**, 225.
- Austerman, S. B. (1965) *J. Am. Ceram. Soc.* **48**, 648.
- Austerman, S. B., Myron, S. B. and Wagner, J. W. (1967) *Carbon* **5**, 549.
- Baker, H. D., Ryder, E. A. and Baker, N. H. (1953, 1961) "Temperature Measurement in Engineering" Vol. I (1953), II (1961) Wiley, New York.
- Ballman, A. A. and Laudise, R. A. (1963) In "The Art and Science of Growing Crystals" (J. J. Gilman, ed.) p. 231. Wiley, New York.
- Baranov, B. V., Prochukhan, V. D. and Goryanova, N. A. (1967) *Inorg. Materials USSR* **3**, 1477.
- Barns, R. L. and Ellis, W. C. (1965) *J. Appl. Phys.* **36**, 2296.
- Bartholomew, R. F. and White, W. B. (1970) *J. Crystal Growth* **6**, 249.
- Bartlett, R. W., McCamont, J. W. and Gage, P. R. (1965) *J. Am. Ceram. Soc.* **48**, 551.
- Belin, C., Brissot, J. J. and Jesse, R. E. (1972) *J. Crystal Growth* **13/14**, 597.
- Bell, R. O., Hemmat, N. and Wald, F. (1970) *Phys. Stat. Sol. (a)* **1**, 375.
- Belruss, V., Kalnajs, J., Linz, A. and Folweiler, R. C. (1971) *Mat. Res. Bull.* **6**, 899.
- Bennett, G. A. (1968) *J. Crystal Growth* **3/4**, 458.
- Bergh, A. A., Saul, R. H. and Paola, C. R. (1973) *J. Electrochem. Soc.* **120**, 1558.
- Berkes, J. S., White, W. B. and Roy, R. (1965) *J. Appl. Phys.* **36**, 3276.
- Berman, I. and Comer, J. J. (1969) *Mat. Res. Bull.* **4**, 107.
- Berman, I. and Ryan, C. E. (1971) *J. Crystal Growth* **9**, 314.
- Berry, R. J. (1966) *Metrologia* **2**, No. 2, 80.
- Best, R. (1967) *Der Elektroniker* **4**, 203.
- Bethe, K. and Welz, F. (1971) *Mat. Res. Bull.* **6**, 209.
- Bezrukov, G. N., Butuzov, V. P. and Korolev, D. F. (1969) *Growth of Crystals* **7**, 91.
- Bezrukov, G. N., Butuzov, V. P., Nikitina, T. P., Fel'dchuk, L. I., Filonenko, N. E. and Khatelishvili, G. V. (1968) *Dokl. Akad. Nauk SSSR* **179**, 1326.
- Blank, S. L. and Nielsen, J. W. (1972) *J. Crystal Growth* **17**, 302.
- Blank, S. L., Hewitt, B. S., Shick, L. K. and Nielsen, J. W. (1973) Proc. AIP Conf. Mag. and Mag. Mat. No. 10, p. 256.
- Block, B. (1930) In "Ullmann's Enzyklopädie der Technischen Chemie", p. 814. 2nd Edition, Berlin-Wien.
- Bonner, W. A. and Van Uitert, L. G. (1967) *Mat. Res. Bull.* **2**, 131.
- Bonner, W. A., Dearborn, E. F. and Van Uitert, L. G. (1965) *Am. Ceram. Soc. Bull.* **44**, 9.

- Bonner, W. A., Dearborn, E. F. and Van Uitert, L. G. (1967) In "Crystal Growth" (H. S. Peiser, ed.) 437. Pergamon, Oxford.
- Bootsma, G. A. and Gassen, H. J. (1971) *J. Crystal Growth* **10**, 223.
- Bovee, B. A. (1953) *Am. Ceram. Soc. Bull.* **32**, 26.
- Bovenkerk, H. P. (1961) *Am Min.* **46**, 952.
- Bradt, R. C. and Ansell, G. S. (1967) *Mat. Res. Bull.* **2**, 585.
- Brauer, G. (1960/1962) "Handbuch der präparativen anorganischen Chemie" Enke, Stuttgart.
- Brice, J. C. (1965) "The Growth of Crystals from the Melt" North-Holland, Amsterdam.
- Brice, J. C. (1973) "The Growth of Crystals from Liquids" North-Holland, Amsterdam.
- Brice, J. C. and Whiffin, P. A. C. (1973) *Platinum Metals Rev.* **17**, 46.
- Bridgman, P. W. (1952) "The Physics of High Pressure" Bell, London.
- Brisot, J. J. and Belin, C. (1971) *J. Crystal Growth* **8**, 213.
- Brixner, L. H. (1959) *J. Amer. Chem. Soc.* **81**, 3841.
- Brixner, L. H. and Babcock, K. (1968) *Mat. Res. Bull.* **3**, 817.
- Brixner, L. H. and Bouchard, R. J. (1970) *Mat. Res. Bull.* **5**, 61.
- Brixner, L. H. and Weiher, J. F. (1970) *J. Solid State Chem.* **2**, 55.
- Broder, J. D. and Wolff, G. A. (1963) *J. Electrochem. Soc.* **110**, 1150.
- Brooks, M. S. and Kennedy, J. K. (1962) (editors) "Ultrapurification of Semiconductor Materials" Macmillan, New York.
- Brunst, W. (1957) "Die induktive Wärmebehandlung" Springer, Berlin.
- Buckley, H. E. (1951) "Crystal Growth" Chapman and Hall, London.
- Bundy, F. P. (1962) In "Modern Very High Pressure Techniques" (R. H. Wentorf, ed.) p. 1. Butterworths, London.
- Bundy, F. P. (1963) *J. Chem. Phys.* **38**, 631.
- Burton, J. A., Prim, R. C. and Slichter, W. P. (1953) *J. Chem. Phys.* **21**, 1987.
- Busch, G., Kaldis, E., Schaufelberger-Teker, E. and Wachter, P. (1970) Rare Earth Conference Paris May 1969, Coll. Intern. C.N.R.S. I, 359.
- Busch, G., Kaldis, E., Muheim, J. and Bischof, R. (1971) *J. Less-Common Metals* **24**, 453.
- Butler, C. T., Russell, J. R., Quincy jr., R. B. and La Valle, D. E. (1966) Report ORNL-3906.
- Caldwell, F. R. (1962) "Thermocouple Materials" NBS Monograph 40, US Government Printing Office, Washington, D.C.
- Campbell, J. E. (1959) (editor) "High Temperature Technology" Wiley, New York.
- Capelletti, R., Fano, V. and Scalvini, M. (1968) *Ricerca Sci.* **38**, 668, 886.
- Capelletti, R., Fano, V. and Scalvini, M. (1969) *J. Crystal Growth* **5**, 73.
- Carruthers, J. R. (1967) *J. Electrochem. Soc.* **114**, 959.
- Carruthers, J. R. and Nassau, K. (1968) *J. Appl. Phys.* **39**, 5205.
- Chamberland, B. L. (1967) *Mat. Res. Bull.* **2**, 827.
- Champion, J. A., Keene, B. J. and Allen, S. (1973) *J. Mat. Sci.* **8**, 423.
- Chandrasekhar, S. (1961) "Hydrodynamic and Hydromagnetic Stability" Clarendon Press, Oxford.
- Chang, C. E. and Wilcox, W. R. (1971) *Mat. Res. Bull.* **6**, 1297.
- Chase, A. B. and Osmer, J. A. (1967) *J. Am. Ceram. Soc.* **50**, 325.
- Chicotka, R. J. (1971) *IBM Techn. Discl. Bull.* **13**, 3037.
- Chrenko, R. M. (1971) *Nature, Phys. Sci.* **229**, 165.
- Cloete, F. L. D., Ortega, R. F. and White, E. A. D. (1969) *J. Mat. Sci.* **4**, 21.
- Cobb, C. M. and Wallis, E. B. (1967) Report AD 655 388.

- Cochran, W. G. (1934) *Proc. Cambridge Phil. Soc.* **30**, 365.
- Cockayne, B. (1968) *Platinum Metals Rev.* **12**, 16.
- Cockayne, B. and Gates, M. P. (1967) *J. Mat. Sci.* **2**, 118.
- Cockayne, B. Chesswas, M., Plant, J. G. and Vere, A. W. (1969) *J. Mat. Sci.* **4**, 565.
- Collins, A. T. (1972) *Diamond Res.*, Suppl. Ind. Diamond Rev. (cited by Strong and Wentorf 1972).
- Corbett, J. D. and Duke, F. R. (1963) In "Techniques in Inorganic Chemistry" (H. B. Jonassen and A. Weissberger, eds.) p. 103. Vol. I, Interscience, New York.
- Cotton, F. A. (1939-1972) (editor) "Inorganic Syntheses" McGraw-Hill, New York.
- Crookes, W. (1912) *Proc. Roy. Soc. (London)* A **86**, 461.
- Crystal Growth (1949) *Disc. Faraday Soc.* No. 5.
- Cuomo, J. J. and Gambino, R. J. (1970) US Patent 3,498,894. (March 3).
- Damen, J. P. M. and Robertson, J. M. (1972) *J. Crystal Growth* **16**, 50.
- Daneman, H. L. and Mergner, G. C. (1967) Instrumentation Technology, May and June 1967, Reprint A 1.2102 RP of Leeds and Northrup, Philadelphia.
- Darling, A. S., Selman, G. L. and Rushforth, R. (1970) *Platinum Metals Rev.* **14**, 54, 95, 124.
- Daval, J. (1974) C.N.R.S. Grenoble, private communication.
- Dawson, R. D., Elwell, D. and Brice, J. C. (1974) *J. Crystal Growth* **23**, 65.
- Deacon, J. A. and Hiscocks, S. E. R. (1971) *J. Mat. Sci.* **6**, 309.
- Derjaguin, B. V., Fedoseev, D. V., Lukyanovich, V. M., Spitzin, B. V., Ryabov, V. A. and Lavrentyev, A. V. (1968) *J. Crystal Growth* **3/4**, 380.
- Dernier, P. D. and Maines, R. G. (1971) *Mat Res. Bull.* **6**, 433.
- DeVries, R. C. (1966) *Mat. Res. Bull.* **1**, 83.
- DeVries, R. C. (1967) *Mat. Res. Bull.* **2**, 999.
- DeVries, R. C. and Fleischer, J. F. (1972) *J. Crystal Growth* **13/14**, 88.
- DiBenedetto, B. and Cronan, C. J. (1968) *J. Am. Ceram. Soc.* **51**, 364.
- Dike, P. H. (1958) "Thermoelectric Thermometry" 3rd Edition, Leeds and Northrup, Philadelphia.
- Dike, P. H., Gray, W. T. and Schroyer, F. K. (1966) Optical Pyrometry, Leeds and Northrup Techn. Publ. A. 1.4000.
- Donohue, P. C. (1972) *Mat Res. Bull.* **7**, 943.
- Dugger, C. O. (1966) *J. Electrochem. Soc.* **113**, 306.
- Dugger, C. O. (1967) In "Crystal Growth" (H. S. Peiser, ed.) p. 493. Pergamon, Oxford.
- Duncan, C. S., Hopkins, R. H. and Mazelsky, R. (1971) *J. Crystal Growth* **11**, 50.
- Eckstein, J., Holas, M., Jindra, J., Uchytlova, A. and Wachtl, Z. (1960) *Czech. J. Physics B* **10**, 247.
- Egli, P. H. and Johnson, L. R. (1963) In "The Art and Science of Growing Crystals" (J. J. Gilman, ed.) p. 194. Wiley, New York.
- Ellis, W. C., Frosch, C. J. and Zetterstrom, R. B. (1968) *J. Crystal Growth* **2**, 61.
- Elmer, T. H. (1953) *Am. Ceram. Soc. Bull.* **32**, 23.
- Epstein, D. J. (1970) Report AD 715'312.
- Espig, H. (1960) *Chem. Tech.* **12**, 6, 327.
- Euler, J. and Ludwig, R. (1960) "Arbeitsmethoden der optischen Pyrometrie" Braun, Karlsruhe.
- Fajans, K. (1921) *Naturwiss.* **9**, 729.
- Fajans, K. and Karagunis, G. (1930) *Z. Angew. Chem.* **43**, 1046.
- Faust jr., J. W. and John, H. F. (1964) *J. Phys. Chem. Solids* **25**, 1407.

- Ferretti, A., Kunnmann, W. and Wold, A. (1962) *J. Appl. Phys.* **34**, 388.
- Filby, J. D. and Nielsen, S. (1966) *Microelectronics and Reliability* **5**, 11.
- Finch, C. B. and Clark, G. W. (1965) *J. Appl. Phys.* **36**, 2143.
- Finch, D. I. (1966) General Principles of Thermoelectric Thermometry, Techn. Publ. D 1.1000, Leeds and Northrup, Philadelphia.
- Fitzer, E. (1956) Plansee Proceed., 2nd Seminary, Reutte, Tirol, p. 56.
- Flicstein, J. and Schieber, M. (1973) *J. Crystal Growth* **18**, 265.
- Flörke, O. W. (1955) *Ber. Dt. Keram. Ges.* **32**, 369.
- Foguel, M. and Grajower, R. (1971) *J. Crystal Growth* **11**, 280.
- Fong, F. K. and Yocom, P. N. (1964) *J. Chem. Phys.* **41**, 1383.
- Foster, L. M. and Stumpf, H. C. (1951) *J. Amer. Chem. Soc.* **73**, 1590.
- Fromm, E. and Jehn, H. (1972) *Metallurg. Transact.* **3**, 1685.
- Frosch, C. J. (1967) In "Crystal Growth" (H. S. Peiser, ed.) 305. Pergamon, Oxford.
- Fukunaga, O. and Saito, S. (1968) *J. Am. Ceram. Soc.* **51**, 362.
- Garrard, B. J., Wanklyn, B. M. and Smith, S. H. (1974) *J. Crystal Growth* **22**, 169.
- Gärtner, K. J., Rittinghaus, K. F., Seeger, A. and Uelhoff, W. (1972) *J. Crystal Growth* **13/14**, 619.
- Garton, G. and Wanklyn, B. M. (1967) *J. Crystal Growth* **1**, 164.
- Garton, G., Hann, B. F., Wanklyn, B. M. and Smith, S. H. (1972) *J. Crystal Growth* **12**, 66.
- Gasson, D. B. (1965) *J. Scient. Instr.* **42**, 114.
- Geary, D. A. and Hough, J. M. (1968) *J. Crystal Growth* **2**, 113.
- Ghez, R. and Giess, E. A. (1973) *Mat. Res. Bull.* **8**, 31.
- Giess, E. A. (1966) *J. Am. Ceram. Soc.* **49**, 104.
- Giess, E. A., Kuptsis, J. D. and White, E. A. D. (1972) *J. Crystal Growth* **16**, 36.
- Gilman, J. J. (1963) "The Art and Science of Growing Crystals" Wiley, New York.
- Givargizov, E. I. and Sheftal, N. N. (1971) *J. Crystal Growth* **9**, 326.
- Goodenough, J. B., Kafalas, J. A. and Longo, J. M. (1972) In "Preparative Methods in Solid State Chemistry" (P. Hagenmuller, ed.) p. 1. Academic Press, New York.
- Goodrum, J. W. (1970) *J. Crystal Growth* **7**, 254.
- Goodwin, A. R., Gordon, J. and Dobson, C. D., (1968) *J. Phys. D* **1**, 115.
- Goss, A. J. and Adlington, R. E. (1959) *Marconi Rev.* **22**, 18.
- Gray, W. T. and Finch, D. I. (1971) *Physics Today* **24**, 9, 32.
- Greenspan, H. P. (1968) "The Theory of Rotating Fluids" Cambridge Univ. Press.
- Griffiths, L. B. and Mlavsky, A. I. (1964) *J. Electrochem. Soc.* **111**, 305.
- Grodziewicz, W. H. and Nitti, D. J. (1966) *J. Am. Ceram. Soc.* **49**, 576.
- Grodziewicz, W. H., Dearborn, E. F. and Van Uitert, L. G. (1967) In "Crystal Growth" (H. S. Peiser, ed.) 441. Pergamon, Oxford.
- Guldborg, C. and Waage, P. (1867) "Etudes sur les affinités chimiques" Christiana.
- Gunn, J. B. (1971) private communication, see also *IBM Techn. Discl. Bull.* **15**, 1050 (1972).
- Habermann, C. E., Daane, A. H. and Palmer, P. E. (1965) *Trans. AIME* **233**, 1038.
- Hall, H. T. (1958) *Rev. Sci. Instrum.* **29**, 267.
- Hall, H. T. (1960) *Rev. Sci. Instrum.* **31**, 125.
- Hall, R. N. (1952) *Phys. Rev.* **88**, 135.
- Hall, R. N. (1953) *J. Phys. Chem.* **57**, 836.
- Hamaker, R. W. and White, W. B. (1968) *J. Appl. Phys.* **39**, 1758.
- Hamaker, R. W. and White, W. B. (1969) *J. Electrochem. Soc.* **116**, 478.
- Hanneman, R. E. and Strong, H. M. (1965) *J. Appl. Phys.* **36**, 523.

- Hanneman, R. E. and Strong, H. M. (1966) *J. Appl. Phys.* **37**, 612.
- Harbaugh, W. E. and Eastman, G. Y. (1970) *Heating, Piping and Air Cond.* **42**, 10, 92.
- Harrison, T. R. (1960) "Radiation Pyrometry and its Underlying Principles of Radiant Heat Transfer" Wiley, New York.
- Hart, P. B. (1965) Brit. Pat. Applicat. 21979/62 (quoted by White 1965).
- Hauptman, Z., Wanklyn, B. M. and Smith, S. H. (1973) *J. Mat. Sci.* **8**, 1695.
- Haussühl, S. (1964) *Neues Jahrb. Min. Abh.* **101**, 343.
- Hayes, A. and Chipman, J. (1939) *Trans. AIME* **135**, 85.
- Hecht, H. (1951) "Präparative anorganische Chemie" Springer, Berlin.
- Hein, C. C. (1956) US Patent 2'747'196.
- Helferich, R. L. and Zanis, C. A. (1973) Report AD 754'092.
- Hemmat, N., Lampert, C. B., Menna, A. A. and Wolff, G. A. (1970) Solution Growth of Electronic Compounds and Their Solid Solutions. Preprint volume, Mat. Engng. and Sciences Div., Biennial Conf., Febr. 15-18, 1970, Atlanta, Amer. Inst. of Chem. Engs., 112-121 (see also AD 722,785).
- Hide, R. and Titman, C. W. (1967) *J. Fluid Mech.* **29**, 39.
- High Temperature Technology (1960) Proc. Int. Symp. 1959, McGraw-Hill, New York.
- Hintzmann, W. and Müller-Vogt, G. (1969) *J. Crystal Growth* **5**, 274.
- Hippel, A. von *et al.* (1963) *MIT Techn. Report* **178**, 45.
- Hoffmann, W. and Scheel, H. J. (1969) *Z. Krist.* **129**, 396.
- Holden, A. N. (1949) *Disc. Faraday Soc.* **5**, 312.
- Holden, A. and Singer, P. (1960) "Crystals and Crystal Growing" Heinemann, London.
- Holonyak, N., Wolfe, C. M. and Moore J. S. (1965) *Appl. Phys. Lett.* **6**, 64.
- Hukin, D. (1971) Paper at ICCG 3, Marseille.
- Hurle, D. T. J. (1966) *Phil. Mag.* **13**, 305.
- Hurle, D. T. J. (1967) In "Crystal Growth" (H. S. Peiser, ed.) p. 659. Pergamon, Oxford.
- Hurle, D. T. J., Mullin, J. B. and Pike, E. R. (1964) *Phil. Mag.* **9**, 423.
- Hurle, D. T. J., Mullin, J. B. and Pike, E. R. (1967) *J. Mat. Sci.* **2**, 46.
- Hurle, D. T. J., Jakeman, E. and Pike, E. R. (1968) *J. Crystal Growth* **3/4**, 633.
- Hurst, J. J. and Linz, A. (1971) *Mat. Res. Bull.* **6**, 163.
- IPTS-68 (1969) Internat. Practical Temperature Scale of 1968, in *Metrologia* **5**, No. 2, 35.
- Jaeger, G. and Krasemann, R. (1952) *Werkstoffe u. Korrosion* **3**, 401.
- Jankelevic, G., Vinarov, I. V., Seka, I. A. and Frajman, I. B. (1967) *Ukrain. Chim. Z.* **33**, 1040 (russ.).
- Janssen, G. A. M., Robertson, J. M. and Verheijke, M. L. (1973) *Mat. Res. Bull.* **8**, 59.
- Janz, G. J. (1967) "Molten Salts Handbook", p. 388. Academic Press, New York-London.
- John, V. and Kvapil, J. (1968) *Kristall u. Technik* **3**, 59.
- Jolly, W. (1970) "The Synthesis and Characterization of Inorganic Compounds" Prentice-Hall, Englewood Cliffs, N.J.
- Jonassen, H. B. and Weissberger, A. (1963-1968) (editors) "Technique of Inorganic Chemistry" Vols. I-VII, Interscience, New York.
- Joubert, J. C. and Chenavas, J. (1975) to be published.
- Kamenetskaya, D. S. (1967) *Sov. Phys.-Cryst.* **12**, 1; (1968) In "Growth and Perfection of Metallic Crystals" (D. E. Ovsienko, ed.) p. 245. Consultants Bureaux, New York.

- Kaneko, K., Ayabe, M., Dosen, M., Morizane, K., Usui, S. and Watanabe, N. (1973) *Proc. IEEE* **61**, 884; (1974), *J. Electrochem. Soc.* **121**, 556.
- Kanzaki, H. and Kido, K. (1960) *J. Phys. Soc. Japan* **15**, 529; (1962), *J. Appl. Phys.* **33**, 482.
- Kawabe, K. and Sawada, S. (1957) *J. Phys. Soc. Japan* **12**, 218.
- Keezer, R. C. and Wood, C. (1966) *Appl. Phys. Lett.* **8**, 139.
- Kelman, L. R., Wilkinson, W. D. and Yaggee, F. L. (1950) U.S. A.E.C. Report ANL-4417.
- Kennedy, G. C., Jayaraman, A. and Newton, R. C. (1962) *Phys. Rev.* **126**, 1363.
- Kennedy, T. N., Hakim, R. and Mackenzie, J. D. (1967) *Mat. Res. Bull.* **2**, 193.
- Kestigian, M. (1967) *J. Am. Ceram. Soc.* **50**, 165.
- Khamskii, E. V. (1969) "Crystallization from Solutions" Consultants Bureau, New York.
- Kim, K. M., Witt, A. F. and Gatos, H. C. (1972) *J. Electrochem. Soc.* **119**, 1218.
- Kingery, W. D. (1959) "Property Measurement at High Temperatures" Wiley, New York.
- Kirgintsev, A. N. and Avvakumov, E. G. (1965) *Sov. Phys.-Cryst.* **10**, 375.
- Kiyama, R. and Minomura, S. (1953) *Rev. Phys. Chem. Japan* **23**, 10.
- Kjems, J. K., Shirane, G., Müller, K. A. and Scheel, H. J. (1973) *Phys. Rev. B* **8**, 1119.
- Kleber, W. and Wilke, K. T. (1969) *Kristall u. Technik* **4**, 165.
- Kleinknecht, H. P. (1966) *J. Appl. Phys.* **37**, 2116.
- Klement, W. and Jayaraman, A. (1967) *Progr. Solid State Chem.* **3**, 289.
- Knippenberg, W. F. (1963) *Philips Res. Repts.* **18**, 161.
- Knippenberg, W. F. and Verspui, G. (1966) *Philips Res. Repts.* **21**, 113.
- Kostkowski, H. J. (1960) In "High Temperature Technology" Intern. Symp. 1959, p. 33. McGraw-Hill, New York.
- Kostkowski, H. J. and Lee, R. D. (1962) "Theory and Methods of Optical Pyrometry" NBS Monograph 41, US Government Printing Office, Washington, D.C.
- Kröger, F. A. (1964) "The Chemistry of Imperfect Crystals" North-Holland, Amsterdam.
- Kunmann, W. (1971) In "Preparation and Properties of Solid State Materials" (R. A. Lefever, ed.) 1. Dekker, New York.
- Kunmann, W. and Ferretti, A. (1964) *Rev. Sci. Instrum.* **35**, 465.
- Kunmann, W., Ferretti, A. and Wold, A. (1963) *J. Appl. Phys.* **34**, 1264.
- Kvapil, J. (1966) *Kristall u. Technik* **1**, 97.
- Kwestroo, W. (1972) In "Preparative Methods in Solid State Chemistry" (P. Hagenmuller, ed.) p. 563. Academic Press, New York.
- Kwestroo, W. and Huizing, A. (1965) *J. inorg. nucl. Chem.* **27**, 1951.
- Kwestroo, W., Huizing, A. and deJonge, J. (1969) *Mat. Res. Bull.* **4**, 817.
- Lange, N. O. (1967) "Handbook of Chemistry" 10th Edition, p. 1432. McGraw-Hill, New York.
- Laudise, R. A. (1963) In "The Art and Science of Growing Crystals" (J. J. Gilman, ed.) Wiley, New York.
- Laudise, R. A., Linares, R. C. and Dearborn, E. F. (1962) *J. Appl. Phys.* **33**, 1362.
- Lebl, M. and Trnka, J. (1965) *Z. Physik* **186**, 128.
- Levin, E. M., Rynders, G. F. and Dzimian, R. J. (1952) Growing Beryllium Oxide Crystals, NBS Report No. 1916.
- Lichtensteiger, M., Witt, A. F. and Gatos, H. C. (1971) *J. Electrochem. Soc.* **118**, 1013.

- Lierde, W. van and Bressers, J. (1966) *J. Appl. Phys.* **37**, 444.
- Linares, R. C. (1960) *J. Phys. Chem.* **64**, 941.
- Linares, R. C. (1962) *J. Am. Ceram. Soc.* **45**, 307.
- Linares, R. C. (1964) *J. Appl. Phys.* **35**, 433.
- Linares, R. C. (1965) *J. Am. Ceram. Soc.* **48**, 68.
- Linares, R. C. (1967) *Am. Min.* **52**, 1554.
- Linares, R. C. (1968) *Trans. Met. Soc. AIME* **242**, 441.
- Linz, A., Belruss, V. and Naiman, C. S. (1965) *Electrochem. Soc.* Spring Meeting, San Francisco, Extended Abstracts **2**, 87.
- Litvin, Y. A., Lisoyvan, V. I., Sobolev, Y. V. and Butuzov, V. P. (1968) *Dokl. Akad. Nauk SSSR* **183**, 144.
- Lord, G. W. and Moss, R. H. (1970) *J. Phys. E: Scientif. Instr.* **3**, 177.
- Lux, H. (1970) "Anorganisch-chemische Experimentierkunst" 3rd Edition. Barth, Leipzig.
- Luzhnaya, N. P. (1968) *J. Crystal Growth* **3/4**, 97.
- Lydtin, H. (1972) private communication.
- Lyons, V. J. (1965) US Patent 3.198.606 (Aug. 3, 1965).
- Makram, H. (1966) *Czech. J. Physics B* **17**, 387.
- Makram, H. and Krishnan, R. (1969) In "Crystal Growth" (H. S. Peiser, ed.) p. 467. Pergamon, Oxford.
- Makram, H., Touron, L. and Loriers, J. (1968) *J. Crystal Growth* **3/4**, 452.
- Malkus, M. V. R. (1954) *Proc. Roy. Soc. (London) A* **225**, 185.
- Manzel, M. (1967) *Kristall u. Technik* **2**, 61.
- Marezio, M. and Remeika, J. P. (1965) *J. Phys. Chem. Solids* **26**, 2083.
- Marezio, M. and Remeika, J. P. (1966) *J. Chem Phys.* **44**, 3348.
- Marezio, M., Remeika, J. P. and Jayaraman, A. (1966a) *J. Chem. Phys.* **45**, 1821.
- Marezio, M., Remeika, J. P. and Dernier, P. D. (1966b) *Mat. Res. Bull.* **1**, 247.
- Margrave, J. L. (1965) (editor) "Refractory Materials, a Series of Monographs" Academic Press, New York-London.
- Mason, D. R. and Cook, J. S. (1961) *J. Appl. Phys.* **32**, 475.
- Matecha, J. and Kvapil, J. (1970) *J. Crystal Growth* **6**, 199.
- Mateika, D. (1971) *J. Crystal Growth* **9**, 249.
- Mateika, D. (1972) *J. Crystal Growth* **13/14**, 698.
- May, E. (1950) "Industrial High-Frequency Electric Power" Wiley, New York.
- Mayer, I., Shidlovsky, I. and Yanir, E. (1967) *J. Less-Common Metals* **12**, 46.
- McLaren, E. H. (1957) *Can. J. Phys.* **35**, 78.
- McWhan, D. B. and Remeika, J. P. (1970) *Phys. Rev. B* **2**, 3734.
- Meyer, A. (1970) *J. Less-Common Metals* **20**, 353.
- Miller, C. E. (1958) *J. Appl. Phys.* **29**, 233.
- Millett, E. J., Brice, J. C., Whiffin, P. A. C. and Whipps, P. W. (1967) In "Crystal Growth" (H. S. Peiser, ed.) p. 673. Pergamon, Oxford.
- Minden, H. T. (1973) *Solid State Technol.* (January, 1973).
- Mlavsky, A. I. and Weinstein, M. (1963) *J. Appl. Phys.* **34**, 2885.
- Monchamp, R. R., Belt, R. and Nielsen, J. W. (1967) In "Crystal Growth" (H. S. Peiser, ed.) p. 463. Pergamon, Oxford.
- Morgan, W. L. and Scheffler, L. F. (1965) US Patent 3.224.843.
- Morozewicz, J. (1899) *Tschermaks Min. Mitt.* **18**, 1, 105, 225.
- Morris, D. F. C. (1968) *Structure and Bonding* **4**, 63; **6**, 157.
- Müller, G. and Gnauck, G. (1965) "Reinste Gase" VEB Deutscher Verlag der Wissenschaften, Berlin.
- Mullin, J. W. (1972) "Crystallization" 2nd Edition. Butterworths, London.

- Mullin, J. B., Straughan, B. W. and Brickell, W. S. (1965) *J. Phys. Chem. Solids* **26**, 782.
- Munro, D. C. (1963) In "High Pressure Physics and Chemistry" (R. S. Bradley, ed.) Vol. 1, p. 11. Academic Press, London.
- Nelson, D. F. and Remeika, J. P. (1964) *J. Appl. Phys.* **35**, 522.
- Nelson, H. (1963) *RCA Review* **24**, 603.
- Neuhaus, A. (1956) *Chem. Ing. Techn.* **155**, 350.
- Neuhaus, A. (1964) *Chimia* **18**, 93.
- Newkirk, H. W. and Smith, D. K. (1965) *Am. Min.* **50**, 22, 44.
- Nielsen, J. W. (1964) *Electronics* (Nov. 30, 1964).
- Nielsen, J. W. (1974) private communication.
- Nielsen, J. W. and Dearborn, E. F. (1960) *J. Phys. Chem.* **64**, 1762.
- Nielsen, J. W., Lepore, D. A. and Leo, D. C. (1967) In "Crystal Growth" (H. S. Peiser, ed.) p. 457. Pergamon, Oxford.
- Niemyski, T., Mierzejewska-Appenheimer, S. and Majewski, J. (1967) In "Crystal Growth" (H. S. Peiser, ed.) p. 585. Pergamon, Oxford.
- O'Kane, D. F., Kwap, T. W., Gulitz, L. and Bednowitz, A. L. (1972) *J. Crystal Growth* **13/14**, 624.
- Oppelt, W. (1964) "Kleines Handbuch technischer Regelvorgänge" 4th Edition. Verlag Chemie, Weinheim.
- Otto, C. A. (1958) "Electric Furnaces" London.
- Oxley, C. E. and Stockton, J. (1966) *J. Scient. Instr.* **43**, 767.
- Parker, H. S. and Brower, W. S. (1967) In "Crystal Growth" (H. S. Peiser, ed.) p. 489. Pergamon, Oxford.
- Patel, A. R. and Bhat, H. L. (1971) *J. Crystal Growth* **11**, 166.
- Paul, W. and Warschauer, D. M. (1963) "Solids under Pressure" McGraw-Hill, New York.
- Perloff, D. S. and Wold, A. (1967) In "Crystal Growth" (H. S. Peiser, ed.) p. 361. Pergamon, Oxford.
- Perry, F. W. (1967) In "Crystal Growth" (H. S. Peiser, ed.) p. 483. Pergamon, Oxford.
- Peters, E. T. and Ryan, J. J. (1966) *J. Appl. Phys.* **37**, 933.
- Petzold, D. R., Schultze, D. and Wilke, K. T. (1971) *Z. Anorg. Allg. Chem.* **386**, 288.
- Pfann, W. G. (1955) *Trans. AIME* **263**, 961.
- Pfann, W. G. (1958) In "Liquid Metals and Solidification" (B. Chalmers, ed.) *Amer. Soc. f. Metals*, Cleveland, Ohio.
- Pfann, W. G. (1966) "Zone Melting" 2nd Edition. Wiley, New York.
- Pfann, W. G., Benson, K. E. and Wernick, J. H. (1957) *J. Electron.* **2**, 597.
- Plaskett, T. S. (1969) *J. Electrochem. Soc.* **116**, 1722.
- Plaskett, T. S., Blum, S. E. and Foster, L. M. (1967) *J. Electrochem. Soc.* **114**, 1304.
- Pohl, D. and Scheel, H. J. (1975) to be published.
- Poiblaud, G. and Jacob, G. (1973) *Mat. Res. Bull.* **8**, 845.
- Pointon, A. J. and Robertson, J. M. (1967) *J. Mat. Sci.* **2**, 293.
- Poland, D. E., Green, J. W. and Margrave, J. L. (1961) Corrected Optical Pyrometer Readings, NBS Monograph 30, US Government Printing Office, Washington, D.C.
- Rabenau, A. (1963/1964) *Philips' Techn. Rundschau* **25**, 365.
- Raksani, K. and Voszka, R. (1969) *Kristall u. Technik* **4**, 227.
- Rea, J. R. and Kostiner, E. (1971) *J. Crystal Growth* **11**, 110.
- Reed, T. B., Fahey, R. E. and Honig, J. M. (1967) *Mat. Res. Bull.* **2**, 561.

- Reed, T. B. (1972) "Free Energy of Binary Compounds" MIT Press.
- Reed, T. B. (1973) Solid State Research Report, Lincoln Lab., No. 1, 25.
- Remeika, J. P. (1954) *J. Amer. Chem. Soc.* **76**, 940.
- Remeika, J. P. (1958) U.S. Pat. **2**, 852, 400.
- Remeika, J. P. (1963) U.S. Patent 3'079'240 (Febr. 26, 1963).
- Remeika, J. P. (1970) Paper presented at Int. Conf. on Ferrites, Kyoto.
- Remeika, J. P. and Marezio, M. (1966) *Appl. Phys. Lett.* **8**, 87.
- Remeika, J. P. and Spencer, E. G. (1964) *J. Appl. Phys.* **35**, 2803.
- Remeika, J. P., Dodd, D. M. and DiDomenico, M. (1966) *J. Appl. Phys.* **37**, 5004.
- Reynolds, G. F. and Guggenheim, H. J. (1961) *J. Phys. Chem.* **65**, 1655.
- Robertson, D. S. (1966) *Brit. J. Appl. Phys.* **17**, 1047.
- Robertson, G. D. and Scholl, R. F. (1971) *Rev. Sci. Instrum.* **42**, 882.
- Robertson, J. M. (1969) *Engelhard Industries Techn. Bull.* **10**, 77.
- Robertson, J. M. and Neate, B. W. (1972) *J. Crystal Growth* **13/14**, 576.
- Robertson, J. M. (1974) private communication.
- Robertson, J. M., Smith, S. H. and Elwell, D. (1969) *J. Crystal Growth* **5**, 189.
- Robertson, J. M., Kamminga, W. and Rooymans, C. J. M. (1975) to be published.
- Robertson, J. M., Wittekoek, S., Popma, T. J. A. and Bongers, P. F. (1973) *Appl. Phys.* **2**, 219.
- Robertson, J. M., Damen, J. P. M., Jonker, H. D., Van Hout, M. J. G., Kamminga, W. and Voermans, A. B. (1974a) *Platin. Metals Rev.* **18**, 15.
- Robertson, J. M., Van Hout, M. J. G., Verplanke, J. C. and Brice, J. C. (1974b) *Mat. Res. Bull.* **9**, 555.
- Rodot, H., Hruby, A. and Schneider, M. (1968) *J. Crystal Growth* **3/4**, 305.
- Roeser, W. F. and Lonberger, S. T. (1958) Methods of Testing Thermocouples and Thermocouple Materials, NBS Circular 590, US Government Printing Office, Washington, D.C.
- Rogers, D. B., Ferretti, A. and Kunnmann, W. (1966) *J. Phys. Chem. Solids* **27**, 1445.
- Rooymans, C. J. M. (1972) In "Preparative Methods in Solid State Chemistry" (P. Hagenmuller, ed.) p. 72. Academic Press, New York.
- Roy, R. (1965) *Bull. Soc. Chim. Franc.* 1065.
- Roy, R. (1966) *Mat. Res. Bull.* **1**, 299.
- Roy, R. and White, W. B. (1968) *J. Crystal Growth* **3/4**, 33.
- Rubin, L. G. Temperature-Concepts, Scales and Measurement Techniques, Report A 1.0001 RP, Leeds and Northrup, Philadelphia.
- Russell, R. G., Morgan, W. L. and Scheffler, L. F. (1962), US Patent 3.065.091.
- Sawada, S., Nomura, S. and Fujii, S. (1951) *Rept. Inst. Sci. Techn., Univ. Tokyo* **5**, 7.
- Schäfer, H. (1964) "Chemical Transport Reactions" Academic Press, New York.
- Scheel, H. J. (1968) *J. Crystal Growth* **2**, 411.
- Scheel, H. J. (1971) *Z. Krist.* **133**, 264.
- Scheel, H. J. (1972) *J. Crystal Growth* **13/14**, 560.
- Scheel, H. J. (1973) Swiss Patent 541.353 (Sept. 15, 1973), US Patent pending.
- Scheel, H. J. (1974) *J. Crystal Growth* **24/25**, 669.
- Scheel, H. J. and Schulz-DuBois, E. O. (1971) *J. Crystal Growth* **8**, 304.
- Scheel, H. J. and Elwell, D. (1972) *J. Crystal Growth* **12**, 153.
- Scheel, H. J. and Schulz-DuBois, E. O. (1971) *IBM Techn. Discl. Bull.* **14**, 2850.
- Scheel, H. J. and Elwell, D. (1973) *J. Electrochem. Soc.* **120**, 818.
- Scheel, H. J. and West, C. H. (1973) *J. Phys. E: Scientif. Instr.* **6**, 1178.
- Schieber, M. (1967) *Kristall u. Technik* **2**, 55.

- Schildknecht, H. (1966) "Zone melting" Academic Press, New York.
- Schönherr, E. (1971) *J. Crystal Growth* **9**, 346.
- Schulz-DuBois, E. O. (1972) *J. Crystal Growth* **12**, 81.
- Seidenstricker, R. G. (1966) *J. Electrochem. Soc.* **113**, 152.
- Senhouse, L. S., Paolis, M. V. de, Loomis, T. C. (1966) *Appl. Phys. Lett.* **8**, 173.
- Shafer, M. W., Torrance, J. B. and Penney, T. (1972) *J. Phys. Chem. Sol.* **33**, 2251.
- Shenker, H., Lauritzen jr., J. I., Corruccini, R. J. and Lonberger, S. T. (1955) NBS Circular No. 561, US Government Printing Office, Washington, D.C.
- Shick, L. K. and Von Neida, A. R. (1971) US Patent 3'627'498.
- Sickafus, E. N. and Barker, D. B. (1967) *J. Crystal Growth* **1**, 93.
- Simpson, P. G. (1960) "Induction Heating Coil and System Design" McGraw-Hill, New York.
- Sip, V. and Vanicek, V. (1962) *Growth of Crystals* **3**, 191.
- Slichter, W. P. and Burton, J. A. (1958) In "Transistor Technology" (H. E. Bridgers, J. H. Scaff and J. N. Shive, eds.) p. 107. Van Nostrand, Princeton.
- Smakula, A. (1962) "Einkristalle" Springer, Berlin.
- Smith, C. L. and Murrill, P. W. (1966) *ISA Journal* **13**, 5, 50.
- Smith, S. H. and Elwell, D. (1968) *J. Crystal Growth* **3/4**, 471.
- Smith, S. H. and Wanklyn, B. (1974) *J. Crystal Growth* **21**, 23.
- Sproull, R. L. (1962) *Scient. Amer.* (December 1962).
- Stambaugh, E. P., Miller, J. E. and Hines, R. C. (1961) "Metallurgy of Elemental and Compound Semiconductors" p. 317. Interscience, New York.
- Stansel, N. R. (1949) "Induction Heating" McGraw-Hill, New York.
- Steininger, J. and England, R. E. (1968) *Trans. AIME* **242**, 436.
- Steininger, J. and Reed, T. B. (1972) *J. Crystal Growth* **13/14**, 106.
- Steininger, J. and Strauss, A. J. (1972) *J. Crystal Growth* **13/14**, 657.
- Stimson, H. F. (1961) Internat. Practical Temp. Scale of 1948—Text Revision of 1960, NBS Monograph 37, US Government Printing Office, Washington, D.C.
- Stone, B. D. (1959) US Patent 3.009.780 (June 20, 1959).
- Stringfellow, G. B. and Greene, P. E. (1971) *J. Electrochem. Soc.* **118**, 805.
- Strong, H. M. (1962) In "Modern Very High Pressure Techniques" (R. H. Wentorf, ed.) p. 93. Butterworths, London.
- Strong, H. M. and Hanneman, R. E. (1967) *J. Chem. Phys.* **46**, 3668.
- Strong, H. M. and Chrenko, R. M. (1971) *J. Phys. Chem.* **75**, 1838.
- Strong, H. M. and Wentorf, jr., H. R. (1972) *Naturwiss.* **59**, 1.
- Tarjan, I. and Matrai, M. (1972) "Laboratory Manual on Crystal Growth" Akademiai Kiado, Budapest.
- "Temperature, its Measurement and Control in Science and Industry" Vol. 1 (1941), Vol. 2 (1955), Vol. 3, Parts I and II (1962) Reinhold, New York.
- Thoma, R. E., Goss, R. G. and Weaver, C. F. (1967) In "Crystal Growth" (H. S. Peiser, ed.) p. 147. Pergamon Press, Oxford.
- Thurmond, C. D. and Struthers, J. D. (1957) *J. Phys. Chem. Solids* **57**, 831.
- Tiche, D. and Spear, K. E. (1972) Report AD 736.639.
- Tiller, W. A. (1963) *J. Appl. Phys.* **34**, 2757.
- Tiller, W. A. (1968) *J. Crystal Growth* **2**, 69.
- Timofeeva, V. A. and Zaleskii, A. V. (1959) *Growth of Crystals* **2**, 69.
- Timofeeva, V. A. and Kvapil, J. (1966) *Sov. Phys. Cryst.* **11**, 263.
- Timofeeva, V. A., Lukyanova, N. I., Guseva, I. N. and Lider, V. V. (1969) *Sov. Phys.-Cryst.* **13**, 747.
- Tolksdorf, W. (1968) *J. Crystal Growth* **3/4**, 463.

- Tolksdorf, W. and Welz, F. (1972) *J. Crystal Growth* **13/14**, 566.
- Tolksdorf, W. (1973) *J. Crystal Growth* **18**, 57.
- Tolksdorf, W. (1974a) private communication.
- Tolksdorf, W. (1974b) *Acta Electron.* **17**, 57.
- Tolksdorf, W. and Welz, F. (1973) *J. Crystal Growth* **20**, 47.
- Trainor, A. and Bartlett, B. E. (1961) *Solid State Electron.* **2**, 106.
- Triebwasser, S. (1959) *Phys. Rev.* **114**, 63.
- Trumbore, F. A., Porbansky, E. M. and Tartaglia, A. A. (1959) *J. Phys. Chem. Solids* **11**, 239.
- Tsushima, K. (1966) *J. Appl. Phys.* **37**, 443.
- Tyco Laboratories Inc., Waltham, Mass. (1971) Report AD 722.785.
- Van Hook, A. (1961) "Crystallization, Theory and Practice" Reinhold, New York.
- Van Uitert, L. G. (1970) *Platinum Metals Rev.* **14**, 118.
- Van Uitert, L. G., Bonner, W. A., Grodkiewicz, W. H., Pietroski, L. and Zydzik, G. J. (1970) *Mat. Res. Bull.* **5**, 825.
- Vergnoux, A. M., Riera, M., Ribet, J. L. and Ribet, M. (1971) *J. Crystal Growth* **10**, 202.
- Vichr, M. (1973) private communication.
- Vidal, C. R. and Haller, F. B. (1971) *Rev. Sci. Instrum.* **42**, 1779.
- Vilms, J. and Garrett, J. P. (1972) *Sol. State. Electr.* **15**, 443.
- Vines, R. F. (1941) "The Platinum Metals and their Alloys" Internat. Nickel Comp., New York.
- Von Neida, A. R. and Shick, L. K. (1969) *J. Appl. Phys.* **40**, 1013.
- Von Philipsborn, H. (1967) *J. Appl. Phys.* **38**, 955; (1967) *Helv. Phys. Acta* **40**, 810.
- Von Philipsborn, H. (1969) *J. Crystal Growth* **5**, 135.
- Von Philipsborn, H. (1971) *J. Crystal Growth* **9**, 296.
- Wagner, C. (1950) *J. Phys. and Coll. Chem.* **53**, 1030.
- Wagner, C. (1954) *Trans. AIME* **200**, 154.
- Wagner, R. S. and Ellis, W. C. (1964) *Appl. Phys. Lett.* **4**, 89.
- Wagner, R. S. and Ellis, W. C. (1965) *Trans. AIME* **233**, 1053.
- Wagner, R. S. (1967) In "Crystal Growth" (H. S. Peiser, ed.) p. 347. Pergamon, Oxford.
- Wagner, R. S. (1968) *J. Crystal Growth* **3/4**, 159.
- Wakatsuki, M. (1966) *Japan. J. Appl. Phys.* **5**, 337.
- Wald, F., Bell, R. O. and Menna, A. A. (1971) Interim Techn. Rept., Contact No. AT(30-1)-4202, Tyco Labs., Waltham, Mass.
- Wallace, C. A. and White, E. A. D. (1967) In "Crystal Growth" (H. S. Peiser, ed.) p. 431. Pergamon, Oxford.
- Wanklyn, B. M. (1969) *J. Crystal Growth* **5**, 279.
- Wanklyn, B. M. (1972) *J. Mat. Sci.* **7**, 813.
- Wanklyn, B. M. and Hauptman, Z. (1974) *J. Mat. Sci.* **9**, 1078.
- Weaver, C. F., Ross, R. G. and Thoma, R. E. (1963) *J. Appl. Phys.* **34**, 1827.
- Webster, F. W. and White, E. A. D. (1969) *J. Crystal Growth* **5**, 167.
- Weeks, J. R. and Gurinsky, D. H. (1958) In "Liquid Metals and Solidification" p. 106. Amer. Soc. for Metals, Cleveland/Ohio.
- Weinstein, M. and Mlavsky, A. I. (1964) *J. Appl. Phys.* **35**, 1892.
- Weisbeck, R. (1964) *Chem. Ing. Techn.* **36**, 442.
- Wemple, S. H. (1964) *MIT Techn. Rept.* **425**, (see also the Thesis, MIT, 1963).
- Wentorf jr., R. H. (1957) *J. Chem. Phys.* **26**, 956.
- Wentorf jr., R. H. (1961) *J. Chem. Phys.* **34**, 809 (see also US Patent 3'192'015).
- Wentorf jr., R. H. (1962) *J. Chem. Phys.* **36**, 1990.

- Wentorf jr., R. H. (1966) *Ber. Bunsenges. Phys. Chem.* **70**, 975.
- Wentorf, jr., R. H. (1971) *J. Chem. Phys.* **75**, 1833.
- Wernick, J. H. (1956) *J. Chem. Phys.* **25**, 47.
- Wernick, J. H. (1957) *J. Metals* **9**, 1169.
- Whiffin, P. A. C. and Brice, J. C. (1971) *J. Crystal Growth* **10**, 91.
- Whiffin, P. A. C. (1973) Mullard Research Labs. Report No. 2848.
- Whipps, P. W. (1972) *J. Crystal Growth* **12**, 120.
- White, E. A. D. (1965) *Brit. J. Appl. Phys.* **16**, 1415.
- White, E. A. D. and Brightwell, J. W. (1965) *Chem. and Ind.* 1662.
- Wickham, D. G. (1970) *Proceed. Intern. Conf. Ferrites (Kyoto)*, 105.
- Widmer, R. (1971) *J. Crystal Growth* **8**, 216.
- Wilcox, W. R. (1968) *Ind. Eng. Chem.* **60**, 13.
- Wilcox, W. R. (1970) *J. Crystal Growth* **7**, 203.
- Wilcox, W. R. and Fullmer, L. D. (1965) *J. Appl. Phys.* **36**, 2201.
- Wilcox, W. R. and Fullmer, L. D. (1966) *J. Am. Ceram. Soc.* **49**, 415.
- Wilke, K. T. (1956) *Fortschritte d. Mineral.* **34**, 85.
- Wilke, K. T. (1963) "Methoden der Kristallzüchtung", Verlag H. Deusch, Frankfurt and VEB Deutscher Verlag der Wissenschaften, Berlin.
- Wilke, K. T. (1973) "Kristallzüchtung" VEB Deutscher Verlag der Wissenschaften, Berlin.
- Wilke, K. T., Töpfer, K. and Schultze, D. (1965) *Z. Phys. Chem.* **230**, 112.
- Windisch, S. and Nowotny, H. (1972) In "Preparative Methods in Solid State Chemistry" (P. Hagenmuller, ed.) p. 533. Academic Press, New York.
- Wirkus, C. D. and Wilder, D. R. (1966) *J. Am. Ceram. Soc.* **49**, 173.
- Witt, A. F. and Gatos, H. C. (1968) *J. Electrochem. Soc.* **115**, 70.
- Witt, A. F. and Gatos, H. C. (1969) *J. Electrochem. Soc.* **116**, 511.
- Wöhler, F. (1823) *Ann. Chim. Phys.* **29**, 43.
- Wold, A., Kunnmann, W., Arnott, R. J. and Ferretti, A. (1964) *Inorg. Chem.* **3**, 545.
- Wolfe, R., Sturge, M. D., Merritt, F. R. and Van Uitert, L. G. (1971) *Phys. Rev. Lett.* **26**, 1570.
- Wolff, G. A. (1965) In "Adsorption et Croissance Cristalline" p. 722. Colloq. Intern. CNRS, No. 152, Paris.
- Wolff, G. A. and Labelle, H. E. (1965) *J. Am. Ceram. Soc.* **48**, 441.
- Wolff, G. A. and Mlavsky, A. I. (1965) In "Adsorption et Croissance Cristalline" p. 711. Colloq. Intern. CNRS, No. 152, Paris.
- Wolff, G. A. and Mlavsky, A. I. (1974) In "Crystal Growth, Theory and Techniques" Vol. 1 (C. H. L. Goodman, ed.) 193. Plenum Press, London-New York.
- Wolff, G. A., Herbert, R. A., Broder, J. D. (1958) *Proc. Intern. Coll. on Semiconductors and Phosphors*.
- Wolff, G. A., LaBelle, H. E. and Das, B. N. (1968) *Trans. AIME* **242**, 436.
- Wolff, G. A., Das, B. N., Lampert, C. B., Mlavsky, A. I. and Trickett, E. A. (1969) *Mat Res. Bull.* **4**, 567.
- Wood, C. and Van Pelt, B. (1972) *Rev. Sci. Instrum.* **43**, 1374.
- Wood, J. D. C. and White, E. A. D. (1968) *J. Crystal Growth* **3/4**, 480.
- Woodall, J. M. (1971) *J. Electrochem. Soc.* **118**, 150.
- Wulff, L. (1884) German Patent DRP 33.190.
- Ziegler, J. G. and Nichols, N. B. (1942) *Trans. ASME* **64**, 759.