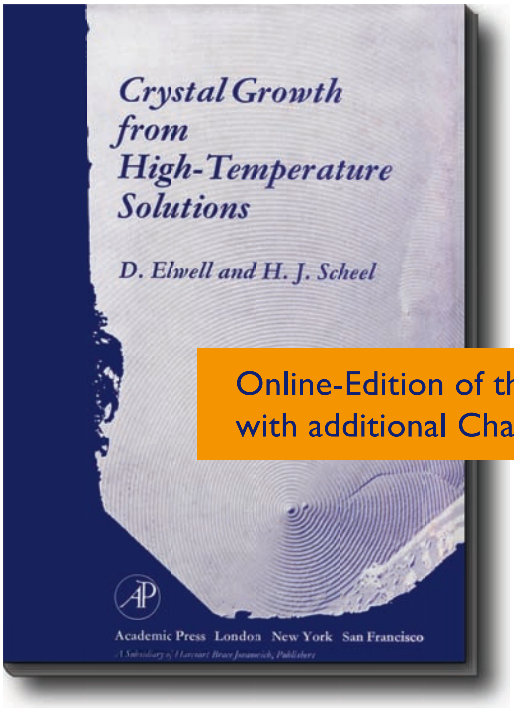

Crystal Growth from High-Temperature Solutions

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with additional Chapter 11 and Appendices A and B

Part 008

5. Crystal Habit

5.1. Historical Development

Interest in the morphology of crystals really began in 1669 when Steno described the law of constancy of angles for the faces on quartz crystals. This law was confirmed by Cappeller (1723) on a variety of crystals. The first examples of habit modification in artificially-grown crystals were described by Romé de L'Isle (1783, rocksalt octahedra in a solution to which urine was added), by Leblanc (1788, alum cubes and octahedra) and by Beudant (1817, 1818), who described the influence of impurities and of mechanical mixing on the habit.

A further stimulus to the growing interest in this field was provided by Haüy (1783, 1784), who postulated a relation between a chemical substance and its individual crystalline form, and another important development was that of Wollaston (1809) with the optical goniometer. An impressive amount of data was accumulated in the 19th and early 20th centuries on the angles between crystal faces, and an enormous variety of careful drawings was prepared. Today the possible morphologies of a crystal having a known structure may be drawn by a computer in a matter of minutes (see Figs 5.8.(II), 5.13, 5.14), but 100 years ago this was a major problem. The famous Goldschmidt atlas (1913) and the works of Groth (1906) contain a compilation of all the faces which had been observed on the known minerals. For example, for quartz 31 common and 369 rare and for calcite 148 common and 381 rare faces are listed, and the occurrence of particular crystal faces on minerals from various deposits was described by statistics.

The situation was changed by the discovery of X-ray diffraction by Friedrich, Knipping and von Laue (1912) and by the first structure determinations by W. H. and W. L. Bragg (1913). The crystal grower is now mainly interested in finding explanations for the habit modifications in artificially-prepared crystals while the crystal consumer is concerned with optimization of the shape of crystals for his particular application or measurement. If impurities are incorporated preferentially at certain faces, it is desirable to ensure that such faces are not present on the growing crystal if the highest possible purity is to be obtained.

The following discussion on the habit and its modification is, of course, only relevant when the crystal grows unconstrained in the solution, when the crystal can form equilibrium faces. This is not the case, for example, in the travelling solvent zone technique, in liquid phase epitaxy or in the pulling of crystals from solution (by a modified Czochralski technique) as will be discussed in Chapters 7 and 8. However, crystals grown by the latter techniques frequently show facets which demonstrate the strong tendency towards facet formation even in constrained crystallization processes.

This Chapter gives a brief survey of the equilibrium shape and of habit modification in crystal growth from solution. More detailed information on special topics has been given by Valeton (1915), Tertsch (1926), Burton, Cabrera and Frank (1951), Buckley (1951), Honigmann (1958), Chernov (1961), Hartman (1969), Kern (1969) and in the conference proceedings of Adsorption et Croissance Cristalline (Colloq. Intern. C.N.R.S. No. 152, Paris, 1965).

5.2. The Equilibrium Shape of a Crystal

Gibbs (1875, 1878) was the first to give a description of the equilibrium form of a crystal based on thermodynamics. The total free energy of a crystal is the sum of the free energies of the volume, of the surface and of the edges and corners. Gibbs showed that the edges and corners have an effect only when the crystals are extremely small, whereas the relative contribution of the surface free energy decreases in proportion to the linear dimensions of the crystal. For crystals of the same volume the equilibrium form is that which has a minimum surface energy. Gibbs' condition demands that $\Sigma\gamma_i A_i$ should have a minimum value, where γ_i is the specific surface free energy of the face i, A_i its area, and the summation is taken over all the faces of the crystal. This principle was also used by Curie (1885).

Wulff (1901) established the relationship between individual faces of the equilibrium shape and their individual specific surface energies by the theorem:

> When a crystal is in its equilibrium shape, there exists within it a point to which the perpendicular distances from all faces are proportional to their

> specific surface free energies; any other possible face, not belonging to the equilibrium shape, has a surface free energy such that a plane drawn with the corresponding orientation and distance from this point would be entirely outside the crystal.

A polar diagram of the specific surface free energy is called a *Wulff plot* (or γ plot) and shows a closed surface, the distance of which from the origin is proportional to the magnitude of γ. The equilibrium shape is then found by drawing all the planes normal to the radius vectors to this surface and taking the innermost envelope. The equilibrium shape will thus be determined by the minima in the Wulff plot. If these are sharp, that is if certain faces have much lower free energy than other possible faces, the crystal will be facetted. A point on the γ surface corresponds to a part of the equilibrium surface if a sphere drawn through the origin to touch the γ surface at this point does not intersect the γ surface. A section through a Wulff plot for a simple crystal shape *CDEF* is shown in Fig. 5.1. The diagonals *CE* and *DF* are first drawn, then circles are drawn with the diameters *OC*, *OD*, *OE*, *OF* between *O* and the corresponding corners. The normals from *O* to *CD* and *DE*, respectively, are then proportional to γ_A and γ_B and meet the minima in the γ plot. This example assumes no other minima, that is no other possible equilibrium facets. It is evident that the Wulff theorem can generally be applied to small crystals only. This is confirmed by careful experiments of Valeton (1915) and of Neuhaus (see Spangenberg, 1934) who did not find differences in solubility of various existing faces on macroscopic crystals. However there is theoretical proof by Volmer (1939), von Laue (1943), Landau (1950), Herring (1953) and Chernov (1961) that in principle the Wulff theorem should hold and that crystals should have singular faces up to their melting point. Bennema

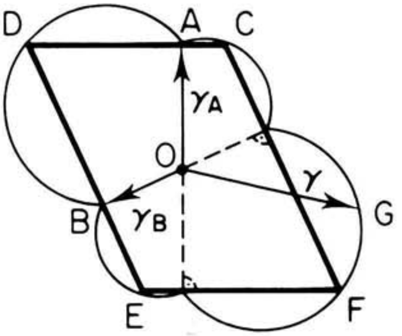


Fig. 5.1. Wulff plot for simple crystal.

(1973) has reviewed Herring's treatment of the equilibrium form and presented his conclusions in the form of seven theorems.

The kinetics of the microscopic growth steps at the growing surface, especially the concept of the *repeatable step*, offer an alternative possiblity of determination of the equilibrium form. Attempts to perform such calculations have been described by Kossel (1927), Stranski (1928) and by Stranski and Kaishev (1934) and were for instance successfully applied by Simon and Bienfait (1965) to the complicated structure of gypsum. However, as a rule the method of Kossel and Stranski will only be applicable to simple structures. Reviews on the Kossel-Stranski model were published by Knacke and Stranski (1952) and by Honigmann (1958).

Qualitative methods of predicting the stable crystal habit have been proposed, notably by Bravais (1866), Niggli (1919, 1920), Sohncke (1888), Donnay and Harker (1937) and by Hartman and Perdok (1955). Stable faces were connected by L. Bravais with a high lattice plane density and by Niggli with surfaces having few unsaturated bonds. Sohncke and later Donnay and Harker proposed that the faces of lowest specific surface free energy will be those of highest reticular density, that is those which have the highest density of atomic packing. Although the equilibrium faces of crystals do normally have a high reticular density, it is also necessary to consider the nature of the chemical bonds between the atoms in the crystal as was stressed by Niggli (1919, 1920).

The Hartman-Perdock PBC method, which was briefly mentioned in Chapter 4, is based on the assumption of Born (1923) that the surface energy of a crystal depends mainly on the chemical bond energies. The attachment energy of Hartman and Perdok depends on the direction (with respect to the surface) of the strong chemical bonds, which are those which release the largest amount of energy during the crystallization process. Uninterrupted chains of strong bonds are called periodic bond chains (PBC). In the example shown in Fig. 5.2, (a) has flat or *F faces* with strong bonds linking neighbouring PBC's, (b) has a stepped or *S face* since these bonds are not directed along the surface. In Fig. 5.3, the *F* and *S* faces

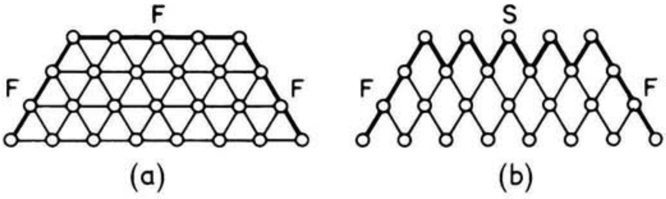


FIG. 5.2. Section of crystal with o representing a PBC. (a) Neighbouring PBC's linked by strong bonds, (b) neighbouring PBC's not linked by strong bonds along the *S* face.

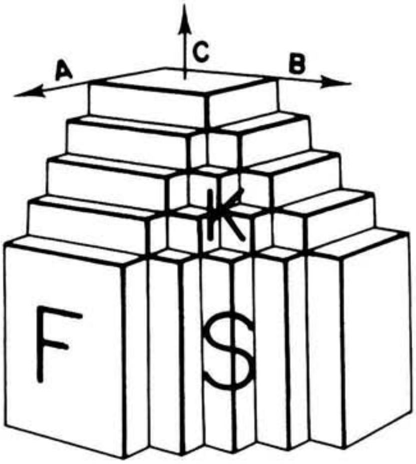


FIG. 5.3. Flat (F), stepped (S) and kinked (K) faces corresponding to the directions of PBC's parallel to A, B and C.

are depicted, together with the kinked or K *faces* which do not contain any PBC vector. Clearly the S and K faces grow very quickly and are therefore rarely, if ever, observed. The habit of a crystal is dominated by the slowly-growing F faces. From a knowledge of the crystal structure it is frequently possible to predict which will be the F faces, and many examples of the application of this method have been published. However, not all the F faces will be present, and it is not possible to predict with confidence which F faces will have the lowest rates of growth and which will be present in the crystal.

There is a certain similarity between the PBC method and the classical Kossel-Stranski theory as outlined by Honigmann (1958). The F and the S and K faces of Hartman and Perdok correspond approximately to the flat and rough faces, respectively, of Stranski (1932). There is, in fact, a variety of terms for the three types of faces, as listed in Table 5.1, and having the same significance. In this connection it is interesting to note that Steno described the stepped and irregular structure of intermediate faces as early as 1669.

In general, the value of theories of the equilibrium habit of crystals is limited because growth occurs under nonequilibrium conditions (except for the few observations of equilibrium forms of small crystals by Lemmlein, 1954; Klija, 1955; Bienfait and Kern 1964). The departure from equilibrium normally increases with crystal size, solute concentration, supersaturation, growth rate and impurity concentration. In addition, the type of solvent may influence the habit according to the type of

TABLE 5.1. Methods of Notation for the Three Types of Face

Kossel (1927) Stranski (1928)	glatt (flat)	vergröbert (rough)	
Stranski and Kaischev (1931)	vollständig, Gleichgewichtsform-Flächen (complete, faces of equilibrium form)	unvollständig (incomplete)	
Burton and Cabrera (1949)	close-packed	stepped	
Hartman (1953), Hartman and Perdok (1955)	F (flat)	S (stepped)	K (kinked)
Honigmann (1958)	A2 two-dimensional nucleation	A1 one-dimensional nucleation	A0 zero-dimensional nucleation
Chalmers (1958) Laudise (1970) etc.	smooth	rough	
Frank (1958), Cabrera (1959)	singular	nonsingular, vicinal	

solvent-solute interaction as discussed in Chapter 3. Frank (1958) stressed the fact, already mentioned by Gibbs (1875, 1878), that for crystals of macroscopic dimensions the energy associated with the driving force for crystallization will be larger than changes in free energy due to departures from the equilibrium shape, so that crystals will not have their equilibrium form except for the cases where the kinetically controlled habit happens to be identical with the equilibrium form. Among the other factors which might influence the habit are the crystal defects (dislocations, twin and low-angle boundaries), as discussed later. In addition the effect of surface roughening (Sections 4.2 and 4.3) will decrease the importance of the predicted equilibrium form. Normally, however, as pointed out in the review by Hartman (1969), morphological changes usually involve only *F* faces and are caused by changes in the relative growth rates of different *F* faces.

5.3. Influence of Growth Conditions on Habit

The habit of crystals growing in solution is determined by the slowest growing faces as noted in Chapter 4. The assumption in the discussion on the equilibrium form was that these faces will be the faces of lowest energy, but it is apparent that crystal habit is governed by kinetic rather than equilibrium considerations. A considerable period may, however, elapse after nucleation before the slowest growing faces dominate the habit, and a dependence of the observed habit on the duration of growth has been noted by numerous investigators (see, for instance, Buckley, 1951; Van Hook, 1961; Alexandru, 1969; Mullin, 1972).

A dependence of crystal habit on *supersaturation* is to be expected since the growth rates of different F faces often exhibit a different dependence on the supersaturation. The linear growth rate may be written as

$$v = k\sigma^m \tag{5.1}$$

where the parameters k and m depend on the face considered and on such factors as the temperature and the solution flow rate. Thus the relative growth rates of two faces denoted by 1 and 2 will be

$$\frac{v_1}{v_2} = \frac{k_1\,\sigma^{m_1}}{k_2\,\sigma^{m_2}}. \tag{5.2}$$

If these growth rates have the form shown in Fig. 5.4, face 2 will tend to dominate at low supersaturations where $v_2 < v_1$. Accordingly face 1 will dominate at higher supersaturations.

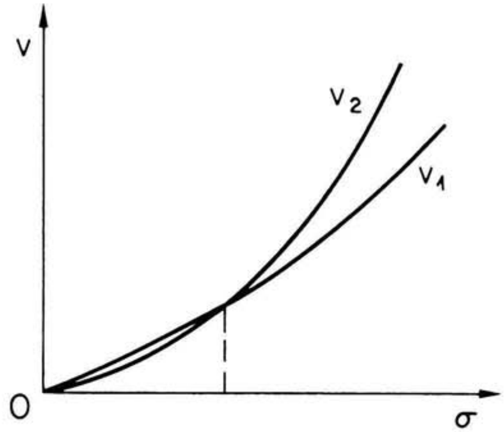


FIG. 5.4. Variation with supersaturation of growth rate of two F faces.

Kern (1969), in a review on crystal morphology and the effects of impurities, quotes potassium iodide as an example of a crystal which exhibits such a dependence of habit on supersaturation. When KI is grown from an aqueous solution at supersaturations below 10%, it is bounded by {100} faces. If the supersaturation is greater than 14%, the dominant faces are {111}. Both types of face are seen on crystals grown at supersaturations between 10 and 14%. The type of behaviour illustrated in Fig. 5.4 has been found for many crystals grown from aqueous solution, particularly by Kern and co-workers. Another example is that of Rochelle salt, which was studied by Belyustin and Dvoryakin (1958). They studied the relative growth rates of several faces and found maxima relative to {100} at different supersaturations.

The variation with *time* of crystal habit for faces inclined at different angles has been discussed by Alexandru (1969), who also considered the practical conditions for the growth of large crystals from aqueous solutions. He also pointed out the effect of the seed crystal shape on the final habit.

Since the parameter k of Eqn (5.1) depends on temperature, habit modifications will normally result from significant changes in the *growth temperature*. In general, experimental studies are not carried out at constant supersaturation and so do not distinguish between the (respective) effects of temperature and supersaturation. Gavrilova (1968) studied the effect of temperature on the morphology of magnesium sulphate $MgSO_4.7H_2O$. The changes in morphology of this substance were mainly changes in the relative elongation. The ratio of the length of the crystals along [100] to the distance between opposite {110} faces varied regularly from 7.8 at 22°C to 2.3. at 42°C. Gavrilova ascribes this effect to modifications in the structure of the solution, due to the change in concentration rather than to the effect of temperature on the growth kinetics. The $MgSO_4$—H_2O system is, however, untypical because of the large degree of solvation: crystallization above 48°C yields the hexahydrate $MgSO_4.6H_2O$. An example of separation of the effects of temperature and supersaturation on the habit for hydrothermal growth of quartz was given by Laudise (1958, 1959). The appearance of new faces, {111} and {012}, was observed on NaCl crystals by Honigmann (1952) when temperature fluctuations of 0.1 to 5°C were applied during growth, and similar observations had already been made in 1914 by Shubnikov on alum. The appearance of rough (non-equilibrium) faces is compared with the face development on spheres (Honigmann, 1958).

As discussed by Egli and Johnson (1963) a directed *flow of solution* around the growing crystal might be used to change the final shape. Alexandru (1969) found no significant difference in the habit of Rochelle salt ($NaKC_4H_4O_6.4H_2O$) crystals grown in static and in stirred solutions. Effects of solution flow have been discussed by Gülzow (1969). In the case of rapid solution flow and high supersaturation, the linear growth rate was found to vary with distance from the leading edge of the crystal. Two equivalent faces then will grow with different speeds as schematically shown in Fig. 5.5. In the "shadow" of the solution stream hopper growth might even occur, as will be discussed in Chapter 6. Gülzow also gives examples of morphology changes due to *defects* having a strong directional property, which will arise because of the increase in the rate of growth with the concentration of defects on certain crystal faces.

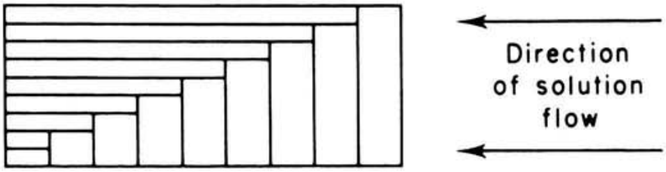


FIG. 5.5. Different growth rate of equivalent faces due to the direction of solution flow.

Twinning and especially the *twin-plane re-entrant edge* (TPRE) *mechanism* and their influence on the habit were described by Scheel and Elwell (1973) and in Section 4.14. Examples of habits of Al_2O_3, $BaTiO_3$ and BeO modified by TPRE are discussed below (Sections 5.5.1–5.5.3). Shlichta (1969) considered the effect on crystal growth of the strain energy associated with *dislocations*. This energy might be large enough to influence the step height of the layers advancing from the growth spirals. Thus crystal faces having the largest value of Burgers vector would have the highest surface energy and therefore the slowest growth rate. On the other hand, Shlichta presented evidence that the contribution of the dislocation strain energy to the morphology is at most rather small. Fordham (1949) measured the growth rates in the same crystallizer of strained and unstrained crystals of ammonium nitrate. He found that the strained crystals grew at a slightly faster rate on average, but the difference was not large compared with the scatter in the results for both sets of crystals.

Sheftal (1958) has proposed that habit changes can arise from differences in the concentration of *inclusions* near a crystal face, but this view does not appear to have received much support. Inclusions are normally seen as an effect rather than a cause of morphological changes.

Ultrasound may have an effect on the habit since the growth rate of various faces seems to be dependent on the direction, the frequency and the intensity of applied ultrasonic waves (Kapustin, 1963).

5.4. Effect of Impurities on Habit

A vast number of papers has been published on observations, largely qualitative, of morphological changes produced by the addition of small quantities of impurity to solutions. Buckley (1951) devotes a major section of his book to this topic, in particular to the effect of organic impurities on the growth of inorganic crystals from aqueous solution, and Mullin (1972) discusses in some detail the use of habit modification in the chemical industry. We shall consider here only briefly the effect of impurities on crystal morphology, and in Chapter 7 we shall discuss the distribution of impurities in solution-grown crystals (in connection with the preparation of doped crystals and of solid solutions).

An important fact to be explained in connection with impurity effects is that only very small traces, typically 0.01%, are often required to produce changes in habit. This means that many observed crystal habits may be caused by unsuspected impurity effects. The impurities normally have little effect on the dissolution rate as they are present in concentrations well below the solubility limit.

Marc (1908, 1912), Gille and Spangenberg (1927), Neuhaus (1928), and Bunn (1933) proposed that impurities form two-dimensional *complexes* on certain crystal faces and that these may become unstable three-dimensional complexes as growth proceeds. The latter complexes break up and have the effect of retarding growth on such faces through their interaction with the solute. On other faces the impurity forms stable complexes which are incorporated into the crystal and have little effect on the growth rate. The effect of the impurity on the crystal habit according to this argument arises through the reduction it causes in the supply of material to the crystal face.

More recent treatments normally consider that the impurity is adsorbed on the crystal surface and that it causes a reduction in the specific surface free energy $\Delta\gamma$. This is related to the temperature and to the packing density of adsorbed particles by the equation

$$\Delta\gamma = kTn_{S_0} \cdot \ln\left(1 - \frac{n_S}{n_{S_0}}\right) \tag{5.3}$$

which was derived by von Szyskowski from the Gibbs adsorption isotherm and the Langmuir equation. Here n_S is the actual number of adsorbed particles per square centimeter and n_{S_0} is the maximum number of adsorbed particles. Stranski (1956) has discussed this change in surface free energy with respect to the equilibrium shape regarding the Kossel crystal (see also Honigmann, 1958).

A recent experimental and theoretical study of the effect of adsorption applying the theory of Gjostein (1963) has been published by Burmeister (1971) for the case of silicon growth from the gas phase. In part these arguments can be applied to growth from solution if the pressures are replaced by the concentrations in the solution. Burmeister's equation for a rough surface is

$$\gamma_l = kTN_{ls} \cdot \ln\left(1 + \frac{p}{p_l^*}\right) \tag{5.4}$$

where γ_l is the surface (line) energy, N_{ls} the maximum number of sites available on ledges, p the actual pressure and p_l^* is a characteristic pressure. The relative density of adsorbed molecules is then

$$\frac{N_l}{N_{ls}} = 1 - \exp\left(-\frac{\gamma s}{kTN_{ls}}\right) \tag{5.5}$$

with N_l the effective number of molecules adsorbed at ledges. The ratio of the line energy γ_l to surface energy is of the order of the lattice constant (Honigmann, 1958).

The review of Kern (1969) discusses two-dimensional adsorption compounds and the specific effects of certain impurities, such as Cd^{2+} ions for habit modification of NaCl, are ascribed to the similarity between the {111} planes of NaCl and the corresponding plane in the $CdCl_2$ structure. If an adsorption layer covers a whole surface of a crystal, growth of that face may be entirely suppressed. Cabrera and Vermilyea (1958) postulate that a fall in the growth rate will occur if the mean distance between strongly adsorbed impurity particles is comparable with the size of a critical two-dimensional nucleus for the corresponding supersaturation (see below). Chernov (1961, 1962) distinguishes between two effects of adsorbed impurities. If these are relatively small and mobile, the main effect will be to reduce the effective number of kinks. Relatively large and immobile impurities, such as organic dye molecules, act as an obstacle for the movement of surface steps. In the former case, the mean separation x_i of unoccupied kinks is increased compared with the value x_o for the same crystal in a pure solution by a relation

$$x_i = x_o + \epsilon n_i \tag{5.6}$$

where n_i is the relative concentration of impurity in the solution and ϵ is given by

$$\epsilon = \frac{a}{2V_I f^3} \cdot \left(\frac{kT}{2\pi m}\right)^{3/2} \exp \frac{W_S + W_{k_1} - W_{k_2}}{kT}. \tag{5.7}$$

Here V_I is the volume and W_S the energy of an impurity molecule, f the vibrational frequency of an impurity particle of mass m in the adsorbed state, W_{k_1} and W_{k_2} are, respectively, the energies of a free and an impurity-occupied kink. Chernov estimates $W_S + W_{k_1} + W_{k_2} \sim 40$ kJ/mole, $f \sim 3.10^{12}\,s^{-1}$, so that $\epsilon \sim 10^4 a$. Thus an impurity concentration of $\sim 10^{-3}$ will increase the distance between impurity-free kinks by a substantial factor. The energy term $(W_S + W_{k_1} - W_{k_2})$ will normally depend on the orientation of the step and the resulting anisotropy of x_i will cause a corresponding anisotropy in the rate of advance of the steps. This would explain polygonization of the growth steps in the presence of impurities which was discussed in Section 4.12. A qualitative confirmation of Chernov's two effects of impurities as mentioned above was given by Slavnova (1958).

The effect of kink poisoning can be included in the BCF theory by introducing into Eqn (4.41) an additional factor C_o to allow for the relatively large separation between kinks in a step. The magnitude of this effect has been calculated by Chernov (1962), who found that it increased the non-linear region of the $v(\sigma)$ variation as well as decreasing the absolute value of v compared to that for a pure system.

Sears (1958) also considered the poisoning of kink sites in a step by impurities. He proposed that the poisoning will only be effective if the impurity covers the whole step, otherwise new kinks are continuously generated by statistical fluctuations. Quantitative calculations are not presented but Sears also discusses the effects of poisons on the nucleation rate and on the spiral shape. In the example considered, potassium chloride, the growth behaviour is changed by only a few parts per million of lead chloride.

The effect of large impurity particles is to retard the growth of layers at the points of contact with the particles while these are captured into the steps. This *step pinning* was considered also by Cabrera and Vermilyea (1958). The condition for the step to re-form on the other side of the impurity particle is fulfilled when the separation between particles is greater than $2r^*$, where r^* is the radius of a critical nucleus. Cabrera and Vermilyea assume that the rate of advance v_{st} of the steps is given by

$$v_{st}/v_{\infty} = (1 - 2r^* d^{1/2})^{1/2} \tag{5.8}$$

where v_{∞} is the step velocity in the absence of impurities and d the density of impurities on a two-dimensional lattice. If new impurity particles are flowing towards the step at a rate $\mathcal{J}_i$ then, just ahead of a step moving with a velocity v_{st}, with step density $1/y_o$,

$$d = \mathcal{J}_i \, y_o / v_{st}. \tag{5.9}$$

Combining (5.8) and (5.9) gives an equation in v_{st}^5 which has a solution only if $2r^*(\mathcal{J}_i \, y_o/v_{\infty})^{1/2} < 0.54$. Thus the steps will flow only if

$$v_{\infty}/y_o > 14 r^{*2} \mathcal{J}_i. \tag{5.10}$$

For small σ, $v_{\infty}/y_o \propto v$ (the linear growth rate) $\propto \sigma^2$ [Eqn (4.43)] and $r^* \propto 1/\sigma$ [Eqn (4.25)] and so growth will only occur if the supersaturation exceeds a minimum value given by

$$\sigma_{\min}^3 \mathcal{J}_i = \text{constant}. \tag{5.11}$$

For high supersaturations where $v \propto \sigma$, this relation should be replaced by

$$\sigma_{\min}^4 \mathcal{J}_i = \text{constant}. \tag{5.12}$$

The latter relation was confirmed experimentally by the studies of Price, Vermilyea and Webb (1958) on the electrolytic growth of silver whiskers in the presence of gelatine. Step pinning on sucrose crystals by raffinose impurities has been measured by Albon and Dunning (1962). As in the theory of Cabrera and Vermilyea, the results are interpreted by assuming that pinning occurs when the distance between two impurity molecules in a step is less than $2r^*$.

Burrill (1972) has proposed a model based on the reduction in the area of crystal face available for adsorption of solute molecules due to the presence of impurity.

Mullin *et al.* (1970) considered that a mechanism of physical blocking of sites on the crystal surface is an oversimplification, and that impurity ions in the vicinity of the surface will retard growth by their interaction with the solvent even if they are not adsorbed on the crystal surface. The presence of impurities may reduce the effective supersaturation by a "dilution", retard diffusion, hinder aggregation of growth units and so a detailed description of their effect is likely to be highly complex.

Whatever the detail of the atomic or kinetic mechanism, impurities will clearly cause habit modification by the varying degree with which they inhibit growth on different faces. However, in some exceptional cases an increase in the growth rate of crystal faces due to impurities has been observed. Such an increase may be caused by a decrease in the surface energy which reduces the size of the critical nucleus. It is likely to occur when the increased surface nucleation rate more than compensates for the decrease in step velocity (Sears, 1958).

The effect of impurity addition is often highly beneficial to the quality of the crystals. For example, Egli and Zerfoss (1949) have pointed out that NaCl is difficult to grow from a pure aqueous solution because the supersaturation for the onset of nucleation is small. If Pb^{2+} ions are added, crystals grow very easily because the critical supersaturation for nucleation is increased and so growth can proceed at much higher supersaturations than in the pure solution. Egli and Zerfoss also noted that the impurities may not enter the lattice. High-quality ammonium dihydrogen phosphate crystals were grown from a solution containing 0.1% Fe at a rate ten times that in a pure solution, but iron could not be detected in the crystals. Wanklyn (1974) listed the cases where the presence of impurities in crystal growth from high-temperature solutions was observed to have a beneficial effect.

As mentioned in the introduction to this chapter, impurities may cause the appearance of faces which are not observed in pure solutions. Hartman (1969) has proposed that certain impurities will cause faces which are normally rough to become flat, due to adsorption of a layer of impurities over the face. This effect is illustrated in Fig. 5.6. Lateral growth is possible only at steps and the growth process is thus similar to that of a normal *F* face. The epitaxial layer of impurities effectively imposes its own PBC's on the face. The example discussed by Hartman is that of $Hg(CN)_2$ grown from methyl alcohol (Ledésert and Monier, 1965). Crystals grown

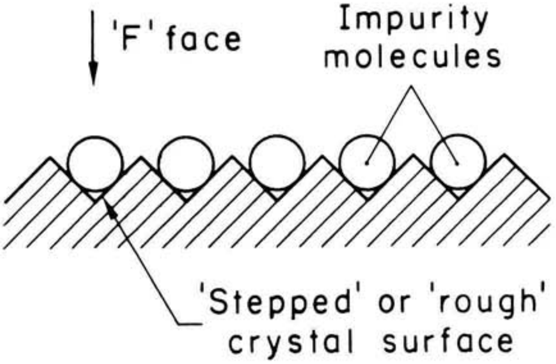


FIG. 5.6. Conversion of *S* and *K* faces by absorbed layer of impurity (schematic).

from this solvent exhibit {211} faces, which do not appear in growth by other methods and which are not *F* faces. This morphology is ascribed to the formation of an adsorption layer of CH_3OH molecules which give an arrangement resembling the flat {100} faces of the complex compound $Hg(CN)_2.CH_3OH$. The effect is of course due to the solvent itself and not to an impurity in this example, but the explanation could be extended to a number of impurity-dependent habit changes. However, for obvious reasons, it is extremely difficult experimentally and theoretically to describe the actual kinetic processes of the role of impurities in habit control.

5.5. Habit Changes in HTS Growth

The literature on the habit of crystals grown from HTS is too extensive for a detailed discussion on all materials. Examples of substances which have been investigated systematically or by several investigators will therefore be discussed. The examples described below illustrate the principles outlined in the previous sections, but some part of the interpretation is still speculative. An extensive tabulation of crystal habits and habit changes in flux growth has been given by Wanklyn (1974), and the influence of solvent and impurities on the habit of semiconductor crystals has been reported by Faust *et al.* (1968).

5.5.1. Aluminium oxide Al_2O_3

Extensive investigations of alumina, with and without the addition of Cr^{3+} to form ruby, have been made because of its application in many fields and its interesting properties. According to Timofeeva and Lukyanova (1967), the faces which are found on crystals grown from PbF_2 and from $PbO/PbF_2/B_2O_3$ solutions are listed in Table 5.2, together with their

TABLE 5.2. Relative Growth Rates of the Most Common Faces of Alumina (after Timofeeva and Lukyanova, 1967)

Face	Terminology	Estimated relative growth rates
{001}	Pinacoid	1
{101}	Main rhombohedron	10
{012}	Small rhombohedron	6
{223}	Hexagonal bipyramid	8
{110}	Prism	20

approximate relative growth rates. Since the {001} face has the slowest growth rate, alumina crystals tend to grow with a plate-like habit with the more rapid growth perpendicular to the *c* axis. Timofeeva and Lukyanova also examined the structure of the faces of their crystals by optical microscopy. They found growth steps on the faces of the three slowest growing faces, and low-angle boundaries on the {101} and {110} faces. No other faces appear to have been seen on Al_2O_3 crystals grown by other workers except by White and Brightwell (1965) who observed {001}, {012}, {104}, {113} and {125} faces (all hexagonally indexed). Of these the latter three are different from those in Table 5.2 and seem to be transient faces. White and Brightwell also mentioned an interesting habit change due to the influence of temperature. Below 1250°C, {001} plates with minor {012} and {104} were predominant, whereas at higher temperatures more equant and inclusion-free crystals with {001} and larger {012} faces were grown. The latter crystals were almost free from the multiple twinning effects observed in the "low-temperature" thin plates. Therefore the presence of twins seems to account for preferred nucleation sites and growth perpendicular to the *c* axis. This was confirmed later by Wallace and White (1967) who examined several plate-like crystals using X-ray diffraction topography. The twinning consists of a 180° rotation in the basal plane.

Linares (1965) found that his plate-like crystals were bounded only by {001} and {223} faces. He also reported that the {110} is the fastest growing face and gave the ratio of the growth rates of {223} and {001} faces as 100 : 1. The tendency of crystals to grow as thin plates is reduced when growth occurs on the walls of the crucible, well below the surface of the melt. The enhancement of growth in the direction of ⟨001⟩ was attributed to conduction of heat of crystallization through the crucible walls, which favoured growth of {001} until the {223} faces became sufficiently established to provide an appreciable area for the dissipation of heat. Increasing the cooling rate from about 0.5°C per hour to 1–5°C per hour was reported to favour the formation of more equidimensional crystals.

Nelson and Remeika (1964) had also found a tendency for crystal plates to grow near the surface and for more equidimensional crystals with fewer defects to grow near the bottom of the solution. Further confirmation is obtained from the work of Adams, Nielsen and Story (1966) who imposed a steep temperature gradient on their crucible in order to encourage growth near the base. Izvekov *et al.* (1968) confirmed the observation mentioned above that Al_2O_3 crystals grown at high temperatures (here above 1135°C) have a more equidimensional habit and attributed this effect to increased surface roughness at higher temperatures. The same tendency was found by Champion (1969), who compared the habit of crystals grown by slow cooling, evaporation and gradient transport from lead flouride. Changing the method of growth had little effect apart from the trend towards thicker crystals at higher temperatures.

Janowski *et al.* (1965) and Chase (1966) found that the addition of La_2O_3 to alumina growing from a PbF_2—Bi_2O_3 solvent greatly reduced the incidence of plate-like crystals. Its effect is to slow down the growth rate of {101} and {102} faces so that these become predominant rather than {001}. The {101} faces are dominant at 0.1–0.2% La_2O_3, and {012} at about 1%. An increase of the impurity beyond 1.5% results in the appearance of irregular {110} faces and in deterioration in quality of the crystals. La^{3+} ions are found to enter the crystal in concentrations up to 0.9%. It is concluded by Chase (1966) that La^{2+} is incorporated into the lattice. However, the incorporation of such a high concentration of the large La^{3+} ion should shift the lattice constants by 0.01 to 0.03 Å, and it is a pity that this was not determined. It seems more probable that a large fraction of the La^{3+} and F^- ions was incorporated as flux inclusions. These can be very tiny and undetectable by the unaided eye, as was demonstrated by Linares (1965). Lanthanum additions probably act by slowing down the rate of step motion on {101} and on {012} faces but are rejected at steps on the former face and enter the lattice at steps or other sites in the latter. Crystals of high optical quality were grown with 0.5% La_2O_3 concentration in the solution.

Similar observations have been made by Scheel and Elwell (1973) during a systematic study of conditions for growth of $GdAlO_3$ and $LaAlO_3$. In Fig. 5.7. a twin of alumina with the twin plane (101) and with typical reentrants, as grown from a solution of equal amounts (by weight) of Gd_2O_3 and Al_2O_3 in PbO—PbF_2—B_2O_3 flux, is shown.

Some typical habits of Al_2O_3 are shown in Fig. 5.8.i, and the corresponding indexed drawings in Fig. 5.8.ii. In addition to the above-mentioned habits of {001} plates and combinations of {001} with {221}, a steep

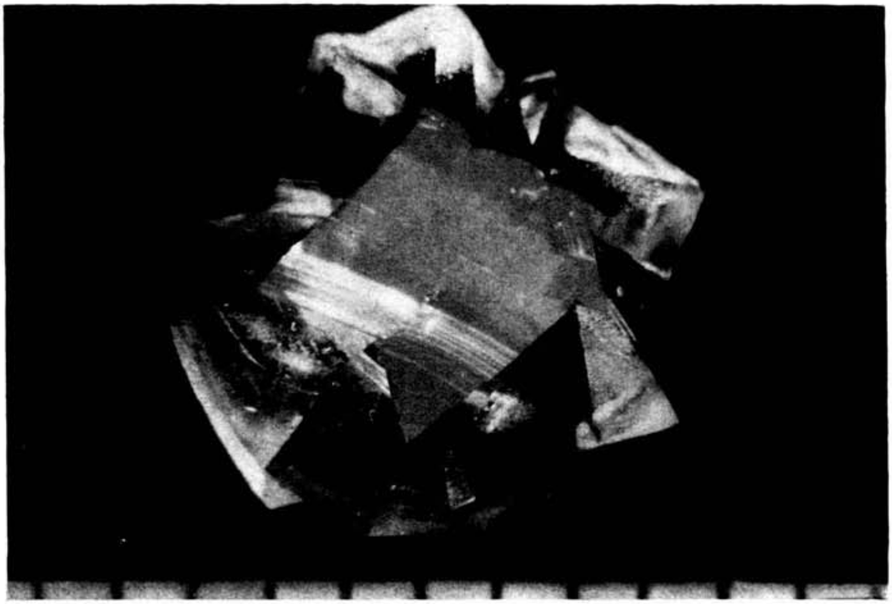
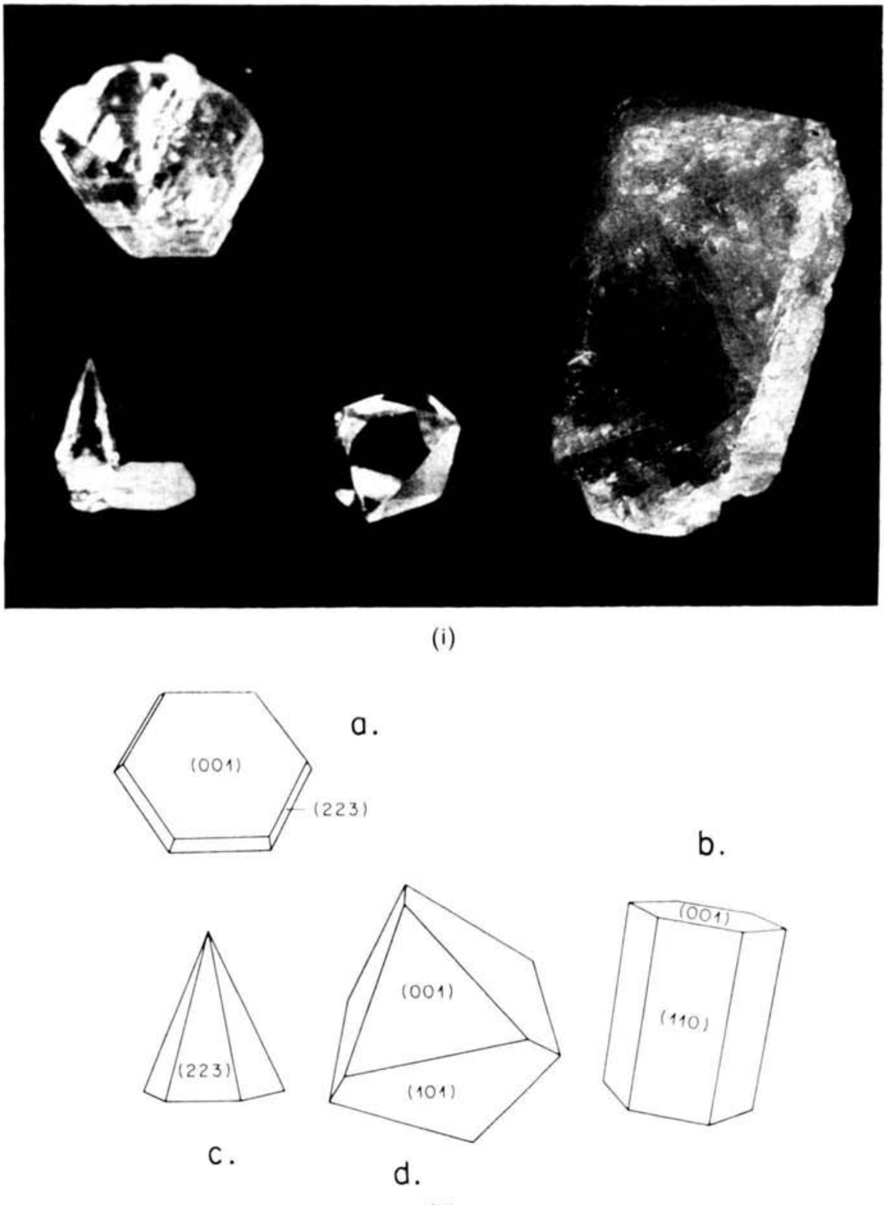


FIG. 5.7. Twinned alumina crystal with re-entrants (Scheel and Elwell, 1973).

pyramid grown from a La_2O_3-containing solution and a typical natural crystal with dominant {110} and {001} faces are shown. The latter habit is frequently found in metamorphic rocks or sediments, and often barrel-like corundum crystals with dominating {221} and minor {001} faces are found in nature. The crystal projections of Fig. 5.8.ii were drawn by computer with a program of Keester (1972).

Chase and Osmer (1970) attempted to correlate morphological changes with the composition of the solvent. Since most crystals had been grown from PbF_2 or mixtures of PbF_2 with other salts, they investigated the growth habit in solvents of different compositions in the systems PbF_2—PbO and PbF_2—MoO_3. Flat plates were found in solutions rich in PbF_2, and crystals tended to become more rhombohedral as the oxide content in the solvent was increased above 50 mole %. Chemical analysis revealed the presence of Pb^{2+} and F^- ions in the platy crystals. The habit was believed to be related to the presence of AlF_6^{3-} ions in the melt. F^- ions entering the crystal enhance the adsorption of Pb^{2+} and so slow down the growth rate, especially of the {001} face which always grows by the lateral propagation of growth layers.

Yanovskii *et al.* (1970) showed that alternative solvents can be found for the growth of non plate-like alumina crystals. They used various alkali and



(i)

(ii)

FIG. 5.8. Habits of alumina crystals. (i) Actual crystals, (ii) corresponding computer graphs: (a) hexagonal plate {001}/{111}, (b) hexagonal prism {110}/{001}, (c) pyramid {223}, (d) typical isometric Al_2O_3 crystal with {001} and {101}.

alkaline-earth tungstates and found that the crystals grew with a bipyramidal habit with only {223} faces, occasionally modified by small {101} facets. The dominance of the {223} faces was attributed to adsorption of a layer of tungstate ions on this face, which is the most favourable for epitaxial adsorption of WO_4 tetrahedron chains. Addition of cryolite, Na_3AlF_6, to a sodium tungstate solvent resulted in the reappearance of {001} faces so that the crystals were again of plate-like habit. Thick plates with {001} and {012} faces were grown from pure cryolite by Arlett *et al.* (1967).

The influence of the growth mechanism, impurities, type of solvent, and temperature on the Al_2O_3 habit is not yet clearly understood. However, the twin growth mechanism of White and Brightwell seems to provide a plausible explanation of the platy habit. In this connection it should be mentioned that other growth mechanisms have been deduced from surface features. Although Wallace and White (1967) did not find growth spirals on a (001) plane of an alumina plate, Sunagawa (1967) observed hillocks, apparently originating from screw dislocations, on the same plane. This indicates that alumina plates often grow rapidly perpendicular to the *c* axis by the twin-plane reentrant-edge mechanism (see Sections 5.3 and 4.14) and slowly along ⟨001⟩ by a screw-dislocation mechanism.

The habit changes of alumina were discussed in detail since here is a very good example of the effect of the various parameters. Also it was demonstrated how by proper choice of solvent, dopant, supersaturation and growth temperature, Al_2O_3 crystals which are untwinned, free from inclusions, of equidimensional shape and low in impurity content, can be obtained from flux.

5.5.2. Barium titanate $BaTiO_3$

The perovskite-type compound barium titanate is one of the most interesting ferroelectric compounds and has been studied in great detail. Its study was particularly stimulated when Blattner, Känzig, Matthias and Merz in 1947, 1949 and Remeika in 1954 grew the first crystals suitable for physical measurements. Of the various phase transitions, that occurring at 1460°C from the high-temperature hexagonal to the cubic form is of particular importance to the crystal grower, since crystals should be grown below this temperature. The tetragonal ferroelectric phase has a Curie temperature of 120–130°C.

The dominating habits of $BaTiO_3$ crystals grown from various solvents are the pseudo-cube with {100} faces and the so-called *butterfly twin*. The latter is preferred for physical studies and is schematically shown in Fig. 5.9. These typically twinned $BaTiO_3$ crystals were first grown to a considerable size by Remeika (1954) using potassium fluoride as solvent. The

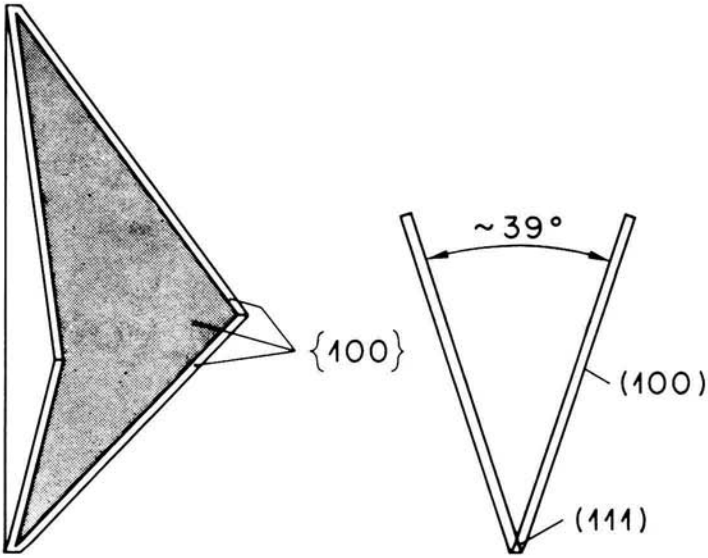


FIG. 5.9. Butterfly twin of barium titanate (after Nielsen *et al.*, 1962).

crystallographic features of the twin were described by White (1955) and by Curien and LeCorre (1955). All faces are {100} and the twin plane is (111). Small differences are reported in the literature for the value of the angle between the "wings", but it is always 39° within a few minutes.

The conditions necessary for the formation of butterfly twins have been studied by De Vries (1959) and by De Vries and Sears (1961), and have been summarized by Nielsen, Linares and Koonce (1962). The presence of excess $BaTiO_3$ powder at the onset of growth is most important, otherwise cubes are formed. Nielsen *et al.* found that the yield of twins depended strongly on the size of the undissolved particles and concluded that growth originated on particles of micron dimensions. The nuclei for twin formation must have {111} faces exposed and may be twinned themselves.

A high supersaturation is also necessary for the growth of the butterfly twins. Timofeeva (1959) found that twins formed on cooling a solution of $BaTiO_3$ in $BaCl_2$ at 20°C/h, but that more equidimensional crystals grew when the cooling rate was 4°C/h. Sasaki (1964) reported that the rapid lateral growth occurred mainly at temperatures above 1000°C, and that it was difficult to grow butterfly twins below this temperature. Sasaki and Kurokawa (1965) observed that the yield of butterfly twins depended on the temperature gradient across the crucible and that the yield was highest with the temperature higher at the base of the crucible.

Since it is difficult to control the concentration and size distribution of undissolved particles remaining in a solution after the initial soak period, the size and yield of butterfly twins are sensitive to minor changes in experimental procedure and to the nature of the barium titanate powder. Impurities in small concentrations have relatively little effect (Nielsen *et al.*, 1962; De Vries, 1959; Sholokhovich *et al.*, 1968) except for lanthanum oxide which is very effective in reducing the yield of twins. De Vries (1959) noted the $BaTiO_3$ faces which developed under various growth conditions ($BaTiO_3$—KF ratio, soak temperature, cooling rate) and also occasionally observed hexagonal $BaTiO_3$ crystals which seem to be stabilized by replacement of Pt^{4+}, Zr^{4+}, Au^{3+} or Fe^{4+} for Ti^{4+}. Hexagonal plates of composition $BaTi_{0.75}Pt_{0.25}O_3$ were obtained by Blattner *et al.* (1947, 1949).

A completely different morphology is obtained by the method used by Linz *et al.* (von Hippel *et al.*, 1963; Belruss *et al.*, 1971) in which $BaTiO_3$ crystals are pulled from a melt containing excess TiO_2 (see Section 7.2.7). Growth on a seed occurs at temperatures between 1396° and 1335°C at a rate of about 0.25 mm/h. The preferred orientation of the seed crystal is [110]. Figure 5.10 shows a typical habit of a $BaTiO_3$ crystal grown by this *top-seeded solution-growth* technique. The fully grown crystals exhibit mainly {210}, {100} and {111} faces, with {210} being the most developed. The crystals also display reentrants (indicated by *R*) which are reminiscent of the (111) twinning in the butterfly twins, but are due to alternating (210) and (120) faces.

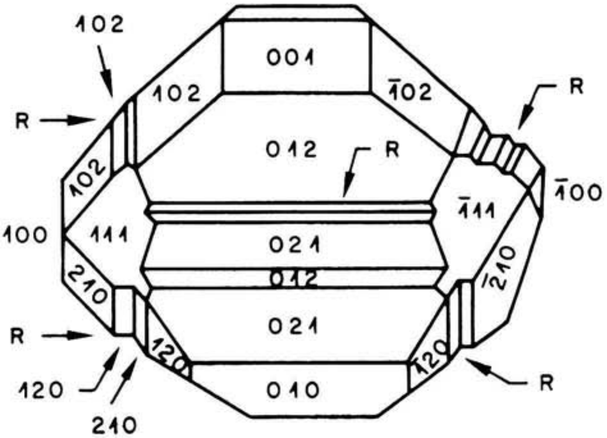


FIG. 5.10. Habit and reentrants (R) of $BaTiO_3$ grown by top-seeded solution-growth technique, growth direction {111} (von Hippel *et al.*, 1963).

Attempts to grow butterfly twins of other perovskites such as $CaTiO_3$, $SrTiO_3$ and $PbTiO_3$ failed, and it was proposed that this fact could be correlated with the nonexistence of a hexagonal phase at high temperatures (Nielsen *et al.*, 1962).

5.5.3. Beryllium oxide BeO

Detailed studies of the growth of BeO from lithium molybdate and other solvents have been reported by Austerman (1964) and by Newkirk and Smith (1965). As in the examples described previously, BeO shows a rather complex set of habit changes which are influenced by the type of solvent, impurities, temperature and supersaturation. The effect of growth temperature and of the solvent composition in the system Li_2MoO_4—MoO_3 on the habit is shown in Fig. 5.11. The principal habits are seen to be plates, prisms and pyramids, often showing the {101} pyramid face which is seen on most crystals. The prismatic and plate crystals are bounded by {101}, {100} and generally by the $(00\bar{1})$ basal plane which by definition is the oxygen side of the polar BeO structure.

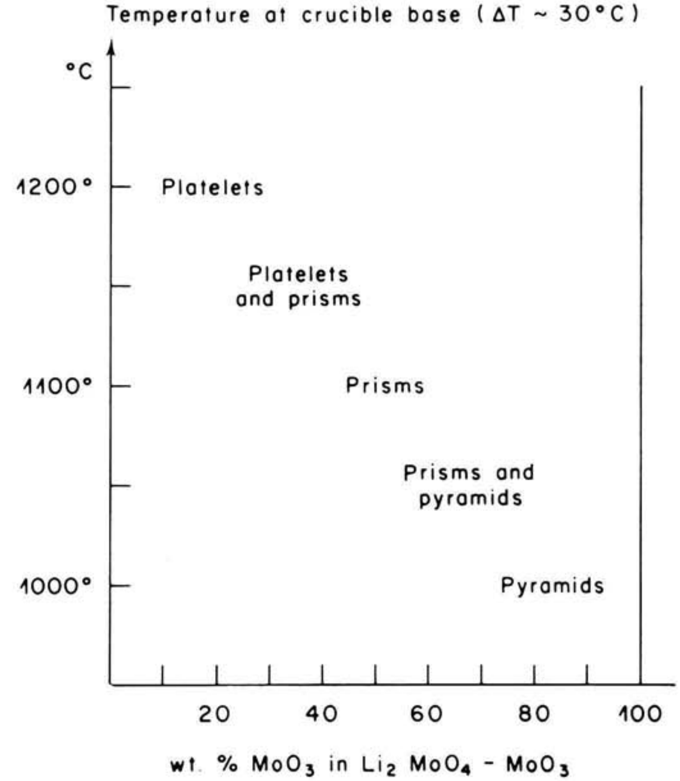


FIG. 5.11. Habits of BeO as a function of growth temperature and flux composition (after Austerman, 1964).

Many crystals seem to exhibit *twinning*, a common form being indicated by a core of reverse polarity running through a prismatic crystal. This core terminates in a small pyramid, bounded by $\{101\}$ and $\{001\}$ faces, which projects from the centre of the $(00\bar{1})$ face. Austerman suggests that the twinning is a discontinuity in the beryllium layers, with the oxygen layers continuing across the twin boundary. This twinning mechanism is shown in Fig. 5.12. The energy to form a twin is presumably very small, and the prevalence of twins is perhaps responsible for the large variety of growth forms.

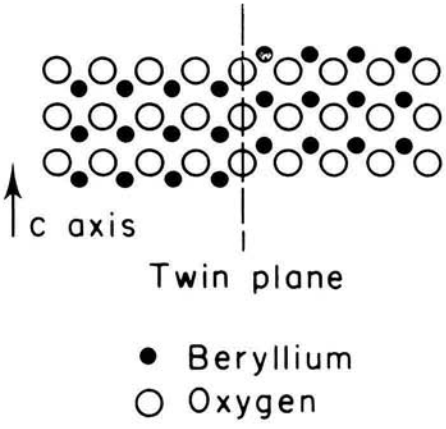


FIG. 5.12. Twinning mechanism in BeO (schematic).

The number of crystal forms may be further increased by the addition of impurities. Austerman (1964) has noted a dozen or so different faces, and mentions in particular $\{111\}$, $\{102\}$, $\{20\bar{1}\}$, $\{12\bar{3}\}$ and $\{11\bar{1}\}$ in addition to the more common faces mentioned above. His paper gives drawings of nineteen different habits observed after adding phosphate, borate or silicate to the lithium molybdate flux or after replacing lithium by potassium. Less regular crystals were due to asymmetric twinning. Newkirk and Smith (1965) also found that borates, silicates and phosphates have the most marked effect on morphology. The addition of phosphate seems to reduce twinning and to improve the crystal quality, whereas Austerman (1965) devoted a paper to the detrimental effect of silica impurities.

Linares (1967) has grown BeO crystals from sodium borate fluxes in which the solubility is much higher than in the alkali molybdates. Prismatic crystals are formed in $NaBO_2$ and rod-shaped crystals in $Na_2B_4O_7$ when cooling rates of 1–5°C/h are used. On increasing the cooling rate to 25°C/h, hollow rods crystallize, and *whiskers* may be grown when a cooling rate of 100°C/h is applied.

Newkirk *et al.* (1967) hoped to find the actual growth mechanism by a careful electron-microscope study of the features. Flat cones (growth hillocks) were detected on the singular (001) face, and the height of the spreading layers was assumed to be below 250 Å, the resolution of the replica technique used. However, the twin boundary evidently showed a multifacetted structure and therefore offered a much larger numbei of reentrant sites. The $(00\bar{1})$ face has vicinal character and appeared highly convoluted near the twin boundary where the lateral motion and traffic of growth steps was greatest. Farther from the boundary, convolutions became more widely spaced as growth layers annihilated and reinforced one another. Thus, as in the growth of the twinned alumina plates described above, a combined twin reentrant-edge and screw-dislocation mechanism can be assumed to be the growth mechanism for the majority of the flux-grown BeO crystals.

5.5.4. Cerium oxide CeO_2 and thorium oxide ThO_2

Ceria and thoria are highly refractory materials both of which have the cubic fluorite structure. They have been grown from high-temperature solutions as crystals with similar habits and are included here to illustrate the fact that similar considerations can be applied to related groups of materials, although significant differences are often observed between members of a group.

Crystals of CeO_2 were probably first synthesized from high-temperature solution by Nordenskiöld (1860, 1861) whose crystals from borax solution showed a combination of {100} with {111} faces, rarely with minor {110}. These observations were confirmed by Grandeau (1886) and by Sterba (1901) who observed the same habit in CeO_2 crystals grown from NaCl, borax, and K_2SO_4 solutions.

Finch and Clark (1966) reported that crystals grown from $Li_2O—WO_3$ solvents had an octahedral habit. Linares (1967), in a systematic study of the effect of different solvents on the habit and quality of CeO_2 crystals, obtained octahedra from $Na_2O—B_2O_3$ solvents with $Na/B \leqslant 1.0$ and from $Li_2O—B_2O_3—MoO_3$ with $Mo/B \leqslant 1.0$. The $PbO—PbF_2—B_2O_3$ solvents always gave CeO_2 cubes, which are usually characterized by large regions of lamellae with flux *inclusions* between these lamellae. Despite the higher solubility of CeO_2 in $PbO—PbF_2$ solvents, the crystallization of inclusion-free CeO_2 crystals seems to necessitate the use of fluxes based on molybdates or alkali borates. CeO_2 grown by Wanklyn (1969) from various PbF_2-based solvents showed mainly {100} faces, as was also described by Zonn and Joffe (1969), who obtained cubes from a 10 PbF_2 : 1 PbO solvent.

According to Linares (1967) crystals of thoria and of ceria grown from various solvent compositions resemble each other as regards habit. The tendency of thoria to form a cubic shape was stronger than with ceria but fewer inclusions were observed in thoria. Finch and Clark (1965) found that the addition of about 1% B_2O_3 to a $Li_2O—WO_3$ flux had a beneficial effect on the solubility and the growth behaviour. They do not discuss the morphology but show a crystal which appears to be mainly octahedral in shape. Chase and Osmer (1967) obtained inclusion-free thoria cubes from $Bi_2O_3—PbF_2$ and from PbF_2 solvents; good quality was obtained particularly by the gradient transport technique. Scheel (unpublished) has confirmed the observations of Linares (1967) and found no influence of small U-, Sb- and Bi-additions on the habit. However, from a flux containing 73% PbF_2, 21% Sb_2O_3, 3% NaF and 3% B_2O_3, yellow octahedral thoria crystals were formed together with black octahedra having the pyrochlore structure.

5.5.5. Yttrium garnets $Y_3Al_5O_{12}$, $Y_3Ga_5O_{12}$, $Y_3Fe_5O_{12}$

Since the discovery of the ferrimagnetic yttrium iron garnet (YIG) by Bertaut and Forrat (1956) and by Geller and Gilleo (1957), the interest in the garnets of yttrium and the rare earths has grown very rapidly, resulting in widespread activity on the crystal growth of these compounds. The structure of the rare-earth garnets is similar to that of natural silicate garnets. The cubic unit cell with a lattice constant of the order of 12 Å contains eight formula units. The rare-earth ions occupy irregular dodecahedral sites, the smaller Al^{3+}, Ga^3, Fe^{3+}, etc. ions being distributed on octahedral and tetrahedral sites. An extensive review of the crystal chemistry of garnets has been published by Geller (1967).

It is normally found that {110} and {211} faces are dominant on flux-grown crystals. The {100} habit reported by Timofeeva (1959, 1960) has not been confirmed since, and the crystals shown were possibly orthoferrite pseudo-cubes or hematite rhombohedra, as were found among the crystallization products of Titova (1962). However, Timofeeva (1971) claimed that garnets usually show {100} and {111} after spontaneous nucleation and only later develop the slowly growing {110} and {211} faces, especially in viscous solutions. Nielsen and Dearborn (1958) found that {110} faces of YIG were dominant when the crystals were grown slowly and that {211} became the most important faces when the cooling rate was increased to 5°/h.

Drawings of garnet habits prepared by computer (Keester, 1972) are shown in Fig. 5.13. Rhombendodecahedral faces {110} (a), ikositetrahedral faces {211} (b), and combinations of {110} with {211} (c) and of {110}, {211} and the rare {321} faces are the dominant garnet habits.

Lefever *et al.* (1961) showed that, for YIG, the ⟨100⟩ are the directions of rapid dendritic growth following nucleation. The ⟨111⟩ are also

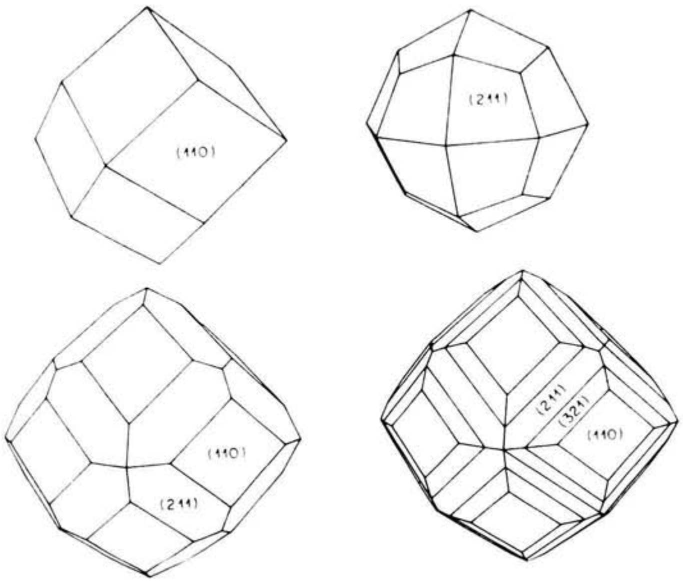


FIG. 5.13. Computer drawings of the garnet habits. (a) {100}, (b) {211}, (c) {110} + {211}, and (d) {110} + {211} + {321}.

rapid growth directions, but not so rapid as ⟨100⟩. Lefever and Chase (1962) examined the surface features of the {110} and {211} faces, which showed growth steps spreading from hillocks and which appeared to grow by a screw-dislocation mechanism. Gendelev (1963) proposed that the relative dominance of {110} and {211} faces depends mainly on the ratio of Y_2O_3 to Fe_2O_3 in the layer of solution adjacent to the growing crystals. In the (110) plane, the ratio of Y^{3+} to Fe^{3+} ions is 0.33 : 1, while in the (211) plane it is 0.60 : 1. A high Y^{3+} : Fe^{3+} ratio in the melt might therefore increase the relative growth rate of the {211}, and so the {110} would become more dominant. Similarly an increase in the Fe^{3+} concentration would favour dominance of the {211} faces. The dominance of {211} on crystals grown at higher cooling rates is explained by the lower solubility of Y_2O_3 and the lower mobility in the solution of the relatively large Y^{3+} ions. Gendelev discusses the influence of the direction of convective solution flow on the morphology, {211} faces dominating on one half of a crystal in which the supersaturation was believed to be highest, and {110} on the opposite side of the same crystal where the solute flow and hence the supersaturation were lower. He concludes that the quality of the YIG crystals depends directly on the dominance of the {110} faces, since these appear to be the slowest growing faces under conditions of low supersaturation and adequate supply of both Y^{3+} and Fe^{3+} ions. However, Tatarskii (1964) criticizes the explanation of the habit changes of YIG in terms of local differences in concentration.

Large crystals of YIG and of YIG–YGaG solid solutions grown by Scheel (unpublished) under the stirring action of the accelerated crucible rotation technique (Scheel, 1972) exhibit a dominance of the {110} faces and are free from flux inclusions. The large YIG crystals grown at the crucible base by Grodkiewicz *et al.* (1967) are dominated by {110} faces, but the crystals contain large regions with flux inclusions.

The morphology of yttrium aluminium garnet (YAG) is discussed by Gendelev and Titova (1968). Crystals of this substance grown from lead-based solvents are normally bounded only by {110} faces. The {211} faces, which appear only occasionally, must therefore have a relatively rapid growth rate. The development of {211} can be increased, as in the case of YIG, by high cooling rates, but crystals with dominant {211} faces usually contain a high concentration of inclusions.

Chase and Osmer (1969) found that YAG crystals grown at the bottom of the crucible have a pure {110} habit but those grown on the melt surface show additional {211} faces. Yttrium gallium garnet (YGaG) crystals have the {211} faces more strongly developed, and grow with a pure {211} habit from a melt rich in Y_2O_3 or PbO. The {110} faces are present when growth occurs in a melt rich in Ga_2O_3 or PbF_2. YAG was found to exhibit a similar dependence on flux composition, growing with a pure {110} habit from a melt rich in PbF_2 or Al_2O_3, and with {110} modified by {211} in a PbO or Y_2O_3 rich melt. The crystals grown from a melt rich in PbF_2 and Al_2O_3 or Ga_2O_3 have much more incorporated lead impurity than those grown from a melt rich in PbF_2 or Y_2O_3. This suggests that the lead, replacing yttrium in the garnet structure, changes the relative surface energies of the {110} and {211} faces, and so retards the relative growth rate of {110}. This tendency is contrary to Gendelev's explanation for YIG and some explanation other than the relative concentration of Y^{3+} in the two types of face must be considered. Chase and Osmer (1969) propose that the habit is mainly governed by the formation of a complex between PbF_2 and yttrium ions and that this complex modifies the behaviour of the surface diffusion or growth step propagation in some way leading to incorporation of the complex. This suggestion has not been substantiated by further evidence, and sytematic studies of the growth habit of garnets from other solvents have not been performed.

The habit of the yttrium garnets seems to be insensitive to the addition of impurities to the solution. Various substitutions have been made in these materials and the habit remains dominated by {110} and {211}, although {321} and other faces have been observed on naturally occurring silicate garnets. However, Wolfe *et al.* (1971) and van der Ziel *et al.* (1971) described a *facet-related site selectivity* for rare-earth ions in YAG. It is probable that such site preference accounts for the facet-related anisotropy in magnetic garnets as indicated by Callen (1971) and by Bobeck *et al.* (1971). These noncubic magnetic properties, introduced during growth, and therefore the habit and the growth direction in liquid phase epitaxial growth of garnets are of considerable importance in the development of magnetic bubble domain devices for logic and memory applications.

5.5.6. Zinc sulphide ZnS and cadmium sulphide CdS

Cubic and hexagonal polymorphs of zinc sulphide (zincblende and wurtzite) have been grown from high-temperature solutions. The cubic-hexagonal transition region at about 1020°C and its relationship to crystal habit in ZnS crystals grown by sublimation was studied by Hartmann (1966).

As listed in Table 5.3, cubic zinc sulphide crystallizes from flux as tetrahedra, octahedra and plates, whereas the hexagonal ZnS grows as prisms and plates. Linares (1968) found cubic {111} plates when $PbCl_2$ solutions of ZnS were cooled rather quickly (5° to 10° per hour), whereas at cooling rates of 1°C/h octahedral ZnS crystals were formed. Mita (1962) tried a number of compounds as solvents for flux growth of zinc sulphide. He obtained crystals only from NaCl, KCl, NaBr, NaI, KI and $CaCl_2$, whereas from $ZnCl_2$, K_2S and other salts no visible crystals were obtained, contrary to crystal-growth experiments of Parker and Pinnell (1968). Mita found that crystal size is closely related to the solubility of ZnS in the various solvents, and observed needles (hexagonal prisms {100} with pyramidal end faces {101}) in all solvents at crystallization temperatures of approximately 1050°C and, in addition, {001} plates of the hexagonal zinc sulphide grown from NaCl and KCl fluxes.

Parker and Pinnell (1968) reported systematic experiments intended to optimize the conditions for growth of cubic ZnS. They used a horizontal gradient transport technique and pure KCl as well as mixtures of KCl with $ZnCl_2$ and KI with $ZnCl_2$, $CdCl_2$ and $PbCl_2$ in order to obtain clear crystals up to 1 cm in size. With potassium chloride as solvent, dendritic platelets were formed at temperatures below 800°C, thin platelets from 800–830°C and thicker platelets at temperatures above 830°C. However, the crystals grown from KCl were small (~1 mm.). From mixed solvents (e.g. 20% KI, 80% $ZnCl_2$, $t=845°C$, $\Delta T=2°$) clear, large and more equidimensional crystals were obtained. These observations were attributed to complex formation in the solution.

Scheel (1974) obtained colourless tetrahedra and hollow crystals of cubic zinc sulphide by cooling sodium polysulphide solutions of ZnS.

Only the hexagonal wurtzite-type modification of CdS was obtained by

TABLE 5.3. Observed Habit Changes in Flux-grown ZnS and CdS

	Habit	Size (mm)	Solvent, exp. conditions	References
Cubic ZnS	Tetrahedra	1 × 1 × 1	KCl, 850°	Parker and Pinnell (1968)
			Na_2S	Doelter (1890, 1894)
		1 × 1 × 1	Na_2S—S, 500–600°	Scheel (1974)
	Octahedra	0.1	K_2CO_3	Schneider (1873)
		3	$PbCl_2$, 1°/hr	Linares (1968)
	Plates {111}	0.1–0.5	K_2S, Na_2S	Malur (1966)
		3 × 3	Ba_2ZnS_3, 1300°, 1.2°/hr	Malur (1966)
		5 × 5 × 1	$PbCl_2$, 5–10°/hr	Linares (1968)
		10	$ZnCl_2$—KI, 845°, $\Delta T = 2°$	Parker and Pinnell (1968)
Hexagonal ZnS	Prisms {100}		$CaF_2 + BaS + ZnSO_4$	St. Claire-Deville and Troost (1861)
		10 × 1 × 1	NaCl, KCl, 1070–1200° → 900–950°C	Mita (1962)
		5 × 0.1	NaBr, NaI, KI, $CaCl_2$, 1050°C, 5°/hr	Mita (1962)
	Plates {001}	5 × 0.2	K_2S	Malur (1966)
			NaCl, KCl	Mita (1962)
Hexagonal CdS	Prisms {100} with minor {101} or {001}		$CaF_2 + BaS + CdO$	St. Claire-Deville and Troost (1861)
			$CdCl_2$	Bidnaya *et al.* (1962)
		15 × 1 × 1	Na_2S—S, 600°	Scheel (1974)
	Prisms {100} and pyramids {101}		$K_2CO_3 + S$	Schüler (1853)
			Na_2S—S, 500°, 5 at.	Scheel (1974)
			Na_2S—K_2S—S	Scheel (1974)
	Plates {001} with minor {100} or {101}		$CdO + BaS + CaF_2$	St. Claire-Deville and Troost (1861)
			$K_2CO_3 + S + C$	Schüler (1853)
			$CdCl_2$, 800–900°C	Bidnaya *et al.* (1962)
		10 × 10 × 0.5	$PbCl_2$, 800° → 500°C	Linares (1968)
		5 × 5 × 0.5	Na_2S—S, 750–800° → 400°	Scheel (1974)

crystallization from high-temperature solutions. Cubic CdS prepared by precipitation from aqueous solutions (Jackson, 1969) seems to transform to the hexagonal phase at about 310–370°C according to Hartmann (1966). However, Cardona *et al.* (1965) described the epitaxial vapour deposition of cubic CdS on the arsenic face of gallium arsenide at 710–730°C.

The morphology of hexagonal CdS grown from the vapour phase was

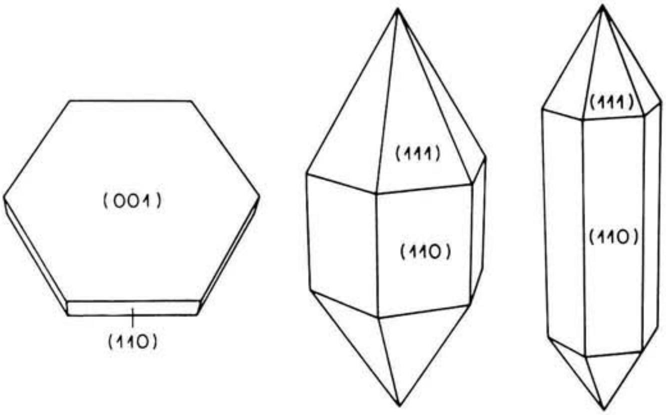


FIG. 5.14. Computer drawings of the main habits of flux-grown CdS: (a) hexagonal plates {001}/{110}, (b) and (c) prisms and pyramids.

studied in detail by Woods (1959), Bulakh (1969) and Kaldis (1969). In flux-grown CdS, a similar variety of habit change has been observed, as may be seen from the Table 5.3 and Fig. 5.14. Linares (1968) and Bidnaya *et al.* (1962) obtained {001} plates when crystallization from $PbCl_2$ and $CdCl_2$ fluxes, respectively, started at relatively high temperatures, of the order of 800°C. Scheel (1974) also obtained hexagonal plates when sodium polysulphide was used as solvent at high temperatures, whereas at lower temperatures, and with the addition of K_2S to the Na_2S—S flux, a prismatic habit with pyramidal end faces is favoured. However, this temperature relationship may not be significant, since the supersaturations are not known.

5.6. Summary on Habit Changes

Only real habit modification, that is the appearance and the change in relative importance of various types of faces on sound crystals, has been discussed in this Chapter. Unusual growth forms such as dendrites, hopper crystals, hollow crystals, whiskers, etc. will be discussed in the next Chapter. The few typical examples chosen demonstrate the influence of the various parameters on the habit. Information on other compounds may be obtained from the original literature listed in the table of flux-grown crystals in Chapter 10. However, the phenomenon of habit change should not be generalized. For instance, there are substances which do not change their habit at all such as compounds of the spinel type which generally grow as {111} octahedra.

It has been shown that habit, growth mechanism, incorporation of inclusions and impurities, and growth conditions are closely interrelated.

The study of the causes of habit modification is and will remain an interesting field for further research because, though not generally considered of great importance, habit often plays a vital role in the growth of large high-quality crystals and in their economical use. It is therefore proposed that crystal-growth publications should include observations on the morphology of flux-grown crystals for the benefit of future development in this field.

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