Crystal Growth from High-Temperature Solutions

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## I.I. The Importance of Materials Research

"We have for some time labelled civilizations by the main material which they have used: The Stone Age, the Bronze Age and the Iron Age . . . a civilization is both developed and limited by the materials at its disposal. . .. Today, man lives on the boundary between the Iron Age and a New Materials Age." These words were used by Sir George Thomson, Nobel prizewinner in 1937, and were quoted in a review of the evolution of materials science and technology by Promisel (1971).

It is more valid today to say that the age of new materials is well and truly upon us. Novel metals such as titanium are increasingly replacing steel for several applications, and metals generally are experiencing competition from ceramics, plastics and composite materials. The rate of innovation is, of course, now so rapid that it has become erroneous to speak of an "age"; the term is still widely used and the particular choice of emphasis—Atomic Age, Electronic Age, Computer Age and so on depends on the writer's personal viewpoint. Nevertheless it cannot be denied that the development of new materials has contributed greatly to the changes which have characterized the 20th century, particularly in aviation, communications and packaging.

The rapid development of new materials has led to the creation of *materials science* as a discipline in its own right. Materials science is an integration of physics, chemistry, crystallography, metallurgy, ceramics and glass technology and the need for new materials has resulted in a breakdown of many traditional barriers. The new concept is that a "consumer" will specify the properties of the material required rather than stipulating that it should be metallic, ceramic or plastic. As a result,

scientific societies have tended to widen their scope with, for example, metallurgical societies including plastics and non-metallic composites in their conferences and discussions.

Materials scientists tend to have varied backgrounds, and are very rarely trained in materials as such because of the slow rate of development of degree courses in this discipline. The normal training of materials scientists is chemistry, physics or metallurgy but it is not uncommon for electrical engineers, mineralogists or geologists to move into materials science or technology.

Crystal growth is a relatively small but important area of materials science. It is clearly more difficult to prepare single crystals than polycrystalline material and the extra effort is justified only if single crystals have outstanding advantages. Their chief merits are the anisotropy, uniformity of composition and the absence of boundaries between individual grains which are inevitably present in polycrystalline materials and which lead, for example, to optical absorption or scattering or to trapping of conduction electrons. Grain boundaries are also absent in glasses, which can be used for laser generation and some other applications, but the absence of an ordered structure often has severe disadvantages. In addition, there are many experiments which can be performed only on single crystals, such as measurements of magnetocrystalline anisotropy, and which are vital for the detailed understanding of the properties even of the polycrystalline material. The relationship between crystal growth (or materials preparation), characterization and physical properties is shown in Fig. 1.1. Careful characterization should be made of all crystals used and the resulting information used by the crystal grower in order to



FIG. 1.1. Interrelation between crystal characterization, growth and properties.

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optimize the crystal growth technique. On the other hand, characterization is necessary in order to validate any physical measurements.

The production by Stockbarger (1936, 1949) of 1500 fluorite crystals, up to 15 cm in diameter, for military application in high-quality lenses and the successful synthesis of quartz crystals by Nacken during the second world war initiated systematic crystal-growth activity, and further stimulation was given by the development of the germanium transistor, by the growth of ferroelectric BaTiO<sub>3</sub> (Blattner *et al.*, 1947; Remeika, 1954), and of magnetic garnets (Bertaut and Forrat, 1956; Geller and Gilleo, 1957; Nielsen and Dearborn, 1958).

The widest use of single crystals is probably that of ruby for bearings (also as a laser material and as a gemstone) and that of silicon in electronic devices such as the transistor. Silicon is normally preferred to germanium because of its larger band gap (1.1 eV compared with 0.72 eV for Ge), which results in a lower sensitivity to changes in temperature, but was initially considered relatively difficult to prepare in single crystal form. The increasing use of silicon, particularly in MOS (metal-oxide-semiconductor) and in LSI (large-scale integration) technology is favoured by its outstanding crystallization properties and by the passivation by an oxide layer formed directly on the silicon surface. It should not be forgotten that the degree of perfection now possible has been attained only as a result of considerable research and development investment of money and effort. The III-V semiconductors have important advantages for certain applications; for example the high mobility of carriers in GaAs favours the use of oscillators, and GaP and its solid solutions with GaAs are now used as light-emitting diodes.

This book describes one method by which single crystals and thin film layers may be obtained, namely by the use of solutions at high temperatures. In the various chapters theoretical and practical considerations will be outlined for the growth of large crystals and of crystalline films having a high degree of perfection. It is hoped that this discussion will stimulate interest in crystal growth from high-temperature solutions and will encourage more crystal growers to adopt solution techniques.

### **1.2. High-temperature Solution Growth**

In the growth of crystals from high-temperature solutions (the abbreviation HTS will be used extensively) the constituents of the material to be crystallized are dissolved in a suitable solvent and crystallization occurs as the solution becomes critically supersaturated. The supersaturation may be promoted by evaporation of the solvent, by cooling the solution or by a transport process in which the solute is made to flow from a hotter to a cooler region.

The principal advantage of using a solvent is that crystal growth occurs at a lower temperature than that required for growth from the pure melt. A reduction in the temperature is desirable or even essential for many materials, in particular those in the following categories.

- a. Those which are *incongruently melting*, that is which decompose before melting so that crystallization from the melt results in some other phase.
- b. Materials which undergo a phase transition which results in severe strain or even fracture; crystals of such materials should be grown at temperatures below this transition.
- c. Materials which have a very high vapour pressure at the melting point.
- d. Materials which have a very volatile constituent and whose chemical composition may therefore change on heating close to the melting point.
- e. Highly refractory materials which require difficult or expensive techniques for crystallization from the melt.

Other advantages of crystal growth from solutions are based on the fact that the growing crystal is not exposed to steep temperature gradients and that the crystal can grow in an unconstrained fashion, that is the crystal can grow free from mechanical or thermal constraints into the solution and so develop facets. This, in combination with the relatively low growth temperature compared with the melting point of the solute, often results in a better crystal quality with respect to point defects, dislocation densities and low-angle grain boundaries, compared to crystals grown directly from their own melt.

The disadvantages of the method are substitutional or interstitial incorporation of solvent ions into the crystal, microscopic or macroscopic inclusions of solvent or impurities, non-uniform doping, a slow growth rate and container problems.

Until recently it was comparatively rare for HTS techniques to be preferred over all possible alternatives on the grounds of crystal quality. One of the principal aims of this book is to propose that these solution techniques should be much more widely used because crystals and crystalline layers of high quality and purity and large size can be produced if careful attention is paid to such questions as the choice of a solvent and the experimental conditions for stable growth. Also homogeneous doping and solid solutions can be achieved under adequately controlled conditions.

The subject of crystal growth from high-temperature solutions includes a number of related techniques which are often treated separately. The most widely used is *flux growth* in which the solvent is a molten salt or oxide, or a mixture such as  $PbO + PbF_2$ . The use of the word "flux" for the solvent is derived from the more general use of this term for a substance used to reduce the melting temperature, or to dissolve oxides as in soldering.

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The term *growth from non-stoichiometric melts* is sometimes used to include all cases where crystals are grown from a liquid containing only the crystal constituents but of a composition which differs from that of the crystal. The scope of this book includes this technique along with "flux growth" and also growth from metallic solvents.

Liquid phase epitaxy (LPE) is a technologically important process in which a thin layer of crystalline material is deposited from solution onto a substrate of similar composition or surface structure.

The literature of high-temperature solution growth, as for all aspects of crystal growth, is very widespread. In addition to the more specialized journals such as the Journal of Crystal Growth, Materials Research Bulletin, Journal of Materials Science, and Kristall und Technik, a very large number of journals on crystallography, physics, chemistry, metallurgy, ceramics, mineralogy and electronic technology may contain articles dealing partly or wholly with HTS growth.

Although this book is the first on the subject an extensive number of review articles have appeared over the last ten years. Reference is made to Laudise (1963), White (1965), Schroeder and Linares (1966), Cobb and Wallis (1967), Roy and White (1968), Luzhnaya (1968), Laurent (1969), Elwell and Neate (1971), Chase (1971), Nielsen (1972), Brice (1973), Elwell (1975) and Wanklyn (1975). Although review articles have been used in the compilation of this book, the subject matter has been synthesized from the original articles and any interpretation of theory and of observations is our own or that of the original authors.

The terms "high temperature" and "solution" are not exactly defined in the context of this book. The experiments described are normally in the range from  $300^{\circ}$ -1800°C and the solute concentration is usually between  $1^{\circ}_{0}$  and  $30^{\circ}_{0}$  in terms of either molar or weight fraction. Some examples will, however, be discussed where the solute concentration is as high as  $80^{\circ}_{0}$  or  $90^{\circ}_{0}$ . Crystals grown from HTS are normally facetted, but again exceptions will be occasionally encountered in the text. Clearly the boundaries between HTS and other growth methods may be only roughly specified; the principal alternative growth methods are described briefly in the next section.

The boundary between solution growth and growth from a doped melt is particularly difficult to define. The distinction which will be made here is that in the latter case the dopant is added in order to change some property of the crystal by virtue of its presence *in the lattice*. In solution growth the "dopant" is added to the melt in order to lower the crystallization temperature and is rejected by the growing crystal under ideal conditions.

The most popular materials grown from high-temperature solution are oxides crystallized from molten salts and this emphasis is reflected in the

subject matter of this book. However, all types of solute and solvent will be considered, with the important exception of *hydrothermal growth* in which the solvent is water at high temperatures and pressures (the hydrothermal technique would justify an independent treatment in the form of a book).

We have included the *vapour*  $\rightarrow$  *liquid*  $\rightarrow$  *solid* (VLS) process in which solute constituents are supplied by transport in the vapour phase. Examples of crystal growth under extreme conditions (e.g. high pressure) will be considered, including the technologically important crystallization of diamonds. In both the VLS process and the growth of diamonds the amount of solvent relative to solute is generally small but the inclusion of these two processes is justified here because of the vital role of the solution stage.

## **I.3. Alternative Methods of Crystal Growth**

Single crystals may be produced by the transport of crystal constituents in the solid, liquid or vapour phase. An introduction to the general problems and classification of crystal growth methods has been given by Laudise (1970), who refers to some earlier reviews. The various methods may be classified as outlined below.

1. Crystal growth from the solid state. Polycrystalline solids contain a very large number of crystallites and crystals of useful size may be obtained if a few of these can be made to grow preferentially with the elimination of their neighbours within the material. Such recrystallization may be achieved by straining the material and subsequently annealing it, or by sintering, and is possible only in those materials which are stable at the high temperatures where appreciable diffusion can occur. Large crystals of several materials, particularly metals, have been obtained by this method which probably deserves more attention than it receives at present. It is, however, unlikely that any process which is carried out in the solid state can reproducibly result in crystals with the necessary high quality required for many applications.

2. Growth from the pure melt. Crystallization by fusion and resolidification of the pure material has many advantages from both the theoretical and experimental viewpoints. Apart from possible contamination from the crucible material and the surrounding atmosphere, no impurities are introduced in the growth process and the rate of growth is normally much higher than that possible by other methods. Mainly for the latter reason, melt growth is commercially the most important method of crystal growth. With favourable materials the crystal quality can be extremely good and the commercial production of dislocation-free silicon is one of the major advances in the field of crystal growth. There are, however, a large number

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of materials which cannot be crystallized from their pure melts for the reasons outlined in the previous section. Even when melt growth is possible, as in the case of alumina  $Al_2O_3$  and spinel MgAl<sub>2</sub>O<sub>4</sub>, a solution method may be preferred on the grounds of crystal quality. Growth from the melt is the subject of a book by Brice (1965, 1973).

3. Growth from the vapour. A wide variety of materials may be grown from the vapour phase and the reaction equilibria are now well understood for many systems. With certain materials growth may occur using a single component system, by sublimation-condensation or sputtering. Molecular beam techniques have also been applied recently to crystal growth problems.

The most frequently used method for the growth of bulk crystals utilizes *chemical transport reactions* in which a reversible reaction is used to transport the source material as a volatile species to the crystallization region. The book by Schäfer (1962, 1964) and the review of Nitsche (1967) are strongly recommended as an introduction to this subject, and Kaldis (1974) discusses the principles of crystal growth from the vapour phase.

The limitations of chemical transport are partly of chemical origin, especially the problem of finding a suitable transporting agent, and formidable difficulties arise if it is necessary to produce uniformly doped materials or solid solutions. In addition, it is rarely possible to grow large crystals because of multinucleation, although exceptions such as  $Al_2O_3$ , CdS, ZnSe, GaP, GaAs and  $Cd_4GeS_6$  are known. The commercial importance of vapour growth is in the production of thin layers by *chemical vapour deposition* (CVD) where usually irreversible reactions (e.g. decomposition of silicon halides or of organic compounds) are used to deposit material epitaxially on a substrate. CVD may often be used as an alternative to liquid phase epitaxy.

4. Growth from aqueous solution. The simplest and oldest method of crystal growth is that from aqueous solutions. Enormous quantities of materials such as sugar, salt and of inorganic and organic chemicals are crystallized from solution in water, and excellent quality crystals of such ferroelectric and piezoelectric materials as ammonium dihydrogen phosphate ADP, potassium dihydrogen phosphate KDP and triglycine sulphate TGS are commercially grown for use in electronic devices. Chemical instability or the requirement of an appreciable solubility in water excludes a number of classes of materials from being crystallized from aqueous solutions, a low solubility arising either from a different type of bonding (metals, semiconductors, covalent compounds) or from a high lattice energy (many metal oxides).

Substances with a low solubility in water can be grown by the gel

technique which has been reviewed by Henisch (1970). The principle relies on the slow migration of crystal constituents (ions) through an inorganic  $(SiO_2 \times H_2O)$  or organic gel so that a very slow reaction occurs with the formation of the sparingly soluble compound. When the concentration of this compound exceeds the solubility limit crystals will be formed, the main function of the gel being to control the slow flow of the reacting ions. From the gel large crystals have not yet been obtained but the gel technique is a useful tool for exploratory research as well as a fascinating hobby for crystal growers who may observe the slow crystallization process in a test tube.

5. Growth from nonaqueous solvents. There are quite a number of ionizing solvents which show similar solvent characteristics in some respects to water, for example the liquids HF, SO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, SbBr<sub>3</sub> and POCl<sub>3</sub>. However, these solvents also show remarkable differences from water and are therefore capable of dissolving a number of elements and compounds insoluble in or chemically reactive with water. Systematic crystal growth from the above ionizing solvents has not yet started.

The growth from solution (in ionizing or covalent solvents) of polymers and crystals of biochemical interest is also a little-explored but very important field. Little crystal growth of organic compounds from covalent solvents is performed although the organic chemist uses recrystallization from solvents or solvent mixtures as a standard purifying process.

6. Hydrothermal growth. A number of metals, metal oxides and other compounds practically insoluble in water up to its boiling point show an appreciable solubility when the temperature and pressure are increased well above 100°C and one atmosphere, respectively. Therefore these materials can be grown by the hydrothermal method reviewed by Ballman and Laudise (1963), oxides generally being grown from alkaline and metals from acid solutions (Rau and Rabenau, 1968). The requirement of high pressures presents practical difficulties and there are only a few crystals of good quality and large dimensions grown by this technique. The outstanding example of industrial hydrothermal crystallization is quartz (SiO<sub>2</sub>) which is produced in large vessels for the manufacture of commercial piezoelectric crystals. Hydrothermal growth might in several other cases be an alternative to HTS growth when large high-quality crystals or layers are needed. One serious disadvantage of this technique is the frequent incorporation of OH- ions into the crystals which makes them useless for many applications.

7. Comparison with high-temperature solution growth. Although no rigorous rules may be established for the general evaluation of a growth method, the following criteria will be of importance in the assessment of any method.

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- a. The universality, that is the number of materials to which the method may be applied.
- b. The size and quality of the crystals grown.
- c. The requirements on apparatus and chemicals.
- d The requirements on experience, theory and time.
- e. Particularly in industrial applications, the crucial factor is the cost per acceptable crystal or layer.

The greatest general advantage of HTS growth is its wide applicability. Except for those organics, hydrates and similar compounds which decompose at relatively low temperatures, there seems to be no limitation to the type of crystal which can be grown from high-temperature solution. In most cases a practical solvent can be found and also growth from nonstoichiometric melts is often possible. The use of HTS growth for the crystallization of oxides is well known but it may not be widely appreciated that such materials as nitrides, borides and carbides may often best be grown from solution.

Until comparatively recently, nucleation was a major problem and the majority of crystals grown from HTS were rather small. This problem has now been largely solved by general advances in techniques and by greater understanding of the growth mechanisms. Large crystals, weighing in some cases over 200 g, have now been produced of a variety of materials ranging from yttrium iron garnet ( $Y_3Fe_5O_{12}$ ), lithium ferrite (LiFe<sub>5</sub>O<sub>8</sub>), gadolinium aluminate (GdAlO<sub>3</sub>) and barium titanate (BaTiO<sub>3</sub>) to Ba<sub>2</sub>MgGe<sub>2</sub>O<sub>7</sub>, ruby and emerald (see Chapter 10).

The quality of HTS-grown crystals may vary considerably but generally it is a function of the effort (experience, cost, time) devoted to the growth of high-quality crystals. Normally the crystals will contain a higher concentration of impurities than crystals grown from the melt, but will have a lower concentration of equilibrium defects such as vacancies and frequently a lower dislocation density. As an example, the dislocation density of Al<sub>2</sub>O<sub>3</sub> crystals grown by a variety of crystal growth techniques is shown in Table 1.1. In this comparison, which looks very favourable for HTS growth, it should be remembered that a number of defects do not depend only on the growth technique but originate from the cooling procedure of the crystal after growth and from any mechanical cutting, grinding and polishing processes. Evidence for the high quality which may be achieved in HTS growth is provided by the observation by Nelson and Remeika (1964) of laser action in an as-grown crystal of ruby a few mm in length, which was silver plated on its natural growth faces.

Apart from the problem of chemical contamination by substitution and

inclusions which may occur as the crystals are grown in the presence of a large mass of impurity (the solvent), the main handicap of HTS growth is that the maximum stable growth rate is relatively slow (see Chapters 6, 7). This limitation can be a severe disadvantage compared with melt growth for the production of large crystals.

Technique	Range of dislocation or etch pit densities per cm	Reference 2
High-temperature	0-<10 <sup>2</sup>	Belt (1967b)
solution growth	0-<10 <sup>2</sup>	Janowski et al. (1965)
	0-~102	Linares (1965)
	10 <sup>2</sup> -10 <sup>4</sup>	Champion and Clemence (1967)
	103-107	Sahagian and Schieber (1969)
	10 <sup>2</sup>	Stephens and Alford (1964)
	102-104	White and Brightwell (1965)
Flame fusion growth	6.104-5.106	Sahagian and Schieber (1969)
	10 <sup>6</sup> -10 <sup>8</sup>	Champion and Clemence (1967)
	3.105-2.106	Alford and Bauer (1967)
Plasma fusion growth	4.105-5.106	Sahagian and Schieber (1969)
	7.105-7.106	Alford and Bauer (1967)
Czochralski growth	2.10 <sup>3</sup> -8.10 <sup>5</sup>	Sahagian and Schieber (1969)
	10 <sup>2</sup> -10 <sup>4</sup>	Belt (1967a)
	10 <sup>2</sup> -10 <sup>3</sup>	Cockayne et al. (1967)
Bridgman-Stockbarger type	105	Schmid and Viechnicki (1970)
Electron beam technique	$1.10^{2} - 5.10^{4}$	Sahagian and Schieber (1969)
Hydrothermal growth	8.104-4.105	Sahagian and Schieber (1969)
Vapour growth	2.104-1.106	Sahagian and Schieber (1969)
	~10 <sup>2</sup>	Schaffer (1964)
Natural crystals	1-5.103	Sahagian and Schieber (1969)

TABLE 1.1. Measured Dislocation Densities of Alumina Al<sub>2</sub>O<sub>3</sub> and Ruby Al<sub>2</sub>O<sub>3</sub>: Cr Crystals Grown by Various Techniques

Although the cost of the furnace and other ancillary equipment is relatively low, a further disadvantage is encountered in the majority of experiments where the only satisfactory crucible material is platinum. This material is very expensive and crucibles often form the major item of capital expenditure. This problem is serious only in the initial stages of development since the cost of reclamation and refabrication of damaged crucibles is low. As with all crystal growth experiments, the cost of materials can be extremely high, but this depends on the amount of contamination which can be tolerated in the crystals grown and therefore on the necessary purity of the starting materials.

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The problems mentioned will be examined, together with the advantages of HTS growth, at various points in the text.

## I.4. Applications

Crystals grown from high-temperature solutions are used both for academic research and by industry, and we shall consider these catagories separately.

### Research use

One of the most important uses of HTS growth is in the synthesis of new materials. Several examples are known of materials which were first formed either by accident or during systematic studies of novel solute-solvent systems. This type of study has been mainly performed on compounds of the transition metals and the rare earths, especially complex oxides. There remains a large area for further study, for example of compounds of the palladium and platinum transition groups, and it is certain that there are many materials with interesting magnetic properties which await discovery.

Of even greater importance is the vital role particularly of flux growth in the preparation of materials in single crystal form for the first time. Many examples may be quoted of materials which were first crystallized from solution prior to the development of now more familiar methods. The synthesis of crystals of new materials has led to important advances, particularly in magnetism, ferro- and piezoelectricity and laser research.

The rapid growth in the number of materials available in single crystal form has led to the establishment of materials information centres in a number of countries,<sup>†</sup> and the excellent service operated by T. F. Connolly has made a valuable contribution to materials research and has benefitted crystal growers and consumers in many countries. The main value of the information centres is that they prevent much duplication of effort and encourage the maximum benefit to the scientific community of centres specializing in the preparation of materials. Where duplication cannot be

† United States: Research Materials Information Centre, P.O. Box X, Oak Ridge, Tennessee 37830 (T. F. Connolly).

*France*: Centre de Documentation sur les Synthèses Cristallines, Laboratoire de Physique Moleculaire et Cristalline, Faculté des Sciences, Chemin des Brusses, 34—Montpellier (Mlle A. M. Vergnoux).

Britain: Electronic Materials Unit, Royal Radar Establishment, Malvern, Worcs. (O. C. Jones).

Germany: Prof. R. Nitsche, Institut f. Kristallographie d. Universität, 78 Freiburg i. Br., and Dr. A. Räuber, Institut für Angewandte Festkörperphysik der Fraunhofer-Gesellschaft, 78 Freiburg i. Br., Eckerstrasse 4.

avoided it is desirable that original crystal growth experiments be repeated with a minimum of effort and therefore that the original publication should contain sufficient information to allow easy repetition.

Exploratory materials research cannot be expected to yield crystals which are large or of very high quality and much further effort may be required to produce crystals which are suitable for more demanding experiments, such as electro-optic modulation or acoustic experiments. The production of large crystals of good quality normally requires more sophisticated techniques and a better understanding of the phase diagram and the growth mechanism.

Increasing attention is being given to the deposition of thin films by liquid phase epitaxy. Provided that the lattice parameter match between the film and the substrate is good and the substrate itself is relatively free from defects, the quality of the films can be extremely high. If the experiment can be performed on such films, their use has the great advantage that relatively little time is required for the growth process, and so one of the major disadvantages of solution methods can be overcome.

## Industrial materials

The materials which have been crystallized from high-temperature solution in industry may be divided into the categories listed below.

1. Magnetic oxides. Insulating magnetic materials, especially yttrium iron garnet or YIG ( $Y_3Fe_5O_{12}$ ), find several applications in the communications field. As an example, small spheres of single crystal YIG are used in the Telstar satellite system. D. A. Lepore of Airtron, the major commercial suppliers of magnetic garnets, has estimated that the current market for such crystals is in the region of \$250–300,000. The plant used at Airtron for their garnet production is shown in Fig. 1.2.

Marriott (1970) describes the design and performance of tunable bandpass filters, which utilize ferromagnetic resonance in YIG, and of power limiters which are based upon the nonlinear processes which occur at high microwave power levels. The same author also discusses the use of a YIG sphere to control the frequency of a Gunn oscillator; the basis of this device is that the oscillator is coupled to a resonant "cavity" provided by the YIG sphere in an applied magnetic field.

Some applications of YIG crystals are also discussed by Schmitt and Winkler (1970), who describe filters, delay lines and magneto-optic modulators. The delay lines are based on phonon propagation in YIG at microwave frequencies and can introduce a variable delay time with low insertion loss. Magneto-optic modulation has been proposed as a means of transmitting information on a laser beam, using the Faraday effect. A device for short-range communication by magneto-optic modulation of an



FIG. 1.2. Plant used for large-scale production of crystals from fluxed melts (courtesy D. A. Lepore, Airtron Division of Litton Industries Inc.).

infra-red beam has been produced. Large YIG crystals (with relatively large regions of inclusions) have been prepared from large (4–8*l*) crucibles by Adams and Nielsen (1966) and by Grodkiewicz *et al.* (1967). Large inclusion-free garnet crystals were produced by Tolksdorf and Welz (1972) for some of the applications mentioned, using a stirring technique developed by Scheel (1972).

The most lively interest in magnetic materials at present concerns the development of devices based on thin garnet films which exhibit cylindrical domains with the axis of magnetization normal to the plane of the film. These cylindrical or "bubble" domains are highly mobile and their use has been proposed for memory devices. Such devices are still in the development stage but the films which have been prepared by the LPE process appear at present to be of greater promise than those grown by

chemical vapour deposition, hydrothermal epitaxy or by sputtering and pilot plants for LPE production of bubble films have recently been constructed.

2. Lasers. Mention has already been made of the observation by Nelson and Remeika (1964) of laser action in as-grown ruby. Comparative studies of the quality of ruby crystals for laser applications such as that of Bradford et al. (1964) show that HTS-grown crystals have important advantages over those grown by other methods. However, crystals grown by the Czochralski method are normally preferred in practice since crystals of adequate quality can be prepared relatively rapidly.

3. Semiconductor devices. The development of the LPE process by Nelson (1963) has ensured an important role for solution growth in semiconductor device technology. Bulk crystals of III-V semiconductors are normally grown from the melt, and LPE is used to form p-n junctions by deposition of a thin layer of doped material. Semiconductor diodes are used as lasers, microwave generators and particularly for light-emitting devices. LPE-grown materials are normally preferred because of a higher efficiency than can be obtained by alternative methods. Examples are reported by Rupprecht (1966) for GaAs lasers and by Panish *et al.* (1971) for Al<sub>x</sub>Ga<sub>1-x</sub>As room temperature continuous lasers, by Kang and Greene (1967) and Solomon (1968) on high resistivity—high mobility GaAs layers with excellent photoluminescent properties, and in a review by Casey and Trumbore (1970) on light-emitting diodes. The latter devices are now produced commercially by LPE and the value of the annual production is probably much higher than that of magnetic garnet crystals.

Thin film microcircuits require insulating substrates, preferably of high thermal conductivity. Comparisons of  $MgAl_2O_4$  substrate crystals grown by various methods were performed by Wang and McFarlane (1968) and by Wang and Zanzucchi (1971) who found that the flux-grown material had much the lowest dislocation density. It seems clear that solution methods would be used for the production of  $MgAl_2O_4$  substrates if large crystals could be grown quickly and reproducibly. The material which is potentially the most attractive for substrates is BeO, on account of its high thermal conductivity. Further work is necessary on establishing the optimum conditions for growth of this material, and it presents hazards because of its high toxicity, but the work which has been done to date has shown that suitable crystals could be grown from HTS with little further development effort.

4. Nonlinear optical materials. Many dielectric materials have been crystallized from high-temperature solutions and several applications have been envisaged, particularly of materials which are piezo-, pyro- or ferroelectric. Potentially the most important application appears at present

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to be as nonlinear optical materials for modulation and second-harmonic generation of laser light as a means of communication with a high density of information transmission.

5. Gemstones. The high value placed on gems for use in jewellery has led to many attempts to synthesize and imitate natural gemstones, and the importance of early experiments in the development of high-temperature solution growth will be discussed in the next chapter. Synthetic emeralds and rubies are marketed on quite a large scale, the most important producers being Union Carbide (Linde Division) and C. F. Chatham in the U.S.A., P. Zerfass in Germany and P. Gilson in France. The wholesale value of synthetic emerald production may be in the region of \$1-2 million.

Chatham and Gilson use a flux method, since the stones produced most closely resemble the natural gems in colour and in the nature of the inclusions. This is one area of solution growth where the solvent inclusions are considered beneficial! Chatham claims that his emeralds take over a year to "mature" but it is unlikely that such a period is really necessary since the process is almost certainly seeded growth from a flux (Flanigen et al., 1967), probably lithium molybdate or tungstate, vanadium oxide or lithium vanadate. The high-quality emeralds grown by Linde are produced hydrothermally. Chatham also produces rubies for gemmological use and flux-grown rubies are also marketed under the name "Kashan". The large difference in price, which can be a factor 10<sup>3</sup> or more, between natural and synthetic gemstones naturally encourages attempts to pass synthetic stones as natural products. It is perhaps remarkable that natural emeralds and rubies have retained their high value when the differences between these and the flux-grown stones are marginal and take an expert to detect, and the gemmological trade need to be extremely vigilant in their tests to distinguish natural from synthetic stones.

Diamonds are now produced synthetically in several countries and synthetic stones account for about a fifth of the world supply of industrial diamonds. The method requires extremely high temperatures and pressures, but the graphite-diamond transition occurs as an exsolution process from a metallic solvent as will be discussed in Chapter 7. Stones weighing several carats (1 carat = 0.2 g) have now been produced (up to 1 carat of gem quality) but the sole application of synthetic diamond at present is in cutting, grinding and polishing in industry. Approximately 20 tons of graphite have been transformed to diamond by the General Electric Company alone.

6. Electro-crystallization. Electrolysis of fused salts is normally used for the commercial production of metals such as aluminium, and has great technological importance. The process of crystal growth from fused salts is analogous in many respects, except for the requirement of electron

transfer in deposition of the metal. Fused salt electrolysis has been used to grow crystals of oxides in reduced valence states (Kunnmann, 1971) and it has also been proposed to use this method for crystal growth of compound semiconductors (Cuomo and Gambino, 1970).

## 1.5. Current Problems and Future Trends

High-temperature solution growth is progressing gradually from an art to a science. At present, experimenters would find it difficult to give a convincing explanation for their choice of several of the operating conditions and other variables. Crystallization from solution is a complex process and only a few experiments are understood quantitatively.

A major problem which awaits clarification concerns the detailed nature of the processes which occur in the solution. Little information is available on the nature of the solute-solvent interaction, the association and dissociation of ions or on the formation of complexes in the high-temperature solutions. It is particularly difficult to give any confident statement regarding the processes in the vicinity of the crystal-solution interface. The questions of prearrangement or clustering of the ions or molecules in the diffusion boundary layer or at the crystal surface and of the nature of the desolvation stage are still largely open. The crystal itself is, of course, relatively easy to examine since it is comparatively stable, but the structure of the solution is a very wide field for future research.

It is fascinating to picture crystallization from solution on an atomic scale. Although this process is slow in comparison with growth from the melt, it does involve the ordered arrangement of 10 to 100 or more molecular layers on the crystal surface every second, with the rejection of an equivalent amount of solvent. One must hope that the latest techniques of physical chemistry will soon be applied to the clarification of the detailed stages involved, as discussed in Chapters 3 to 6.

The theory of crystal growth generally is at best understood only semiquantitatively, since there remain several parameters which appear in any detailed theoretical treatment which cannot be assigned a value any more reliable than an order-of-magnitude estimate. At present most progress is hoped from computer simulation of nucleation and crystallization processes and from comparison of the results obtained with surface observations or with measured nucleation and crystal growth data. More quantitative studies are required of crystal growth under carefully controlled conditions, and measurements of such parameters as the viscosity of the solution and the diffusion coefficient of the solute are normally lacking for systems of interest in crystal growth.

Many more materials could be crystallized from solution than at present. Until now, flux growth has been used almost exclusively for oxides and the

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LPE process has been mainly concentrated on III-V semiconductors and on magnetic garnets. There has been, for example, little work on carbides (except for SiC), borides, sulphides, selenides and tellurides, pnictides, intermetallic compounds and on some complex oxides such as germanates.

In only very few cases have intensive efforts been made to grow crystals weighing more than a few grams. It is clear that many more crystals could be grown to 100 or 200 g if systematic attempts were made to find a good solvent and to optimize the conditions of growth.

As industrial uses of more sophisticated materials grow, a stage could be envisaged where high-temperature solution growth will be used for industrial crystallization with batches of say 100 kg of crystals. Criteria for the design of such crystallizers are available for some systems, at least to approximately the level of confidence now used for crystallization from aqueous solutions. Production on such a scale might be necessary if solution methods are to be competitive for a wide range of materials on economic grounds.

In summary, we believe that the subject of crystal growth from hightemperature solution is still relatively unexplored. Major advances are likely in the next few years in the understanding particularly of the nature of solutions and of the interface kinetics. Other problems such as nucleation and the effects of impurities are also little understood at present. On the practical side there remain many interesting materials which have still not been crystallized and many more of which crystals are not available in good size or quality. Increasing use of technologically important materials such as yttrium iron garnet may require the development of apparatus for bulk crystallization from high-temperature solutions.

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### APPENDIX B

lowed by several others but serve to illustrate a need for intensive development so that this important technology of LPE can achieve its true potential. This requires the education of crystal/epitaxy technologists (Scheel 2003&2004).

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