JOURNAL OF MATERIALS SCIENCE 1 (1966) 199–210

Bibliography on Crystal Growing

Annotated References 1960 to 1965

E. A. D. WHITE
Department of Electrical Engineering, Imperial College of Science and Technology, London, SW7, UK

1. Introduction

The emphasis given to the study and development of crystal growing over the past few years has resulted in an ever-increasing spate of publications. There has been no completely appropriate venue for reporting work in this field; the choice of journal usually has been made according to the properties of the crystals or the application for which they were grown. Thus, reports on corundum crystal growing have been distributed in ceramic, optical, mineralogical, physical, and chemical journals, making it difficult for interested parties to keep abreast of developments without spending an excessive amount of time scanning journals which are of restricted interest. The present contribution is intended to bring together references to recent publications dealing with the subject of crystal growing, particularly from the aspect of materials research.

It is not intended that the list of references should be comprehensive, but that they should be representative of the materials currently being grown, and of the techniques used for research purposes. They have been selected to cover a reasonably broad range of subject matter. Where several papers on a particular technique or material exist, only those references are included which seem to the compiler to be novel or important for future development.

Since the journal in which this bibliography appears is intended to cater for a wide spectrum of materials interests, an attempt has been made to classify the references according to the characteristics of the crystals grown. For a description and comparison of the basic crystal growing techniques used, and for references to earlier works on crystal growing, a number of books and review articles are included in the final section entitled "Growth Techniques".

Many of the references quoted could be included in more than one section, and a choice was made on the basis of the most important property or application.

2. Maser and Laser Materials

Since microwave and optical devices employing the principle of stimulated emission have been the *raison d'être* for much of the current crystal growth investigations, this section is given pride of place. Included in it are crystals which have been grown for electron spin resonance investigations as potential maser materials and also certain crystals of optical interest which have been used for laser investigations.

1. I. ADAMS and J. W. NIELSEN, "Growth of Large Ruby Crystals from Molten Salt Solutions", Electrochem. Soc. Meeting, Abstract No. 88 (Toronto, Spring 1964).

The growth of ruby crystals, several cm across, from PbF_2 solutions was described. Solubility data were presented, together with some details of the growth technique. This work represents the largest scale application of the fluxed-melt growth technique yet recorded.

2. J. BUTCHER and E. A. D. WHITE, "A Study of the Hydrothermal Growth of Ruby", *Min. Mag.* **33** (1964) 974-85.

The hydrothermal process for the growth of ruby was investigated using different aqueous solvents. The conditions for growth on seed crystals were established, and growth rates were found to be limited because of the restrictions imposed by the structural materials used for the autoclaves. The need for equipment operating at much higher temperatures and pressures, while retaining a reasonably large working volume, was apparent from this work.

3. B. COCKAYNE, "The Growth of Calcium Tungstate Single Crystals Free from Low-Angle Boundaries", *Brit. J. Appl. Phys.* **16** (1965) 423-4.

An interesting approach to the control of crystal perfection by modifying the vacancy concentration in the neck region of Czochralski-grown crystals of $CaWO_4$. This was achieved by: (a) quenching-in thermal vacancies present at the melting point by increasing the growth rate; and (b) altering the stoichiometry of the crystal to produce defect structures by the use of a reducing atmosphere. The formation of low-angle boundaries in the neck region of crystals grown under low thermal stress was avoided by growing the neck region at a fast rate.

4. B. COCKAYNE, D. S. ROBERTSON and W. BARDSLEY, "Growth Defects in Calcium Tungstate Single Crystals", *Brit. J. Appl. Phys.* **15** (1964) 1165.

Crystals of $CaWO_4$ grown for laser studies suffer from a number of defects which are described in this paper. The principal defects are low-angle boundaries which arise in the neck region (cf. reference 3) and striations in crystals doped with Nd and other rare earth ions.

5. L. D. FULLMER and W. R. WILCOX, "Growth of Potassium Tantalum Niobate Crystals", *Bull. Amer. Phys. Soc.* **9** (1964) 726.

Crystals of $K(Nb,Ta)O_3$ were grown by Czochralski pulling from melts contained in 100 ml Pt crucibles. Optical quality crystals were obtained using [111] seeds at pulling rates below 1.5 mm/h. A good example of the versatility of the Czochralski technique for materials which can be melted and contained by suitable crucibles.

6. E. F. FARRELL and J. H. FANG, "Flux Growth of Chrysoberyl and Alexandrite", *J. Amer. Ceram. Soc.* **47** (1964) 274-6.

Chrysoberyl, $BeAl_2O_4$, and the chromium-doped form, alexandrite, are interesting materials structurally, chemically, and physically, as well as gemmologically. Crystals grown from PbO and from Li_2O-MoO_3 solutions, respectively, were obtained up to 10 mm across by slow cooling. Small crystals of Cr_2BeO_4 were also obtained.

7. A. L. GENTILE, D. M. CRIPE and F. H. ANDRES, "The Flame-Fusion Synthesis of Emerald", *Amer. Miner.* **48** (1963) 940-3.

Synthetic emerald of gem quality has been marketed for many years ("Chatham" emerald). The process has never been divulged, and little scientific interest was shown until its potential as a maser material was discovered. Crystals have recently been grown by a variety of processes (references 12 and 14) other than the one described. No information of the crystal perfection is given.

8. E. A. GIESS, "Solubility and Crystal Growth of $ZnAl_2O_4$ and Al_2O_3 in Molten PbF_2 Solutions", *J. Amer. Ceram. Soc.* **47** (1964) 388-92.

The fluxed-melt technique was applied to the growth of Al_2O_3 and, for no obvious reason, the spinel, $ZnAl_2O_4$. Lead fluoride is well known as being a versatile solvent for fluxed-melt growth. Solubility data for the systems studied are given.

9. M. A. HILLER and O. M. STAFSUDD, "Czochralski Growth of Doped Single Crystal Lanthanum Trifluoride for Lasers", *J. Appl. Phys.* **35** (1964) 693-5.

LaF_3, another contender for laser applications, provides a convenient host lattice for lanthanide ions, having the advantage that no charge-compensating additives are required. The raw material was prepared by fluorinating 5N La_2O_3, and crystals were pulled in a helium atmosphere from an iridium crucible. Crucible and crystal were rotated in opposite directions.

10. R. A. LAUDISE, J. H. CROCKET and A. B. BALLMAN, "The Hydrothermal Crystallisation of Yttrium Iron Garnet and Yttrium Gallium Garnet and a Part of the Crystallisation Diagram Y_2O_3-Fe_2O_3-H_2O-Na_2CO_3", *J. Phys. Chem.* **65** (1961) 359-61.

The title of this article is virtually an abstract of the contents, and it only remains to comment upon the application of the hydrothermal process to the important class of garnet-structured materials. It would seem to offer the possibility of controlled growth of large crystals free from the flux inclusions characteristic of fluxed-melt crystals.

11. R. A. LEFEVER, "Flame-Fusion Growth of C-Type Rare Earth Oxides", *Rev. Sci. Inst.* **33** (1962) 1470-1

The conventional form of flame-fusion apparatus has been used for comparatively few substances. The flame temperatures attainable using H_2/O_2 mixtures are just sufficient to melt some of the rare earth oxides. Crystals of Y_2O_3, Er_2O_3, and Yb_2O_3 were obtained. These grew with a coating of polycrystalline material, which was thought to reduce radiation losses and consequently reduce the sharp thermal gradient which is responsible for many of the imperfections in flame-fusion ruby.

12. R. A. LEFEVER, A. B. CHASE and L. E. SOBON, "Synthetic Emerald", *Amer. Miner.* **47** (1962) 1450-3.

Another successful synthesis of emerald crystals by the fluxed-melt technique. Solvents used were PbO-PbF_2, B_2O_3 and Li_2O-MoO_3. The best results were obtained from a complex mixture, $BeO + Al_2O_3 + Li_2SiO_3 + Cr_2O_3 + MoO_3$, by slow cooling. Growth on seed crystals was obtained.

13. R. A. LEFEVER, J. W. TORPY and A. B. CHASE, "Growth of Single Crystals of Yttrium Aluminium Garnet from Lead Oxide-Lead Fluoride Melts", *J. Appl. Phys.* **32** (1961) 962-3.

The garnet structure has proved to be one of the most versatile for compositional variations. Following work on YIG ($Y_3Fe_5O_{12}$), the potentialities of the lattice as a host for lanthanide ions are now being realised in the laser field. The growth process described is similar to that used for YIG, viz., by slow cooling melts of Y_2O_3 and Al_2O_3 in PbO-PbF_2. Crystals up to 13 mm across were obtained, although this has now been improved upon (see reference 24).

14. R. C. LINARES, A. A. BALLMAN and L. G. VAN UITERT, "Growth of Beryl Single Crystals for Microwave Applications", *J. Appl. Phys.* **33** (1962) 3209-10.

Crystals of beryl (undoped emerald) were grown by the fluxed-melt technique from a variety of solvents including $Li_2Mo_2O_7$, $Li_2W_2O_7$, $PbMoO_4$, $PbWO_4$, and V_2O_5; the latter was preferred.

15. K. NASSAU, "Application of the Czochralski Method to Divalent Metal Fluorides", *J. Appl. Phys.* **32** (1961) 1820-1.

Apparatus used for pulling a variety of fluorides (including CaF_2, BaF_2, SrF_2, CoF_2, MnF_2, and $KMnF_3$) is shown. Crystals were pulled in argon atmospheres and cracking was evidently a problem. However, this work predated many of the innovations and improvements to the pulling technique described in other references.

16. K. NASSAU and A. M. BROYER, "Calcium Tungstate: Czochralski Growth, Perfection and Substitution", *J. Appl. Phys.* **33** (1962) 3064-73.

A comprehensive statement of crystal growing, doping and the imperfections occurring in $CaWO_4$ crystals for laser applications. Although this material has been the subject of many subsequent papers, this work contains much useful information.

17. D. F. NELSON and J. P. REMEIKA, "Laser Action in Fluxed Grown Ruby", *J. Appl. Phys.* **35** (1964) 522-4.

Ruby crystals of "rhombohedral" type were grown from solution in PbO-B_2O_3 by slow cooling. Although they were comparatively small (cf. reference 1), the perfection of the crystals obtained was demonstrated by silvering opposing as-grown faces and obtaining laser action in a conventional cavity. No obvious advantage appears to be attached to the PbO-B_2O_3 system as a solvent.

18. S. O'HARA and G. M. MCMANUS, "Czochralski Growth of Low Dislocation Density Zinc Tungstate Crystals", *J. Appl. Phys.* **36** (1965) 1741.

The recent tendency to study growth conditions and factors affecting crystal perfection, rather than to pursue an all-out empirical approach, is reflected in this work. Strain, due to thermal gradients, was shown to be responsible for the high dislocation density of crystals grown in steep gradients. If the crystals were not widened initially from the diameter of the seed, the new growth was of superior quality. The changes in temperature applied to produce widening resulted in increased dislocation densities.

19. A. E. PALADINO and B. D. ROITER, "Czochralski Growth of Sapphire", *J. Amer. Ceram. Soc.* **47** (1964) 465.

Yet another technique applied to ruby and sapphire growth; but one which may well prove to be most successful for the production of large high-quality crystals, when it has been developed sufficiently. This particular study employed tungsten crucibles with RF heating, using either the crucible or a concentric carbon sleeve as the susceptor. The growth atmosphere was purified N_2. At a pulling rate of 2·5 cm/h, no Tyndall scattering was observed, the crystals could be cut without shattering, and impurities other than Si and W were mainly $<0.0001\%$.

20. J. D. RIDLEY and B. COCKAYNE, "An After-Heater for Use with High-Temperature Vertical Crystal Pullers", *J. Sci. Inst.* **41** (1964) 647.

The imperfections resulting from stresses in the crystals, arising from excessive thermal gradients, can be reduced by providing additional heating above the growth interface. In the simplest form, this can be achieved by providing heat-shielding round the pulled crystal. In the work described, ceramic alumina tubes were used for $CaWO_4$ crystals grown for lasers. An appreciable improvement in quality resulted.

21. J. J. RUBIN and R. A. THOMAS, "Preparation and Fabrication of Molybdate Single Crystals for Optical Maser Studies", *J. Amer. Ceram. Soc.* **48** (1965) 100.

Large crystals of $CaMoO_4$ were grown by Czochralski pulling. The addition of Nb^{5+} as a charge-compensator enabled high quality crystals of $CaMoO_4{:}Nd^{3+}$ to be produced.

22. P. S. SCHAFFER, "Vapour Phase Growth of Single Crystals", US Air Force Contract No. AF19(628)-2383, Final Report, Lexington Laboratories Inc (January 1964).

The growth of small Al_2O_3 platelets and whiskers by vapour transport in wet hydrogen has long been known. This work described a controllable reaction which led to growth on seed crystals. The basic process involves reacting $AlCl_3$ vapour, CO_2, and H_2. The material produced has a low etch pit concentration ($\sim 10^2/cm^2$) and an impurity level of 40 ppm.

This type of vapour deposition technique offers the advantage of control of reactant concentrations, and hence growth rates, by pressure regulation. The complexity of the equipment needed and the comparatively slow growth rate detract from advantages it may have over the Czochralski technique. It is nevertheless a powerful technique which should find application to other refractory oxides.

23. F. STERZER, D. BLATTNER and S. MINITER, "Cuprous Chloride Light Modulators", *J. Opt. Soc. Amer.* **54** (1964) 62-8.

The use of CuCl crystals as a light modulator for lasers resulted in attention being diverted to this material. The structure transition at 407° C from wurtzite to blende forms prevented growth from the pure melt. A flux was used to depress the melting point to a temperature below the transition temperature.

24. L. G. VAN UITERT, W. G. GRODKIEWICZ and E. F. DEARBORN, "Growth of Large Optical-Quality Yttrium and Rare-Earth Aluminium Garnets", *J. Amer. Ceram. Soc.* **48** (1965) 105-8.

Two improvements to the usual fluxed-melt process are claimed. Firstly, the addition of 2 wt % B_2O_3 to suppress excessive nucleation and give larger crystals; secondly, the use of excess Al_2O_3, which leads to the initial formation of corundum crystals and lowers the lead content of the garnet crystals. The beautiful crystals illustrated apparently justify these claims.

25. L. G. VAN UITERT and R. R. SODEN, "Single Crystal Tungstates for Resonance and Emission Studies", *J. Appl. Phys.* **31** (1960) 328-30.

This early work on tungstate crystals grown from the fluxed melt illustrates the usefulness of this technique for the provision of small crystals for preliminary studies. Crystals of $MgWO_4$, $ZnWO_4$, $CdWO_4$, $CaWO_4$, $SrWO_4$, and $BaWO_4$ were grown from Na_2WO_4-WO_3 melts by slow cooling. Crystals up to 10 mm in length were obtained. Specimens of $NaYW_2O_8$ were also grown.

Since this publication, several of these crystals have been grown in more massive form by pulling and have been the subject of extensive investigations.

26. E. A. D. WHITE and J. W. BRIGHTWELL, "The Growth of Ruby Crystals from Solution in Molten Lead Fluoride", *Chem. and Ind.* (September 1965) 1662-8.

The work reported describes the application of the flux technique, on a reasonably large scale, to the growth of highly perfect crystals. The details of the experimental conditions given warrant inclusion of this reference (cf. reference 1).

27. W. R. WILCOX and L. D. FULLMER, "Turbulent Convection in Czochralski Crystal Growth", *J. Appl. Phys.* **36** (1965) 2201.

Convection was observed visually and by measurement with thermocouples in melts of CaF_2. Fluctuations of 30° C caused growth rate fluctuations and gave rise to striations in the crystals. The temperature fluctuations were reduced or eliminated by reduction of the vertical gradient by using reflectors and after-heaters around the crystal. An additional benefit of after-heating is suggested, which is of importance in relation to the gross striation effects so troublesome in the pulling of doped crystals.

3. Magnetic Materials

Following early work on the growth of spinel-type ferrite crystals by fluxed-melt, Verneuil, and hydrothermal techniques, the discovery of the ferrimagnetic properties of YIG opened an enormous field for further crystal growing. The incongruent melting of YIG has led to the use of a variety of techniques for its growth; the most successful, however, is probably the fluxed-melt process. The current interest in ferrites for microwave devices has fostered the growth of hexagonal ferrite crystals related to the β-alumina structure for device studies, as well as the growth of a wide variety of transition metal and rare earth oxides for fundamental investigations.

28. I. L. ABERNATHY, T. H. RAMSEY, JR, and J. W. ROSS, "Growth of YIG Single Crystals by the Floating-Zone Technique", *J. Appl. Phys.* **32** (1961) 376S.

A vertical floating-zone apparatus employing RF heating and a $MoSi_2$ susceptor was used to melt a polycrystalline rod. It was necessary to grow from an iron-rich melt because of the incongruence at the melting point. An oxygen atmosphere of 7 kg/cm² was used, and a 0.6 cm diameter rod was traversed at 0.25 cm/h. A line width of 1 to 2 Oe was obtained.

Next to the fluxed-melt technique, this is probably the most successful growth of YIG; it could well be of value if the need for large specimens becomes acute. The comparatively high line width may reflect the purities of the materials used.

29. R. E. BARKS, D. M. ROY and W. B. WHITE, "Growth of Haematite Crystals by the Flux Method", *Ceram. Bull.* **43** (1964) 255.

Platy crystals of α-Fe_2O_3 were grown from solution in $Na_2B_4O_7$ by cooling at a comparatively fast rate of 45° C/h. Crystals up to 6 mm across were claimed, the addition of ZnO to the melt giving enhanced size without contamination.

30. G. P. ESPINOSA and S. GELLER, "Growth of Single Crystal Garnets of the System $(Bi_{3-2x}Ca_{2x})Fe_2(Fe_{3-x}V_x)O_{12}$", *J. Appl. Phys.* **35** (1964) 2551.

In addition to the constituents implied in the title, excess Bi_2O_3 or Bi_2O_3 + PbO was used as the solvent. Crystals were grown by slow cooling from 1200° C to about 1000° C at 3 to 10° C/h. Crystals of composition $x = 1.36$ were grown, but the end member $x = 1.5$ was not obtained.

The problem of determining the ionic or molecular species in the solution would appear to be severe. However, this example illustrates the usefulness of the technique for the preparation of crystals of complex composition.

31. R. J. GAMBINO and F. J. LEONHARD, "Growth of Barium Ferrite Single Crystals", *J. Amer. Ceram. Soc.* **44** (1961) 221-4.

Hexagonal crystals of up to 13 mm edge were grown from solution in Na_2CO_3, by slow cooling at 0.75 to 4 deg/h from 1375° C. Crystals of this type are of interest as hard magnetic materials; the method provided a means of growing a variety of Ba and Sr compounds suitable for microwave measurements.

32. F. H. HORN, "Growth of Single Crystal Iron Ferrites by the Czochralski Method", *J. Appl. Phys.* **32** (1961) 900-1.

The application of the pulling technique to ferrite crystal growing yielded specimens of mixed ferrite, such as $Zn_xFe_{3-x}O_4$. Iridium crucibles were used in a CO_2 atmosphere. Heat reflectors reduced thermal gradients in the crystal, and suppressed oxidation of the surface of the grown crystal.

33. W. KUNNMANN, A. FERRETTI and A. WOLD, "Flux Growth of $NiFe_2O_4$ Crystals by the Czochralski Method", *J. Appl. Phys.* **34** (1963) 1264.

A combination of Czochralski pulling and fluxed-melt growth yielded crystals of about 1 cm^3 volume. The very slow rate of pulling (about 0.8 mm/day) hardly warrants such a description and is a far cry from the original Czochralski process. The flux used was $Na_2Fe_2O_4$ and growth was initiated on a water-cooled platinum probe.

34. W. KUNNMANN, A. WOLD and E. BANKS, "Cobalt Ferrite Crystal Growth from the Ternary Flux System Na_2O-CoO-Fe_2O_3", *J. Appl. Phys.* **33**(suppl.) (1962) 1364-5.

An earlier paper describing similar growth and nucleation of $CoFe_2O_4$ crystals without the refinement of pulling. A mixture of $CoFe_2O_4$ and $Na_2Fe_2O_4$ in ratio 3:2 was heated to 1350° C and cooled at 2 deg/h. The cold-finger technique for nucleation gave crystals 25 mm diameter by 18 mm length. Isotherms for the Na_2O-CoO-Fe_2O_3 ternary system are given.

35. R. A. LAUDISE and E. D. KOLB, "Hydrothermal Crystallisation of Yttrium Iron Garnet on a Seed", *J. Amer. Ceram. Soc.* **45** (1962) 51-3.

A further process for YIG growth. The slow growth rates (0.08 mm/day) and the development of the flux process to give larger and more perfect crystals appear to have discouraged the development of the hydrothermal technique. It is worth recording as an example of the forgotten versatility of the hydrothermal process.

36. R. A. LAUDISE, R. C. LINARES and E. F. DEARBORN, "Growth of Yttrium Garnet on a Seed from a Molten Salt Solution", *J. Appl. Phys.* **33**(suppl.) (1962) 1362-3.

The first recorded successful growth of YIG on a seed using the flux technique. The record is also notable for the use of a temperature gradient to transport source material to the crystal growing zone via a baffle. However, it was found necessary to slowly cool in addition, to avoid re-solution of the seed crystal. Barium borate was used as solvent.

Although the products appear to offer little advantage over crystals grown from PbO-PbF_2 melts, the control of nucleation and transport in this process make it attractive for future development.

37. R. C. LINARES, "Growth of Yttrium-Iron Garnet from Molten Barium Borate", *J. Amer. Ceram. Soc.* **45** (1962) 307-10.

Although duplicating to some extent the information recorded in reference 36, the present work is of interest as in addition it briefly refers to the growth of crystals of YBO_3, ZnO, $YAl_3B_4O_{12}$, TiO_2, ZrO_2, CeO_2, and ThO_2 from barium borate melts. No indication of the crystal size obtainable is given, and, from the compiler's experience, in some cases it can be very small indeed.

38. R. C. LINARES, "Growth of Single Crystal Garnets by a Modified Pulling Technique", *J. Appl. Phys.* **35** (1964) 433.

This later paper reports the continued development of garnet growth from barium borate flux. Reasonably full experimental details are given and, characteristically, it is reported that sapphire, $LiFe_5O_8$, $TbPO_4$, and CaF_2 crystals were also grown.

39. J. W. NIELSEN, "Improved Method for the Growth of Yttrium-Iron and Yttrium-Gallium Garnets", *J. Appl. Phys.* **31** (1960) 515-25.

The improved flux composition for the growth of garnet crystals has been the basis for the majority of the YIG crystals produced by the flux method. Its success may be judged from the following reference.

40. J. W. NIELSEN, "Big YIG's Grow in Salt", *Electronics* **44** (January 1964).

This popularised article describes crystals up to 300 g with line widths of 0.3 Oe or less, obtained from lead salt solutions. The necessity for good temperature control and the use of large crucibles is emphasised. ZnO, ruby, and Ga or Al garnet crystals were also grown.

41. R. P. POPLAWSKY, "Ferrite Crystals Grown Using an Arc-Image Furnace", *J. Appl. Phys.* **33** (1962) 1616-7.

The advantages of the arc-image furnace with respect to atmosphere control are particularly appropriate for the growth of ferrite crystals. Growth rates of 0.5 mm/min were achieved by establishing a floating molten zone at the junction of two cylinders of ferrite.

42. J. P. REMEIKA, "$GaFeO_3$: A Ferromagnetic-Piezoelectric Compound", *J. Appl. Phys.* **31**(suppl.) (1960) 263-4.

J. P. Remeika's prowess in exploiting the fluxed-melt process is demonstrated with the growth of $Ga_{2-x}Fe_xO_3$ from solution in Bi_2O_3-B_2O_3 mixtures by slow cooling. The value of x is determined by the Fe_2O_3:Ga_2O_3 ratio used and by the temperature of crystallisation.

43. R. O. SAVAGE and A. TAUBER, "Growth and Properties of Single Crystals of Hexagonal Ferrites", *J. Amer. Ceram. Soc.* **47** (1964) 13-8.

The growth of ferrite crystals based on the β-Al_2O_3 structure has been developed to give several variations including those designated Y, Z, U, and W. Solutions containing $NaFeO_2$, Fe_2O_3, BaO, and MeO (where Me $\equiv$ Zn, Co, Ni, or Mg) were slow cooled from temperatures above 1250° C. A vertical temperature gradient of 20 to 30° C was used to promote circulation in the crucible.

44. M. SCHIEBER and L. HOLMES, "Crystal Growth and Magnetic Susceptibilities of Some Rare-Earth Sodium Molybdenum Scheelites", *J. Appl. Phys.* **35** (1964) 1004.

The crystals were grown by slow cooling a ternary melt, R_2O_3-Na_2O-MoO_3 (where R $\equiv$ rare earth). The compositions, $Na_2R_2Mo_4O_{16}$, are derived by substituting Na + R for the divalent ions in the usual scheelite compounds, in the manner used for charge compensation in laser crystals.

45. G. A. SLACK, "$FeAl_2O_4$-$MgAl_2O_4$: Growth and Some Thermal, Optical and Magnetic Properties of Mixed Single Crystals", *Phys. Rev.* **134** (1964) A1268-80.

The crystals were produced by a modified Bridgman technique in which a graded RF coil was moved upwards past a stationary coil at 1 cm/h. An interesting modification of the usual type of Bridgman apparatus, which is convenient for high temperature operation.

46. H. J. VAN HOOK, "Thermal Stability of Barium Ferrite ($BaFe_{12}O_{19}$)", *J. Amer. Ceram. Soc.* **47** (1964) 579-81.

It was found that barium ferrite crystallises congruently from the melt under an oxygen pressure of 40 atmospheres at 1540° C. The work was carried out in a pressure vessel internally heated by a Pt/Rh-wound furnace, which unfortunately is not described. The use of this technique for other ferrites would be useful.

47. D. G. WICKHAM, "Use of Lead Pyrophosphate as a Flux for Crystal Growth", *J. Appl. Phys.* **33** (1962) 3597-8.

A novel flux was used for the growth of $MgFe_2O_4$ and Fe_2O_3 crystals by slow cooling. The advantage claimed for $Pb_2P_2O_7$ was the low volatility, but the crystal products were not outstanding in any particular.

4. Semiconductor Materials

The growth of conventional semiconductor crystals is now a well-established industry and has led to the development of sophisticated and well-engineered pulling equipment. Other familiar materials have been produced by a variety of directional-freezing techniques, which need little description. The references described below deal with less familiar materials, or with new techniques which have evolved in recent years.

48. J. J. BARLIČ, "Single Crystal Pulling without Temperature Programming", *J. Sci. Inst.* **42** (1965) 361-2.

An ingenious arrangement in which a molten layer is formed in a restricted hot zone. The rate of feed of polycrystalline ingot is balanced by the rate of withdrawal of the crystal; regulation of crystal diameter occurs automatically, according to the position of the melt level with respect to the temperature gradient. The process is probably limited to materials which can be melted in silica tubes.

49. R. L. BARNES and W. C. ELLIS, "Whisker Growth of GaAs and GaP Grown by the Vapour-Liquid-Solid Mechanism", *J. Appl. Phys.* **36** (1965) 2297.

The V-L-S growth technique is one of the few new processes which have appeared recently. As the name implies, it involves three phases and bears some relationship to solution growth, vapour transport, and travelling solvent techniques. Following its discovery for Si crystal growth (R. S. WAGNER and W. C. ELLIS, "The Vapour-Liquid-Solid Mechanism of Crystal Growth and its Application to Silicon", *Trans. Amer. Inst. Min. Metall. Engrs.* **233** (1965) 1053-64), it has now been applied to other materials and has been investigated in greater detail. In the present work, the metals Au, Pd, Pt, and Ga were used to provide the liquid layer on which the crystal material condenses from the vapour and from which it solidifies on to the substrate.

50. G. E. J. BECKMANN, "The Growth of Silicon Carbide from Molten Silicon", *J. Electrochem. Soc.* **110** (1963) 84-6.

Examples of solution growth for non-metallic crystals other than oxides are comparatively few. In the present instance, higher temperatures than those normally used for fluxed-melt growth are involved (e.g. 1450 to 2600° C), but the growth rates are also higher. Both α and β forms of SiC were obtained.

51. J. S. BERKES, W. B. WHITE and R. ROY, "Growth of Controlled Composition Non-Stoichiometric Rutile from Borate Fluxes", *Ceram. Bull.* **43** (1964) 255.

Crystals were grown from $Na_2B_4O_7$-B_2O_3 solution at 1200° C under oxygen partial pressures of $10^{-0.7}$ to 10^{-12} torr. The products were prisms up to 15 mm in length and varied in colour from yellow to black. The use of the flux technique under such conditions is interesting and suggests that it may be usefully applied to the growth of sub-oxides of transition elements.

52. J. C. BRICE and P. A. C. WHIFFIN, "The Temperature Distribution in Pulled Germanium Crystals during Growth", *Solid State Electronics* **7** (1964) 183-7.

Fine thermocouples were grown into the crystal and used to measure supercooling at the interface. Values of the thermal conductivity of the solid and liquid phases were deduced. This work is an example of the imaginative yet simple approach to the study of crystal growth processes, which is too often omitted.

53. J. D. BRODER and G. A. WOLFF, "A New Method of GaP Growth", *J. Electrochem. Soc.* **110** (1963) 1150-3.

The need for a distinction between the terms *method*, *process*, and *techniques* is illustrated here. The method involved is basically a modification of the Pfann travelling solvent technique. A thin layer of a solution of GaP in Ga was made to traverse a polycrystalline specimen of GaP heated by induction.

54. R. T. DELVES, "Constitutional Supercooling and Two-Liquid Growth of HgTe Alloys", *Brit. J. Appl. Phys.* **16** (1965) 343.

A novel technique, which has the advantage of low temperature solution growth without the disadvantage of constitutional supercooling. However, it is restricted in its applicability, since it requires equilibrium of the solid with two immiscible liquids which preferably differ markedly in density. It was successfully applied by the author to the Hg-Te and Hg-Mn-Te systems.

55. L. B. GRIFFITHS and A. J. MLAVSKY, "Growth of α-SiC Single Crystals from Chromium Solutions", *J. Electrochem. Soc.* **111** (1964) 805-10.

Another example of solution growth of SiC. The interest here lies in the use of a thin film passage technique (reference 53) to recrystallise a layer of SiC on a SiC substrate. Lasing action at the p-n junction formed between the seed and new growth was claimed.

56. G. HAACKE and G. A. CASTELLION, "Preparation and Semiconducting Properties of Cd_3P_2", *J. Appl. Phys.* **35** (1964) 2484.

An example of the application of a vapour phase technique to new semiconductor materials. The crystals were formed by passing a sealed evacuated tube through a temperature gradient at a slow speed. Transport in a Hg atmosphere gave the largest crystals (2 cm length).

57. D. E. HARRISON and W. A. TILLER, "Growth of Large Single Crystals of Hexagonal Se from the Melt at High Pressures", *J. Appl. Phys.* **36** (1965) 1680.

The freezing point of Se is increased by pressure, and it was found that crystals could be grown at rates several orders of magnitude faster than at ordinary pressures. Crystals up to 1 cm diameter by 10 cm length were grown at 5 kbar.

58. J. HOLT, "Refining and Growth of Rutile Single Crystal by RF Zone Melting", *Brit. J. Appl. Phys.* **16** (1965) 639-44.

Zone refining has seldom been applied to materials other than metals, semimetals, and low melting point compounds. The application to a comparatively refractory oxide is of great interest. The comparatively high electrical conductivity of oxygen-deficient TiO_2 allowed RF heating by direct coupling.

59. D. W. F. JAMES and C. LEWIS, "Si Whisker Growth and Epitaxy by the Vapour-Liquid-Solid Mechanism", *Brit. J. Appl. Phys.* **16** (1965) 1089.

The reduction of silicon tetrachloride by hydrogen was used to deposit Si via thin liquid alloy zones of Au/Si and Ni/Si on to single crystal substrates. The use of Au film gave epitaxial layers and whiskers, while Ni film gave random growth. A further example of the potentially important V-L-S method.

60. E. P. A. METZ, R. C. MILLER and R. MAZELSKY, "A Technique for Pulling Single Crystals of Volatile Materials", *J. Appl. Phys.* **33** (1962) 2016-7.

The use of a non-volatile, non-reactive liquid of lower density than the melt to prevent sublimation of volatile constituents is described. Crystals of PbTe and PbSe were grown using B_2O_3 as the confining liquid. The solution to this particular problem is much simpler than the use of complex apparatus in a high ambient temperature.

61. A. I. MLAVSKY and M. WEINSTEIN, "Growth of GaAs from Gas by Travelling Solvent Method", *J. Appl. Phys.* **34** (1963) 2885-92.

A detailed account of the use of the thin film travelling solvent technique is given. Crystals, 6 mm diameter × 6 mm long, were grown in a temperature gradient of 1.5 to 2 deg/ml at 900° C. The method was claimed also to have been used for the growth of GaP from Ga, SiC from Cr, and $SrTiO_3$ from $BaO\text{-}B_2O_3$. The latter example illustrates the applicability of the thin film configuration to fluxed-melt systems for oxide materials.

62. R. NITSCHE, H. U. BOLSTERLI and M. LICHTENSTEIGER, "Crystal Growth by Chemical Transport Reaction, I", *J. Phys. Chem. Solids* **21** (1961) 199.

The wide applicability of the vapour phase transport technique is illustrated here by the growth of binary, ternary, and mixed crystal chalcogenides. A disadvantage of the process would seem to be the probable incorporation of halogen in the crystal products.

63. A. C. PRIOR, "Growth from the Vapour of Large Single Crystals of Lead Selenide of Controlled Composition", *J. Electrochem. Soc.* **108** (1961) 82-7.

Large and good quality crystals of PbSe were grown by sublimation of the material. The apparatus used enabled the Pb:Se ratio to be varied by controlling the partial pressure of Se during growth. This technique is appropriate to a wide variety of semiconductor materials containing an easily volatilised component.

64. M. WEINSTEIN and A. L. MLAVSKY, "Growth of GaP Crystals and p-n Junctions by a Travelling Solvent Method", *J. Appl. Phys.* **35** (1964) 1892-4.

The authors, having exchanged roles (cf. reference 61), report the application of the thin film travelling solvent process to GaP crystals. Growth rates of 0.5 mm/h are claimed, using a Ga zone of 0.025 mm thickness. The p-n junctions were formed by using a 2% Ge-Ga solvent zone.

5. Refractory Materials and Synthetic Minerals

For convenience, the opportunity is taken to include in this section some crystals which are of interest from the point of view of mineral synthesis rather than for their heat-resisting properties.

65. S. AUSTERMAN, "Growth of Beryllia Single Crystals", *J. Amer. Ceram. Soc.* **46** (1963) 6-10.

The fluxed-melt technique was used for the growth of

BeO crystals from Li_2MoO_4:MoO_3 solutions, by evaporation of MoO_3. It has been shown that the solubility of BeO in these solutions is related to the MoO_3 content, and that they may be regarded as solutions of BeO in MoO_3, to which Li_2MoO_4 is added to suppress the vapour pressure of MoO_3.

The useful solvent properties of Li_2MoO_4:MoO_3 have also been demonstrated by other workers for a variety of oxide materials. It has the advantages of being water-soluble, non-toxic and has a conveniently low melting point.

66. A. A. BALLMAN, "A New Series of Synthetic Borates Isostructural with the Carbonate Mineral Huntite", *Amer. Miner.* **47** (1962) 1380-3.

New materials with the general formula $RAl_3B_4O_{12}$, where R is a rare earth ion, were prepared by the fluxed-melt process. In two cases, the $RCr_3B_4O_{12}$ compounds were prepared. The solvents used were K_2SO_4-MoO_3 and PbF_2-B_2O_3 mixtures. Crystals up to 10 mm in size were obtained by slow cooling.

67. A. B. CHASE and J. A. OSMER, "Synthesis of Thorianite Crystals from Bismuth Oxide-Lead Fluoride Melts", *Amer. Miner.* **49** (1964) 1469-71.

Crystals of ThO_2 up to 6 mm across were grown from solution in PbO-PbF_2, Bi_2O_3-PbF_2, and PbF_2 melts. The Bi_2O_3-PbF_2 mixtures were considered to give the best results. Crystals were grown by the conventional slow cooling process with spontaneous nucleation.

68. C. B. FINCH and G. W. CLARK, "Single Crystal Growth of ThO_2 from Lithium Ditungstate Solvent", *J. Appl. Phys.* **36** (1965) 2143.

An alternative fluxed melt for ThO_2 growth, but in this instance a temperature gradient was used to transport nutrient material to seed crystals. Crystals doped with lanthanide elements were also grown. The multi-purpose additive, B_2O_3, was used in this work to increase growth rates.

69. C. B. FINCH, L. A. HARRIS and G. W. CLARK, "The Thorite-Huttonite Phase Transformation as Determined by Growth of Synthetic Thorite and Huttonite Single Crystals", *Amer. Miner* **49** (1964) 782-5.

Although the applicability of the results (thorite formed below 1225° C and huttonite above) to conditions other than those used might be questioned, successful growth of $ThSiO_4$ crystals from alkali ditungstate or dimolybdate melts using a temperature gradient process was achieved. This work is of interest as an example of the use of the solution technique to prepare crystals at a temperature below that at which a structure transition occurs.

70. R. J. GAMBINO, "Growth of Europium-Doped Single Crystals of BaO and SrO", *J. Appl. Phys.* **36** (1965) 656.

An example of the use of the induction-coupled plasma torch. Powders fed through the plasma in the normal manner vapourised, and an oblique arrangement of the torch was used in which the powder was passed through the cooler tip of the hot gas stream. The plasma torch obviously presents severe difficulties in its use for crystal growing, and in the present case the problems have been overcome by a somewhat awkward arrangement. It would seem preferable to reduce the heat of the plasma by operation at lower pressures.

71. F. A. HALDEN and R. SEDLACEK, "Verneuil Crystal Growth in the Arc-Image Furnace", *Rev. Sci. Inst.* **34** (1963) 622-6.

The arc-image furnace, used as a heat source for crystal growth by the Verneuil process, offers advantages with respect to atmosphere control and temperature stability. It is particularly appropriate for the growth of materials which require reducing conditions, but initially it has been used by the authors for the growth of TiO_2, Al_2O_3, $MgAl_2O_4$, CaO:ZrO_2, and other refractory oxide materials. Surprisingly little information on its use for other materials has been forthcoming.

72. W. JORDAN and J. J. NAUGHTON, "Growth of Forsterite Crystals in a Reactive Crucible", *Amer. Miner.* **49** (1964) 806-8.

An unusual process in which pellets of forsterite composition are fed into a graphite susceptor shaped like a Bridgman crucible. Considerable evolution of gas occurs by reaction with the crucible, which tends to limit contact between the crucible and contents. Crystals were grown by lowering the crucible through the RF work coil. The applicability of this process appears to be limited.

73. R. C. LINARES, "The Growth of Refractory Oxide Single Crystals", *J. Appl. Phys.* **33** (1962) 1749-59.

The fluxed-melt process was used for the growth of a variety of materials including Al garnets, rare earth aluminates, spinels, β-Al_2O_3-type materials, α-Al_2O_3, BeO, MnO, and $GaFeO_3$. This work provides convincing evidence of the versatility of solution growth for oxides.

74. K. NASSAU and A. M. BROYER, "Application of Czochralski Crystal Pulling Technique to High-Melting Oxides", *J. Amer. Ceram. Soc.* **45** (1962) 474-8.

The authors describe the use of the pulling technique to a number of oxide materials including $CaWO_4$, TiO_2, $BaTiO_3$, and ferrite crystals. The melt is heated by RF in a Rh crucible which is also the susceptor. The criteria for the applicability of the technique are discussed.

75. T. B. REED, "Growth of Refractory Oxide Crystals Using the Induction Plasma Torch", *J. Appl. Phys.* **32** (1961) 2584-5.

The first description of a plasma generated by RF induction used as a heat source for Verneuil-type crystal growing. The difficulties associated with this very high temperature heat source have been referred to in reference 70. Apart from crystal growing, the process is also of interest for the preparation of spheroidal refractory powders.

6. Miscellaneous Materials

Many different crystals have been prepared in recent years in the search for new and improved materials for electronic devices, as well as for fundamental research purposes. Some of these have occurred incidentally; for example, in studies of fluxed-melt systems. It is difficult to classify some of these materials, which are of interest in more than one respect, and consequently they are amalgamated in this section.

76. L. M. BELYAEV, G. P. SHAKNOVSKOI, S. P. SMIRNOV and J. P. KUZ'MINA, "Preparing Crystals of CdS at High Pressures", *Soviet Physics Crystallography* **6** (1962) 516-8.

Crystals were grown from the melt in graphite crucibles and an inert atmosphere, at pressures ranging from 150 to 180 atmospheres. This is one of the few examples of crystal growth under high pressure conditions – presumably the complexity of the high pressure apparatus deters more widespread application of such techniques.

77. F. BERTAUT, F. FORRAT and P. F. FANG, "Growth of Rare Earth Manganites", *Compt. rend.* **256** (1963) 1958.

Crystals were prepared by slowly cooling melts containing Mn_2O_3, R_2O_3, and BiO_3 (where R ≡ rare earth). Growth by evaporation of Bi_2O_3 at constant temperature was also employed. The crystals are reported to be ferroelectric.

The term "manganite" is presumably used in an analogous manner to "ferrite".

78. F. BROWN and W. H. TODT, "Floating Zone $BaTiO_3$: Preparation and Properties", *J. Appl. Phys.* **35** (1964) 1594-8.

This work is unusual in the application of the floating zone technique to $BaTiO_3$ and in the use of gas burners to provide the molten zone. Boules, 2.5 cm length by 0.32 cm diameter, of ferroelectric $BaTiO_3$ containing 1.5 % $SrTiO_3$ were grown. The additive was used to avoid the troublesome hexagonal-cubic transition in melt-grown $BaTiO_3$.

79. R. A. LAUDISE, E. D. KOLB and A. J. CAPORASO, "Hydrothermal Growth of Large Sound Crystals of Zinc Oxide", *J. Amer. Ceram. Soc.* **47** (1964) 9-12.

The careful and detailed work by the Bell Telephone Laboratories team on the hydrothermal growth of quartz is repeated for ZnO. This material is of considerable current interest, both as a piezoelectric and as a semiconductor material.

80. R. C. LINARES and A. D. MILLS, "Growth of $7ZnO.Sb_2O_5$ Spinel Crystals", *Acta Cryst.* **15** (1962) 1048.

Crystals of this unusual spinel composition were grown as octahedra, with edges up to 6 mm long, by slowly cooling solutions in PbF_2, $Na_2B_4O_7$, and $Zn_3(PO_4)_2$. Apart from demonstrating the near-universal solvent properties of PbF_2, the use of another phosphate flux is of interest (see reference 47). The properties of this defect spinel are not recorded, but its formula is more recognisable if written – $(Zn,Sb)_3O_4$.

81. J. W. NIELSEN and E. F. DEARBORN, "The Growth of Large Single Crystals of Zinc Oxide", *J. Phys. Chem.* **64** (1960) 1762-3.

This records earlier work on ZnO growth from solution in lead fluoride by slow cooling. The process was presumably superseded by hydrothermal growth and was probably useful for provision of seed crystals for that work.

82. J. W. NIELSEN, R. C. LINARES and S. E. KOONCE, "Genesis of the Barium Titanate Butterfly Twin", *J. Amer. Ceram. Soc.* **45** (1962) 12-7.

The mysteries of the growth process of the butterfly twin crystal, by the technique devised by Remeika, are finally cleared up. Unlike most examples of fluxed-melt growth, the formation of the crystals depends on the presence of undissolved crystal nuclei and on a relatively rapid cooling rate. The effect of the size of the persistent nuclei is described.

83. T. B. REED and W. J. LAFLEUR, "Vapour Growth of SnO_2 Crystals", Lincoln Lab. Report No. 1 (1963) 19.

An unusual and apparently crude, if successful, process for growing SnO_2 crystals is described. An oxy-hydrogen burner of the premix type was used to heat a charge of SnO_2 in a muffle, at 1700 to 1800° C. Crystals several cm in length were obtained. These tended to be hollow at the lower growth temperatures.

84. J. P. REMEIKA and A. A. BALLMAN, "Flux Growth, Czochralski Growth and Hydrothermal Synthesis of Lithium Metagallate Single Crystals", *Appl. Phys. Letters* **5** (1964) 180.

One of the latest piezoelectric crystals to be discovered, $LiGaO_2$ can be crystallised by a variety of techniques. The authors are to be commended for saving time and space by condensing their publications.

85. D. B. ROGERS, A. FERRETTI and E. J. DELANEY, "Single Crystal Growth of V Spinels by Electrolytic Reduction", Lincoln Lab. Report No. 2 (1964) 73.

Electrolysis is seldom used for crystal growing. It is combined here with the fluxed-melt process for the preparation of $Co_{1+x}V_{2-x}O_4$ $(O<x<1)$. The value of x depended upon the composition of the melt and upon the temperature used. This combined process appears to be applicable to the growth of lower valency compounds of other oxide materials.

86. L. G. VAN UITERT and L. EGERTON, "Bismuth Titanate: A Ferroelectric", *J. Appl. Phys.* **32** (1961) 959.

Several complex ferroelectric materials have been prepared by incorporating Bi_2O_3 in titanate compositions. This material, $Bi_4Ti_3O_{12}$, was grown from solution in Bi_2O_3, and made use of the common ion to reduce unwanted flux contamination. A phase transformation at 643° C is considered to be the Curie point.

87. A. VON HIPPEL *et al*, "$BaTiO_3$ Crystals Pulled from Solution in $BaCl_2$ or TiO_2", MIT Lab. for Insulation Research, Tech. Report No. 178 (March 1963) 44.

Unlike conventional fluxed-melt growth, the proportions of solvent to solute are reversed here, to provide a comparatively slight lowering of the liquidus temperature. The growth conditions are consequently comparable with those for pulling crystals from heavily doped melts. The object of the flux addition is again to avoid the destructive hexagonal-cubic transition in $BaTiO_3$. Comparatively large "boules" of good quality were prepared.

88. R. W. WARREN, "Floating-Zone Growth of Single Crystal Alkali Halides", *Rev. Sci. Inst.* **33** (1962) 1378-86.

The application of floating-zone melting to poorly conducting materials using induction heating is discussed. In the case of alkali halides, it was necessary to preheat the materials to make them sufficiently conducting for RF coupling to occur. An example of the application of the floating-zone technique to nonmetals, which provides a means of obtaining high purity crystals.

89. YO MITA, "Growth of Zinc Sulphide Single Crystals from Fluxes", *J. Phys. Soc., Japan* **17** (1961) 784-7.

An unusual example of non-oxide crystal growth by the flux technique. Several halide fluxes as well as K_2S were used; the best of these were found to be NaCl and KCl. Crystals up to 10 mm in length were obtained by cooling the melts in silica tubes from 1070° C in an inert atmosphere. The crystals grown were presumably heavily doped with Cl.

7. Crystal Growth Techniques

This final section contains references to work on crystal growth processes where the emphasis is on the apparatus, mechanism, or technique, rather than on the materials grown. For those unfamiliar with general crystal growing technology, the applicability of the techniques to particular classes of materials may be ascertained by reference to the text books or review articles which are also included in this section.

90. G. A. CHADWICK, "Monotectic Solidification", *Brit. J. Appl. Phys.* **16** (1965) 1095.

The mechanism of the growth process used by Delves (reference 54) is considered, particularly with respect to the interfacial energies between the two immiscible liquids and the solid substrate. Changes in the magnitude of these energies can result in differences in the microstructure of the grown crystal.

91. T. CHERON, "Crystal Growth and Crystallography: A Literature Survey", Aerospace Corp. Report, USAF Contract No. 04(647)-930 AD 274,642 (1962).

A list of references with abstracts is given, of papers referring to materials which are of interest in electronic devices. These mainly cover the few years prior to 1962 and the list is not comprehensive.

92. G. R. CRONIN, M. E. JONES and D. WILSON, "The Growth of Crystals from Compounds with Volatile Components", *J. Electrochem. Soc.* **110** Sect. 1 (1963) 582-4.

An apparatus is described, in which the correct atmosphere necessary for growth is maintained by balancing the chamber pressure with an applied inert gas pressure. Examples of materials grown are InAs, GaAs, and PbTe.

93. D. B. GASSON, "The Preparation of Calcium Tungstate Crystals by a Modified Floating-Zone Recrystallisation Technique", *J. Sci. Inst.* **42** (1965) 114-5.

A clever device which employs an iridium strip heater to melt the end of a vertically-positioned polycrystalline rod. Holes in the strip allow molten material to pass through and crystallise on a seed. The feed rod moves vertically through the strip heater to give a long cylindrical crystal.

94. P. GERTHSEN, "Ein neues Verfuhren zur Kristallzüchtung von hochschmelzenden Stoffen", *Z. Angew Phys.* **15** (1963) 301.

The use of an electric arc for the production of a floating zone is described. Two electrodes were held horizontally on opposite sides of a vertically-mounted rod of the material to be melted, and two arcs were struck between the electrodes and the sides of the central rod. The molten zone so formed in the central rod carried the arc current. For materials which were poor conductors, or which could not be readily preheated a four-electrode system was used.

95. J. J. GILMAN (editor), "The Art and Science of Growing Crystals" (John Wiley, New York, 1963).

A collection of articles by leading authorities on a variety of crystal growing topics. Most growth techniques are included but the standard varies, as might be expected. A useful and reasonably up-to-date book which tries to reverse the emphasis of the title.

96. H. K. HENISCH, J. DENNIS and J. I. HANOKA, "Crystal Growth in Gels", *J. Phys. Chem. Solids* **26** (1965) 493-500.

An unusual process based on effects studied by Liesegang and others. Crystallisation occurs by reactants diffusing

through a silicic acid gel. It is particularly useful for the growth of materials with low solubilities, which cannot easily be prepared by other methods. The authors have prepared crystals of a number of metal citrates, oxalates, and tartrates, but have obviously not fully explored the limitations of the process. An interesting dependence of nucleation on U V irradiation was noted.

97. D. T. J. HURLE, "Mechanism of Growth of Metal Single Crystals from the Melt", *Progress in Materials Sci.* **10** (1962) 79-147.

A very comprehensive and complete review based on a thesis by the author. It is of particular interest with respect to imperfections in metal or semiconductor crystals.

98. R. W. JOHNSON, "Use of Induction Heating for Floating-Zone Melting above 2000° C", *J. Appl. Phys.* **34** (1963) 352-5.

The use of an eddy current concentrator to focus energy on a small length of 6 mm diameter rod is described. This equipment was used to zone-melt at temperatures above 2600° C. The advantages of the use of an inert atmosphere are emphasised, making the technique particularly suitable for refractory metals.

99. M. KESTIGAN, G. J. GOLDSMITH and M. HOPKINS, "A High Intensity Carbon-Arc-Image Furnace and its Application to Single Crystal Growth of Refractory Oxides", *J. Electrochem. Soc.* **111** (1964) 260-2.

The arc-image equipment described consisted of a pair of arcs with a double ellipsoid mirror optical system. This is a comparatively complex and refined version of the apparatus used by other workers. The asymmetric heating conditions resulting from this configuration seem to be a possible disadvantage.

100. R. A. LAUDISE and J. W. NIELSEN, "Hydrothermal Crystal Growth", "Solid State Physics, Vol. XXI", edited by F. Seitz and D. Turnbull (Academic Press, New York 1961) pp. 149-222.

A descriptive review of this valuable but not widely used technique. The authors are among the leading exponents of hydrothermal practice for research purposes.

101. J. C. LEWIS, B. REDFERN and F. C. COWLAND, "Vitreous Carbon as a Crucible Material for Semiconductors", *Solid State Electronics* **6** (1963) 251-4.

Vitreous carbon is a comparative newcomer to the materials field and is of some interest as a crucible material for crystal growing. Its particular virtues are associated with the high purity, high lustre, and mechanical strength. It is now commercially available in the form of boats and crucibles.

102. V. K. LYAPIDEVSKII and I. V. FALOMKIN, "The Influence of Ultrasonics on Directed Crystallisation", *Soviet Physics-Acoustics* **8** (1963) 288-9.

The influence of ultrasonics on segregation during freezing was studied using $KMnO_4$ solution. Improved segregation was obtained and attributed to improved solute transport in the liquid-solid boundary layer. The results obtained suggest that the application of ultrasonics to high temperature solution-growth techniques would be of value in improving solute rejection at the growth interface.

103. F. R. MONFORTE, F. W. SWANEKAMP and L. G. VAN UITERT, "RF Technique for Pulling Oxide Crystals without Employing a Crucible Susceptor", *J. Appl. Phys.* **32** (1961) 959-60.

A closely-wound RF coil with a water-cooled solid base was used to contain the melt. The cooling was sufficient to leave a layer of solid material, which acted as crucible for the melt. Auxiliary heating was necessary to make the material sufficiently conducting for coupling to the RF coil. Crystals of $MnFe_2O_4$ were grown, but it seems likely that the technique could not be applied to materials of lower electrical conductivity.

104. A. MUAN, "Silver-Palladium Alloys as Crucible Materials in Studies of Low Melting Iron Silicates", *Ceram. Soc. Bull.* **42** (1963) 344-7.

The use of crucible materials cheaper than platinium is of considerable interest for fluxed-melt growth.

105. T. B. REED and W. J. LAFLEUR, "Constitutional Supercooling in Iodine Vapour Crystal Growth", *Appl. Phys. Letters* **5** (1964) 191.

The work is particularly novel in applying the concept of constitutional supercooling, familiar in melt growing, to vapour phase growth. Iodine vapour, with argon as a carrier gas, was used, and the maximum velocity of gas to produce a smooth interface on a seed crystal was measured for different thermal gradients. This work could have a considerable bearing on several vapour growth processes in current use.

106. H. F. STERLING and R. W. WARREN, "High Temperature Melting without Contamination in Cold Crucibles", *Metallurgia* **67** (1963) 301-7.

The use of crucibles and boats constructed from water-cooled silver tubing for containing molten materials is described. The melt does not wet the silver surface and consequently contamination does not occur. These containers have introduced an important new technique in zone melting and crystal pulling by RF heating, since they can be used to contain materials at temperatures in excess of 2000° C. Crystals of refractory metals such as Nb and Mo, as well as metal borides, have been pulled using this equipment.

107. H. SASAKI and S. KISADA, "Raising Crucible Method for Growing Single

Crystals of Volatile Materials", *J. Appl. Phys., Japan* **3** (1964) 170.

A sealed ampoule containing the volatile material, and having a tapered top, is raised slowly through a temperature gradient to a cooler zone. Nucleation occurs at the constriction. The growth of HgS crystals is described.

108. J. L. TORGENSEN, A. T. HORTON and C. P. SAYLOR, "Equipment for Single Crystal Growth from Aqueous Solutions", *J. Res. Nat. Bur. Stand.* **67c** (1963) 25-32.

Crystal growth from aqueous solutions is still used for the production of ADP, EDT, and related crystals. Although comparatively little effort has been directed to the development of the technique in recent years, the apparatus described is probably the most refined of its type.

109. E. A. D. WHITE, "Crystal Growth Techniques", *GEC Journal* **31** (1964) 43-53.

The compiler may perhaps be forgiven for having the last word, by drawing attention to a simplified and condensed description of crystal growing methods which may be of value to those unfamiliar with some of the basic techniques referred to above.