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 PbF₂ 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 CaWO₄. 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.

Crystals of CaWO₄ 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.


Crystals of K(Nb,Ta)O₄ 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.


Chrysoberyl, Be₃Al₂O₆ and the chromium-doped form, alexandrite, are interesting materials structurally, chemically, and physically, as well as gemmologically. Crystals grown from PbO and from Li₂O-MoO₃ solutions, respectively, were obtained up to 10 mm across by slow cooling. Small crystals of Cr⁺BeO₂ were also obtained.


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.


The fluxed-melt technique was applied to the growth of Al₂O₃ and, for no obvious reason, the spinel, ZnAl₂O₄. Lead fluoride is well known as being a versatile solvent for fluxed-melt growth. Solubility data for the systems studied are given.


LaF₃, 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 La₂O₃, and crystals were pulled in a helium atmosphere from an iridium crucible. Crucible and crystal were rotated in opposite directions.


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.


The conventional form of flame-fusion apparatus has been used for comparatively few substances. The flame temperatures attainable using H₂/O₂ mixtures are just sufficient to melt some of the rare earth oxides. Crystals of Y₂O₃, Er₂O₃ and Yb₂O₃ 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.


Another successful synthesis of emerald crystals by the fluxed-melt technique. Solvents used were PbO-PbF₂, B₂O₃ and Li₂O-MoO₃. The best results were obtained from a complex mixture, BeO + Al₂O₃ + Li₂SiO₃ + Cr₂O₃ + MoO₃, by slow cooling. Growth on seed crystals was obtained.


The garnet structure has proved to be one of the most versatile for compositional variations. Following work on YIG (Y₂Fe₅O₁₂), 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 Y₂O₃ and Al₂O₃ in PbO-PbF₂. Crystals up to 13 mm across were obtained, although this has now been improved upon (see reference 24).


Crystals of beryl (undoped emerald) were grown by the fluxed-melt technique from a variety of solvents including Li₃Mo₂O₆, Li₂W₂O₆, PbMoO₄, PbWO₄, and V₂O₅; the latter was preferred.