Growth Of Oxides Single Crystals By The Optical Floating Zone Method

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ABSTRACT

Single crystals growth of various, congruently and incongruently melting oxides has been performed by the floating zone and traveling solvent techniques. In the case of incongruently melting materials the use of a carefully determined solvent allows the establishment of steady state much faster, leading to better, more stable growth conditions. As examples the growth of a few, different oxides are discussed.

INTRODUCTION: VERSATILITY LIMITATIONS OF THE METHOD

The floating zone technique using halogen lamps and ellipsoidal mirrors has been used for crystal growth of wide range of materials, from metals and semiconductors through to oxides including high temperature superconductors and new magnetic materials [1,2,3,4,5]

The crystals grown by the floating zone (FZ) technique are of high quality but relatively small (usually not bigger than few mm in diameter and few cm long), so most of the work has concentrated on new materials, mainly for research purposes. Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> [2,7,8] and TiO<sub>2</sub> [9] are the only oxides grown by this technique for industrial applications.

In this review, the advantages and disadvantages of the FZ technique for the growth of oxide crystals, both, congruently and incongruently melting as well as their solid solutions will be discussed, on the basis of work conducted at McMaster University and that found in the literature.

The most obvious advantages of the Floating Zone Technique come from the fact that:
- no crucible is necessary
- both, congruently and incongruently melting materials can be grown
- the relatively high thermal gradient on the crystallization front decreases the chance for constitutional supercooling and allows for more rapid growth of incongruently melting ones
- oxides melting as high as 2500 °C can be grown
- the growth can be conducted at high pressure (up to 10 atm) and in specific atmosphere
- solid solutions with controlled chemical composition can be prepared
- in contrast to crucible methods, a steady state can be achieved. This is beneficial for
crystal growth of doped materials (with distribution coefficient different than 1) and for
incongruent crystallization

The floating zone technique supported by other characterization methods (such as
differential thermal analysis (DTA) or X-Ray diffraction) is an effective way of
construction and investigation of phase diagrams.

This method has some disadvantages as well.

It is not suitable for materials
- with high vapor pressure
- low surface tension
- high viscosity
- materials which undergo a phase transition during cooling are also not suitable, as the
crystal usually crushes after growth.

Depending on the melting properties of the oxides either a direct crystallization
or a traveling solvent zone (TSZM) approach should be applied. These melting
properties are either known from previous work and published literature or - for new
materials and solid solutions - they must be assessed by the DTA.

EQUIPMENT

Optical furnaces

Three types of optical floating zone furnaces are commercially available, with
one (fig. 1), two (fig. 2) and four (fig 3) ellipsoid mirrors. They all employ halogen or
Xenon arc lamps of different power as an energy source and the experiment can be
carried in a controlled gas atmosphere at high pressure.

The price of the furnace is usually high and - even if the furnaces are relatively
simple to operate for routine growth, the process requires continuous attention and
understanding by the operator (especially if new approaches are being attempted). Even
if some attempts have been made with the automatic control of these machines [10] we
do not know any commercial systems offering this feature or of any paper in the
literature describing such automation.

Our crystal growth experiments have been performed in two image furnaces
installed in our laboratory. One is a two mirror NEC Apparatus (Fig 2), and the other one
is a four ellipsoidal mirror Crystal System Apparatus (Fig 3). There is one main
difference between these furnaces: in the Crystal System one the lamps move, whereas in
the NEC furnace the seed (and feed) rods move but the lamps stay in one position. This is an important difference which should be carefully addressed when discussing the values of feeding speeds.

Both furnaces are equipped with video cameras, allowing for the observation in situ of the crystal growth processes as well as for appropriate adjustment of the growth conditions.

**Other equipment**

Successful preparation of starting materials for crystal growth requires additional important equipment:
- muffle furnace, for preliminary ceramics preparation
- furnace with controlled atmosphere
- hydrostatic press
- grinders, pelletisers and ceramic and Pt containers

**MATERIALS PREPARATION**

The list of oxide materials grown in our laboratory includes $\text{Al}_2\text{O}_3$, $\text{TiO}_2$, $\text{Ga}_2\text{O}_3$, $\text{CuCo}_2\text{O}_4$, Yb$\text{Co}_2\text{O}_4$, La$_2$CuO$_4$, La$_3$Cu$_2$O$_6$, Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$, Y$_2$Ti$_2$O$_7$, SrCu$_2$(BO$_3$)$_2$, Sr$_2$RuO$_4$, Sr$_1$Ca$_2$Cu$_3$O$_{6+x}$ and Sr$_x$La$_{1-x}$MnO$_3$. Much wider list of oxide materials prepared by the optical floating zone technique in other laboratories is presented in Table 1.

**Ceramic rods preparation**

The stability of the growth process - and the quality of crystal obtained depend strongly on the quality of the ceramic rod which acts as the source of material for crystallization.

The first step is a typical powder synthesis. The batch of weighed appropriate powders is carefully prepared by ball mixing and by manual mixing using a mortar. The powders are pelletized and annealed at the appropriate temperature and for appropriate time. The quality of resulting ceramics is then assessed by X-ray diffraction and - if found correct - the material is re-grinded, formed as a rod (8 mm diameter and 120 mm long) by cold or hot pressing under 2500 bar and subsequently re-annealed (fig.4).

The density of these rods is measured as it is very material dependant and varies dramatically from 60 to 93% of the crystallographic density of the material. In many cases, when evaporation is not an issue it is advisable to pre-melt a ceramic rod before performing the final crystal growth. It was found to be especially important for slower grown, incongruently melting compounds (e.g. HTC superconductors).
Crystal growth process

For congruently melting materials (i.e. Al₂O₃, TiO₂, Ga₂O₃, CuGeO₃, YbCoGaO₄, Sr₂RuO₄, Y₂Ti₂O₇) the process starts by melting the tips of polycrystalline rods, bringing them together and establishing a liquid floating zone between the bottom (seed) rod and a top (feed) rod (Fig 5).

For the above mentioned oxides, the growth rates are relatively fast and vary from 1 to 25 mm/h. Both rods rotate in opposite directions for temperature uniformity as well as to mix material inside the molten zone. For compounds which undergo a peritectic transition [3,5] (incongruently melting materials, which decompose upon melting, leading to a new solid phase and a liquid of composition different from that of the original solid) a Traveling Solvent Zone (flux) approach is usually adopted [Fig 6].

This approach can be realized in two ways:

1. a flux pellet is synthesized and mounted between the feed and seed rods. As the temperature increases the flux pellet melts and the rods are joined. At this point the temperature has to be adjusted again carefully to allow for establishment of steady state conditions. The growth should initially be slow, sometimes as slow as 0.1 mm/h, allowing for crystallization of appropriate composition from the melt of different composition.

2. sometimes, mostly when a new material is being grown, it is advisable to start from the self-flux. In this case the zone is created by melting the ceramic rod and adjusting the temperature and growth speed until (thanks to precipitation of the high temperature solid phase) enough liquid is created to support the growth.

After quenching the zone can be analyzed and the composition of the flux can be assessed.

The examples of incongruently melting materials presented in this work are La₃CuO₄, Bi₂Sr₂CaCu₂O₈, Sr₂RuO₄, Sr₁₀Ca₁₀Cu₂O₄₁ and SrCu₂(BO₃)₂.

In any case it is easier to start the growth on a crystalline seed, as this facilitates the beginning of crystallization and prevents soaking of the molten zone into the porous seed rod. The quality of obtained crystals depends on the stability of the growth and the quality of the feed rod.

CHARACTERIZATION

Characterization of both prepared ceramics and the crystals grown depends on the material and on the information already available in the literature (the character and temperature of melting, crystallographic and physical properties).

Differential thermal analysis (DTA) was performed on all the samples, either to establish the melting properties of the material or to calibrate the furnaces.

Optical observation of crystals obtained under a polarizing microscope allowed us to observe the continuity of the growth process and to connect the changes in the
growth conditions with changes in grown material grown (fig 7).

All the materials, feed rods and resulting crystals were the subject of X-ray analysis. Powder diffraction allowed us to determine the uniformity of the material (address the problem of presence or absence of more than one phase).

The Laue technique was applied to orient the as-grown crystal boule. It also allowed to look for problems related to twinning and for an initial assessment of the crystallographic quality if obtained materials. Single crystal X-ray diffraction, supported by Guinier lattice constant assessment, lead to solving of crystallographic structure of the new materials (YbCoGaO₄).

Energy dispersive X-ray analysis (EDAX) and electron microprobe analysis (EPMA) confirm the exact chemical composition of the crystals and the solid solutions grown under different conditions and allow phase analysis of obtained materials. Physical properties of the grown oxides were generally investigated by the users of the crystals. The high temperature superconducting (HTS), magnetic (by SQUID and NMR), electrical and crystallographic properties are the most important ones.

In Table 1 the examples of crystals obtained as well as the growth conditions are presented.

CONCLUSIONS

This fascinating field of crystal growth is relatively unexploited. Recently, with a growing number of highly computerized furnaces operating the number of works reported on new and already studied materials is rising. Some of this work deal with the method itself, investigating temperature oscillations in the zone [11] and detailed lamp irradiation/thermal flows analysis [12].

In addition to the continuous preparation of new solid solutions of oxides displaying different and modified physical properties the future work will include:
- investigation of phase diagrams,
- understanding/assessing high temperature properties of molten oxides and salts
- correlation of crystal features with changes in the growth conditions
- creating a user friendly theoretical approach connecting crystal growth conditions with obtained results.

To achieve all this the continuous cooperation between a crystal grower and scientists who characterize the crystals is absolutely essential. Without good characterization of crystals grown, progress in crystal growth will be very slow.

ACKNOWLEDGEMENT

The continuous help and support of Drs Graeme Luke, John Preston, John E. Greedan and
A. Dabkowski is acknowledged. The help of Mr Marek Kiela with technical problems and Mr Israel Crooks and Jessie Gare in sample preparation is greatly appreciated. This work was supported by NSERC of Canada and by Materials and Manufacturing of Ontario.

REFERENCES

[11] [Balbaszow, private communication]

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[23.] Il, N. and Shindo, I., Single Crystal Growth of Akermanite (Ca₃MgSi₂O₇) and Gehlenite (Ca₃Al₂Si₂O₇) by the Floating Zone Method., Journal of Crystal Growth 46 (1979) 569-574


[27] Urushibara, A., Moritomo, Y., Arima, T., Asamitsu, A., Kido, G., Tokura, Y.,
Insulator-Metal Transition and Giant Magnetoresistance in La$_{1-x}$Sr$_x$MnO$_y$, Physical Review B Volume 51, Number 20


[42] Ito, T., Oka, K., New Technique for the Crystal Growth of La$_{1.6}$Ba$_x$Cu$_{2.4}$O$_y$ (x = 70.5), Physica C 231 (1994) 305-310


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(Ca,La)$_{1.6}$Cu$_{2.3}$O$_{4.1}$ and Observation of One-Dimensional Disorder, Journal of Crystal Growth 197 (1999) 825-832


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<th>Material</th>
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<td>6 70 atm O$_2$</td>
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Fig. 1 Schematic drawing of one mirror FZ furnace [2,19]

Fig. 2 Schematic drawing of two mirrors FZ furnace [NEC]

Fig. 3 Schematic drawing of four mirrors FZ furnace [3]

Fig. 4 Ceramic rod of SrCu₂(BO₃)₂ after annealing

Fig. 5 Crystal growth of congruently melting materials by FZ

Fig. 6 [5]

Fig. 7 Polished crosssection of Sr₁₄Cu₂₄O₄₁
Fig. 8 Crystals of congruently melting materials scale in mm

A Al₂O₃ : Cr ; B Y₂Ti₂O₇ ; C YbCoGaO₄

Fig. 9 Crystals of incongruently melting materials scale in mm

A La₂CuO₄ ; B SrCu₂(BO₃)₂ ; C crystals separated from grown Bi₂SrCa₂Cu₃O₈