Growth Of Oxides Single Crystals By The Optical Floating Zone Method

Hanna A. Dabkowska and Bruce D. Gaulin

Brockhouse Institute for Materials Research, and
The Department of Physics and Astronomy,
McMaster University,
1280 Main Street West,
Hamilton,
Ontario L8S 4M1,
Canada

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. $Y_3Fe_5O_{12}$ [2,7,8] and TiO_2 [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/and 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
- of 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 equipement

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 Al_2O_3, TiO_2, Ga_2O_3, $CuGeO_3$, $YbCoGaO_4$, La_2CuO_4, $La_2Cu_2CaO_6$, $Bi_2Sr_2CaCu_2O_n$, $Y_2Ti_2O_7$, $SrCu_2(BO_3)_2$, Sr_2RuO_4, $Sr_{11}Ca_3Cu_{24}O_{41}$ and $Sr_xLa_{1-x}MnO_3$. 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 (8mm 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. Al_2O_3, TiO_2, Ga_2O_3, $CuGeO_3$, $YbCoGaO_4$, Sr_2RuO_4, $Y_2Ti_2O_7$) 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 0.1mm/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 La_2CuO_4, $Bi_2Sr_2CaCu_2O_n$, Sr_2RuO_4, $Sr_{11}Ca_3Cu_{24}O_{41}$ and $SrCu_2(BO_3)_2$.

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 preprepared 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 then 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 Guinner lattice constant assessment, lead to solving of crystallographic structure of the new materials ($YbCoGaO_4$).

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.

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Table 1

Material	Method	Growth			Comments ref.
		rate, mm/h	atmosphere	rotation rpm	
Al_2O_3	FZ	10	air	30	[13] and this work, fig 8
TiO_2	FZ	0.5-5	air, O_2	30	[2,9] and this work, fig 8
Ga_2O_3	FZ	10		20	volatile, this work
$CuGeO_3$	FZ	1-2	air	20	[5,14] and this work
$YbCoGaO_4$	FZ	1.7		20	[15] and this work, fig 8
Sr_2RuO_4	FZ	25	$2Ar{:}1O_2$	30	volatile, [16,32,33] and this work
$Y_2Ti_2O_7$	FZ	6	air	10	[17] and this work
$CaTiSiO_5$	FZ	0.5-12	air	20	phase transition[18]and this work
$Sr_{0.2}La_{0.8}MnO_3$.	FZ	7	air	15	[19, 25,27] and this work
$Sr_{0.3}Nd_{0.7}MnO_3$	FZ	2.5-10	air/O_2		[19]
$Ca_{0.5}La_{0.5}MnO_{3-}$	FZ	2.5-10			[19,26]
Mg_2SiO_4 :Cr	FZ		Ar/O_2		[20,21]
$Ca_2Al_2SiO_7$	FZ	3		25	[22,23]
$Ca_2MgSi_2O_7$	FZ	2-3	air, N_2	30-45	[23]
$Sr_2CuO_2Cl_2$	FZ	5	Ar, Ar/O_2		[24]
$Tb_2Ti_2O_7$	FZ	5-20	Ar,O_2	10-20	[17]
$SrTiO_3$	FZ	15	15 atm O_2		[2,28]
$CoTiO_3$	FZ	2			[29,30]
YVO_4 : Er	FZ	7		30	[31]
$Ca_{2-x}La_xRuO_4$	FZ	50			[34[

$Sr_3Ru_2O_7$	FZ	fast			[35]
La_2CuO_4	TSZM	1	O_2	20	[36] and this work, fig 9
$La_{2-x}Sr_xCuO_4$	TSZM	1	O_2	20	[37,38,39,40, 41] and this work
$La_{2-x}Ba_xCuO_4$	TSZM	0.5	10^{-2} atm O_2		[36,42]
$Bi_2Sr_2CaCu_2O_n$	TSZM	0.2	O_2		[43,44,45,46, 47] and this work, fig 9
$Bi_2Sr_2CaCu_2O_n$:Li	TSZM	0.5			[53]
$SrCu_2(BO_3)_2$	TSZM	0.2-0.5	O_2	10-20	low surface tension, [54] and this work, fig 9
$Sr_{14-x}Ca_xCu_{24}O_{41}$	TSZM	1	10 atm O_2	20	[55,56] and this work
$La_{14-x}Ca_xCu_{24}O_{41}$	TSZM	1-1.5	13 atm O_2	40	[56,57]
$SrCuO_2$	TSZM	1	1 atm O_2		[56,58]
Sr_2CuO_3	TSZM	1	1 atm O_2		[56]
Ca_2CuO_3	TSZM	1	1 atm O_2	30	[59]
Li_3VO_4	TSZM	0.5-1	Ar,O_2, air		[60]
$Y_3Fe_5O_{12}$	TSZM	1.5-3	15-20 atm O_2		[2,5,61]
$Y_3Fe_{5-x}Al_xO_{12}$	TSZM	1.5-3	50 atm O_2		[2,7,8]
$SrFe_{12}O_{19}$	TSZM	6	50 atm O_2		[2]
$RFeO_3$	TSZM	3-10	70 atm O_2		[2]
$R_3Ga_5O_{12}$	TSZM	10	air		[2]
$MgFe_2O_4$	TSZM	5	50 atm O_2		[2]
$BaFe_{12}O_{19}$	TSZM	6	70 atm O_2		[2]

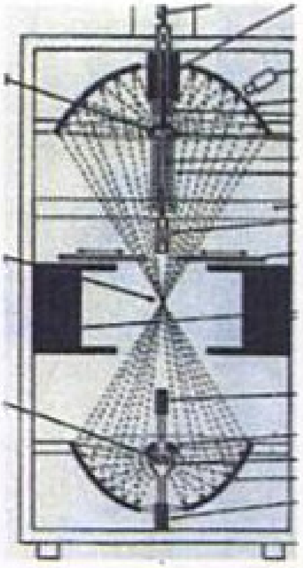

Fig. 1 Schematic drawing one mirror FZ furnace [2,19]

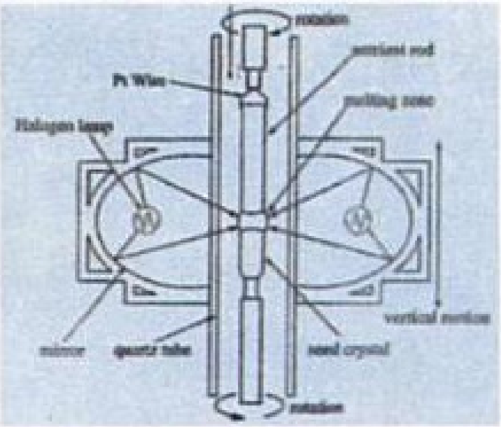

Fig. 2 Schematic drawing of two mirrors FZ furnace [NEC]

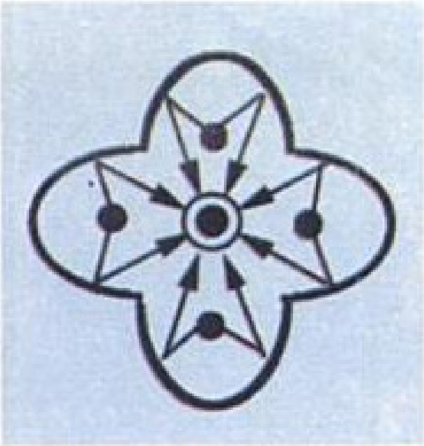

Fig. 3 Schematic drawing of four mirrors FZ furnace [3]

Fig. 4 Ceramic rod of $SrCu_2(BO_3)_2$ after annealing

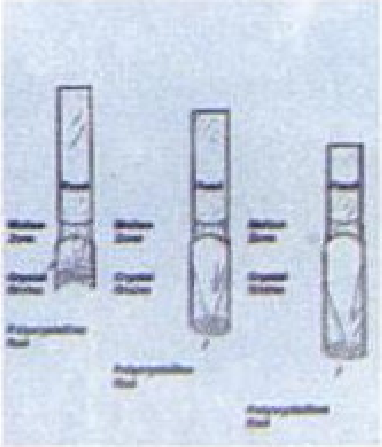

Fig.5 Crystal growth of congruently melting materials by FZ

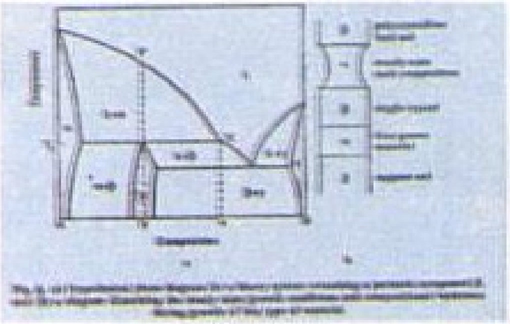

Fig. 6 [5]

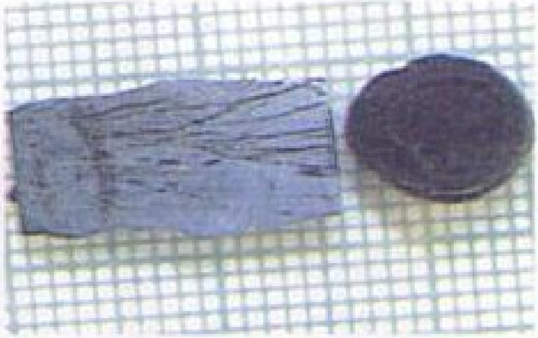

Fig. 7 Polished crossection of $Sr_{14}Cu_{24}O_{41}$

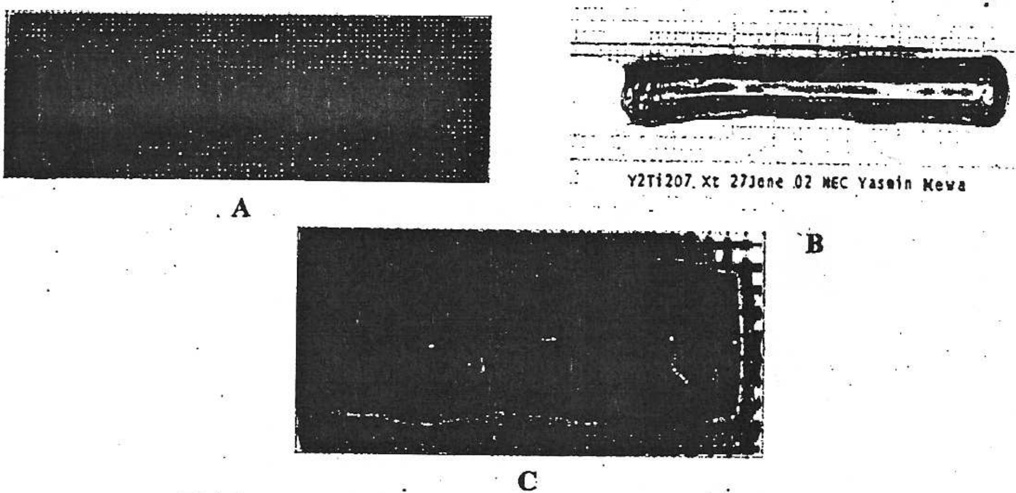

Fig. 8 Crystals of congruently melting materials scale in mm

A $Al_2O_3 : Cr$; **B** $Y_2Ti_2O_7$; **C** $YbCoGaO_4$

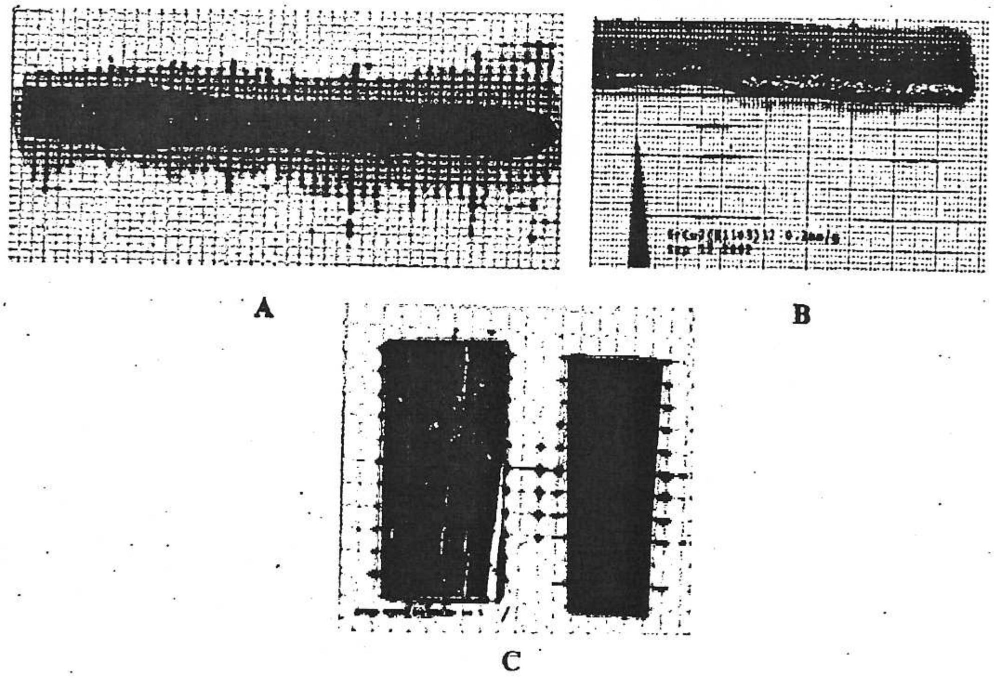

Fig.9 Crystals of incongruently melting materials scale in mm

A La_2CuO_4 ; **B** $SrCu_2(BO_3)_2$; **C** crystals separated from grown $Bi_2SrCa_2Cu_2O_n$