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Invited Paper

Growth of single crystals of selected cuprates by the optical Floating Zone Technique

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Cuprates are complicated oxides with fascinating properties. They often disclose a layered type structure and are anisotropic, so to reliably investigate their physical, crystallographic and optical properties high quality single crystals are essential. The optical Floating Zone [FZ] technique and the related Travelling Solvent Floating Zone [TSFZ] technique are among the newest, most sophisticated crucible-free methods for the growth of various single crystals of cuprates. Using optical heating, it is possible to crystallize congruently [e.g. $CuGeO_3$] as well as incongruently melting materials [e.g. high temperature superconductor Sr_xLaCuO_4 or the Shastry-Sutherland 2-x material SrCu(BO)]. Copper oxide tends to react with all common crucible materials (refractory metals and ceramics) at elevated temperatures, so a crucible-free method is essential to obtain single crystals of cuprates. Careful control of the partial pressure of oxygen is important in order to sustain the proper oxidation state of copper cations. This presentation discusses the application of both the FZ and the TSFZ methods in growth of high quality single crystals of selected cuprates. The materials grown require either very slow (slower than 0.3 mm/h) or very fast (faster than 25 mm/h) growth speed each presenting its own challenges. The relevant processes and reactions are explained on the basis of known phase diagrams. The growth of high quality single crystals of $SrCu_2(BO)_2$, and $CuGeO_3$ as well as some high temperature superconductors [LaSr CuO_4 and LaBa CuO] is discussed in detail.

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1. Introduction

The floating zone technique using halogen lamps and ellipsoidal mirrors as a heat source has been used for crystal growth of wide range of materials, from metals and semiconductors to oxides, including high temperature superconductors and new magnetic materials [1-5].

The crystals grown by the optical floating zone (FZ) technique are of high quality but relatively small (usually not bigger than few mm in diameter and few cm long). Most of this work concentrats on new materials, mainly for research purposes.

High quality single crystals of cuprates are routinely grown on the image furnace and these work have been the subject of the excellent review published by Revcolevschi et al. [5,6].

In the present update, recently grown cuprates are being discussed and the advantages and disadvantages of the FZ technique for the growth of oxide crystals, both, congruently and incongruently melting will be addressed.

The most obvious advantages of the Floating Zone Technique come from the fact that:

- no crucible is necessary
- congruently as well as incongruently melting materials can be grown -the relatively high thermal gradient on the crystallization front decreases the chance for constitutional supercooling and allows for controlled 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 a controlled atmosphere
- solid solutions with controlled chemical composition can be prepared, as - in contrast to the crucible methods-a near-steady state can be achieved. This is beneficial for crystal growth of doped materials (with distribution coefficient different than 1) and for crystallization of incongruently melting materials.

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

This method also has some disadvantages as high thermal gradients cause stress leading to cracks in the cooling crystal. It is also very difficult to grow materials

- with high vapor pressure
- low surface tension - of high viscosity
- materials which undergo a phase transition during cooling

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

2. Materials preparation

2.1 Ceramic rods

The stability of the growth process -and the quality of resulting single crystal depend strongly on the quality of the ceramic rod which provides the source of material for crystallization.

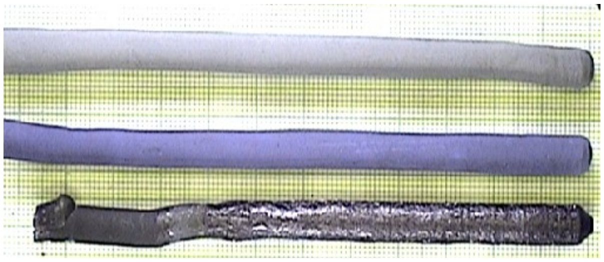

Fig. 1. Ceramic rods for preparation of single crystals of SrCu$_2$(BO) (annealed once, annealed twice and premelted).

The first step is a typical ceramics synthesis. A batch of carefully weighed appropriate materials is prepared by ball mixing and than by manual mixing in the mortar. The powder is pelletized and annealed under appropriate conditions. The quality of prepared ceramic is then assessed by X-ray diffraction and -if found to be correct - the material is re-ground, formed as a rod (about 8 mm diameter and 100 mm long) by cold or hot pressing under 70 MPa and then re-annealed (Fig 1). The density of the rods can vary dramatically from 50 to 93% of crystallographic density of the material. In many cases, when evaporation is not an issue it is advisable to pre-melt a ceramic rod before preforming the final crystal growth. This densification procedure was found to be especially important for slower grown, typically incongruently melting compounds (e.g. high temperature superconductors).

3. Crystal growth procedure

3.1 Optical furnaces

The crystal growth experiments have been performed in two image furnaces installed in our laboratory. One is a four ellipsoidal mirror Crystal System Apparatus [1] and the other one is a two mirror NEC Apparatus [2]. They both employ halogen lamps of different power as the energy source and the experiment is carried in a sealed tube -so that controlled gas atmosphere at high pressure can be applied. There is one main difference between these furnaces: in the Crystal System INC one, the lamps move, whereas in the NEC the seed (and feed) rods move and 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 adjusting of the growth condition.

For congruently melting materials (e.g. $CuGeO_3$) 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 the top (feed) rod as shown on Fig 2. Congruently melting materials grow relatively quickly (from 1 to 20 mm/h). Both rods rotate in opposite directions to achieve temperature uniformity and also to mix the material within the molten zone.

Fig. 2. Stable zone (growth of Ba01La1.9CuO4), 1mm/h.

For the compounds which undergo a peritectic transition (incongruently melting materials) a Traveling Solvent Zone (flux) approach is usually adopted [3,6]. 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 carefully to allow for the creating a steady state. The growth -when started -should be slow, sometimes as slow as 0.1mm/h, allowing for crystallization of the appropriate composition from the melt of starting composition.

(2) sometimes, mostly when a new material is being grown, it is advisable to create a self -flux. In this case the zone is established by melting the ceramic rod and careful adjustment of the temperature and the growth speed until enough of the liquid is created to proceed with the growth. The zone can be analyzed if quenched, and the composition of the flux can be assessed. Examples of incongruently melting cuprates grown by the TSFZ method are $SrCu_2(BO_3)_2$, $Bi_2Sr_2CaCu_2On$, $SrCuO_2$, Sr_2CuO_3, Ca_2CuO_3, $NdCu_2O_4$, $BiSrCuO_6$, (La1-xCax)$_2$CaCu$_2$O$_6$, $Sr_{11}Ca_3Cu_{24}O_{41}$ and La_2CuO_4 -pure and doped with Sr or Ba. The start of the growth on an oriented single crystal seed facilitates the beginning of crystallization, prevents from soaking of the molten zone into the porous seed rod and allows for a controled orientation of the obtained crystal. Its quality depends heavily on the growth stability and the uniformity of the feed rod.

4. Characterization

Characterization of both, preprepared ceramics and the resulting single crystals depends on the material and the information available in the literature (character and temperature of the phase transitions, crystallographic and physical properties).

Differential thermal analysis (DTA) is performed on all the samples (unless the melting temperature is to high) to define the melting properties of the material and to calibrate the furnaces.

Optical observation of the obtained crystals under a polarizing microscope allows further observation continuity of the growth process and explains the changes in the material grown with changes in growth conditions (Fig 3). Non-transparent materials require a lot of effort (cutting and polishing) in order to obtain reliable information.

Fig. 3.Crossection of beginning of crystallization of Sr11Ca3Cu24O41 (grain growth and core visible) [7].

All the materials, feed rods and resulting crystals were subject of X-ray analysis. Powder diffraction allowed us to find out about the uniformity of the material (address the problem of presence or absence of more then one phase). Neutron diffraction confirms the monodomain nature of the crystals and the scan on preferred reflection shows a FWHM for each analyzed crystal.

The Laue technique was applied to orient the as-grown crystal boule. It helps to address problems related to grain growth and to assess the crystallographic quality of materials obtained. Single crystal X-ray diffraction, supported by Guinner lattice constant assessment, leads to resolving the crystallographic structure of new and doped materials.

Energy dispersive X-ray analysis (EDAX) and electron microprobe analysis (EPMA) confirm the chemical formula of crystals and solid solutions grown in different conditions and allow advanced phase analysis of obtained materials. The physical properties of the grown oxides were generally investigated by the crystal users, according to the physical properties and applications. Superconducting, magnetic, thermal (specific heat), electrical, and crystallographic properties are of the most important onesmost interest within our laboratory.

5. Examples of cuprates grown by the floaing zone technique

$CuGeO_3$: a quasi -one dimensional inorganic chain compound, and a spin-Peierls (SP) material. Its structure is composed of linear Cu-O chains running along the *c* axis, well separated each from others by Ge-O chains. The magnetism of this system is well described within a model of spin S=1/2 Heisenberg linear chain that undergo a spin-Peierls transition; in the particular case of $CuGeO_3$ at temperature » 14 K the SP transition occurs as a consequence of the spin lattice dimerization below TSP, accompanied by spontaneous strains along all three crystal axes. The crystal structure of the material is orthorhombic (Pb21m space group with the lattice parameters a = 4.81 Å, b = 8.47 Å, c = 2.94 Å). It grows well by the Floating Zone method and is one of a few congruently melting cuprates (melts at 1173 ^oC). Transparent, blue crystals cleave easily along (011) plane (Fig. 4) and can be doped with many elements [6,8]. Optical properties of pure and doped CuGeO3 are presented in [9,10]

$(La_{1-x}Ca_x)_2CaCu_2O_6$ high temperature superconductor

Cubic centimeter size single crystals of $(La_{0.95}Ca_{0.05})_2CaCu_2O_{6+y}$ were successfully grown under 1 bar pressure of oxygen. The growth rate was rather slow at 0.35 mm/h. The crystals grown were not superconducting. Only when grown grown at the pressure of 11 bars of oxygen they do display a superconducting transition temperature of 28 K. Application of high pressure of oxygen during crystal growth is often an effective method to obtain bulk superconducting single crystals. The crystals are tetragonal (I4/mmm, a ~ 3.84 Å, c ~ 19.39 Å) with a mosaic spread FWHM on (110) peak (neutron diffraction) about 0.3 deg [11].

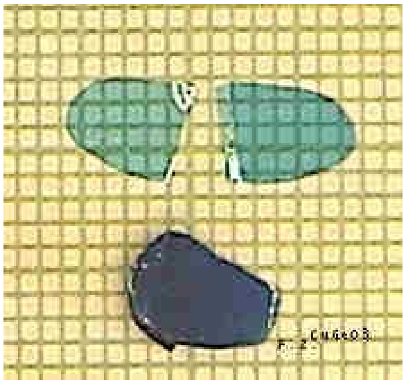

Fig. 4. Pieces cleaved from CuGeO3 crystals grown at rate 5 mm/h.

$Sr_{14-n}Ca_nCu_{24}O_{41}$ – a spin ladder material (Tperitectic = 955 ^oC) Crystals of these solid solutions (1< n < 12) have to be grown in high oxygen pressure (up to 13 bar) with a growth speed of about 1 mm/h. They cleave along (010) and for n > 11 become superconducting at high pressure. They display an orthorombic structure, Cccm, a =11.46 Å, b = 13.40 Å and c = 27.65 Å. The resulting crystals are single domain, as confirmed by neutron diffraction [12 -14].

$Bi_2Sr_2CaCu_2O_{8+d}$ high temperature superconductors This material is one of the most extensively studied high temperature superconductors with Tc up to 91K [15-23]. It has orthorombic symmetry and lattice parameters a ~ b = 5.4 Å, c = 30.8 Å. Thin single crystals up to 5 cm long can be separated from the very slowly (about 0.2 mm/h) grown boule (Fig. 5).

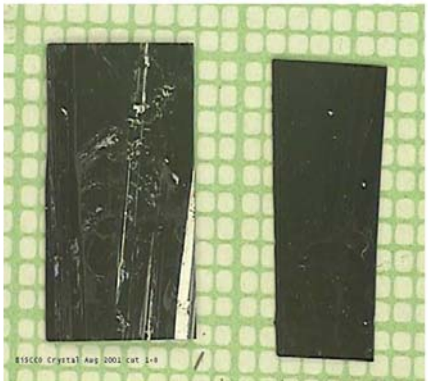

Fig. 5. $Bi_2Sr_2CaCu_2O_{8+d}$ 0.2 mm/h growth Fig 6 $La_{1.925}Ba_{0.075}CuO_{4}$,1mm/h growth.

La_2CuO_4,$La_{2-x}Sr_xCuO_4$,$La_{2-x}Ba_xCuO_4$ tetragonal crystals (I4/mmm, a=3.781 Å, c=13.248 Å) were intensively grown in previous years in many laboratories. Substituting part of La with Sr, Ca, Ba (from 0.01 to 0.3 molar %) (Fig. 6) allows for investigation of **high temperature superconductivity** on high quality single crystals [24 - 30].

Tetragonal **$SrCu_2(BO_3)_2$** (I-4m, a =8.99 Å c = 6.65 Å) is a realization of the Shastry-Sutherland model for two-dimensional Heisenberg antiferromagnets. The high-resolution, inelastic neutron scattering measurements on undoped $SrCu_2(BO_3)_2$, confirmed that slowly (less than 0.3 mm/h) grown crystal (Fig. 7) is a single domain with a mosaic spread of the (110) Bragg peak of 0.3 deg. To obtain high quality crystals of this borate substituted with Mg for Cu and Na or La for Sr even slower growth rates and self-flux have to be applied [31-33].

Crystals of **orthorhombic chain cuprates $SrCuO_2$** (Cmcm, a = 3.573 Å, b = 16.33 Å, c = 3.913 Å, T = 1085 °C), **Sr_2CuO_3** (Immm, a = 12.71 Å, b = 3.915 Å, c = 3.503 Å, T = 1225 °C) and **Ca_2CuO_3** (Immm, a = 12.23 Å, b = 3.779 Å, c = 3.259 Å), previously grown by TSFZ method at 1mm/h, were found to be monodomain over their total length of several cm [6,34,35].

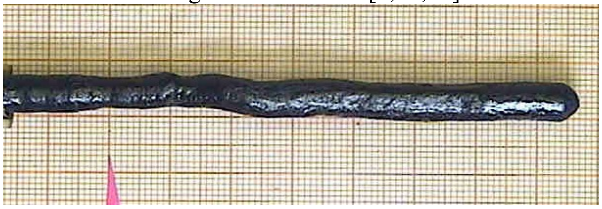

Fig. 7. $SrCu_2(BO)_2$crystal grown 0.22 mm/h in 2 atm of O2 .Beginning of the growth marked.

$CaCu_3Ti_4O_{12}$ giant dielectric constant material This cubic, perovskite related material (Im-3, a = 7.39Å) has attracted a lot of of attention due to the high values of the static dielectric constant greater than or similar to 10 000 at room temperature, which drops to about 100 below or close to 100 K . Relatively large crystals were grown using a speed about 6 mm/h [36,37].

Semiconducting Nd_2CuO_4 and superconducting $Ce_{0.15}Nd_{1.85}CuO_{4-d}$ single crystals were grown slowly (< 0.6 mm/h). They are tetragonal (I4/mmm a = 3.945 Å c = 12.17 Å and a = b = 3.94 Å, c = 12.07 Å respectively). For Nd doped material supeconductivity was achieved when the growth was preformed in Ar/O2 mixture [38]

In Table 1 an extended list of cuprates obtained as well as the growth conditions are presented.

Table 1. Growth conditions for crystals grown by optical floating zone method.

Material	Growth			References
	rate, mm/h	atmosphere	rotation rpm	
$CuGeO_3$	1-5	< 1atm O_2	30	5,6,8,9,10
$CaCu_3Ti_4O_{12}$	6	O_2	30	36,37
$CdCu_3Ti_4O_{12}$	6	O_2	30	37
$CaYCu_5O_{10}$	0.5	O_2	15	*39*
La_2CuO_4	1	O_2	20-30	6,25
La_{2-x}SrxCuO_4	1	O_2	20-30	26,27,28,29
$La_{2-x}Ba_xCuO_4$	0.5	10-2 atm O_2	20-30	24,28,30
$Bi_2Sr_2CaCu_2$On	0.2	O_2	30	15-23
$(La_{1-x}Ca_x)_2CaCu_2O_6$	0.35	1-11atm O_2	30	11
$Bi_2Sr_2CaCu_2$On:Li	0.5	O_2		40

$SrCu_2(BO_3)_2$	0.2-0.5	O_2	10-30	31,32,33
$Sr_{14-x}Ca_xCu_{24}O_{41}$	1	10 atm O_2	30	13,14
$La_{14-x}CaxCu_{24}O_{41}$	1-1.5	13 atm O_2	40	14,15
$SrCuO_2$	1	1 atm O_2	30	34
Sr_2CuO_3	1	1 atm O_2	30	13
Ca_2CuO_3	1	1 atm O_2	30	35
Nd_2CuO_4	0.5-0.6	O_2	30	38
$Nd_{1.85}Ce_{0.15}CuO_4$	0.5-0.6	$1Ar/_{30}O_2$	30	27,38

5. Conclusions

The field of crystal growth by floating zone method is relatively new and not fully developed. Recently, with growing number of highly computerized furnaces the number of reported studies on new and previous known materials is rising. A very limited number of these studies deal with the method itself, investigating temperature oscillation in the zone [41] and detailed lamp irradiation/thermal flows analysis [42].

Besides the continuous preparation of new solid solutions of oxides with different and modified physical properties the future work has to include:

- investigation of the influence of growth conditions on crystal quality
- creating a "user friendly" theoretical approach connecting crystal growth conditions with single crystals obtained.
- understanding/assessing the high temperature properties of molten oxides and salts
- investigation of phase diagrams, To achieve all this the, continuous cooperation between a crystal grower and crystal characterizer is imperative. Without excellent characterization of grown crystals no progress in crystal growth can be achieved.

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