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Influence of heat distribution and zone shape in the floating zone growth of selected oxide compounds

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Abstract The effects of heat distribution, process parameters, and the ambient atmosphere on the characteristics of the molten zone are considered for floating zone (FZ) crystal growth of selected oxide compounds with special reference to cuprates. The outer shape of the FZ, which is stabilized only by capillary forces, and the interfaces between melt and growing crystal are decisive for process stability and crystal perfection. They do not only depend on external parameters such as zone heights, growth velocity, and rotation mode but are closely related to the phase diagram and the constitution of the individual substance. Therefore, the choice of the optimum process conditions is a subtle balance of parameters like appropriate focusing or defocusing of the light, the direction of growth and the ambient atmosphere, which are adapted to the individual substance. A pyrometric method of FZ temperature measurement was developed as an appropriate tool for process control.

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Introduction

In the floating zone (FZ) technique, a stationary molten zone between feed rod and crystal is produced by contactless heating. The crystal grows by moving the zone through the cylindrical feed rod. The crucible free FZ method avoids any contamination with the crucible material and is often applied if the melts have high chemical activity or high-melting temperatures. Besides silicon, single crystals of a broad variety of other substances such as metals, intermetallics, and oxide compounds are grown by the FZ method [1]. The basic difference of most oxide compounds, e.g., oxides, compared with metals is their low electrical conductivity. Therefore, optical heating with diverse modifications of image furnaces has become a well-established method for FZ growth of oxides [1–4]. Oxides exhibit much smaller heat conductivities than metals and intermetallics. Temperature gradients in the crystal become big and precautions, like an additional resistance heater are often required to avoid cracks and other defects caused by inherent thermal stresses [2].

The control of the FZ is of outmost importance for the crystal growth processes, which does not only mean a stable height, but also a proper crystal–melt interface shape, chemical composition, and homogeneity of the melt. The latter items are of particular importance in the traveling solvent floating zone (TSFZ) mode. Here we report effects of process parameters in FZ crystal growth experiments with vertical optical furnaces of some novel classes of oxide compounds. Cuprates have attracted tremendous attention after the discovery of their high-T_c superconducting properties [5, 6], but also the low-dimensional spin ordering in some cuprates is a unique subject for basic research [7, 8]. Here we deal with the crystal growth of CuO, the prototype of this class of compounds, $CaCu_2O_3$,

$Ca_xSr_{14-x}Cu_{24}O_{41}$ and $Ca_{2+x}Y_{2-x}Cu_5O_{10}$. Li-compounds, such as $LiMnPO_4$, are attractive as active materials for Li-ion batteries [9]. The influences of irradiation parameters of optical heating, wetting of the melt, velocity and direction of growth, and the composition and pressure of the ambient atmosphere on the size and stability of the FZ, outer contours of the crystal, the shape and the stability of the crystal/melt interface are considered.

Experimental details

The FZ crystal growth was accomplished in a vertical optical furnace URN-2ZM (MPEI, Moscow) [2] and alternatively in the new Smart Floating Zone (SFZ) facility designed and constructed at IFW Dresden [10]. In both methods, a 3- or 5-kW xenon lamp positioned near the focal point of the lower elliptic mirror is utilized for heating the zone. The cylindrical growth chamber is located near the focal point of the upper mirror (Fig. 1a). The construction of the growth chambers made from quartz or sapphire enables the use of high-pressure gas atmospheres up to 80 bar or rather 150 bar (SFZ). Counter-rotation of feed rod (15 rpm) and crystal (25 rpm) has been applied, which improves mixing of the melt in the FZ. For the SFZ gas mixtures of Ar/O_2 for high pressure can be realized.

Normally, the high radiation density in FZ methods with optical heating does not enable temperature measurements by a pyrometer. A new method of pyrometric technique was realized [11], which permits temperature measurements on the crystal and melt surface during the growth process. The light flux is interrupted for 60 ms by closing a stroboscopic light shutter (Fig. 1a). In this short time interval, the temperature is measured by a two-color pyrometer. Thus, the temperature of the FZ and temperature gradients can be optimized.

Experimental results

Effects of process characteristics on height and outer shape of the floating zone

The height of the molten zone is one decisive parameter of the FZ method, which is normally enlarged by increasing the lamp power or wider opening of the mechanical light shutter for the radiation flux (cf. Fig. 1a). The maximum zone height is determined by equating the capillary forces of the surface tension and the hydrostatic pressure of the melt column [1].

Model calculations have proved that the irradiation profile is strongly affected by the lamp position [3]. In Fig. 1b, the effect of a displacement z of the lamp with respect to the focus of the lower elliptic mirror on temperature profiles of Al_2O_3 is shown, which is exemplary for the oxide materials. The temperature profile is scanned by the pyrometer from the crystal via the surface of the FZ up to the adjacent part of the feed rod. It is evident that the temperature gradient on the crystal and the heights of the molten zones (defined by the intersection points with $T_m = 2,050$ °C, the melting temperature of Al_2O_3) can be

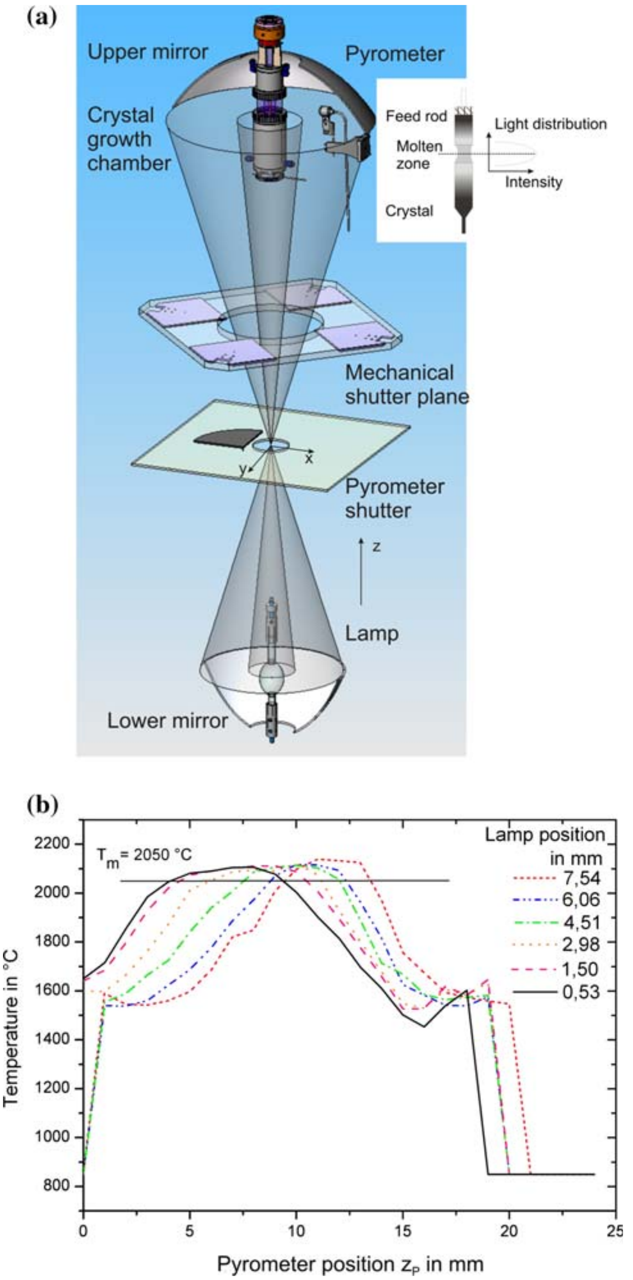

Fig. 1 **a** Scheme of the vertical optical FZ furnace. The inset is a sketch of the FZ crystal growth process with corresponding light profile at the surface. **b** Measured temperature profiles on crystal, floating zone (FZ) and feed rod of Al_2O_3 (melting temperature $T_m = 2050$ °C) for different lamp positions

adjusted by the lamp position. Moving the lamp out of the focus in vertical direction on the optical axis toward the crystal, the zone is shifted to a higher position z and the zone height first increases and then decreases. The temperature profile strongly depends on the heat conductivity of the material. For Al_2O_3, a gradient of 105 ± 5 K/mm was realized in the crystal, which weakly varies with the lamp position. This may be compared with Ni where the gradient is strongly increased from 100 to 170 K/mm.

The shape of the free surface of a FZ is defined by the equilibrium of the acting forces [1]. The requirement of a constant growth angle β at the tri-junction point, which is specific material dependent quantity, determines the zone shapes for upward and downward growth directions. The faceting in crystal growth experiments of cuprates is shown in Fig. 2. During the FZ growth of CuO, the facets become apparent from the different reflectivity of the rotating crystal (Fig. 2a). If faceting occurs, the external shape of the crystal is not longer determined by a constant meniscus angle and the FZ deviates from cylinder symmetry. The growth is governed by rather intricate kinetics mainly caused by the inherent crystal anisotropy. Elaborately considered, the growing FZ crystal is not a perfect cylinder. The cross section shown in Fig. 2b for a $(Sr, Zn)_{14}Cu_{24}O_{41}$ crystal exhibits some flat surfaces and bulges.

Many oxide compounds melt incongruently. Here the TSFZ method is applied where the composition of the traveling zone deviates from the growing crystal. The melt/feed rod interface is not always smooth but can form a mushy zone, which reflects the finite melting interval. For materials with a high-wetting affinity of the melt, such as cuprates, in vertical optical TSFZ facilities melting and resolidification on the feed rod can occur (cf. Fig. 3a). This was observed for small focused light incidence and if properitectic high-melting phases exist. For example, CaO is formed in crystal growth of Ca-doped $Ca_xSr_{14-x}Cu_{24}O_{41}$ and Nd_2O_3 in the case of $Nd_{1,85}Ce_{0,15}CuO_4$. As a result of resolidification, the zone gets narrower and its concentration is changed, which finally leads to a worse wetting of the feed rod. Especially for high-pressure experiments, this kind of growth instability was observed. The high-melting phases crystallize as needles as shown schematically in Fig. 3b. Remelting of undesired phases during the growth in most cases requires the increase of power. This leads to a sudden change of the zone composition and to solidification of narrow rims of properitectic phase particles in the crystal, which mark the pattern of the solidifying interface. Less sharp light focusing can improve the growth process and partially prevent the formation of the undesired phase. In vertical FZ facilities, the light rays with small incidence angle can be cut off by using a light blocker in the central part of the growth facility close to the optical axis. The high-incidence angle at the radiated zone leads to a sharper interface at the feed rod.

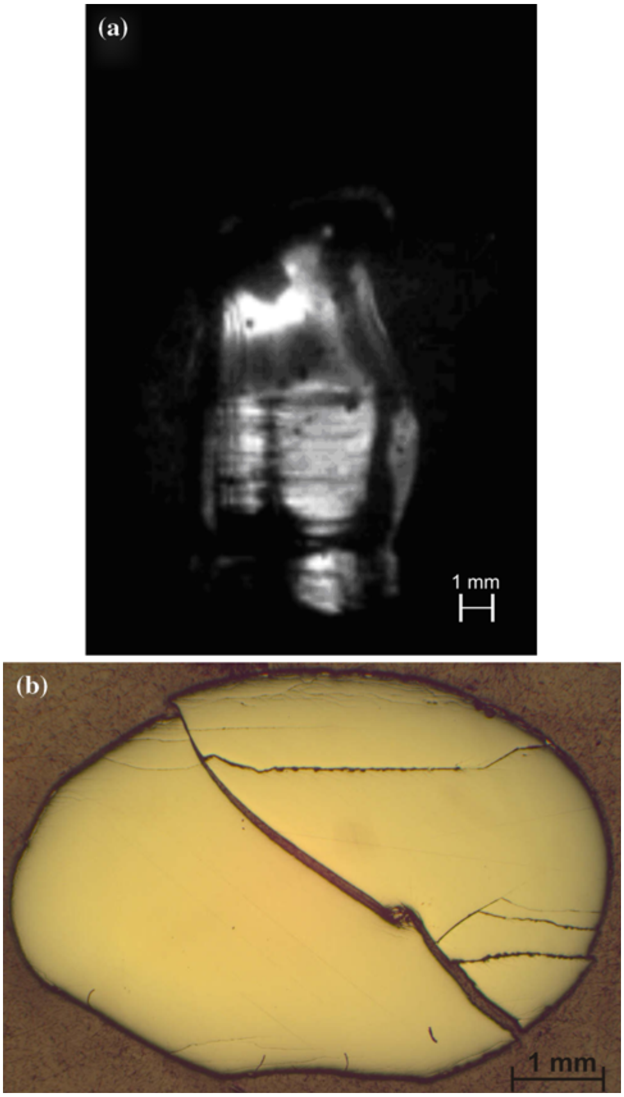

Fig. 2 **a** Facets formed on a CuO crystal (*bottom*) grown with 10 mm/h from the FZ (*top*) under 55 bar O_2. **b** $(Sr, Zn)_{14}Cu_{24}O_{41}$ crystal cross section showing sharp edges due to the formation of facets on its surface (The crystal has been broken because of thermal stresses on cooling)

Factors governing the crystal–melt interface shape

Besides the outer shape of the FZ, the control of the crystal–melt interface is another crucial point of the crystal growth. In unseeded crystal growth, only a convex interface enables a proper grain selection. A concave interface is also unfavorable because it enhances the concentration of inclusions and dislocations along the core of growing crystals. In contrast to inductive radio frequency (rf) heating, a convex interface is mostly observed for radiation heating by both Halogen and Xenon lamps. However, some

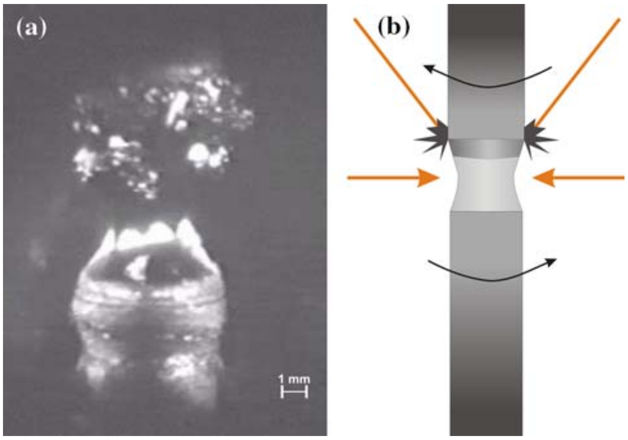

Fig. 3 **a** Video image of a FZ growth experiment of $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ at 2 bar O_2 showing crystal, FZ and feed rod from bottom to top. **b** Scheme of needle growth on the feed rod (*arrows* indicate the optical radiation)

cuprates, such as $SrCuO_2$ or $CaCu_2O_3$, tend to an extremely convex interface shape as illustrated in Fig. 4a. Comparing the FZ method with inductive rf heating to FZ crystal growth with optical radiation heating, the melt convection in the FZ in the latter case is very weak and dominated by thermocapillary forces [12, 13]. This can lead to solute accumulation and finally to second-phase formation in the back standing regions close to the surface. The cross section of $(Ca_{0.75}Cu_{0.25})Cu_2O_3$ grown with an extremely convex crystal–melt interface is shown as an example where the inner crystal is surrounded by a polycrystalline eutectic CuO layer in Fig. 4b. This low melting eutectic (with CuO phase) is formed from the Cu-enriched melt of the diffusion boundary layer close to the surface. To avoid the deficiencies in the growth process for these materials, a less sharp focusing of the radiation is required. Counterrotation of the crystal with a high rate is beneficial for both a less curved interface and better convective mixing in the melt.

For materials such as $LiMnPO_4$, there is a tendency to form an undesired concave interface, which can be illuminated and heated though the transparent liquid zone. Because of the asymmetric light incidence in our FZ facilities, a concave phase border is created for growth from bottom to top. This direction is normally preferred because larger crystal diameters can be achieved. In an additional experiment, it was shown (Fig. 5) that the interface curvature can be reversed to convex by changing the growth direction. In this case, the irradiation of the crystal/melt interface by the light reflected from the upper mirror is prevented.

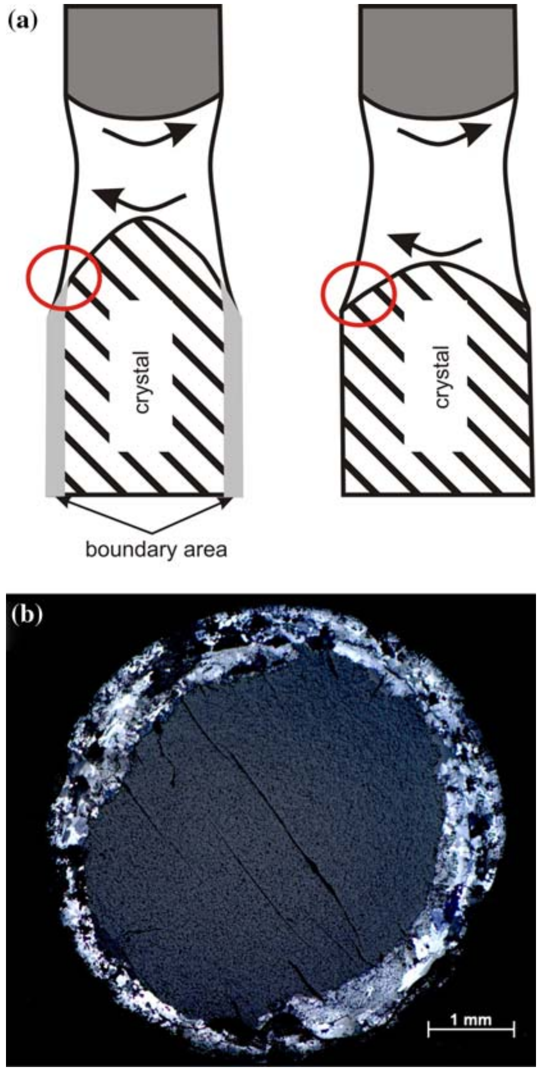

Fig. 4 **a** Schematic illustration of the effect of curved crystal–melt interface, which can lead to defect layers in boundary areas of grown crystals. **b** Single crystal of $(Ca_{0.75}Cu_{0.25})Cu_2O_3$ grown with an extremely convex crystal–melt interface. The crystal is surrounded by a polycrystalline rim of a second phase (eutectic with CuO)

Another challenge in crystal growth of cuprates, which is only mentioned here, is the release of gaseous oxygen at the melting interface, because copper can change its valence [14]. With rising oxygen partial pressure, the melting temperature of CuO increases and reduces the concentration difference (with respect to oxygen) between the melt and the CuO phase, which enables higher growth rates [15]. The oxygen released at the melting interface can form gas bubbles and destabilize the FZ in crystal growth of CuO or ternary cuprates by the TSFZ. On the other hand, oxygen lost during melting must be built in at the crystallization cuprates. An exchange of oxygen via the free surface of the FZ can support this transport process. This was achieved by using Ar/O_2 gas mixtures as ambient atmosphere. Here, the gradient of the thermodynamic potential supports the diffusive transport of oxygen released at the melting interface through the melt into the diluted gas. The formation of bubbles is prevented, and the

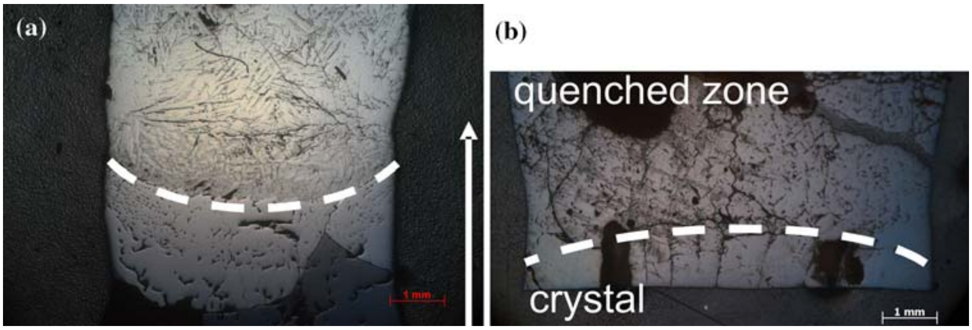

Fig. 5 The effect of growth direction on the interface shape in FZ crystal growth of $LiMnPO_4$ at 10 mm h^{-1} and 50 bar Ar. **a** Concave interface for downward growth and **b** convex interface for upward growth

FZ is stabilized. By slow growth velocities and suitable rotation, a back diffusion during crystallization is enabled. These processes, which are of enormous practical importance, must be further elaborated.

Summary

In this work, we have reported experimental details for optimizing FZ crystal growth of oxide compounds with special reference to cuprates. The outer shape of the FZ, which is stabilized only by capillary forces, and the interfaces between melt and growing crystal (resp. feed rod) are decisive for process stability and perfection of the growing crystal. They do not only depend on external parameters such as zone heights, growth velocity, and rotation mode, but are also closely related with the constitution of the individual substance. Therefore, the choice of the optimum process conditions is a subtle balance of parameters such as appropriate focusing or defocusing of the light, the direction of growth, and the ambient atmosphere, which are adapted to the individual substance.

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