Growth of high-temperature superconductor crystals from flux

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Abstract. Crystallization of high-temperature superconductors was studied in La–Sr–Cu–O, Y–Ba–Cu–O and Bi–Sr–Ca–Cu–O systems. Platelet crystals $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ were obtained by spontaneous crystallization from homogeneous nonstoichiometric melts enriched in barium and copper oxide. $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ was prepared by slow cooling of melts enriched in copper oxide. $\text{Bi}_2(\text{Sr}, \text{Ca})_{n+1}\text{Cu}_n\text{O}_y$, ($n = 1, 2$) was obtained by melting zone travelling. The crystals show transition to superconducting state at $T = 93 \text{ K}$, $\Delta T = 0.2\text{--}0.5 \text{ K}$ (Y, Ba cuprate), $T = 87 \text{ K}$, $\Delta T = 2 \text{ K}$ (Bi, Sr, Ca-cuprate). La, Sr-cuprate single crystals obtained by Czochralski method did not show transition to superconducting state. For flux-grown crystals T_c was $5\text{--}26 \text{ K}$ depending on the composition, growth and heat treatment. The short characterization of some accessory phases ($\text{Ba}_3\text{Y}_2\text{Cu}_3\text{PtO}_{10}$, $\text{Ca}_{1.75}\text{Sr}_{1.5}\text{Cu}_{0.75}\text{PtO}_6$, BaCuO_2 , $\text{Ba}_{41}\text{Cu}_{44}\text{O}_{84}\text{Cl}_2$) is reported.

Keywords. Superconductivity; single crystals; La–Sr–Cu–O system; Y–Ba–Cu–O system; Bi–Sr–Ca–Cu–O system.

1. Introduction

The peculiarities of chemical composition and structures of superconducting cuprates indicate that flux growth is the most appropriate method for growing single crystals of cuprate high- T_c superconductors. Most HTSC-single crystals in different systems were grown by flux technique both in its classical variant (using a mineralizer, mainly, of compounds of alkali or alkali-earth metals) and in its rather new modification (growth from so-called nonstoichiometric melts, the excessive components serving as mineralizer).

In spite of the similarities of HTSC-cuprates (perovskite-like structures, nonstoichiometric compositions) every compound demands an individual approach for growing single crystals. The problems connected with the specific structures of these cuprates relate to layer character, twinning, cleavage and phase transitions and the peculiarities of composition and thermal behaviour relating to nonstoichiometry on oxygen, variable valency of the basic elements, high reactivities of the melts and incongruent melting. Another important problem concerns the inert container.

We discuss below some results on single-crystal growth of superconducting cuprate phases in the systems La–Sr–Cu–O, Y–Ba–Cu–O and Bi–Sr–Ca–Cu–O.

2. La–(Sr)–Cu–O system

The state diagrams of the systems $\text{La}_2\text{O}_3\text{--CuO}$, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4\text{--CuO}$ (Hidaka *et al* 1987; Oka and Unoki 1987; Picone *et al* 1988) show peritectic decomposition of La-cuprate at 1375°C and formation of eutectics $\text{La}_2\text{CuO}_4\text{--CuO}$ (88 mol.% CuO, 1050°C). This explains the use of melts enriched in copper oxide for crystal growing in La–Sr–Cu–O system.

We obtained single-crystals La_2CuO_4 , $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ from nonstoichiometric melts (CuO excess, figure 1) using the slow cooling of the melt or the Czochralski technique. In the first case the platelet or prismatic single crystals with sizes up to several mm were obtained. The cooling rate was 0.5–2 deg/h in the temperature range 1200–1100°C, the crystals growing spontaneously or with localization of nucleation on Pt-rod (figure 2). The crystals had a tetragonal symmetry with the space group 14/mm, $a = 3.7802$, $c = 12.2139$ Å (Bykov *et al* 1987). The crystals were characterized by a transition into superconducting state at $T \lesssim 26$ K, $\Delta T \sim 1$ K.

Single crystals of La,Cu- and La,Sr,Cu-oxides in the shape of large boules were grown following the Czochralski method. The direction of pulling was [010], the rotation rate of the seed was 20 rpm and the pulling rate was 0.1–0.2 mm/h (Bykov *et al* 1988). La_2CuO_4 crystals were pseudotetragonal with orthorhombic unit cell parameters $a = 5.36$, $b = 5.40$ and $c = 13.17$ Å. Single crystals of Sr-doped cuprates showed no phase transition to superconducting state or transition at low temperature $\lesssim 5$ K.

Figure 1. Field of starting compositions for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ single crystal growth from flux.

Figure 2. $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ crystals grown by spontaneous crystallization from nonstoichiometric melt (a) and by Czochralski technique (b).

This is much lower than the T_c for polycrystalline specimens or even for spontaneously-grown single crystals. This may be due to appreciable deviation of the composition from stoichiometry (La(Sr) deficiency up to 2–10%) with the low distribution coefficient for Sr or with ordering of strontium.

Single crystals of La_2CuO_4 , $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ were used for a detailed study of their optical and electrical properties (Denisov *et al* 1989a,b; Ivanov *et al* 1989).

3. Ln–Ba–Cu–O system

The single crystals $\text{LnBa}_2\text{Cu}_3\text{O}_{6.5+x}$ where Ln–Y or rare-earth elements were grown from nonstoichiometric melt (excess of CuO and BaO) by slow cooling. Eutectic composition BaO–CuO served as a solvent. Mechanical mixture of sintered 123 and solvent (18–28 mol.% BaO to 82–72 mol.% CuO) in molar ratio 1:(10–15) (figure 3) were placed in Pt-crucible and heated up to 1200°C. After soaking for 1–3 hours the temperature was slowly decreased up to 970–960°C (cooling rate 5–10 deg/h). The liquid was then quickly decanted and the platelet single crystals cooled to room temperature. The crystals grew at the bottom of the crucible, the face (001) closely perpendicular to the melt surface. The crystal size depends on growth conditions and the starting ratio of the initial components. Usually $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ crystallized in large thin orthogonal plates (figure 4) $8 \times 8 \times 0.1 \text{ mm}^3$ in size. As-grown crystals were tetragonal with unit cell parameters $a = 3.860$, $c = 11.815 \text{ \AA}$. After annealing in oxygen the crystals became orthorhombic, the typical unit cell parameters were $a = 3.825$, $b = 3.890$, $c = 11.70\text{--}11.74 \text{ \AA}$ depending on chemical composition (oxygen content). By changing the annealing conditions one can obtain crystals with an oxygen content from 6.24 to 6.97 (Avdeev *et al* 1987). Some crystals with Cu deficiency (for example, $\text{Y}_{0.94}\text{Ln}_{0.02}\text{Ba}_2\text{Cu}_{2.88}\text{O}_x$) remain tetragonal after annealing in oxygen, T_c 60–80 K, unit cell parameters are $a = 3.865$, $c = 11.704 \text{ \AA}$ (before annealing) and $a = 3.868$, $c = 11.604 \text{ \AA}$ (after annealing) (Makarenko *et al* 1988). $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ crystals show T_c at 93 K and $\Delta T_c > 0.5 \text{ K}$. The crystals are characterized by large anisotropy of electrical resistance and the $\rho_{\perp}/\rho_{\parallel}$ value is strongly linked with the quality of the samples

Figure 3. Field of starting compositions for $\text{LnBa}_2\text{Cu}_3\text{O}_{6.5+x}$ single crystal growth from flux.

Figure 4. Single crystal plate of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$.

(Makarenko *et al* 1988). The magnetic properties of Y-123 single crystals were described by Avdeev *et al* (1988) and the optical properties by Aleksandrov *et al* (1988).

4. Bi–Sr–Ca–Cu–O system

We grew the single crystals of high- T_c superconductors in Bi–Sr–Ca–Cu–O system by horizontal melting zone technique. The starting material was prepared on the basis of 2212-compound with addition of excess Bi- and Cu-oxides to decrease the melting point of the mixture. The charge was sintered in accordance with the standard ceramic technology (two-stage sintering, 450–600, 800–850°C, with intermediate homogenization). The prepared charge was pressed into tablets and placed in Pt-boat of U- or V-like configuration with dimensions: 120 mm in length, 10–15 mm in width, 10–15 mm in height. Resistive heating was used, the width of melted zone was about 20 mm and the maximum temperature was 900°C. The velocity of boat displacement with respect to a stationary heater was 0.5–2 mm/h. Several passages were used in some experiments.

The experiments resulted in the formation of textured crystalline ingots consisting of black plates packed in parallel with the structure type of 2212-compound. Between these plates three phases were determined; calcium cuprate $\text{Ca}_2\text{Cu}_{1.3}\text{O}_{3.3}$, calcium-strontium bismutate $\text{Bi}_7\text{Ca}_4\text{SrO}_x$ and bismuth-strontium cuprate 2201 (24 Å phase). The quantity of the first two phases in the bulk of ingot did not exceed 5% because they were not determined by X-ray analysis but by electron-microprobe analysis. Figure 5 shows the field of the initial compositions used for crystal growth in the system Bi–Sr–Ca–Cu–O. The ratio of Sr/Ca in crystals was less than 2 due to partial separation of Ca in the other phases Ca_2CuO_3 and $\text{Bi}_7\text{Ca}_4\text{O}_x$. These phases usually contain admixture

Figure 5. Field of starting compositions for Bi-cuprates single crystal grown by horizontal melted-zone travelling.

Figure 6. Plate of Bi, Sr, Ca-cuprate in the ingot.

($\text{Bi}_7\text{Ca}_4\text{SrCu}_{0.5}\text{O}_{16}$) or excess ($\text{Ca}_2\text{Cu}_{1.3}\text{O}_{3.3}$) of copper. Calcium cuprate can also be found on the open surface of the ingot as 10-mm long needle-like crystals of golden colour. Bi–Sr–Ca cuprates are represented by the plates prolonged along the ingot axis, the plate size is about $20 \times 5 \times (0.1\text{--}0.2)$ mm and the *ab*-surface nearly perpendicular to the melt surface. The thin plates can be easily separated along the cleavage plane (001) (figure 6). The crystals obtained had unit cells with parameter

Figure 7. Plot $\rho(T)$ for the middle part of the ingot; a— as-grown specimen; b— annealing in oxygen with quenching; c— annealing in oxygen with slow cooling.

$c = 30.776 \text{ \AA}$ and $c = 24.32 \text{ \AA}$. The intensity ratios of the main reflections and the T_c values indicate different ratios of these two phases in different parts of the ingot. The middle part contains mainly $30 \text{ \AA}$ phase. T_c values were determined from the data of $\rho(T)$ dependance on the samples which were cut from four different parts of the ingot. All the specimens prepared from as-grown ingot showed transition into superconducting state without any additional thermal treatment; T_c (end) 40–55 K, T_c (onset) was 80–100 K depending on the specimen composition and the ingot. Minimum T_c was observed for specimens which, according to microanalysis data, were enriched with Bi. Annealing in O_2 increased the T_c values up to 87 K (figure 7); the annealing parameters were: temperature 830 K, duration 24 h, cooling rate 40–50°C/h down to 150°C. Some data on optical properties of these Bi-compounds were described by Aleksandrov *et al* (1989).

5. Accessory phases

The high reactivity of alkali-earth containing melts leads to the appearance of a new component in complex systems used for high T_c single crystal growth. This component is a crucible material (Pt), which transforms into melt at high temperatures and can deteriorate superconducting crystals or form individual compounds. In Y–Ba–Cu–O, Bi–Sr–Ca–Cu–O we obtained cuprate-platinates $Ba_3Y_2Cu_2PtO_{10}$, $Ba_4(Pt, Cu)O_6$, $Ca_{1.75}Sr_{1.5}Cu_{0.75}PtO_6$. These compounds were obtained as large single crystals up to 10 mm in size (figure 8). The $Ba_3Y_2Cu_3PtO_{10}$ crystals are characterized by a monoclinic system with the unit cell parameters $a = 12.500$, $b = 7.343$, $c = 5.812 \text{ \AA}$, $\gamma = 105.0^\circ$, sp.gr. $B2/m$ (Genkina *et al* 1989). The crystals of Ca, Sr, Cu–platinate are isostructural with Sr_4PtO_6 , the unit cell parameters are $a = 9.442$, $c = 11.125 \text{ \AA}$, sp.gr. $R\bar{3}c$.

Among the other accessory phases, the $BaCuO_2$ phase is the most typical for flux growth. In the presence of chloride solvent a new phase, $Ba_{41}Cu_{44}O_{84}Cl_2$ can be obtained; $a = 18.27 \text{ \AA}$, sp.gr. $Im3m$ (Yakubovich *et al* 1989).

Figure 8. Accessory phases: a. $\text{Ba}_3\text{Y}_2\text{Cu}_3\text{PtO}_{10}$ ($\times 50$); b. $\text{Ba}_4(\text{Pt}, \text{Cu})\text{O}_6$; c. $\text{Ca}_{1.75}\text{Sr}_{1.5}\text{Cu}_{0.75}\text{PtO}_6$; d. BaCuO_2 ($\times 15$).

6. Conclusions

- (i) The single crystals of high T_c -superconductors have been grown in La-Sr-Cu-O, Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O systems.
- (ii) The crystals show transition to superconducting state at $T = 93\text{ K}$, $\Delta T = 0.2\text{--}0.5\text{ K}$ ($\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$); $T = 87\text{ K}$, $\Delta T \sim 2\text{ K}$ ($\text{Bi}_{2.1}\text{Sr}_{1.6}\text{CaCu}_2\text{O}_x$). $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ crystals

have lower T_c compared to polycrystalline materials, the T_c value depends on growth and heat treatment condition (T_c 0–5 K for Czochralski grown crystals for $x \lesssim 0.2$, 5–26 K for spontaneous flux-grown crystals).

(iii) The short characterization of some accessory phases ($\text{Ba}_3\text{Y}_2\text{Cu}_3\text{PtO}_{10}$), $\text{Ca}_{1.75}\text{Sr}_{1.5}\text{Cu}_{0.75}\text{PtO}_6$, $\text{Ba}_{41}\text{Cu}_{44}\text{O}_{84}\text{Cl}_2$ is given.

References

- Aleksandrov I V, Bykov A B, Goncharov A F, Denisov V N, Mavrin B N, Mel'nikov O K and Podobedov V B 1988 *JETP Lett.* **47** 184
- Aleksandrov I V, Bykov A B, Goncharov A F, Denisov V N, Mavrin B N, Mel'nikov O K, Podobedov V B and Romanova N I 1989 *JETP Lett.* **49** 150
- Avdeev L Z et al 1987 *JETP Lett.* **46** 196
- Avdeev L Z, Volkozub A V, Snigirev O V, Khanin V V, Makarenko I N and Stishov S M 1988 *JETP Lett.* **47** 474
- Bykov A B et al 1987 *JETP Lett. Supp.* **46** 19
- Bykov A B, Demianets L N, Zibrov I P, Kanunnikov G V, Melnikov O K and Stishov S M 1988 *J. Cryst. Growth* **91** 302
- Denisov V N, Mavrin B N, Podobedov V B, Bykov A B, Goncharov A F, Zibrov I P and Melnikov O K 1989a *Phys. Lett. A* **140** 141
- Denisov V N, Mavrin B N, Podobedov V B, Goncharov A F, Bykov A B, Zibrov I P and Melnikov O K 1989b *Superconductivity: Physics, Chemistry, Engineering* **2** 123
- Genkina E A, Melnikov O K, Bykov A B and Maksimov B A 1989 *Crystallography* **34** 1426
- Hidaka Y, Enomoto Y, Suzuki M, Oda M and Murakami T 1987 *Jpn J. Appl. Phys.* **26** L377
- Ivanov A S, Mitrofanov N L, Rumyantsev A Yu, Chernoplekov N A, Bykov A B and Melnikov O K 1989 *Physica* **B156–157** 910
- Makarenko I N, Nikiforov D V, Bykov A B, Mel'nikov O K and Stishov S M 1988 *JETP Lett.* **47** 52
- Oka K and Unoki M 1987 *Jpn J. Appl. Phys.* **26** L1590
- Picone P J, Jenssen H R and Gabbe D K 1988 *J. Cryst. Growth* **91** 463
- Yakubovich O V, Bykov A B and Melnikov O K 1989 *Crystallography* (in Russian) (in press)