Crystal growth of YBaCuO and BaKBiO systems from half-melt flux

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Abstract. Single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Ba}_{0.88}\text{K}_{0.12}\text{BiO}_3$ have been grown from the half-melt flux. Largest crystals with size up to $12 \times 7 \times 0.5 \text{ mm}^3$ have been obtained from previously synthesized powders of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, BaCuO_2 and copper oxide on MgO single crystal plates. The $3.5\text{BaO} \cdot \text{B}_2\text{O}_3 \cdot \text{BaF}_2 \cdot (1-x)\text{CuO} \cdot x\text{Cu}_2\text{O}$ solvents is a promising system for controlled growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals on seeds.

Keywords. Single crystal growth.

1. Introduction

The three main obstacles in the attainment of large single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductors are: incongruent melting, high aggressivity of flux-melts to all materials of technological equipment and extremely low coefficient of oxygen diffusion. The first two necessitated the choice of the technique used for single-crystal growth from the flux-melt and the third requires a search for a new efficient approach to oxygen saturation of high-quality single crystals. Timofeeva (1978) showed that successful growth of single crystals is feasible on a restricted number of seeds from the flux-melts featuring good rheological properties like high concentration of crystal-forming substances and, conversely, low viscosity, wetting of technological equipment and a wide metastable range. The flux-melts enriched in copper and barium oxides (Sadowski and Scheel 1989) currently used do not possess these properties resulting in the small crystal size, twinning, intergrowth of single crystals and difficulties in removing the crystals from the frozen flux.

2. YBaCuO system

All the known successful experiments of growing single crystals of $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ reduce to variations on the method of spontaneous crystallization from the half-melt flux of $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with an excess of BaO and CuO oxides. Using this growth technique we have obtained a considerable body of experimental evidence. The results are summarized in table 1 and figure 1.

Good results have been obtained particularly in growing single crystals in man-made cavities (compositions 1, 3, 4) or on seeds from magnesium oxide single crystals. The largest crystals with size up to $12 \times 7 \times 0.5 \text{ mm}^3$ have been grown from previously synthesized powders of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, BaCuO_2 and copper oxide (composition 8) on MgO single crystal plates. The cavities in half-melt flux were formed in two ways: (i) rapid cooling of the flux-melt from the temperature of homogeneity: $1080\text{--}1150^\circ$ to 300°C with subsequent warming up to 1000°C ; (ii) formation of thin cracks in a two-crucible system.

Table 1. Experimental growth conditions and characteristics of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals.

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$					
Mixture composition mol.%			Temperature range of synthesis (°C)	Cooling rates (°C/h)	Single crystal characteristics
$\text{YO}_{1.5}$	BaO	CuO			
2.6	31.2	66.2	1050–880	2–3	High-quality ($5 \times 3 \times 0.1$)mm ³
6.7	27.1	66.2	1100–889	4	Large ($3 \times 3 \times 0.05$)mm ³
6.7	27.1	66.2	1080–880	4	Free from melt
5.0	33.1	61.9	1050–780	3–4	High-quality ($1.0 \times 0.7 \times 0.05$)mm ³
8.7	26.6	64.7	1150–790	4	Size ($0.5 \times 0.5 \times 0.02$)mm ³
6.8	27.1	66.1	1050–790	4	Components: $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, BaCuO ₂ , CuO Size ($1.2 \times 1.2 \times 0.1$)mm ³
5.0	32.5	62.5	1050–750	3	Mixture: $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ BaCuO ₂ , CuO Best crystals ($1.2 \times 1.2 \times 0.1$)mm ³
1.8	30.4	67.8	940–830	0.5	Large ($7 \times 12 \times 0.5$)mm ³

Figure 1. Single crystal of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grown from half-melt flux.

However, despite some advantages in the method of spontaneous crystallization used we failed to restrict the number of nucleation centres, with flux-melts exhibiting unsatisfactory rheological properties. Also the absence in practice of a metastable temperature range in the flux-melt prevented the application of the well-known temperature oscillation method to set a limit on the number of seeds.

All these disadvantages create a need for: (i) a quest for new flux-melts; (ii) development of new methods of creating directed diffusion towards the crystallization boundary and supply of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ to low concentration nonstoichiometric solutions of this compound in the BaO-CuO flux; (iii) manufacture of containers or utilization of protective coatings of single-crystal materials which actually do not substitute the metal ions (for instance MgO or ThO_2).

The major requirements imposed on the flux-melts during controlled synthesis are: low pressure of vapour over the flux-melt, wetting, viscosity and solidus temperature. Moreover, it is essential that the superconductor phase should be the highest temperature phase.

Oxide solutions of $\text{Y}_2\text{O}_3\text{-BaO-CuO}$ in solvents of: (1) $\text{B}_2\text{O}_3\text{-BaO-CuO}$, (2) $\text{B}_2\text{O}_3\text{-Na}_2\text{O}$, (3) $\text{B}_2\text{O}_3\text{-K}_2\text{O}$, (4) Na_2MoO_4 , (5) NaBiO_3 , (6) $\text{Na}_2\text{O-K}_2\text{O}$, (7) Y_2O_5 , (8) $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3$ and (9) $\text{Cu}_2\text{O-B}_2\text{O}_3$ have been examined. In the flux-melts with solvents (2)–(5) and (9) the CuO phase is the highest temperature phase. Solvents (6) and (8) did not satisfy the synthesis conditions owing to high vapour pressure over the flux-melt. Vanadium pentoxide (7) is unsuitable as a solvent for high T_c superconductor synthesis due to low solubility. $\text{B}_2\text{O}_3\text{-BaO-BaF}_2$ solvent shows the most desirable solubility and rheological properties. We have investigated the phase formation in the narrow range of pseudo-ternary phase diagram of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} - 3.5 \text{ BaO} - \text{B}_2\text{O}_3\text{-BaF}_2$. In the temperature range of the existence of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ phase in air the copper oxide and barium borate phases occur. In the $17.0\text{B}_2\text{O}_3 - 40.5 \text{ BaO} - 42.5 \text{ BaF}_2$ solvent with the best rheological properties the CuO phase has been crystallized with the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ concentration varying from 17 to 25 wt%. The change of $\text{BaO} + \text{BaF}_2$ concentration in the flux-melt to 72 wt% caused the formation of the barium borate phase. The increase in concentration of crystal-forming oxides to 35 wt% did not affect the phase picture. Higher concentration led to unallowable increase in viscosity of the flux-melt. Precipitation of copper oxide and barium borate phases first gives evidence that the concentration of the crystal-forming oxides in the investigated flux-melt is not high enough. Further search for the phase field of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ results, in our opinion, in broader range of concentration. This range can be expanded to a greater extent by partial substitution of fluoride- and barium oxide by $\text{CuO/Cu}_2\text{O}$ in the solvent. We believe this flux-melt to be promising for controlled growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals.

Along with the search for barium borate-based solvents we have studied the temperature and concentration ranges of the existence of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ phase in the low concentration superstoichiometric melts. It has been established that the desired phase in the temperature range $970\text{--}920^\circ\text{C}$ precipitates steadily from the flux-melt containing 4–10 mol% $\text{YBa}_2\text{Cu}_3\text{O}_7$, 96–90 mol% eutectic solvent (28 mol% BaO –72 mol% CuO). In this case the solution ranging from 5–7 mol% $\text{YBa}_2\text{Cu}_3\text{O}_7$ reveals the best rheological properties. We consider this flux-melt to be prospective for growing of large single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the dynamical regime on seeds from single crystals of MgO , provided the technological problems of directed diffusion

Figure 2. Growth scheme of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals on seeds: 1. Supercooled crystal holder from single crystal MgO. 2. Alumina crucible with flux-melt. 3. Porous container from MgO. 4. Pellet from ceramic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

and supply to the flux-melt (the scheme as indicated in figure 2) as well as those of rust protection of technological equipment are resolved.

The crystals grown in air were either nonsuperconducting or had T_c varying from 40–60 K. Prolonged annealing time (up to 700 h) in flowing oxygen between 480 and 520°C was required for the narrow temperature range of superconducting transition to be obtained.

2. Morphology of growth, microstructure and chemical composition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals

The as-grown single crystals were in the form of rectangular parallelepipeds faceted, as demonstrated by X-ray analysis by the (100), (010) and (001) planes.

The chemical composition of these crystals was checked by neutron activation and EPM analysis. The results are shown in tables 2 and 3. Table 2 compares the analysis

Table 2. Analytical data from two methods for sample 1.

Method	Chemical composition of sample I (wt.%)				
	Y :	Ba :	Cu :	O :	Al
NAA	19	39	27	13	1.3
EPMA	20.51	40.7	25.8	11.7	1.3
Stoichiometric composition					
	20.2	38.5	26.7	14.6	—

Table 3. EPMA data for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals

Starting mixture	Chemical composition of single crystal (wt.%)					
	Y	Ba	Cu	Al	Ni	O
6	1.46	61.52	35.15	0.14	0.44	1.30
7	2.03	61.36	35.05	—	0.32	1.24
8	2.12	62.26	33.35	—	—	2.25

data obtained with two methods for sample I. Table 3 gives the EPMA data for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals grown from the mixture 6–8.

As seen from the comparison of tables 1 and 3 the single crystals grown from MgO and mixture (8) do not contain impurities within the accuracy of the method.

3. BaKBiO system

Single crystals of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ composition were grown as described by Schneemeyer *et al* (1988). The starting compounds were K_2CO_3 (99.95%), BaO (99.98%), BaO_2 (99.98%), KOH (99.98%) and $\text{Bi}_2\text{O}_3 \cdot \text{K}_2\text{O}$ and KOH were used as a flux. The best results with KOH flux were obtained when the Ba/Bi ratio was equal to 0.25 (in metal) with 40 wt% of flux. But the as-grown crystals with the maximum size $0.2 \times 0.2 \times 0.2 \text{ mm}^3$ were highly hygroscopic in air and their analysis was very difficult. Using K_2O flux we obtained better results. The starting compounds were taken in the stoichiometric ratio corresponding to the $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ formula and carefully mixed 45 wt% K_2O . The mixture obtained was placed in a Al_2O_3 crucible and homogenized for 10 at $T = 850^\circ\text{C}$, then the temperature was reduced at 50°C/h to 750°C and the melt was cooled at $0.5\text{--}1^\circ\text{C/h}$ till solidification. The results are listed in table 3. The single crystals of the BaKBiO system ($0.25 \times 0.25 \times 0.25 \text{ mm}^3$) in size obtained by the above methods were examined. Both the samples show similar patterns. The samples possessed a cubic symmetry with the parameter $a = (4.33 \pm 0.02) \text{ \AA}$ and the space group $\text{Pm}\bar{3}\text{m}$ (figure 3). XRD patterns by the oscillation method display the multiplicity of reflections which allows one to assume the presence of isostructural compounds with somewhat different parameters. The most probable way of obtaining sufficiently large single crystals of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ ($0.3 < x < 0.5$) is growing from previously synthesized compounds.

4. Conclusions

Single crystals of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ ($x \leq 0.12$) and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have been grown from the half-melt flux. A number of compositions of the $3.5\text{BaO-B}_2\text{O}_3\text{-BaF}_2\text{-(1-x)CuO} \cdot \text{Cu}_2\text{O}$ solvents have been found to be promising for a controlled growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals.

Figure 3. a. Plate-like single crystal of $\text{Ba}_{0.88}\text{K}_{0.12}\text{BiO}_{3-\delta}$ and b. as-grown single crystal of $\text{Ba}_{0.98}\text{K}_{0.02}\text{BiO}_{3-\delta}$.

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