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Single crystals of $(Bi, Pb)_2Sr_2CaCu_2O_y$ grown by the flux method using KCl as the flux

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Abstract

Single crystals of Bi-based oxide superconductors including Pb were successfully obtained by the flux method using KCl as a flux. Nitrates of Bi, Pb, Sr, Ca and Cu were used as raw materials. Carefully prepared solute calcined at a low temperature (500 °C) was used with a KCl flux. The solvation of this solute to the KCl flux proceeded very smoothly. Platy single crystals of $Bi_{1.8}Pb_{0.4}Sr_{1.6}Ca_{1.2}Cu_2O_y$ having a smooth surface and good crystallinity were extracted near the melt surface, and bulky crystals of $Bi_{1.8}Pb_{0.5}Sr_{1.5}Ca_{1.2}Cu_2O_y$ were solidified at the bottom of the crucible. Basically, these as-grown crystals belong to so-called 2:2:1:2 phase, $(Bi, Pb)_2Sr_2CaCu_2O_y$, and show superconducting transitions at 83.5 K and 88 K for platy and bulky crystals respectively.

Keywords: Single crystals; Crystal growth; Superconductivity; KCl flux

1. Introduction

Bi-based perovskite related compounds are well known as high temperature superconductors above 80 K [1–3]. Large and high quality single crystals are necessary for many measurements of physical properties to elucidate the superconducting mechanism. However, these compounds are regarded as incongruent melting compounds according to phase diagrams [4,5]. Therefore the flux method has been accepted as an important synthesis technique for obtaining single crystals. The self-flux method using CuO as a solvent has usually been applied to the Bi–Sr–Ca–Cu–O system [5,6]. On the contrary, the method using alkali halide KCl flux has also been reported [7–17]. Recently, $Bi_2Sr_2CaCu_2O_y$ films have been grown from KCl solution on several kinds of ceramic substrate, e.g. $SrTiO_3$ [17], by the liquid-phase epitaxy (LPE) [15–17] technique. This technique is promising in view of the possibility of growing a large epitaxial film of the $Bi_2Sr_2CaCu_2O_y$ phase. Thus KCl can be an important intermediate for the synthesis of single crystals belonging to the Bi–Sr–Ca–Cu–O system.

Here we report the growth and superconductivity of single crystals of Bi-based oxides including Pb (in the Bi–Pb–Sr–Ca–Cu–O system) from an alkali chloride KCl ($d_{20} = 1.989$ g cm^{-3}; melting point, 776 °C; boiling point, 1500 °C) flux (solvent). Highly dispersed mixed oxides, which were carefully prepared by pyrolysis of raw material nitrates, were used as the solute.

2. Experimental

2.1. Sample preparations

A solute was prepared from $Bi(NO_3)_3 \cdot 5H_2O$ (purity, 99.9%), $Pb(NO_3)_4$ (purity, 99.9%), $Sr(NO_3)_2$ (purity, 99.9%), $Ca(NO_3)_2 \cdot 4H_2O$ (purity, 99.9%+) and $Cu(NO_3)_3 \cdot 3H_2O$ (purity, 99.9%). These reagents were weighed in the molar ratio 2:0.8:2:2:3, dispersed in pure water, and then stirred to mix well, followed by the evaporation of water by heating. The resultant residue was further heated to 500 °C in air and maintained at this temperature for 20 h for the calcination. The calcined material was used as a solute (nutrient). A 25 wt.% mixture of the solute together with KCl solvent

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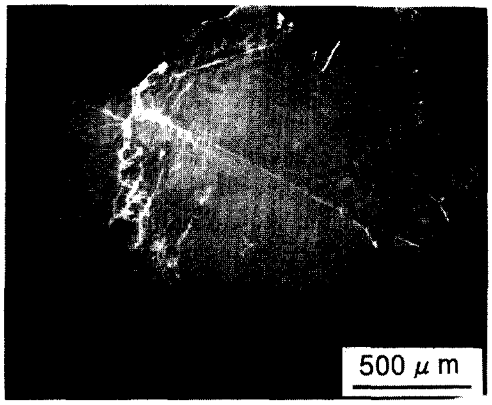
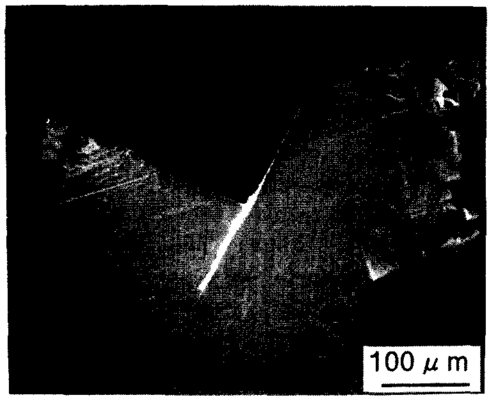
(flux) was put into a platinum crucible of 70 mm diameter and 70 mm height and was then heated up to 890 °C. The mixture was kept at that temperature for 3 h, slowly cooled at 5 °C h^{-1} to 750 °C and then rapidly cooled to room temperature. Single crystals were separated from the solidified material by dissolving KCl in warm water.

2.2. Characterizations

All scanning electron micrographs were taken using a Hitachi-S-800 scanning electron microscope. The composition was determined on the surface of the crystals by means of energy-dispersive X-ray analysis (EDXA). The crystals were then observed with a JEM-2010 transmission electron microscope at an acceleration voltage of 200 kV. A crystal structure analysis was carried out using an X-ray powder diffractometer. The magnetization of the samples was measured with an a.c. magnetometer (f=80 Hz; $H \approx 1$ Oe), where the temperature of the sample was determined with a Pt thermometer.

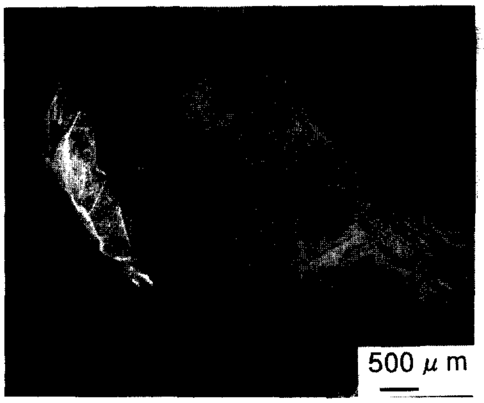


(a)

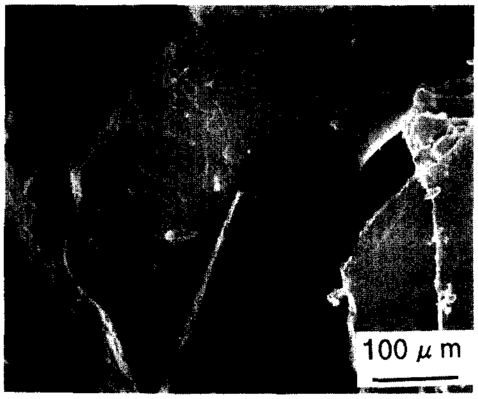


(b)

Fig. 1. (a) Scanning electron micrograph of a platelet grown near the melt surface. (b) An enlargement of the region indicated by an arrow in (a).



(a)



(b)

Fig. 2. (a) Scanning electron micrograph of a block solidified at the bottom of the crucible. (b) An enlargement of the region indicated by an arrow in (a).

Table 1
Cationic compositions of the grown crystals in the system of Bi–Pb–Sr–Ca–Cu–O and of the initial mixture

	Atomic fraction of the following				
	Bi	Pb	Sr	Ca	Cu
Platy crystal	1.8	0.4	1.6	1.2	2
Bulky crystal	1.8	0.5	1.5	1.2	2
Initial mixture	2	0.8	2	2	3

3. Results and discussion

The preparation of the solute is very important in applying a flux growth method. Highly dispersed mixed oxides by pyrolysis of nitrate precursors were prepared. The solvation of this solute to the KCl solvent proceeded very smoothly. Surface roughening of the crystals under study and adhesion of many needle-like crystals [7,8] were successfully prevented. In addition, the flux reported here is easily removed from the crystals.

Thin plates with a black luster were grown near the KCl melt surface (Fig. 1), and bulky crystals (Fig. 2) were solidified at the bottom of the crucible. The

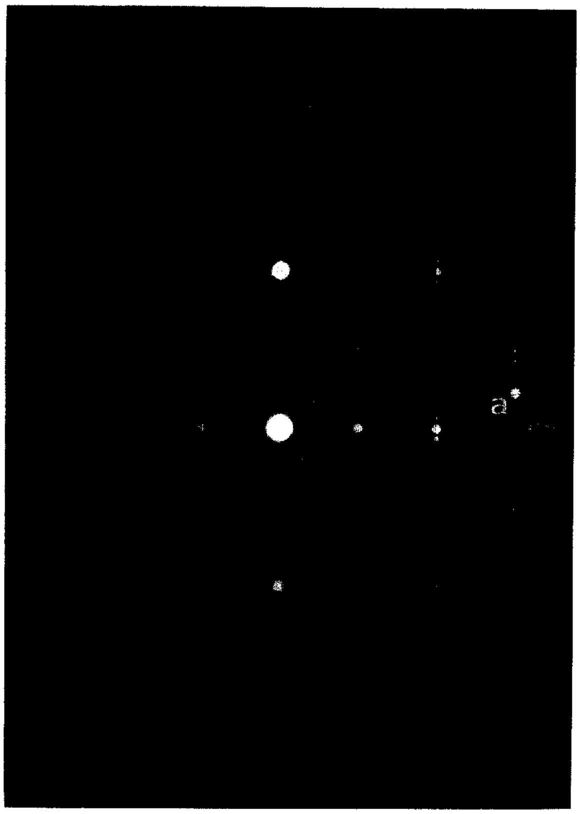


Fig. 3. Electron diffraction pattern of the platy crystal taken with the incident beam parallel to the [001] direction.

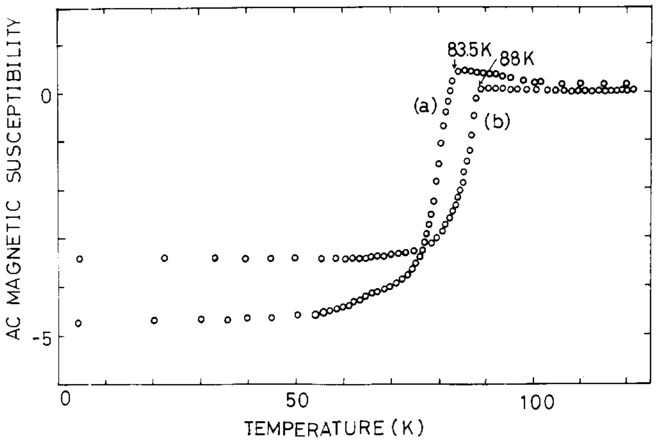


Fig. 4. Magnetization curves as a function of temperature: (a) platelets; (b) block.

distance from the melt surface to the bottom is about 40 mm, and the temperature at the bottom is slightly higher than that at surface. The chemical compositions of the platy crystals and bulky crystals are $Bi_{1.8}Pb_{0.4}Sr_{1.6}Ca_{1.2}Cu_2O_y$ and $Bi_{1.8}Pb_{0.5}Sr_{1.5}Ca_{1.2}Cu_2O_y$ respectively. The Pb and Sr contents of these crystals are different from each other. Basically, these crystals were of so-called 2:2:1:2 phase. The chemical compositions of the present samples are shown in Table 1, together with that of the starting mixture. No evidence of the incorporation of Pt, K or Cl from the crucible and the flux was obtained by EDXA. Fig. 3 shows an example of the electron diffraction pattern obtained from the platy sample. The incident electron beam was parallel to the [001] direction. It is noted that there is a structural modulation along the *b* axis which is characterized by the superlattice reflections indicated by the arrows as reported previously [18–21]. The period of the superstructure is about 7.5*b*.

As shown in Fig. 4, the temperature dependences of the magnetic susceptibilities of these crystals are slightly different from each other; it shows the superconducting transition temperatures at 83.5 K and 88 K for platy crystals and for bulky crystals respectively.

In conclusion, studies of the single-crystal growth of oxide superconductors in the Bi–Pb–Sr–Ca–Cu–O system by the flux method using KCl as the flux has been carried out. Materials carefully calcined at a low temperature derived from nitrates of Bi, Pb, Sr, Ca and Cu were used as a solute with a KCl solvent. The solvation of this solute to the KCl solvent proceeded very smoothly. Platy single crystals of Bi-based oxide superconductors containing Pb having a smooth surface and good crystallinity were successfully extracted near the melt surface. On the contrary, bulky crystals of the superconductor were solidified at the bottom of the crucible. The growth, compositions and fundamental superconducting properties of the crystals have been reported.

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