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Superconductivity and morphological studies on $Bi_2Sr_2CaCu_2O_8$ single crystals grown from stoichiometric and nonstoichiometric melts

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Abstract. Single crystals of $Bi_2Sr_2CaCu_2O_8$ (2212) have been grown by self-flux technique using stoichiometric and non-stoichiometric melts of excess CuO and Bi_2O_3. Single-crystal and powder X-ray diffraction studies have been made on the grown crystals to confirm their single crystallinity and structure respectively. Resistivity and susceptibility measurements provide information on the superconducting nature of the crystals. The effects of fluxing agents and starting composition on surface morphology and superconducting properties have been discussed.

Keywords. Oxide superconductors; flux technique; resistivity; susceptibility.

1. Introduction

The occurrence of superconductivity in Bi-Sr-Cu-O (Michel *et al* 1987) and Bi-Sr-Ca-Cu-O (Maeda *et al* 1988) has stimulated considerable research activity on this system. This system exhibits three different phases of compositions viz. $Bi_2Sr_2CuO_y$ (2201), $Bi_2Sr_2CaCu_2O_y$ (2212) and $Bi_2Sr_2Ca_2Cu_3O_y$ (2223) with T_c near 20, 80 and 110 K respectively (Rao *et al* 1988; Tarascon *et al* 1988; Oka *et al* 1989; Li *et al* 1989). Single crystals of these materials are important for resolving the structure fineness. To grow large size crystals, a basic understanding of the crystallization and growth processes is important.

Several reports are available on the crystal growth of $Bi_2Sr_2CaCu_2O_8$, like the growth from off-stoichiometric starting composition (Balestrino *et al* 1988), using alkali halide fluxes (Schneemeyer *et al* 1988; Sureshkumar *et al* 1990), by laser-heated floating zone process (Feigelson *et al* 1988), from liquid phase by slow cooling (Shigematsu *et al* 1990), by the modified Bridgman technique (Pinol *et al* 1990) and by the travelling solvent float zone technique (Shigaki *et al* 1990).

The problems encountered in the growth of single crystals of Bi-Sr-Ca-Cu-O system were (i) extreme anisotropy in layered habit, (ii) tendency for syntactic intergrowths (Han and Payne 1990), (iii) oxygen defects and (iv) the narrow crystallization temperature region in the phase diagram (Shigematsu *et al* 1990). One line of approach for further experimental investigations is to study the growth aspects and superconducting properties with different flux materials.

The present paper describes the single-crystal growth of $Bi_2Sr_2CaCu_2O_8$ from stoichiometric and non-stoichiometric melts as well as their surface features and morphology. The phases of the grown crystals have been confirmed by powder X-

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ray diffraction analysis. Resistivity and susceptibility have been measured to confirm the superconducting property.

2. Experimental

Single crystals of $Bi_2Sr_2CaCu_2O_8$ were grown by slow-cooling technique from Bi_2O_3-$SrCO_3$-$CaCO_3$-CuO solutions of three different compositions. The starting atomic proportions of the mixtures were 2:2:1:2, 25 mol% of excess CuO with 2:2:1:2 and 2:2:1:2 with 50 mol% of excess Bi_2O_3. Each of the above mixtures was fused in a 25 cc alumina crucible and the growth experiments were carried out in a high temperature furnace in air. The maximum and the crystallization temperatures for different fluxes are listed in table 1. For all experiments the cooling rate was 5°C/h.

The crystals were extracted by careful breaking of the crucibles. In the stoichiometric melt, while removing the contents of the crucible, it was found that small platelets of crystals were packed together, which often spanned the entire breadth of the crucible bottom and it was very difficult to dislodge them from the solidified matrix. In the case of non-stoichiometric melt with excess CuO, crystals were found on the surface of the melt. For excess Bi_2O_3 solution large plate-like crystals were observed at the bottom of the crucible and were easily separated from the solidified mass.

The grown crystals were viewed through an optical microscope to study the surface morphology and growth mechanism. Powder X-ray diffraction patterns were recorded by using CuK_α radiation. Samples were prepared by grinding several crystalline blocks. All crystals possessed tetragonal structure.

Resistivity was measured using a standard dc four-probe technique with an input current of 1 mA. For the stoichiometric melt-grown crystals, the measurement was made on an ingot of crystals. Measurements could be made perpendicular to c-axis for the crystals grown from excess CuO and Bi_2O_3 fluxes. The temperature dependence of susceptibility was studied for the crystals grown from stoichiometric melt using ac susceptometer (Lake shore model 7000). Data were taken at 400 A/m rms applied field and at applied field frequency of 100 Hz.

Table 1. Different flux materials used for the growth of $Bi_2Sr_2CaCu_2O_8$ single crystals.

Starting composition	Excess flux	Temperature range (°C)	Lattice constants (Å)	Results
$Bi_2Sr_2CaCu_2O_8$ (BSCCO)	---	1050–970	$a = b = 5{\cdot}41$ $c = 30{\cdot}73$	Very thin crystals ($1 \times 0{\cdot}5 \times 0{\cdot}3$ mm^3) $T_c = 79$ K
BSCCO	CuO (25 mol%)	990–930	$a = b = 5{\cdot}45$ $c = 30{\cdot}69$	Bigger size crystals ($1 \times 1 \times 0{\cdot}5$ mm^3) $T_c = 68$ K
BSCCO	Bi_2O_3 (50 mol%)	980–930	$a = b = 5{\cdot}52$ $c = 30{\cdot}58$	Non-superconducting crystals ($3 \times 1{\cdot}8 \times 1$ mm^3)

3. Results and discussion

Figure 1a shows the optical photomicrograph of crystals grown from $Bi_2Sr_2CaCu_2O_8$ melt. In most of the trials several plate-like crystals were found intimately juxtaposed. The surface morphology of the as-grown crystal shown in figure 1b indicated that the growth took place layer by layer. This characteristic layered growth was due to the 2D nucleation mechanism in this system.

The crystal grown from excess CuO melt is shown in figure 2a. These crystals were found to be shiny, irregularly-shaped and several times thicker (0·5 mm) than the crystals grown from alkali halide fluxes (Sureshkumar *et al* 1990). Figure 2b shows the sculptured shape patterns on the crystal surface, which were formed due to the non-uniform supersaturation of the solvent during growth. A black, irregular-shaped crystal grown from Bi_2O_3 solution is shown in figure 3a. The surface of the crystal (figure 3b) shows interlaced layer patterns which were due to unstable growth conditions.

Though all the crystals from the same batch visually looked alike under optical microscope, the Laue X-ray diffraction study revealed that all the crystals in the same batch need not necessarily be single crystals. Some of them were found to be

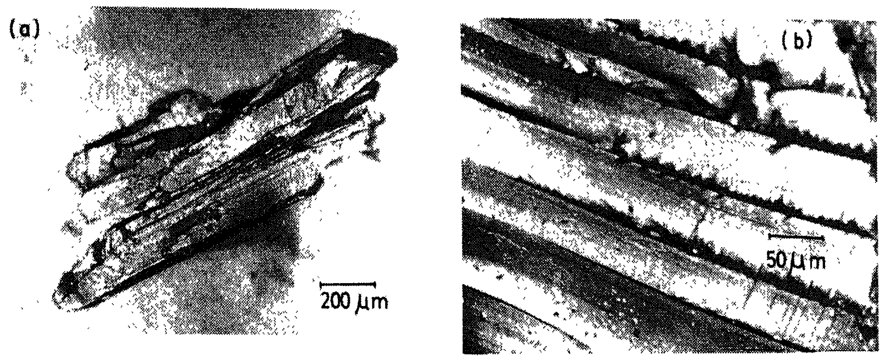

Figure 1. Optical photomicrograph of $Bi_2Sr_2CaCu_2O_8$ crystal (**a**) grown from stoichiometric melt and (**b**) surface showing layer growth mechanism.

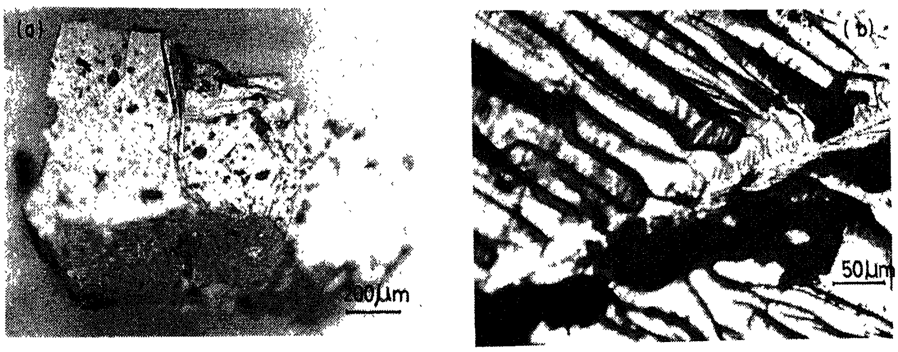

Figure 2. (**a**) $Bi_2Sr_2CaCu_2O_8$ crystal grown from excess CuO flux and (**b**) sculptured shape patterns observed on the surface.

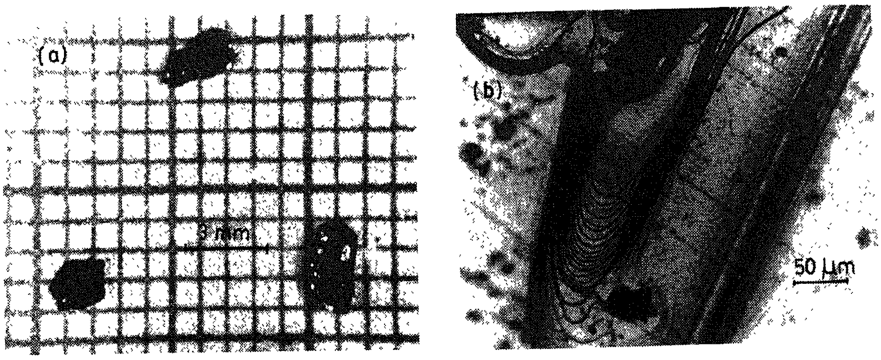

Figure 3. (a) $Bi_2Sr_2CaCu_2O_8$ crystals grown from excess Bi_2O_3 melt and (b) optical photomicrograph of the crystal surface.

Figure 4. Laue photograph of 2212 crystal grown from stoichiometric melt.

polycrystalline too. The Laue photograph of one of the crystals is shown in figure 4. Lattice parameter values calculated from the powder X-ray diffraction patterns showing a tetragonal structure are listed in table 1. For non-stoichiometric melt-grown crystals, a few peaks corresponding to the 2201 intergrowths and CuO phase have been observed.

The temperature dependence of resistance for the grown crystals is shown in figure 5. For an ingot of crystals grown from stoichiometric melt, the superconducting transition began at 95 K and reached the zero resistance state at 79 K. Crystal grown from CuO solution showed double transition, first with a T_c onset at about 100 K and the second at about 85 K. Zero resistance T_c was observed only at 68 K presumably due to some chemical inhomogeneity and existence of 2201 intergrowths. No evidence of superconductivity was observed for crystals grown from excess Bi_2O_3 melt. This may possibly be because of high Sr deficiency in the crystal. The actual amount of Sr incorporated into the crystals depended on the rate of evaporation of Bi_2O_3 solution, the strain effect during the growth and the degree of reaction between the melt and crucible walls.

Figure 6 shows the ac susceptibility data for $Bi_2Sr_2CaCu_2O_8$ crystal grown from stoichiometric melt. As the temperature increased, the diamagnetic curve slowly increased completing the transition by 80 K and indicating the superconducting transition temperature.

4. Conclusions

The effect of different fluxing agents on the crystal growth of $Bi_2Sr_2CaCu_2O_8$ has been studied. Crystals have been grown from both stoichiometric and non-stoichiometric melts. A layer growth pattern which was indicative of the 2D nucleation mechanism has been observed. It has been found that the flux material which was favourable for the growth of bigger size crystals decreased the crystal

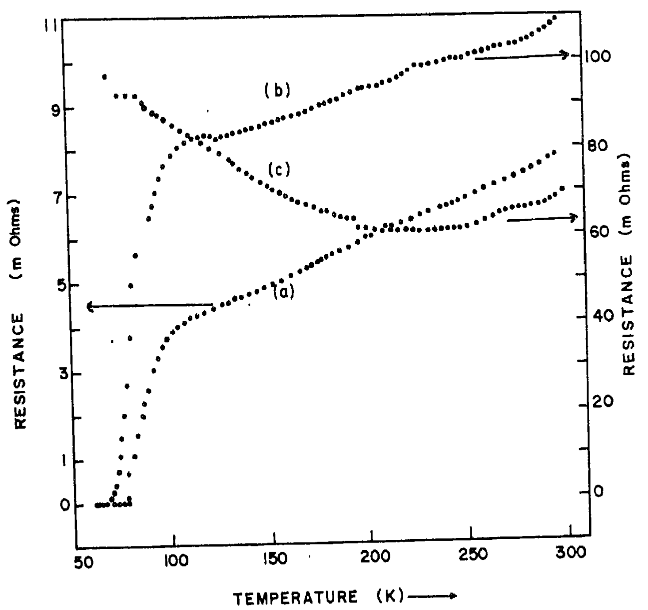

Figure 5. Temperature dependence of resistance of Bi-2212 crystals grown from (a) stoichiometric melt, (b) excess CuO flux and (c) excess Bi_2O_3 flux.

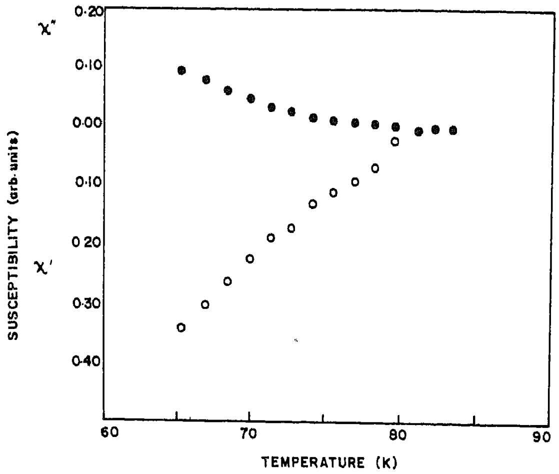

Figure 6. ac susceptibility data for Bi-2212 crystal grown from stoichiometric melt.

quality. Studies relating to anisotropy in resistivity, susceptibility and field and frequency dependence of susceptibility are in progress.

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