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Studies on simultaneous substitution of Pb and Y in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ single crystals

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Abstract

The effect of simultaneous substitution of Pb for Bi and Y for calcium in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ has been studied. Phase pure single crystals of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+\delta}$ have been grown for $x = 0$ to 0.5. Variation in lattice parameters and the change in superconducting transition temperature for different x values have been studied. The optical micrograph revealed the layer growth mechanism and occurrence of some growth twins which are not removed even after annealing. Chemical etching with a bromine–ethanol solution revealed elongated diamond shaped etch pits reflecting the orthorhombic symmetry of the crystal. © 1997 Elsevier Science B.V.

Keywords: Surface morphology; Etching; Substitutional study; Susceptibility; Twins

1. Introduction

Among the three superconducting phases of the Bi-system, the Bi-2212 phase is highly stable and has been studied extensively. Many substitutional studies have been made on this compound as it offers a wide range of isomorphous replacements [1,2]. The substitution in the charge reservoir layer affects the amount of charge on the conduction planes thereby causing an increase or decrease in the transition temperature [3]. The doping also creates structural defects which may affect the transport properties in turn. Substitutional studies on single crystals infer more information on the structural perturbation and physical properties compared to the polycrystalline materials. It has been reported that the partial

substitution of Bi by Pb increases the volume fraction of the high T_c phase [4,5]. Also, the substitution of Y for the divalent Ca causes a decrease in the carrier concentration and thereby decreasing the transition temperature [6,7] in Bi-2212 single crystals. Here we report on the single crystal growth of Bi-2212 with the simultaneous substitution of Pb and Y in the Bi and Ca sites, respectively. Since the incorporation of Pb ions into the crystal lattice causes the formation of a higher volume fraction of the high T_c phase, there has been a considerable interest in studying the chemical and physical properties of Bi–Sr–Ca–Cu–O by adding foreign elements or substituting partially one or more ions in the parent compound. The valence-equality principle is taken care of by the substitution of Pb and Y, i.e., for a formal valence of Bi^{3+} , the substitution of Pb^{2+} is isoelectronic to Y^{3+} substituting for Ca^{2+} . Single crystals have been grown for various Y concentra-

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tions using KCl flux. The crystal growth temperature is much reduced with the KCl flux and the crystallization of the high temperature Bi-2201 phase is avoided and pure 2212 crystals are obtained. The grown crystals have been characterized using optical microscopy, powder X-ray diffraction and Inductively Coupled Plasma (ICP) analysis and etching studies have also been performed using a bromine–ethanol solution.

2. Experimental

High purity chemicals of Bi_2O_3 , SrCO_3 , CaCO_3 , CuO , PbO and Y_2O_3 were taken in the appropriate ratio in a recrystallized alumina crucible after mixing them carefully using acetone in an agate mortar. The mixture was calcined in air at the subsolidus temperature, i.e., between 700°C and 750°C . The calcined mixture was then added with KCl flux in the flux charge ratio 70:30 mol% and heated up to 980°C in a silicon carbide resistive heating furnace. After soaking for about 5 h the temperature was lowered down to 800°C at the rate of $1^\circ\text{C}/\text{h}$ and then to room temperature at a faster rate. The temperature was monitored and the thermal cycle programme was controlled by means of a PID controller using Pt–Pt–Rh thermocouple. A cluster of crystals well-oriented in one direction was found on the solidified matrix. As most of the KCl flux evaporated during crystal growth the crystals were easily separated by breaking the crucible. For all the compositions, the crystals were found over the entire volume of the crucible. The dimensions of the crystals were of the order of $3 \times 2 \times 1 \text{ mm}^3$ and the surface was black and shiny. ICP analysis was carried out to determine the crystal composition. The as-grown crystals were subjected to etching and AC susceptibility studies without any post growth treatment. For the etching study, a shiny crystal was dipped into the bromine–ethanol solution for about 30 s. The etched surface was then dried and its surface was observed through an optical microscope.

3. Results and discussion

The use of KCl flux helps in separating the crystals very easily, unlike in the case of stoichio-

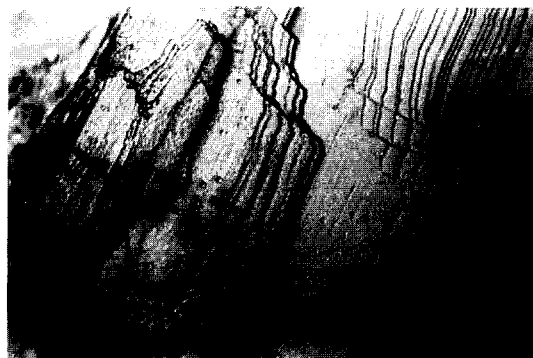


Fig. 1. Optical micrograph of the crystal ($x = 0.1$) depicting the layer growth pattern (200 times).

metric melt or excess CuO flux. However, due to the evaporation of KCl during the initial crystallization, the solution becomes supersaturated and the crystals grow on the surface of the melt. These crystals grown on the surface of the melt obstruct further evaporation of the KCl and hence the degree of supersaturation becomes lower thereby limiting the size of the crystals found at the bottom of the crucible.

3.1. Morphology and etching studies

Thin shiny platelet crystals were used for optical microscopic studies. Fig. 1 shows the optical micrograph of the crystal $x = 0.1$. Layer growth patterns are observed on the surface indicating that the crystal grows by means of two-dimensional nucleation mechanism. Fig. 2 shows the twin patterns observed on one of the crystals grown from $x = 0.3$. In the

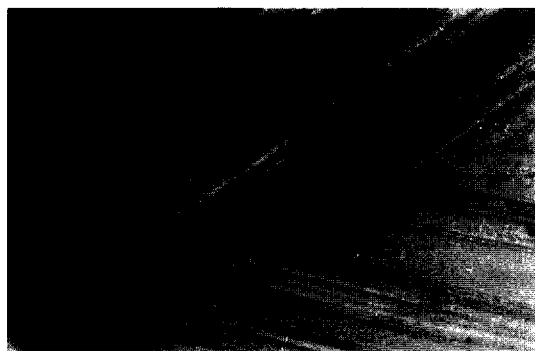


Fig. 2. Twin patterns observed on the crystal for $x = 0.3$ (180 times).



Fig. 3. Etch patterns observed on the crystal (450 times).

Bi-2212 system the twins are generally formed during growth and cannot be removed by any post-growth methods [8–10]. In the present case also, it has been found that the twins are not removed when the indentations are performed on the crystals by heating up to the partial melting temperature of the crystal (845°C) thereby confirming the twins are growth twins.

In order to perform the etching studies, after

trying with several etchants the bromine–ethanol solution was found to be a suitable etchant, which does not diffuse into the crystals and change the stoichiometry. For the bromine concentration of more than 1% in absolute alcohol or the etching time of more than 60 s, insoluble reaction products are formed on the surface and no significant patterns are observed. At the same time, when the etching time is reduced below 30 s the surface of the crystal is found to be polished and etch patterns are observed as shown in Fig. 3. The optimised etching time leads to elongated-diamond-shaped etch patterns reflecting the orthorhombic symmetry of the crystal. The etching studies reveal the accumulation of defects near the crystal edge and the defects appear in the form of chain and the dislocation lines are not in perfect manner.

3.2. X-ray and superconductivity studies

The powder XRD revealed that the crystals are phase pure with no intergrowth of high and low T_c

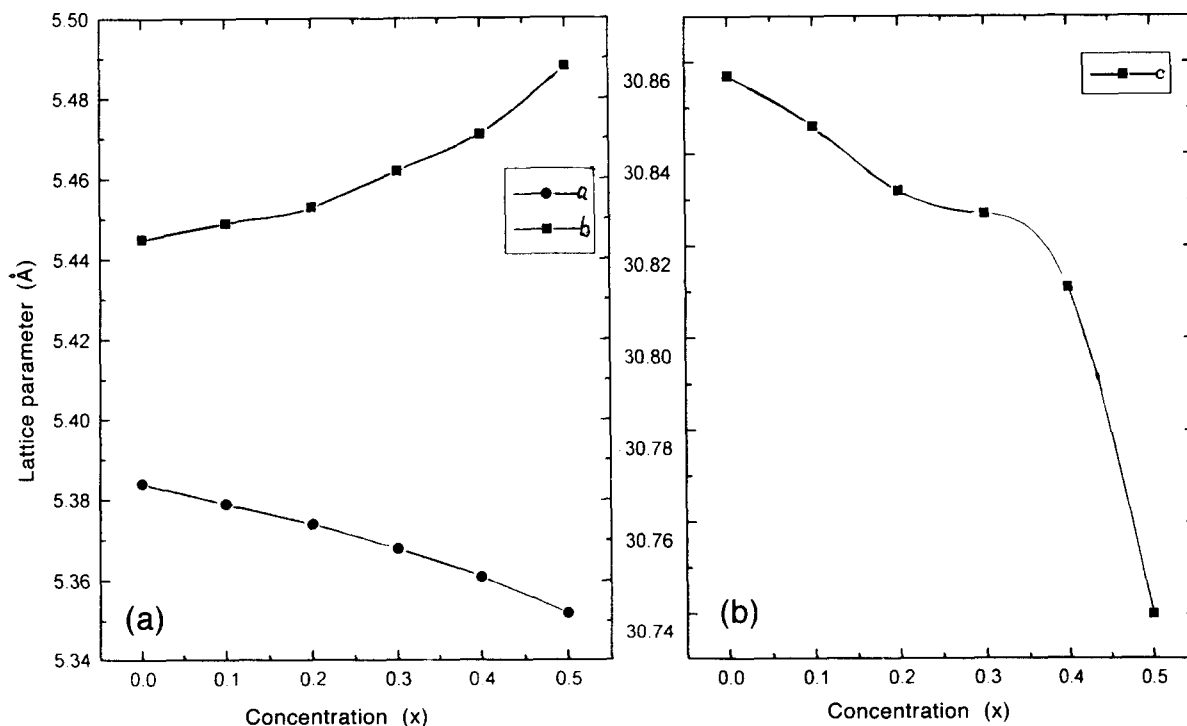


Fig. 4. (a) Variation in the a and b lattice parameters with Y concentration; (b) variation in the c lattice parameter with Y concentration.

Table 1
Variation of lattice parameters and T_c values with Y concentration

x	Lattice parameter (Å)			T_c (K)
	a	b	c	
0.0	5.384	5.445	30.857	96
0.1	5.379	5.449	30.846	90
0.2	5.374	5.453	30.832	87
0.3	5.368	5.462	30.827	80
0.4	5.361	5.471	30.811	72
0.5	5.352	5.484	30.740	n.s.

phases. All the reflections are indexed to orthorhombic structure with cell parameters close to those of Bi-2212 ($a = 5.364$ Å, $b = 5.402$ Å, $c = 30.891$ Å). A plot of the cell parameter versus the concentration of yttrium is shown in Fig. 4. From the graph it is seen that the substitution of Y into the Bi-2212 superconductor leads to a sharp decrease of the c parameter and to a large increase of the orthorhombic distortion with increasing Y concentration. The variation in lattice parameters and T_c values are listed in Table 1. The T_c is found to decrease with increasing Y concentration. The decrease in the transition temperature may be attributed to the replacement of divalent Ca by trivalent Y which involves an excess of oxygen with respect to the stoichiometric formula [11], and also due to a decrease in the carrier concentration. For $x = 0$, the T_c is 96 K and this enhancement in T_c may be attributed to the formation of oxygen vacancies as a result of partial substitution of Pb^{2+} ions at Bi^{3+} sites [12]. Though the powder XRD reveals single phase for various concentrations of yttrium, the crystals with a higher yttrium concentrations ($x = 0.5$) are not superconducting down to 50 K. Hence, it can be concluded that the T_c is restricted to a narrow compositional range, in spite of the isostructural phase formation. From the ICP results, it has been observed that the starting and the crystal composition are nearly equal.

4. Conclusion

Single crystals of $Bi_{1.7}Pb_{0.3}Sr_2Ca_{1-x}Y_xCu_2O_{8-\delta}$ have been grown for various Y concentrations. The use of KCl flux resulted in the easy separation of the

crystals from the solidified matrix. The lattice parameters are found to vary with Y concentration and the orthorhombic distortion also increases with the yttrium concentration. The morphological study revealed that the crystals grow by means of two dimensional nucleation mechanism. A decrease in the transition temperature with increasing Y concentration may be due to the replacement of divalent Ca by the trivalent Y. For higher concentration of yttrium ($x = 0.5$) the crystals are not superconducting, indicating that T_c is restricted to a narrow compositional range.

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