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The Effect of Sb Substitution of Cu in $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_{3-x}Sb_xO_y$ Superconductors

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The effect of partial substitution of Cu in $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_{3-x}Sb_xO_y$ at $x = 0.0$, 0.05, 0.1, 0.15, and 0.2 levels on the electrical and structural properties was investigated in this work. X-ray diffraction analysis shows that these materials have a multiphase structure. Two different types of particles with different morphologies were observed in scanning electron micrographs. The T_c values decreased from 103.5 to 87 K for $x = 0.1$ Sb substitution level with a subsequent increase to 101 K at $x = 0.2$.

1. Introduction

Bi-based copper oxide superconductors have received considerable attention because of their high transition temperature. Since the discovery of high-T_c superconductivity in “BSCCO” cuprate ceramics [1], significant effort has been devoted to prepare high quality single phase bulk BSCCO superconductors. There may be several phases present in the BSCCO system depending on the preparation conditions. The low-T_c (80 K) $Bi_2Sr_2CaCu_2O_x$(2212) and the high-T_c (110 K) $Bi_2Sr_2CaCu_3O_x$(2223) phases are the most dominant ones of these phases. The high-T_c 2223 phase belongs to the orthorhombic crystal system. Both phases have a characteristic common property, namely the perovskite structure as a basic structure which contains several CuO_2 layers in the unit cell. It is well known that the critical transition temperature T_c, and the critical transport current density, J_c, of copper oxide superconductors are very sensitive to the hole concentration and the oxygen content in the system [2, 3]. In order to improve the superconducting properties and increase the volume fraction of the high-T_c phase, modifications of the structure by the incorporation of various cations like Pb, Ag, Sb, V etc. have been tried [4 to 6]. Partial substitutions of bismuth by Sb and Pb have been reported to cause improvements in the superconducting properties (see Kijima et al. [7]). Sb doping alone without Pb was reported to have an adverse effect on the critical temperature in our earlier work [8]. A new phase called as 4441 with the most intense peaks located at about $2\theta = 30^\circ$ in Sb-doped BSCCO superconductors was reported in a number of studies [8, 9]. Although it is commonly suggested that Sb doping brings down the sintering temperature by enhanced sintering kinetics, the reports on its effects on T_c varies significantly. T_c values as high as 150 and 132 K along with low values like 70 K have been reported in Pb and Sb-doped superconductors [10 to 12]. All these significantly different research findings (with different compositions and preparation techniques) call for further research on the effects of Sb doping in the BPSCCO superconducting system. Although there is a significant amount of work on the partial substitution of bismuth by Sb and Pb, work on the partial substitution of Cu by Sb is missing. Sb was suggested to have an oxygen-incorporating effect whereas Pb has an oxygen-depleting effect [13]. The ionic radii of Cu^{2+} and Sb^{3+} are 0.72 and 0.76 Å and the electronegativities of these ions are $\chi = 2.0$ and 1.8, respectively. Since these properties are very similar, Sb may enter the Cu sites easily. It was previously stated that the investigation of Sb addition to a copper deficient system may be of interest [14]. The purpose of the present work was the investigation of the effects of partial Sb substitution of copper on the electrical and structural properties of Pb-doped BSCCO ceramics and to examine whether 4441 phase forms in these superconductors.

2. Experimental Procedures

The $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_{3-x}Sb_xO_y$ superconducting ceramics were prepared by the conventional solid-state reaction of the starting components. High purity (99.99% Aldrich Chem. Co.) Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, CuO, and Sb_2O_3 powders were mixed at five different ratios to give $x = 0.0$, 0.05, 0.1, 0.15, and 0.20 (samples A to E, respectively) in the final ceramic. These powder mixtures were well ground and mixed in a mortar and calcined in alumina crucibles at 800 °C in air for 40 h in a furnace. The calcined powders were well ground again and pellets 10 mm in diameter and 1 to 1.5 mm thick were prepared by uniaxial pressing at 450 MPa. These pellets were further sintered in air at 845 °C for 120 h followed by furnace cooling to room temperature. For all samples resistance was measured as a function of temperature using the ac four-point probe technique. X-ray diffraction (XRD) patterns in the $2\theta = 4°$ to $60°$ Cu K_α range were obtained by using a JEOL JSDX 100S Diffractometer. Scanning electron microscopy (SEM) images were taken by using a JEOL JJXA 733 microscope. The bulk densities were obtained from the bulk dimensions and an Archimedes water displacement technique.

3. Result and Discussions

The temperature dependence of the resistance of all samples is shown in Fig. 1. The onset temperature is defined as the temperature corresponding to the temperature where the resistance–temperature plot deviates from linearity. All samples display a metallic character above the onset temperature. The onset temperature is about 110 K for the undoped sample A and decreases to 106 K for samples B and C ($x = 0.05$ and 0.1). The onset temperature increases to 107 K for sample D ($x = 0.15$) and 109 K for sample E ($x = 0.2$). The critical temperature T_c was determined as the temperature at zero resistance. The variation of T_c with Sb content x is given in Fig. 2. The similar trend for the onset temperatures is observed for T_c, too. T_c for the undoped sample is 103.5 K, and it decreases to 96.5 K for $x = 0.05$, and to 87 K for $x = 0.0$. For samples D and E ($x = 0.15$ and 0.20), T_c increases back to about 101 K.

The XRD patterns of all samples are given in Fig. 3. The high-T_c and low-T_c phase peaks were identified by using the tables given by Bansal et al. [15] and Pandey et al. [16, 17]. All samples have a multiphase nature with high and low-T_c peaks along with

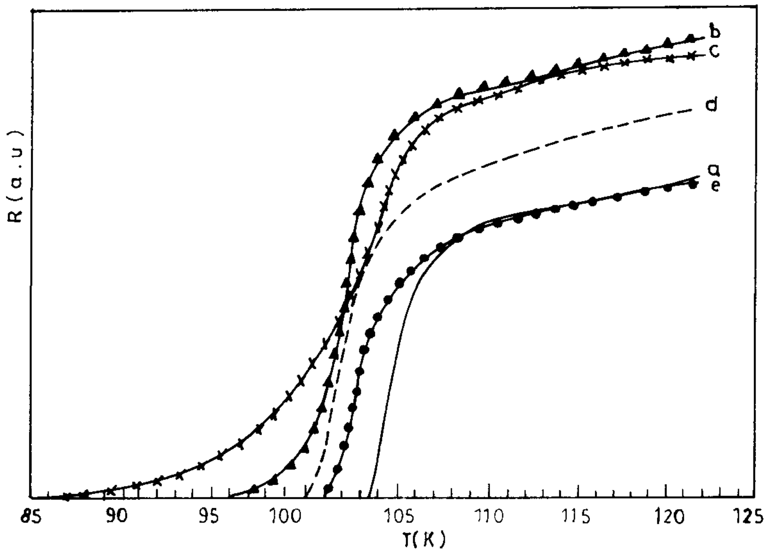

Fig. 1. Temperature dependence of electrical resistance for samples: (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.1$, (d) $x = 0.15$, (e) $x = 0.2$

two impurity phases CuO and Ca_2PbO_4. The two CuO peaks were identified in all samples at 2θ values of 38.6° and 35.1°. A weak characteristic impurity phase Ca_2PbO_4 peak at $2\theta = 17.8°$ was identified in all samples. A cluster of strong peaks were identified in the $2\theta = 29°$ to 31.5° range for the Sb-doped samples with two strongest peaks at 29.58° and 30.05°. The presence of a new 4441 phase was identified in a number of papers and it was also reported to have a high onset temperature near 140 K [9, 11, 18]. The 4441 phase was represented by $Bi_3Sb_{0.8}Pb_{0.2}Sr_{4.1}Ca_{3.9}CuO_{15}$ [18] which was reported to be nonsuperconducting. The intensities of the 4441 peaks in the cluster increase with Sb doping from 0.05 to 0.20. There are strong high-T_c and low-T_c phase peaks in sample A. The intensities of these peaks decrease significantly with Sb doping from 0.05 to 0.10 (samples B to C). The intensities of the high-T_c and low-T_c phase peaks increases again in samples D and E along with significant increases in the 4441

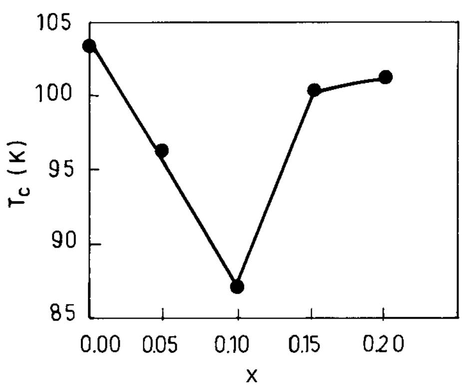

Fig. 2. Variation of critical temperature of Sb-doped samples of $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_{3-x}Sb_xO_y$ with Sb content

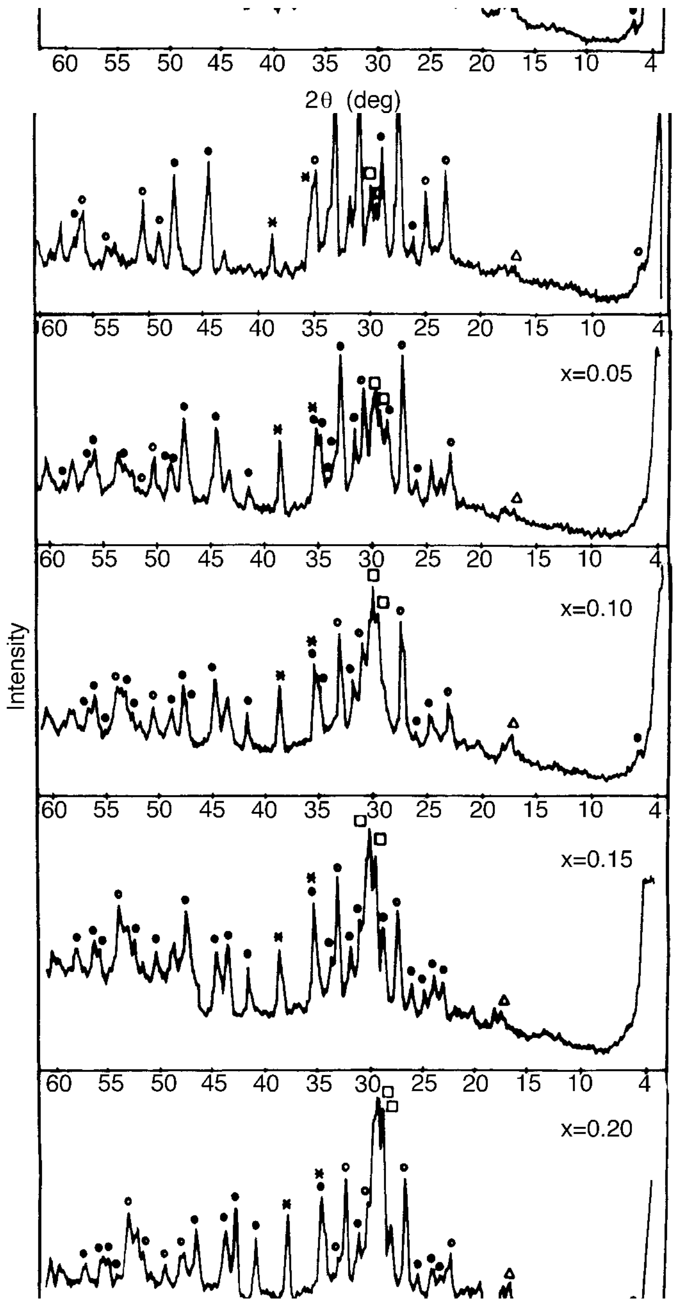

Fig. 3. XRD patterns of samples; ○ low-T_c phase, ● high-T_c phase, $*$ CuO, △ Ca_2PbO_4, □ monoclinic phase

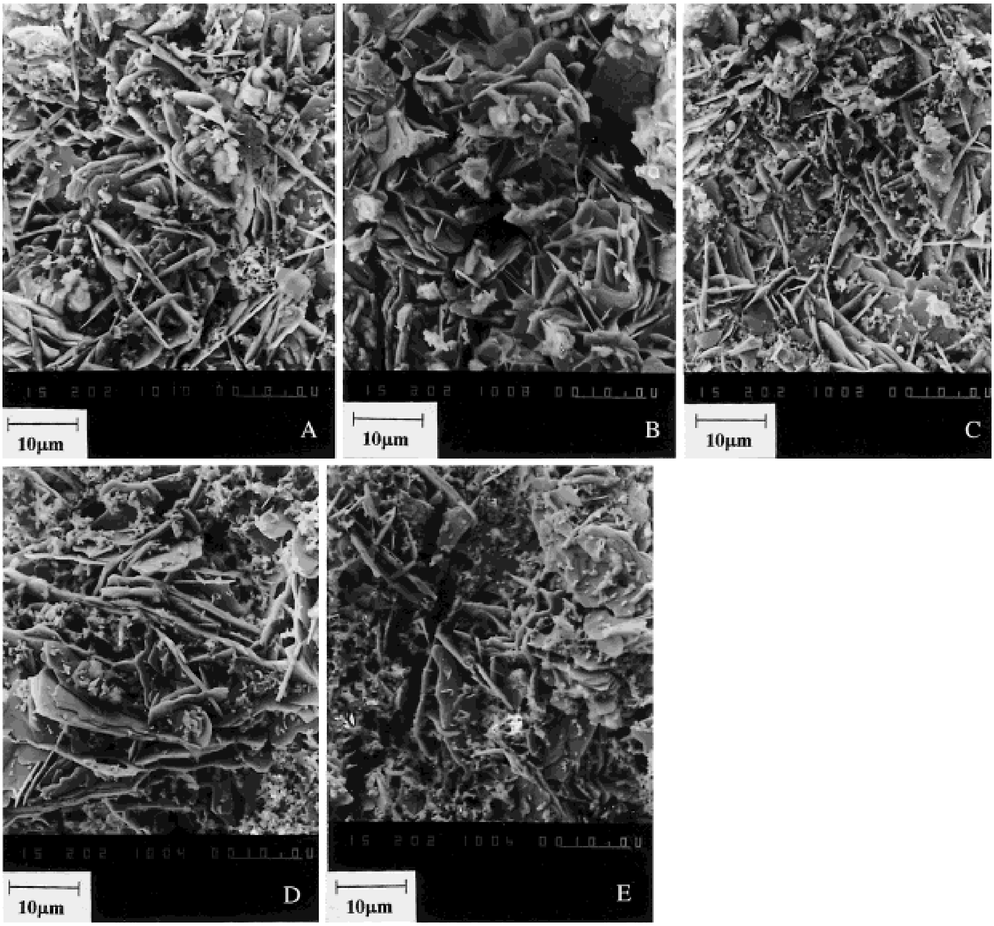

Fig. 4. Scanning electron microscopic images of the top surfaces of the samples: A) $x = 0$, B) 0.05, C) 0.1, D) 0.15, E) 0.2

phase peak cluster intensity. These observations support the variation of T_c schematically shown in Fig. 2.

The microstructures of the top surfaces of all samples are shown in the SEM photographs taken at the same magnification in Fig. 4. Platelike grains about 5 to 10 µm in size seem to dominate these structures which are probably responsible for superconductivity [17, 19]. The platelike grain size seems to be smallest in sample C and largest in sample D. Along with these platelike grains a second finer phase can be easily identified in these micrographs. These particles vary in size and the number of these particles seems to increase in samples C to E. A large number of fine particles along with relatively larger irregular particles can be identified in the micrograph of sample C. Lumps of these second phase particles are visible in all micrographs but especially in higher numbers in samples C to E. The 4441 phase was observed as fine particle piles especially on the surface of pellets and was determined to correspond to Sb-rich regions [20]. It was also claimed that the 2223 phase grows on these finer particles and has a distorted structure. The lumps of finer second phase particles observed in the SEM images of samples C to E (Sb content from 0.10 to 0.20) may most likely be due to the 4441 phase. The XRD peak cluster intensities for the 4441 phase (around $2\theta = 30°$) also was observed to increase significantly from sample C to E as was previously discussed. The relatively smaller size of the platelike grains along with a large number of irregular finer second phase particles (which may be a nonsuperconducting phase) may be the reason for T_c to decrease to 87 K for sample C.

The theoretical density of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$ was obtained as 6.313 g/cm^3 from the lattice parameters [21]. The density calculated from the lattice structure was reported as 6.2 g/cm^3 for Sb and Pb-doped BSCCO ceramics [18]. The bulk densities of Pb-doped BSCCO pellets were evaluated by using a theoretical density of 6.45 g/cm^3 [22]. The densities of the pellets in this work were determined to be in the 5.1 to 5.4 g/cm^3 range by a water displacement Archimedes method. Most of the open pore volume was intruded by water during these tests. The densities of the same pellets were estimated to be in the 3.3 to 3.5 g/cm^3 range from their dimensional measurements. If the theoretical density of these pellets is taken as 6.3 g/cm^3, this indicates that these pellets have 45 to 47% porosity. The bulk densities determined by the Archimedes technique is in the 81 to 86% range of theoretical density. This shows that about two thirds of the pores were filled by water during the density determinations.

4. Conclusions

Substitution of Cu partially by Sb in $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_{3-x}Sb_xO_y$ superconductors resulted in the formation of a phase commonly known as 4441 phase. The presence of a cluster of peaks at about $2\theta = 30°$ in Sb-rich samples was a strong evidence for this statement. The formation of this phase may actually be unavoidable irrespective of composition in Sb-doped BPSCCO superconductors. A finer second phase besides platelike particles was attributed to the 4441 phase. The initial relative decrease and the subsequent increase in the size of the platelike particles along with the increase in the number of finer particles were held responsible for the decrease of the critical temperature T_c from 103.5 to 87 K and the subsequent increase to 101 K. These pellets were highly porous with porosities in the 45 to 47% range.

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