

Effect of cobalt on the high T_c phase of the $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ system

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A.c. susceptibility, X-ray diffraction (XRD), SEM and porosity studies have been performed on $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_y$ ($x=0, 0.05, 0.1$) superconductors. XRD and SEM results have shown that (i) the compound with $x=0$ contains mixed phases of 2223 and 2212, (ii) the increase in concentration of cobalt (from $x=0$ to 0.1) helps the compound to attain a structure of strong 2201 and a small amount of Ca_2CuO_3 impurity phase. The onset temperatures of the diamagnetic signal of these superconductor samples with $x=0, 0.05$, and 0.1 as observed from a.c. susceptibility measurements are 106, 60 and 50 K, respectively. The highest onset temperature, 50 K, observed in the sample with $x=0.1$ rather than the usually reported value of 20 K associated with 2201 phase in bismuth oxide compounds, may be due to the presence of Ca_2CuO_3 impurity phases. SEM and porosity results show that the cobalt helps to increase the grain and pore sizes.

1. Introduction

The discovery of high T_c (110 K) phase along with low T_c phase (85 K) by Maeda *et al.* (1) with bismuth oxide superconductors, has given a new initiative to studies of this compound. With various dopants and preparation conditions, scientists have been continuing their efforts to stabilize the 110 K phase [2–4]. Cava *et al.* [2] have shown stabilization of the high T_c phase (110 K) by the addition of lead to the extent of $x = 0.4$ in place of bismuth, i.e. in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$. With lead substitution, the volume fraction of high T_c phase (2223) was increased by suppressing the low T_c phase (2212). Before this lead substitution, it was reported that excessive calcium and copper over the ideal $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ composition also stabilized the high T_c phase [3]. A relation between charge carrier density and transition temperature was shown to exist in 2212 and 2223 bismuth systems doped with different single-element substitutions [5–7].

Study of double dopants in bismuth oxides is interesting to determine the different phases present in the sample, stabilization of the phases and the variation of the transition temperature with dopant concentration. Komatsu *et al.* [8] and Sato *et al.* [9] prepared $(\text{Bi,Pb,Sb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ ceramics by the melt-quenching method and found that the formation of the high T_c phase was remarkably enhanced by the addition of a small amount of elemental antimony. Luo *et al.* [10] obtained, with antimony addition, a higher T_c near 125 K for $(\text{Bi}_{0.85}\text{Pb}_{0.10}\text{Sb}_{0.05})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$. Kouki Jyodoi *et al.* [11] studied the doping effects of metallic elements on the superconductivity in the $(\text{Bi,Pb})\text{-Sr-Ca-Cu-O}$ system. They observed that

aluminium, indium and bismuth metals increased the superconducting volume fraction and high-temperature shifts of T_c zero, whereas zinc and cadmium metals caused the disappearance of the high T_c phase and an increase in the low T_c phase. Sato *et al.* [12] studied $\text{Bi}_{1.6-x}\text{Pb}_{0.4}\text{Mo}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ and $\text{Bi}_{1.6}\text{Pb}_{0.4-x}\text{Mo}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ ceramics prepared by the melt-quenching method and found that the formation of the high T_c phase was largely enhanced by the coexistence of lead and molybdenum elements. Natsume [13] have studied the effect of nickel substitution for copper in the 110 K phase of the $(\text{Bi,Pb})\text{-Sr-Ca-Cu-O}$ superconductor. The single phase was obtained up to a nickel concentration of $x = 0.015$ for $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2(\text{Cu}_{1-x}\text{Ni}_x)_3\text{O}_3$ ceramics. The zero-resistance temperature decreased monotonically in the region of $x < 0.03$ and became 90 K thereafter. Nagabhooshanam *et al.* [14], also studied samples of $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ doped with a fixed amount of lead in place of bismuth and different amounts of iron in place of copper and observed that both the transition temperature and charge carrier density decrease with increasing iron concentration. Tarascon and co-workers [15, 16] studied the cobalt-doped $\text{YBa}_2\text{Cu}_3\text{O}_y$ in place of copper and concluded that T_c decreased sharply from 93 K to 22 K (for $x = 0.3$), the hole carrier concentration and its temperature dependence decreased with x and the concentration becomes almost temperature independent for $x = 0.3$. Effects with double dopants in Bi–O ceramic superconductors, particularly with lead and cobalt in place of bismuth and copper, respectively, on charge carrier concentration and zero transition temperature, are not only of basic

interest to understand the conditions for the phase stabilization but are also interesting for determining their usability in new superconducting devices.

In this work, a.c. susceptibility, XRD, SEM and porosity studies were performed on samples of $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ superconductors doped with a fixed amount of lead (0.4) in place of bismuth and different amounts of cobalt ($x = 0, 0.05$, and 0.1) in place of copper in order to determine the effect of double dopants (lead and cobalt) on T_c and the effect of cobalt on high T_c phase transformation. It is observed that (i) the multiphase nature (2223 and 2212) of 0.4 lead-doped bismuth compound changes to a strong 2201 phase with increasing cobalt concentration, (ii) the zero transition temperature is nearly 50 K in the sample with $x = 0.1$. The results are explained in terms of impurity phase, grain growth and porosity.

2. Experimental procedure

Samples of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_y$ ($x = 0, 0.05$, and 0.1) were prepared by high-temperature solid-state reaction. Appropriate amounts of Bi_2O_3 , PbO , CaCO_3 , SrCO_3 , CuO and CoCO_3 powders, taken in their molar ratios, were thoroughly mixed and ground in a mortar. The mixed powder was pre-fired in air at 820°C for 24 h followed by an intermediate grinding. Then it was reground and pressed into pellets of 15 mm diameter and 2 mm thickness by applying a load of 10 ton force. The pellets were sintered at $850 \pm 5^\circ\text{C}$ for 48 h and then slowly cooled to 700°C at the rate of 20°C h^{-1} . The solidified samples were subsequently cooled to room temperature at a relatively high rate of 200°C h^{-1} .

A Philips X-ray diffractometer (PW 1700) was used to record powder diffraction patterns of samples. No extra peak corresponding to PbO or Co_2O_3 was detected. A.c. susceptibility measurements were made using the mutual inductance bridge method. The output of the bridge was detected by a Lock-in-Amplifier (Standard Research Systems model no. SR 530) operating in the $10 \mu\text{V}$ sensitivity range. All the a.c. susceptibility measurements were performed by applying an alternating magnetic field of 0.3 Oe at 83.1 Hz frequency. Each time about 150 mg powdered sample was taken in the quartz ampoule. Liquid helium surrounded by liquid nitrogen was used as coolant and nitrogen gas was used as the exchange gas in a cryostat. The temperature of the sample was measured using a copper-constantan thermocouple which was kept just above the sample. The temperature measurement was accurate up to ± 1 K. Scanning electron micrographs of all the samples were taken using Cambridge Instruments Stereoscan Scanning Electron Microscope (CIS 150). The percentage porosity in the samples was measured by an immersion method in which kerosene, specific gravity 0.778, was used as the liquid. The percentage porosity is computed using the formula

$$\text{percentage of porosity} = \frac{S - d}{S - i} \times 100 \quad (1)$$

where d is the dry mass, S the saturated mass, and i the immersion mass of the sample.

3. Results and discussion

Fig. 1 shows the temperature variation of a.c. susceptibility for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_y$ samples with $x = 0, 0.05$ and 0.1 . Fig. 1a corresponds to the sample with $x = 0$ and shows the onset temperature of the diamagnetic signal at 106 K and the fall at 102 K, indicating that the sample possesses the high T_c 2223 phase ($T_c = 105\text{--}110$ K) as a major fraction. Similar results in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ have also been observed by other workers [17–19]. Fig. 1b and c, corresponding to the samples with $x = 0.05$ and 0.1 , show the T_c onset at 60 and 50 K, respectively, indicating that the substitution to cobalt in place of copper reduces the transition temperature drastically from 106 to 50 K, i.e. the high T_c phase (105–110 K) changes to the low T_c phase of $T_c = 50$ K. Literature results [20–22] indicate that the addition of lead modifies the general characteristics of the reaction at high temperatures, allowing an increase in the volume fraction of the 110 K phase. The present result shows that the 110 K phase is modified to nearly 60 and 50 K with 0.05 and 0.1 cobalt substitution in place of copper, respectively, i.e. a low T_c phase is strengthened.

XRD patterns of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_y$ samples corresponding to $x = 0, 0.05$ and 0.1 are shown in Fig. 2. The diffraction peaks of all samples have been indexed on the basis of Chavira *et al.* [22], Chen Jian *et al.* [23], and Matheis and Synder [24]. The following observations are made on comparing the X-ray diffraction patterns of the three samples.

(a) The characteristic line of the semiconducting phase [24] at $d = 0.405$ nm, which may exhibit superconducting characteristics at low temperatures, is very weak in all the samples. In addition, a small decrease in resistance with increase in temperature is also observed in all the samples (not shown).

(b) The X-ray diffraction lines at $d = 0.374$ (0010), 3.072 (0012) and 2.656 nm (0010) which appear characteristic of the 110 K phase (2223), and lines at

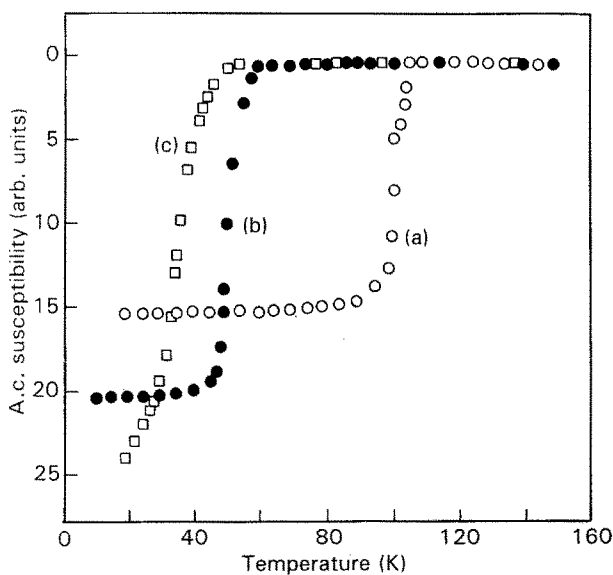


Figure 1 Variation of a.c. susceptibility with temperature in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_y$ samples with (a) $x = 0$, (b) $x = 0.05$ and (c) $x = 0.1$.

0.356 nm (1 1 3) and $d = 0.323$ nm (1 1 5), which are characteristic of the 80 K phase (2212), are present in the sample with $x = 0$ (Fig. 2a). The remaining lines are characterized by those peaks of either 2223 or 2212, as indicated in the figure. This shows clearly the presence of multiphase 2223 and 2212 in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_y$ sample with $x = 0$. This has also been evinced from the a.c. susceptibility measurements with a large variation in the diamagnetic signal at 106 K and a small kink at approximately 85 K.

(c) Not all the characteristic peaks of 2223 and 2212 phases are observed in samples with $x = 0.05$ and 0.1 (Fig. 2b and c), whereas the lines at $d = 0.298$ (1 1 5) and 0.268 nm (2 0 0), which are characteristic of the 20 K phase (2201), are present. The rest of the lines are also identified clearly with the diffraction peak positions of the 2201 phase [22]. In addition, the susceptibility measurements have shown any evidence of neither 110 K nor 80 K phase.

(d) Lines at $d = 0.232$ and 0.250 nm, which are characteristics of CuO, are present in both the samples

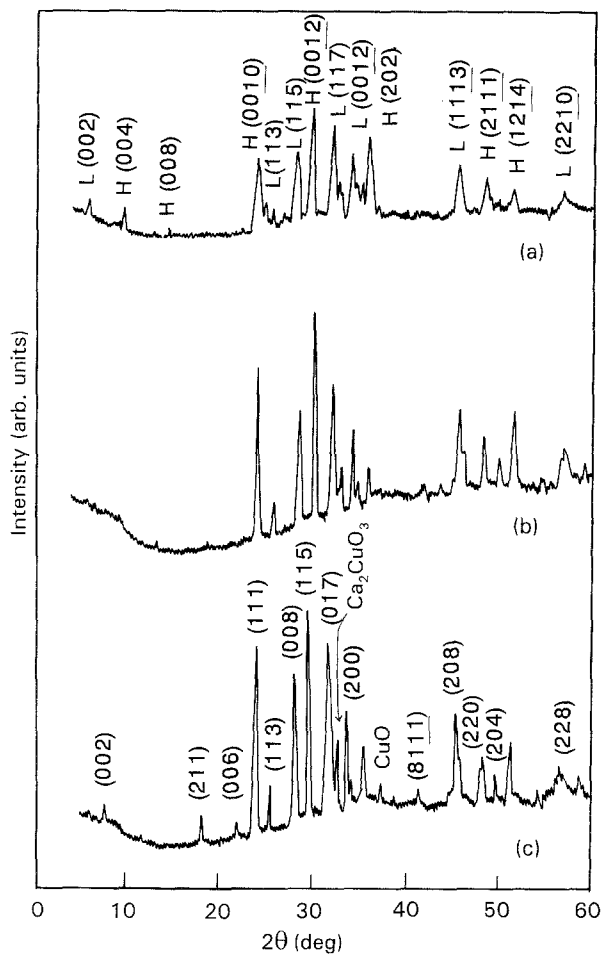
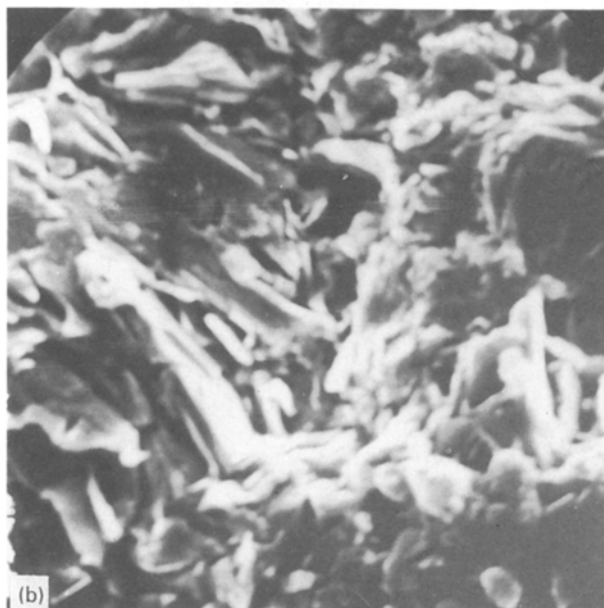
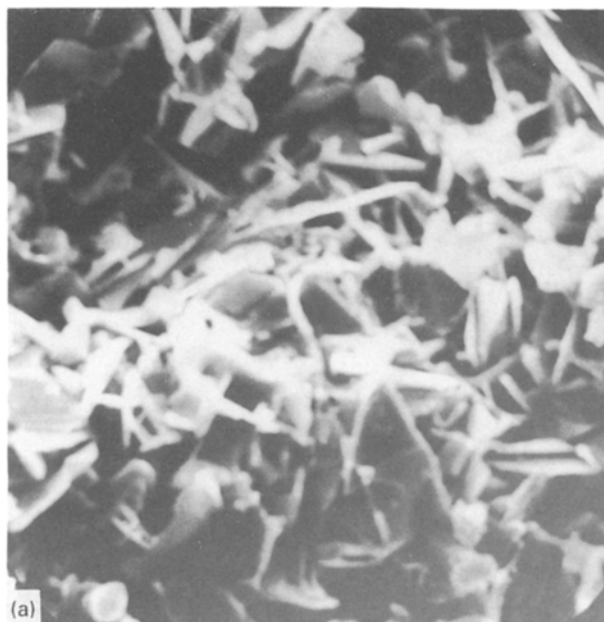
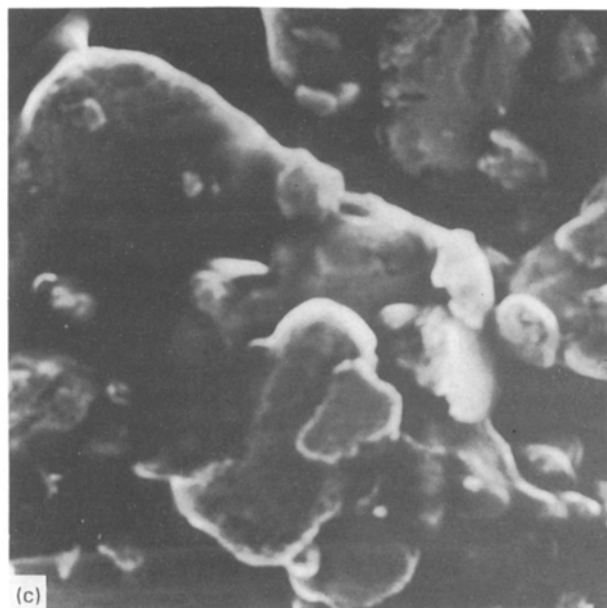


Figure 2 X-ray diffraction patterns of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_y$ samples with (a) $x = 0$, (b) $x = 0.05$ and (c) $x = 0.1$. (a) Low and high T_c peaks corresponding to 2212 and 2223 phases. (b, c) Peaks of 2201 phase. Indices are given against the peaks.

Figure 3 Scanning electron micrographs of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_y$ samples with (a) $x = 0$, (b) $x = 0.05$, and (c) $x = 0.1$. The number of platelets responsible for the high T_c phase is more in (a) for $x = 0$ whereas the number of platelets in the sample with $x = 0.05$ (b) is less. The increase in pore size and the curved nature of the grains are seen clearly in (c) for the sample with $x = 0.1$.



with $x = 0.05$ and 0.1 and they become clear and their intensity becomes slightly greater in the sample with $x = 0.1$, whereas such lines are not observed in samples with $x = 0$.

(e) The line at $d = 2.75$ nm, which is characteristic of Ca_2CuO_3 impurity phase, is barely present in the sample with $x = 0$, but becomes clearly resolvable in samples with $x = 0.05$ and 0.1 . The observed intensities of the Ca_2CuO_3 peaks in these samples with $x = 0, 0.05$ and 0.1 are nearly 20%, 33% and 36%, respectively, indicating that the Ca_2CuO_3 impurity phase increases with increasing cobalt doping concentration.

Increasing evidence of Ca_2CuO_3 and CuO phases in samples with $x = 0.05$ and 0.1 when compared to the sample without cobalt, indicates that cobalt is not going into the lattice but is acting like a poison, and separates the calcium and partly copper atoms, to form impurity phases, thereby causing the formation of 2201 phase.

Scanning electron micrographs of the samples with $x = 0, 0.05$ and 0.1 are shown in Fig. 3. These micrographs show that the number of platelets in the pure sample is more and decreases with increasing cobalt concentration, the size of the platelets increases and the platelets become curved in doped samples. The curved nature of the platelets is seen more clearly in the sample with $x = 0.1$. The micrographs also show that the intergrain distance increases greatly in this sample. The observed porosity values in the samples with $x = 0, 0.05$ and 0.1 are 18, 22 and 29, respectively. These values are also in agreement with the results shown by electron micrographs.

In conclusion, XRD, a.c. susceptibility, SEM and porosity studies of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_y$ ($x = 0, 0.05$, and 0.1) samples indicate that the partial substitution of copper with cobalt in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$, basically with 2223 dominating phase, causes the formation of 2201 low-temperature phase, and this appears more clearly in the sample with $x = 0.1$. However, the observed transition temperature (50 K) of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_{2.9}\text{Co}_{0.1}\text{O}_y$ is more than the T_c of 20 K usually associated with 2201 phase. This may be due to the partial lead substitution and the presence of Ca_2CuO_3 impurity phases in small amounts (Fig. 2). Recently, Kishore *et al.* [25] also observed that the Ca_2CuO_3 impurity phase, added intentionally to Bi-Sr-Ca-Cu-O compounds, would increase the fraction of high T_c phase and would not cause changes in T_c up to 1.2 mol% Ca_2CuO_3 in the compound. In our samples, we expect an impurity mole per cent much smaller than 1.2, because the impurities were not intentionally added. Therefore, the low concentration of Ca_2CuO_3 impurities might be helping by not allowing further reduction in T_c . Thus, the cobalt impurity replacing copper in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_4$ superconductor compound is acting like an agent for increasing the Ca_2CuO_3 impurity phase, porosity and for converting the dominating phase of 2223 to 2201. However, further study of impurity effects on cobalt-doped bismuth oxide compounds with 2201 dominating phase may

add to the above conclusions. Such studies are in progress in our laboratory.

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