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Synthesis and characterization of Y–Ba–Cu–O and Bi(Pb)–Sr–Ca–Cu–O superconductors from the oxine co-precipitation method

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Abstract. Oxide superconductors in the Y–Ba–Cu–O and Bi(Pb)–Sr–Ca–Cu–O systems with $T_c^?$ of 93.6 K and 115 K, respectively, have been prepared by the co-precipitation process via the oxine route using nitrates as the starting materials. Chemical homogeneity, stoichiometry and fine particles of the precursor obtained by this process permit a relatively short time for the production of Y- and Bi-based superconducting compounds compared with that obtained by the conventional solid state reaction method. The resulting densities of the sintered samples were typically greater than 90%. X-ray diffraction analysis, energy dispersive spectral analysis and scanning electron microstructural analysis are also reported in this study.

1. Introduction

As the high quality of ceramic superconductors is a prerequisite for the bulk material applications, it is desired that the starting ceramic powder should be chemically homogeneous, stoichiometric and fine. These conditions become more stringent when the enhancement of J_c in particular is required [1, 2]. Although the solid state reaction method, which is mostly used for the preparation of the bulk high-T_c YBCO [3], BSCCO [4] and TBCCO [5] ceramic superconductors from their respective oxides, has many advantages it meets the above requirements only partially. Incomplete mixing of the constituents of the starting materials due to non-uniformity of particle-size, necessity of repeating the process to get homogeneous powder and lack of reproducibility [6, 7] are the difficulties encountered in the solid state reaction method. It is possible that these difficulties may be overcome by an alternative chemical route or co-precipitation method, where the powder obtained is chemically homogeneous, ultrafine and stoichiometric using short processing durations. Hence, for large scale production, the co-precipitation method is an obvious choice.

Various researchers have employed the co-precipitation method for the preparation of Y–Ba–Cu–O [8–10] and Bi–Sr–Ca–Cu–O [11–13] by using different complexing agents like oxalic acid, citric acid and acetic acid. Though all these routes produced a better quality superconductor than that produced by the solid state reaction method, they suffer from incomplete precipitation, non-uniformity and material loss during

precipitation and washing. However, oxine which has an advantage over these complexing agents, of forming slightly soluble complexes with most of the metals, has not been tried so far.

Recently, we have reported [14] that the Bi(Pb)–Sr–Ca–Cu–O superconductor can be successfully prepared by the co-precipitation method using oxine as the complexing agent. In this paper, we present a detailed study of the YBCO and BSCCO samples synthesized using the oxine co-precipitation technique to elucidate their superconducting properties. These samples were characterized with the help of resistivity, x-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques.

2. Experiment

2.1. Preparation of Y–Ba–Cu–O and Bi(Pb)–Sr–Ca–Cu–O samples

2.1.1. Y–Ba–Cu–O. A mixture of 1.13 g of Y_2O_3, 5.22 g of $Ba(NO_3)_2$ and 7.35 g of $Cu(NO_3)_2 \cdot 3H_2O$ for a cation ratio of 1:2:3 were dissolved in dilute nitric acid. All the powders used here were of reagent grade purity. 20 g of oxine were dissolved in a minimum quantity of acetic acid and diluted with double-distilled water. This solution was added, with constant stirring, to the above solution containing Y, Ba and Cu. During the whole reaction, the pH of the solution was adjusted to 11 by the addition of liquor ammonia. This solution was stirred and digested on a hot plate in the range 100–150 °C for about half an hour. In the present system, more than 90% of all the constituent elements could be precipitated with oxine. The resultant green coloured fine powder was filtered and washed several times with boiling double-distilled water to remove the excess of ammonia and oxine and then dried in an oven at 150 °C for about 2 h so as to eliminate water. Then these dry oxine precipitates were heated at 400 °C for about an hour to initiate the decomposition of the organic constituents. At such a temperature a vigorous reaction was noticed. It is to be mentioned that no oxine salts ignited separately. The residue consisted of homogeneous flakes of sub micron diameter observed under the electron microscope.

The residue was precalcined at 500 °C for half an hour in a furnace to avoid any loss of the compound due to instantaneous decomposition, and the temperature was slowly increased to 800 °C for calcination. This reaction mixture was calcined in air for 5 h first at 800 °C and then at 850 °C. The black coloured powder thus obtained was then pressed into pellets at room temperature at a pressure of 4 tons cm^{-2} and sintered at 900 °C in O_2 atmosphere for 5 h followed by slow cooling.

2.1.2. Bi(Pb)–Sr–Ca–Cu–O. The BSCCO samples were made in a similar manner to that described above using oxine as the co-precipitating agent; starting materials were reagent-grade nitrates of Bi, Pb, Sr, Ca and Cu. Complete precipitation of the nominal composition $Bi_{1.6}(Pb_{0.4})Sr_2Ca_2Cu_3O_y$ (henceforth called 2223) was achieved by dissolving the required amount of each reagent (4.23 g of strontium nitrate, 4.40 g of calcium nitrate, 7.23 g of copper nitrate and 1.3 g of lead nitrate) in hot double-distilled water. 6.5 g of $Bi(NO_3)_3$ was dissolved separately in dilute HNO_3 to prevent hydrolysis and then mixed with the above mixture. To this nitrate solution, a saturated aqueous solution of 30 g of oxine dissolved in acetic acid was then mixed with constant stirring. The pH of the solution was kept around 11 by adding liquor ammonia. Similarly, the complete precipitation of the other nominal compositions $Bi_{1.6}(Pb_{0.4})Sr_2Ca_3Cu_4O_y$ and

$Bi_{3.2}(Pb_{0.8})Sr_3Ca_3Cu_4O_y$ (henceforth called 2234 and 4334, respectively) was also achieved. This mixture was stirred and heated on a hot plate in the temperature range 100–120 °C for about half an hour. The chocolate brown coloured fine precipitates thus obtained were filtered, washed several times with boiling distilled water, and then dried at 100 °C. These dry oxine precipitates were heated at 350 °C for an hour and then precalcined in a furnace at 500 °C for 5 h. The reaction mixture was ground and calcined at 800 °C for 5 h. The black coloured powder thus obtained was then ground and pressed into pellets (15 mm in diameter and 2 mm in thickness) at a pressure of 4 tons cm^{-2}. These pellets were then sintered at 830 °C for 92 h.

2.2. Characterization

Chemical analysis of the oxine precipitates of YBCO and BSCCO samples was performed using the spectrochemical technique by taking data from a large number of points and then averaging the results.

Identification of the phases in the calcined powder and in the sintered pellets was carried out by means of x-ray diffraction studies on a Siemens D-500 diffractometer using CuKα radiation. T_c measurements were carried out using resistivity measurements performed on pellets at 300 to 77 K using a four-probe AC method (73 Hz) with an electric current of 10 mA. J_c was measured at 77 K and zero-magnetic field on bar shaped samples ($0.5 \times 1.5 \times 15$ mm^3) using a four-probe DC-pulse (1 s) method adopting a 1 μV cm^{-1} criterion. The electrical contacts to the samples were made by fine copper wires attached to the sample with a conducting silver paint. The temperature was measured with a calibrated copper–constantan thermocouple attached close to the sample. The density of the sintered pellets was also measured by the conventional xylene absorption technique.

The calcined powder and sintered pellets were also characterized for their compositional and microstructural properties using EDS (KEVEX-7000-77) and SEM (JEOL:JSM-35CF) and the results are discussed below.

3. Results and discussion

According to the spectrochemical analysis of the oxine precipitates of both the samples of YBCO as well as BSCCO, no marked depletion in metals was observed during the precipitation process. These precipitates were calcined and analysed for their composition and particle size using EDS and SEM, respectively. Different parts of the compacted calcined powders of both YBCO and BSCCO samples were checked for Y, Ba and Cu, and for Bi, Pb, Sr, Ca and Cu, respectively. The analysis showed that the YBCO powders consist mainly of $YBa_2Cu_3O_x$ particles. However, the presence of other minor phases like $Y_2Ba_1Cu_1O_5$, $BaCuO_2$ and CuO was also detected. The BSCCO powders were found to contain mainly the low-T_c (2212) phase. A few particles of Ca_2PbO_4 and CuO were also observed.

The particle analysis of these powders performed by SEM showed that the size of the particles was nearly uniform and that the average particle sizes were around 1 and 0.8 μm for the YBCO and BSCCO powders, respectively. All these results, therefore, indicate that the calcined powders obtained by the present oxine route were nearly chemically homogeneous and fine. These calcined powders were also analysed with the help of XRD.
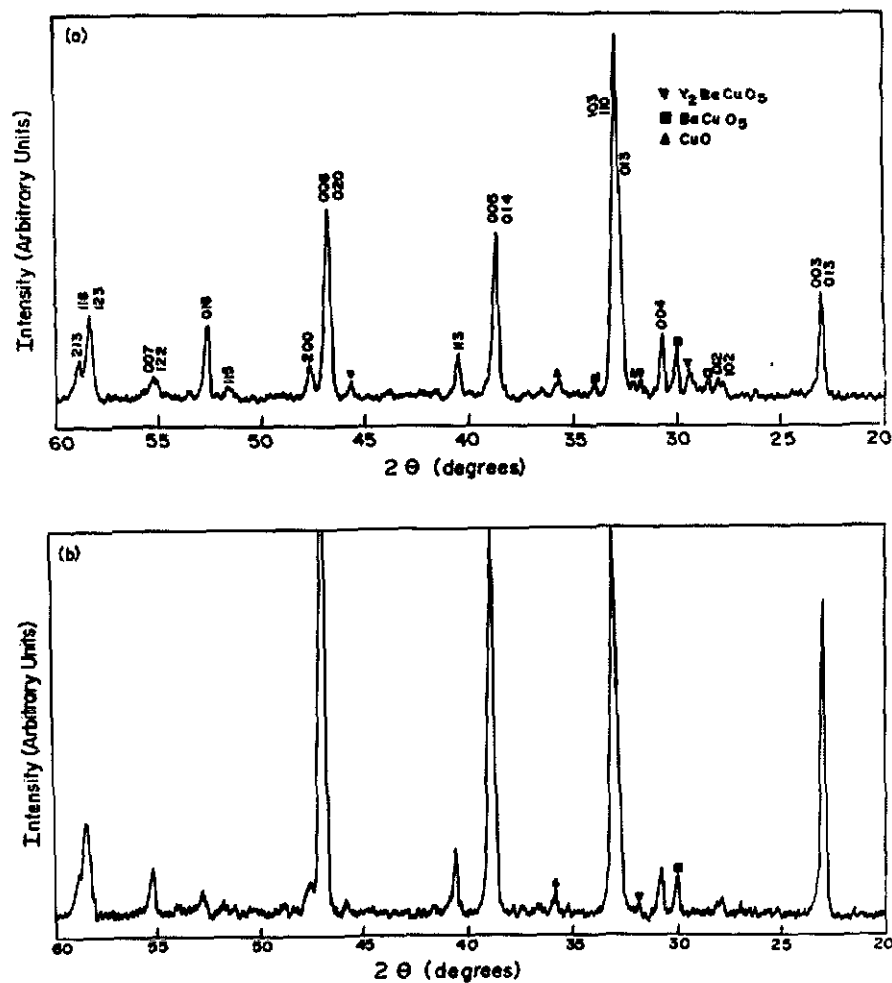
Figure 1. XRD patterns of the precursor of YBCO calcined in air for 5 h at (a) 800 °C and (b) 850 °C.

3.1. Y–Ba–Cu–O

Figure 1 shows the XRD patterns of the precursor of YBCO calcined in air for 5 h, first at 800 °C (a) and then at 850 °C (b). It is evident from the figure that most of the reflections on the XRD pattern in the former case can be indexed as an orthorhombic phase of $YBa_2Cu_3O_x$ with traces of non-superconducting phases, including $Y_2Ba_1Cu_1O_5$ (green phase) at $2\theta = 29.3°$, $31.6°$ and 45.6; $BaCuO_2$ at $2\theta = 28.5°$, $29.9°$ and $34.6°$; and un-reacted CuO at $2\theta = 32.5°$, $35.6°$ and $38.8°$. On recalcining this powder at 850 °C, the intensity of the peaks belonging to $Y_2Ba_1Cu_1O_5$ and $BaCuO_2$ phases were found to decrease as shown in figure 1(b). These results indicate that recalcination at 850 °C reduces the amounts of the green phase and $BaCuO_2$, whereas it enhances the amount of orthorhombic phase $YBa_2Cu_3O_x$. This calcined powder was formed into pellets and sintered at 900 °C for 5 h in O_2 atmosphere and then T_c was measured from the resistance–temperature curve.
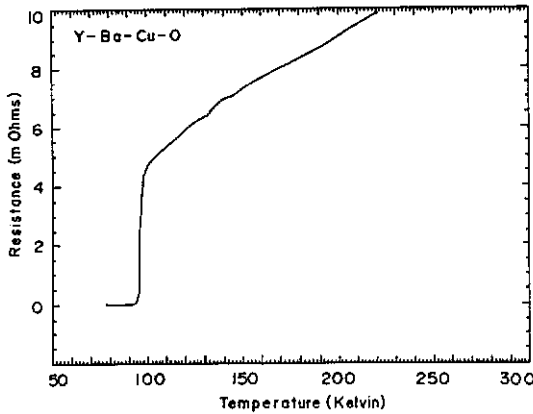
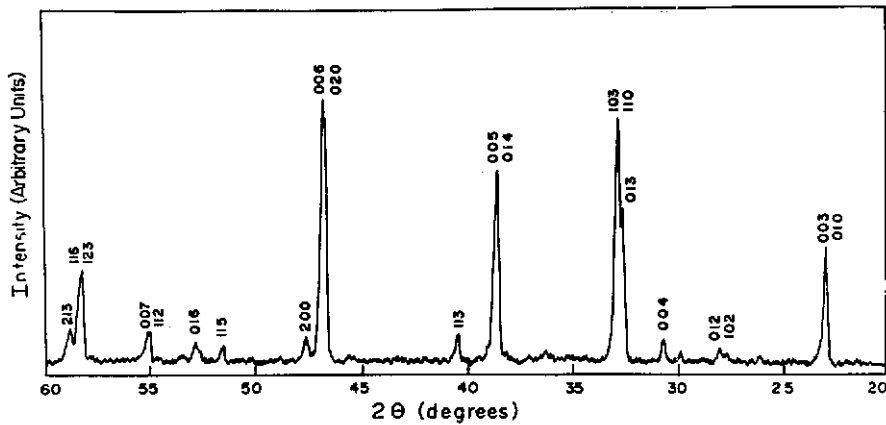Figure 2. Resistance–temperature curve of the $YBa_2Cu_3O_y$ pellet sintered at 900 °C for 5 h in O_2 atmosphere.

Figure 3. XRD pattern of the $YBa_2Cu_3O_x$ pellet sintered at 900 °C for 5 h in O_2 atmosphere.

The resistance–temperature curve for the above sintered sample is depicted in figure 2. The resistance drops at about 95 K (T_c^{on}) and becomes zero at 93.6 K (T_c^o). Above T_c^o, the material shows a metallic behaviour. No degradation in the T_c^o value after thermal cycling was observed; this indicates the formation of a stable superconducting phase. It should be noted that the sintering time required for obtaining the superconducting phase in the present method is only 5 h, and is much less than that required in the conventional solid-state reaction route, which is generally about 10 h [3]. To see the presence of non-superconducting phases in these pellets, an XRD pattern was taken.

Figure 3 shows the XRD pattern of the sintered pellet that can be indexed on the basis of an orthorhombic 1:2:3 structure with lattice parameters $a = 3.81$ Å, $b = 3.88$ Å and $c = 11.63$ Å which are in close agreement with the results of Cava *et al* [15]. The sharpness of the $YBa_2Cu_3O_x$ reflections indicates the presence of homogeneous crystalline grains.

The SEM study of these samples revealed the microstructure over the entire sample area and a representative micrograph of the fractured surface of the $YBa_2Cu_3O_x$ sintered pellet is shown in figure 4. The grains have a well defined parallelepiped shape and are closely packed with little porosity. The closely packed grains are indicative of the better density of this sample. Furthermore, the EDS analysis of the entire sample area shows
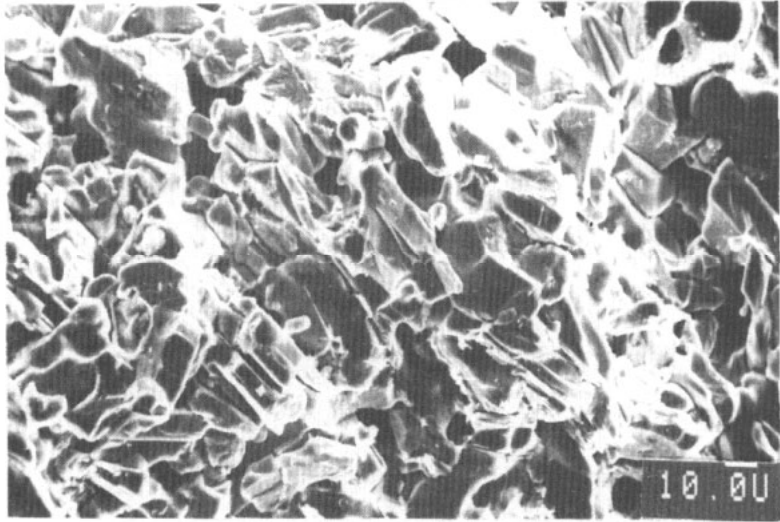
Figure 4. Scanning electron micrograph of the fractured surface of the $YBa_2Cu_3O_x$ pellet sintered at 900 °C (O_2 atmosphere) for 5 h.

Table 1. Various parameters of the oxine co-precipitated YBCO and BSCCO sintered samples.

Sample (notational composition)	XRD data (phases)	SEM data (grain structure)	T_c^c K	J_c (A cm^{-2})	d (gm cm^{-3})
$YBa_2Cu_3O_x$	Orthorhombic (1:2:3)	Crystalline parallelopiped	93.6	100	5.77
$Bi_{1.6}(Pb_{0.4})Sr_2Ca_2Cu_3O_y$	2212	Majority regions: flakes (2212) Minority regions: plate-like crystals (2223)	85	40	5.15
$Bi_{1.6}(Pb_{0.4})Sr_2Ca_3Cu_4O_y$	2212 and 2223	Majority regions: plate-like crystals (2223) Minority regions: flakes (2212)	110	65	5.32
$Bi_{3.2}(Pb_{0.8})Sr_3Ca_3Cu_4O_y$	2223	Plate-like crystals (2223)	115	135	5.87

that the sample comprises mainly $YBa_2Cu_3O_x$ grains having nearly the same composition (nearly 123) thus indicating the presence of nearly homogeneous and stoichiometric grains.

Since the samples contain nearly homogeneous and stoichiometric closely packed crystalline grains they should have higher values of density (d) and critical current density (J_c) [16]. Critical current densities (J_c) of these samples were measured and the results are presented in table 1. The values of d and J_c obtained are 5.77 g cm^{-3} and 100 A cm^{-2}, respectively. These results indicate that the $YBa_2Cu_3O_x$ samples obtained by the present method are more than 90% dense with reasonably good values of J_c.
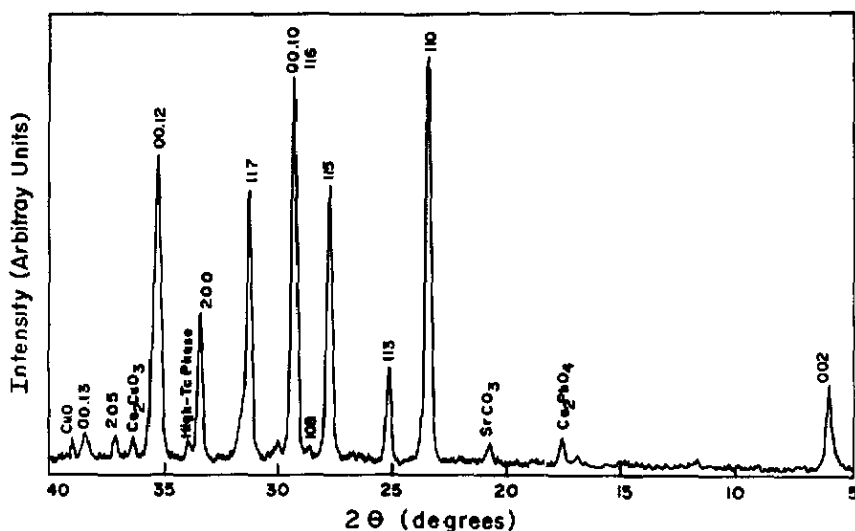
Figure 5. XRD pattern of the precursor for the $Bi_{3.2}(Pb_{0.8})Sr_3Ca_3Cu_4O_y$ powder calcined in air at 800 °C for 5 h.

The BSCCO samples were also studied in a similar manner and the results are presented below.

3.2. Bi(Pb)–Sr–Ca–Cu–O

The XRD patterns of all the powders calcined under similar conditions for the three nominal compositions; 2223, 2234 and 4334 were taken and it was found that the precursor for the first two compositions mainly contained the low-T_c phase. However, other phases like Ca_2CuO_3 and CuO were also observed in the 2234 composition, whereas the nominal composition 4334 produced a precursor containing both the low-T_c as well as the high-T_c phases and small traces of non-superconducting phases.

Figure 5 shows the XRD pattern of the precursor for the powder of the nominal composition 4334 calcined in air at 800 °C for 5 h. Most of the reflection on the XRD pattern could be indexed as a tetragonal (or pseudotetragonal) unit cell [17] with lattice constants of $a = 5.35$ Å and $c = 30.50$ Å for the low-T_c phase $Bi_2Sr_2Ca_1Cu_2O_8$ (2212) that also co-existed with other minor phases, including the high-T_c phase $Bi_2Sr_2Ca_2Cu_3O_{10}$ (2223) with lattice constants $a = b = 5.41$ Å and $c = 37.01$ Å that closely matched the results of Zandbergen *et al* [18]. Moreover, traces of non-superconducting phases were also detected in the sample, consisting of Ca_2PbO_4 ($2\theta = 17.6°$), Ca_2CuO_3 ($2\theta = 36.1°$), and the CuO phase ($2\theta = 38.8°$).

The calcined powders obtained from each of these three starting compositions were formed into pellets and sintered under identical conditions at 830 °C for 92 h in air. The resistivity measurements for specimens are shown in figure 6. In this figure, we show the variation of resistance as a function of measurement temperature for the specimens $Bi_{1.6}(Pb_{0.4})Sr_2Ca_2Cu_3O_y$, $Bi_{1.6}(Pb_{0.4})Sr_2Ca_3Cu_4O_y$ and $Bi_{3.2}(Pb_{0.8})Sr_3Ca_3Cu_4O_y$. The sample with 2223 composition showed a two-step transition with a characteristic foot at 120 K and zero-resistance at 85 K (T_c^0) indicating the presence of two phases: a high-T_c (2223) as well as a low-T_c (2212) phase. By comparison, the other two compositions:
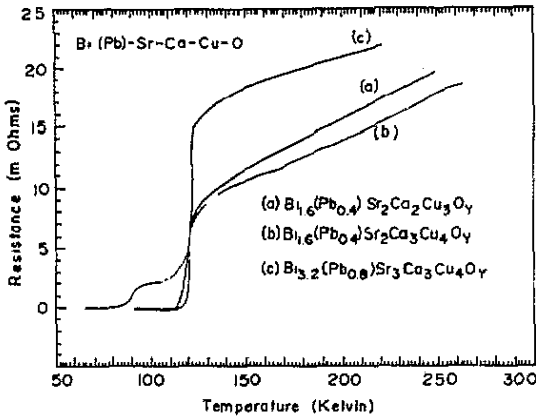
Figure 6. Resistance–temperature curves for the samples: (a) $Bi_{1.6}(Pb_{0.4})Sr_2Ca_2Cu_3O_y$; (b) $B_{1.6}(Pb_{0.4})Sr_2Ca_3Cu_4O_y$; and (c) $Bi_{3.2}(Pb_{0.8})Sr_3Ca_3Cu_4O_y$, sintered at 830 °C for 92 h in air.
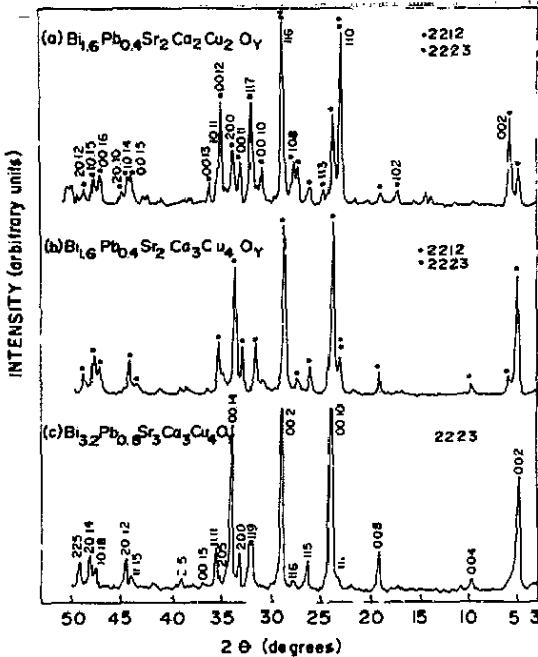
Figure 7. XRD patterns of the pellets of $Bi_{1.6}(Pb_{0.4})Sr_2Ca_2Cu_3O_y$, $Bi_{1.6}(Pb_{0.4})Sr_2Ca_3Cu_4O_y$ and $Bi_{3.2}(Pb_{0.8})Sr_3Ca_3Cu_4O_y$ sintered at 830 °C in air for 92 h.

2234 and 4334 resulted in samples having single transitions with T_c^o at 110 K and 115 K, respectively, indicating the presence of an enhanced amount of the high-T_c phase as compared with that found in the 2223 composition. In addition, as in YBCO samples, no decrease in the T_c^o value was observed after thermal cycling. This indicates the formation of a stable high-T_c phase.

XRD patterns of these pellets (figure 7) clearly indicate the related changes in phase composition. For the 2223 and the 2234 compositions, appearance of the (002) reflections at $2\theta = 5.01°$ and $5.7°$ corroborates the presence of both the 2212 and 2223 phases. However, the peaks of the 2223 phase in the latter composition were made much more intense than those in the former case—indicating a higher content of the high-T_c phase—by the increased content of Ca and Cu. The other nominal composition 4334 resulted in samples with diffraction peaks of the high-T_c phase only, indicating that addition of

excess of Bi and Cu was also found to enhance the formation of the high-T_c phase. We should also mention that, like YBCO samples, these BSCCO samples (for all three nominal conpositions) did not show the presence of non-superconducting phases either; this indicates the formation of a nearly single-phase high-T_c compound. Furthermore, (001) peaks are found to be most prominent, which indicates preferential growth of (001) planes.

Both the resistivity and the XRD results have shown that the sintering time required for obtaining a larger amount of the high-T_c phase and the high zero-resistance temperature for the Bi system in the oxine route is much less than that required in the conventional solid state reaction method, which is about ten days [19]. Therefore it seems that the present method is more efficient. Furthermore, to see the formation of the 2223 grains and the other phases and porosity etc, we studied the fractured surface of these pellets using SEM.

The scanning electron micrographs of the fractured surface of these three compositions are shown in figure 8. The micrographs display clearly that there are two types of region observed in these samples: (i) flakes and (ii) large plate-like crystals. Flakes had an average composition which was rich in Bi (Bi = 22.5, Sr = 23.6, Ca = 16.2 and Cu = 37.7 at.%) whereas the compositions of the plate-like crystals are poor in Bi (Bi = 18.7, Sr = 19.2, Ca = 21.3 and Cu = 40.8 at.%). In the 2223 composition (figure 8(*a*)) most of the microstructure consisted of flakes with a few large plate-like crystals. However, for the other two compositions: 2234 (figure 8(*b*)) and 4334 (figure 8(*c*)), the microstructure mainly consisted of large plate-like crystals with a few flakes. The grains were closely packed. On the basis of compositional analysis and crystal growth observations [20], the flakes belong to the low-T_c phase, whereas the crystals belong to the high-T_c phase. These results indicate that the quantity of high-T_c phase formation is maximum in the nominal composition 4334 and minimum in the nominal composition, 2223, confirming the resistivity and the XRD results shown in figures 6 and 7, respectively. Furthermore, the micrographs indicate that the 2234 and 4334 samples are more homogeneous and less porous than the 2223 sample. Therefore the samples with 2234 and 4334 compositions should show higher values of density and J_c. It was mentioned earlier that the density and J_c values of these samples were also calculated; the values are given in table 1. It is found that the highest and the lowest values of density and J_c are obtained for the 4334 and 2223 compositions, respectively.

All these results imply that for similar calcination and sintering conditions, the amount of high-T_c phase is found to depend upon the starting composition. Starting with the correct stoichiometry (2223) does not yield single-phase materials with high zero-resistance temperatures. We observed that better and reproducible results are generally obtained by going slightly away from stoichiometry. The 2234 composition, which is rich in Ca and Cu in comparison to the 2223 phase, has a high T_c° of 110 K, whereas a starting composition of 4334 which is rich in Bi and Cu yields a nearly single-phase of 2223 with a T_c° of 115 K. It was reported earlier by other workers [4, 21, 22] that, for any nominal composition, the more stable 2212 phase is formed during the initial stages of reaction between mixed oxides and carbonates. It is subsequently transformed into the 2223 phase by the diffusion of Ca and Cu. Depending upon the diffusion rate, a single phase of a 2223 phase can be synthesized by long-duration sintering—as long as 300 h $\sim$ 2 weeks. It was also reported earlier that addition of excess Ca and Cu [21] or presence of liquid flux [23] is found to enhance the diffusion process. Since the stoichiometric composition 2223 has insufficient amounts of Ca and Cu, these are limits
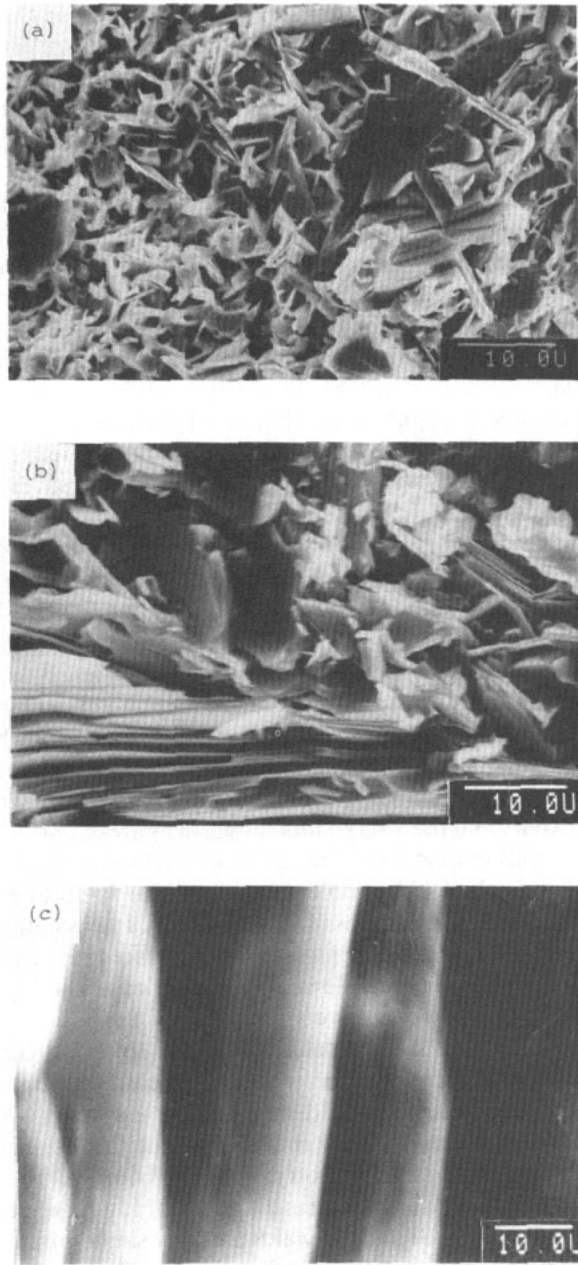
Figure 8. Scanning electron micrographs of the fractured surface of the samples of (a) $Bi_{1.6}(Pb_{0.4})Sr_2Ca_2Cu_3O_y$, (b) $Bi_{1.6}(Pb_{0.4})Sr_2Ca_3Cu_4O_y$ and (c) $Bi_{3.2}(Pb_{0.8})Sr_3Ca_3Cu_4O_y$ sintered in air at 830 °C for 92 h.

to the diffusion and hence the formation of 2223 phase decreases. However, the 2234 starting composition contains excess Ca and Cu, which therefore leads to increased diffusion and thereby enhances the formation of 2223 phase. On the other hand, the

4334 composition provides a liquid flux containing both bismuth as well as copper oxides in excess and hence accelerates the diffusion process to enhance the formation of 2223 phase.

5. Conclusions

High-T_c superconducting compounds Y–Ba–Cu–O and Bi(Pb)–Sr–Ca–Cu–O have been successfully synthesized using the oxine co-precipitation process. Nearly single-phase, homogeneous and more than 90% dense sintered samples were obtained in shorter periods and with lower temperature treatments. The present method exhibited stable and bulk superconducting properties with $T_c^o = 93.6$ K and $J_c = 100$ A cm^{-2} for the YBa$_2$Cu$_3$O$_x$ samples, and $T_c^o = 115$ K and $J_c = 135$ A cm^{-2} for the Bi$_{3.2}$(Pb$_{0.8}$)Sr$_3$Ca$_3$Cu$_4$O$_y$ samples.

Acknowledgment

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