J Supercond Nov Magn (2009) 22: 749–754
DOI 10.1007/s10948-009-0491-8

ORIGINAL PAPER

The Effect of Zn Substitution of Ca in BiPbSrCaCuO Superconductors Sintered at 830 °C

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Received: 10 May 2009 / Accepted: 15 May 2009 / Published online: 4 June 2009

Abstract The effect of partial substitution of Ca by Zn in $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}Zn_xCu_3O_y$ at $x = 0.00, 0.05, 0.10, 0.15$ and 0.20 levels on the electrical and structural properties was investigated in this work. The characterization of the ceramics prepared by the conventional solid-state reaction method were done by resistance–temperature measurements, XRD, SEM and density analysis. Low levels of Zn substitution of Ca caused significant changes in the properties of the ceramics. The low-T_c superconducting properties were enhanced and the fraction of the low-T_c (2212) phase were found to increase at $x = 0.15$ level of Zn substitution at 830 °C sintering temperature. Zero resistance was observed only in sample D with $x = 0.15$ and the T_c was determined as 92 K. The SEM micrographs and the density analysis have shown that this was the densest packed ceramic.

Keywords Bi-based superconductors · Zn substitution · Scanning electronic microscopy · X-ray diffraction

1 Introduction

Bi-based ceramic superconductors with $T_c = 110$ K may have important implications in various applications. The interest is mainly due to a great potential of this material for it is possible use in superconductor devices operated at liquid nitrogen temperatures. $Bi_2Sr_2Ca_nCu_{n+1}O_y$ ceramics ($n = 0$, 1 and 2 with 10, 85 and 110 K transition temperatures respectively) commonly have a multiphase structure. The most important problem in these systems is the difficulty of obtaining phase-pure high-T_c ($n = 2$, 2223) materials.

Research on the doping of the ceramics or substitution of the basic elements with various other cations in high-T_c superconductors may contribute to a better understanding of superconductivity by the determination of the physical origin of T_c suppression and enhancement. The improvement/suppression of superconducting properties depend on the physical properties of the dopant cations. Several substitution studies have been done to obtain desired properties in Bi(2223). It was previously reported that partial substitution of Bi, Ca, and Cu commonly by Sn, Sb, Ag, Hg and Pb has increased T_c and Ca_2CuO_3 has improved J_c–B characteristics in Bi(2223) superconductors [1–6]. Especially Pb substitution forms a liquid phase which aids in the 2223 phase formation.

The superconducting properties are commonly believed to be related to the hole concentration and oxygen content in the copper oxide superconductors. Moreover, it is suggested that in Bi-based systems T_c depends on oxygen content in the structure and maximum T_c occurs at optimum oxygen concentration. Important parameters in Bi-based systems are the substitution sites and the change in the charge balance. In the work done by Nanda et al. [7] it is pointed out that in the Bi-based system the substitution of Ca^{+2} by Sm^{+3} ($r_{Sm} = 0.964$ Å, $r_{Ca} = 0.99$ Å) causes a decrease in the superconducting phase volume fraction and T_c depending on the change in hole concentration. The substitution of Ca^{+2} by rare-earth Sm^{+3} provides additional electrons, which in

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turn decreases the hole carrier concentration leading to a decrease of T_c and of other superconducting properties. Similar results were obtained when Ca was replaced by Y^{+3} ($r_Y = 0.893$ Å) [8] and it was reported that in Bi-based systems, hole concentration may change with substitution of Y, La, and Nd (trivalent cations) for Ca or Sr (divalent cations). Khan and Khizar [9] have worked on the effects of the substitution of R(Eu, Yb, Ag) for Ca. They have reported that by the increase in the Eu, Yb, Ag substitution level, the volume fraction of (2223) phase was decreased while the volume fraction of (2212) phase was increased. Halim et al. [10] replaced Ca by Ba^{+2} ($r_{Ba} = 1.34$ Å) and Zn^{+2} ($r_{Zn} = 0.74$ Å) and measured ac susceptibility of the samples. They compared structural changes in the system and pointed out that there is S–I–S type weak coupling between grains in Zn doping while there is S–N–S type weak coupling in Ba doping. Kanai et al. [11] reported that the substitution of rare-earth ions for Ca brings about a transition from the 2223 to the 2212 phase. The sintering temperature is an important parameter for obtaining the high-T_c phase. The sintering temperature is commonly in the 845–855 °C range [12, 13]. Ca_2PbO_4 phase which is formed during heat treatment, plays an important role in the formation of the high-T_c (110 K) phase.

Based on the results of SEM and XRD analysis of BiPbSrCaCuO ceramic superconductors, Karaca et al. [14] concluded that the structure of samples has dominant low-T_c phase (2212) and c lattice parameter is increasing with increasing Zn content from X-ray diffraction analysis. Moreover, they observed that the grain size of the samples decreases with Zn enrichment in scanning electron microscopy examination. They observed that Bi-2223 phase decreases and Bi-2212 phase increases with increasing Zn addition.

In their study, Kozuka et al. [15] prepared $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_{10+x}$ compound and doped it with ZnO by the solid-state reaction method. They investigated the influence of ZnO doping on the crystal structure in the Bi-2223 phase, and what kind of site is replaced by Zn^{2+} ions. They suggested that Zn^{2+} ions are substituted for Cu^{2+} ions in Cu(2) sites based on the calculation of the bond valence sum, and the crystal structures of the Bi-2223 phase with ZnO were refined. In addition, it is recognized that the solid-solubility of Zn in the Bi-2223 phase is 2 wt.%, based on the variations in the lattice parameters. Moreover, it was reported that the ZnO doping up to approximately 50 wt.% did not influence the T_c values of (Bi, Pb)-2223 ceramic.

Oqowa et al. [16] concluded that when the 0–50 wt.% ZnO-doped thick film was sintered at 835 °C for 1 hour in air, the highest J_c value of 1200 A/cm^2 was obtained for 0.5 wt.% ZnO-doped (Bi, Pb)-2223 thick film. Based on these results, they suggested that the small amount of ZnO doping improves the intragranular weak bonding or Josephson junction.

Although there are extensive studies on the 2212 and 2223 materials where Ca has been replaced by rare-earths and other cations, the normal-state properties of these materials have not been studied in detail. The carrier concentration dependence of the superconducting properties of the 2223 phase is also not yet clearly understood.

The purpose of the present work was the investigation of the effects of partial Zn substitution of calcium (ionic radii is smaller relative to Ca) on the structural properties of Pb-doped BSCCO ceramics sintered at 830 °C which is about 15–25 °C lower than in the previous studies. The presence of probable positive effects of Zn on the formation of the low-T_c phase and whether there is any effect of this substitution on the probable formation of the high-T_c phase which is usually not expected at 830 °C, was investigated in this work.

2 Experimental Procedure

$Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}Zn_xCu_3O_y$ superconducting ceramics were prepared by the conventional solid-state reaction method. High-purity (99.99% Aldrich Chem. Co.) Bi_2O_3, PbO, $SrCO_3$, CuO and ZnO powders were mixed at five different ratios to give $x = 0.00$, 0.05, 0.10, 0.15 and 0.20 (samples A to E respectively). These powder mixtures were well ground and mixed in a mortar and calcined at 775 °C for 30 hours in a furnace (Nabertherm). The calcined powders were well ground and calcined again under the above conditions. The calcined powders were ground again and pellets which are 1–1.5 mm in thickness and 13 mm in diameter were prepared by uniaxial pressing at 500 MPa. These pellets were further sintered at 830 °C for 250 hours in a furnace by using 7 °C/min heating rate. After sintering, pellets were cooled to room temperature in the furnace at 2 °C/min. For all samples, resistance was measured as a function of temperature using the four-point probe technique. X-ray diffraction pattern in the 3–52° CuK_α radiation was obtained by using JEOL JSDX 100S diffractometer. The SEM photographs of the microstructure were taken by using JEOL JJXA733 microscope. The bulk densities were obtained from the dimensions and the Archimedes water displacement technique.

3 Results and Discussion

The temperature dependence of the electrical resistance of the $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}Zn_xCu_3O_y$ ceramics sintered at 830 °C for 250 hours (samples A, B, C, D and E respectively) is given in Fig. 1. The resistance–temperature curve is linear up to the onset temperature which is in accordance with the metallic character of the samples. The onset-temperature is defined as the temperature corresponding to

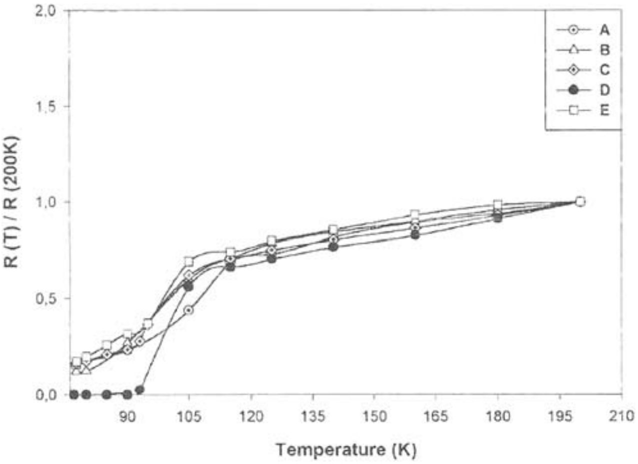

Fig. 1 Temperature dependence of normalized electrical resistance of samples. (**A**) $x = 0.00$, (**B**) $x = 0.05$, (C) $x = 0.10$, (**D**) $x = 0.15$, (**E**) $x = 0.20$

Table 1 The critical temperatures $T_{c,\text{zero}}$ (K), $T_{c,\text{onset}}$ (K) and mass density of the samples $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_{2-x}\text{Zn}_x\text{Cu}_3\text{O}_y$

Sample	Zn (x)	T_c (onset) K	T_c ($R = 0$) K	Mass density (g/cm^3)
A	0.00	108	–	5.26
B	0.05	109	–	5.02
C	0.10	110	–	5.48
D	0.15	114	92	5.35
E	0.20	104	–	5.27

the temperature where the resistance–temperature plot deviates from linearity. The onset temperature is about 108 K for sample D. The resistance of the other samples started to decrease significantly and the curves deviated from their linear shape in the 104–114 K range (Table 1). The variation of $T_{c,\text{onset}}$ with Zn content, x, is given in Fig. 2. Up to the liquid nitrogen temperature, samples A, B, C, E have not yet shown zero resistance while sample D ($x = 0.15$) has shown zero resistance at 92 K. The presence of three zones for the resistance decrease for all samples except D is apparent in Fig. 1. The 180 K resistance of the undoped sample A is higher than for the Zn-doped samples. The ratio of the 180 K resistance of sample A to B, C, E was 5.9, 5.8, 6.3 respectively while the same ratio was 8.8 for sample D. These results indicated that 830 °C sintering temperature for $x = 0.15$ Zn doping level may contribute to the stabilization of the low-T_c phase and the volume fraction of the low-T_c phase increases with increasing substitution level.

The XRD patterns of all samples are shown in Fig. 3. The high-T_c and low-T_c phase peaks were identified by using the tables given by Bansal et al. and Pandey et al. [17–19]. All samples have a multiphase nature with dominant low-T_c phase along with high-T_c, CuO, Ca_2PbO_4 and ZnO

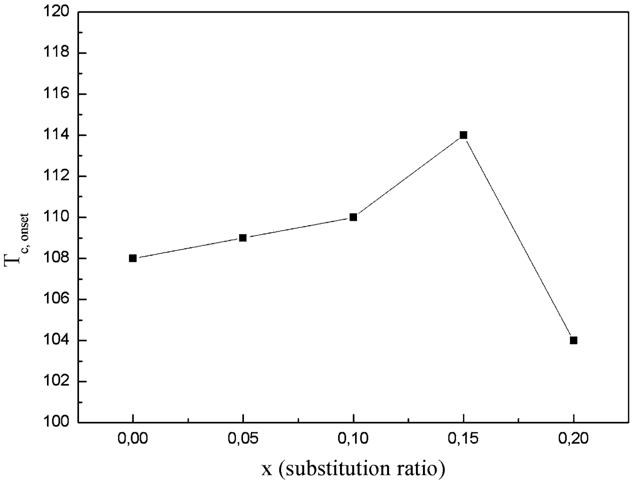

Fig. 2 Variation of onset temperature of Zn-doped samples of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_{2-x}\text{Zn}_x\text{Cu}_3\text{O}_y$ ($x = 0.00$–0.20)

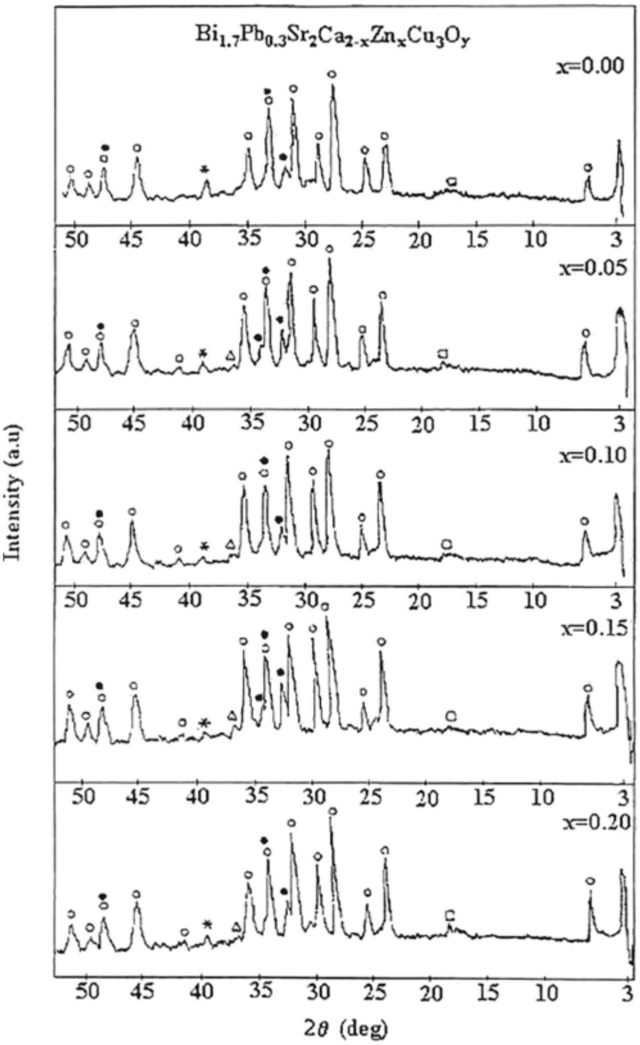

Fig. 3 XRD patterns of samples; ○ low-T_c, ● high-T_c phase, ∗ CuO, □ Ca_2PbO_4, △ ZnO

Fig. 4 Scanning electron microscope photographs of the top surfaces of the samples: (**A**) $x = 0.00$, (**B**) $x = 0.05$, (**C**) $x = 0.10$, (**D**) $x = 0.15$, (**E**) $x = 0.20$

phases, which indicates the difficulty in obtaining a single-phase material by the conventional ceramic method. Single-phase ceramics were obtained by melt-quenching technique and under controlled atmospheres at shorter sintering periods. The intensities of the low-T_c phase peaks located at 2θ values of 29° (0010), 35° (119), 49° (224), 50° (115) were observed to be the highest in sample D pattern. The relative intensities of almost all low-T_c phase peaks increased in Zn-doped samples compared to the undoped sample A. The number of peaks with similar intensities increases from three (sample A) to six (samples B, C, and D) in the 2θ range of about 23–36°. Three peaks were identified as high-T_c phase and also low-T_c peaks at $\approx 2\theta$ values of 32, 33.25, 47.75 by using the tables given in the literature [17–19]. An extra low intensity high-T_c phase peak at $\approx 2\theta = 33.8$ was detected only in samples D and B. (002)L characteristic peak appears around near $2\theta = 5.76°$ ($d = 15.331$ Å). No (002)H peak at $2\theta = 4.7°$ has been observed in this work, which is a very important peak in bismuth-based superconductors.

The CuO peaks were identified in all samples at the 2θ value of 38.6. A weak characteristic impurity-phase Ca_2PbO_4 peak at $2\theta = 17.8°$ was identified in all samples. The intensities of both of these phases were determined to be the lowest in sample D which was the only sample with zero resistance above liquid nitrogen temperature with a T_c of 92 K. The ZnO impurity phase was identified in all doped samples but had the highest peak intensity for sample D at $2\theta = 37°$. These results may support the fact that Zn doping

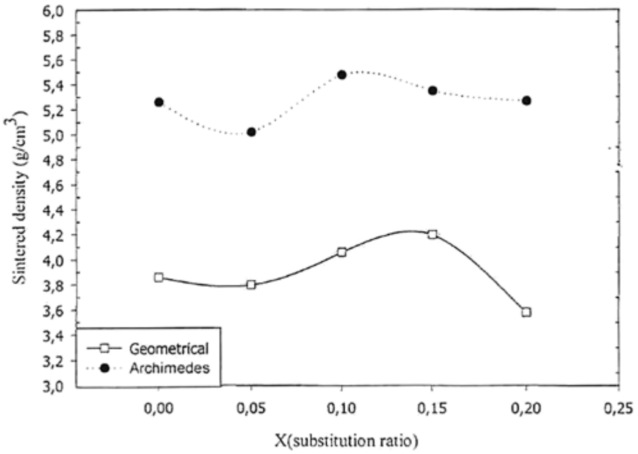

Fig. 5 Variation of the sintered densities with the extent of substitution, X

may aid in the higher consumption of the CuO and $CaPbO_4$ phases in sample D with enhanced 2212 phase formation.

The presence of 2212 phase in all samples may be due to low sintering temperature. It is well known that for the formation of 2223 phase, the required sintering temperature is about 850–865 °C, and to achieve complete 2223 phase, partial substitution of Pb for Bi is preferred. Grivel and Flükiger [20] pointed out that partial melting might occur in the sample at about 850 °C, which coincides with the formation of 2223 phase. The formation of liquid phase is believed to be an origin of the enhancement of the formation of the high-T_c phase. The stability range of the 85 K phase is 600–830 °C. At >830 °C, it reacts with excess oxides to form a 110 K phase. Above 870 °C, 85 K and 110 K phases decompose with oxygen loss. The phase of $Bi_2Sr_2CuO_y$ (2201) with minor peaks of Ca_2PbO_4 and 2212 was formed as the major phase at 700 °C. On the other hand, the formation of major low-T_c 2212 and minor high-T_c 2223 phases was observed in ceramics annealed at 800 °C [21]. Ca_2PbO_4 phase plays a crucial role in the formation of high-T_c superconducting films and bulk specimens. It is well established that for an optimum hole concentration the T_c has a maximum value and above and below this optimum, T_c decreases. The decrease in the hole concentration might be responsible for degradation of the superconducting properties.

The 2000× magnified SEM photographs are given in Fig. 4. In all samples, the dominant structure is plate-like grains randomly distributed due to the presence of pores between the grains in these low density compacts. While observing all the samples respectively from A to E, surface contacts have become dominant instead of point contacts, and the plates have been placed one above the other. In addition, the photographs also show that the location of the plates has changed during the same observation. Sample D possesses a denser structure and its photograph indicates the presence of rod-like particles. The densities of samples have been obtained by two different methods: their geometric dimensions and the Archimedes method. The dependence of the densities determined by the two methods on the substitution level is given in Fig. 5. While the densities which were determined through geometric dimensions have been (from A to E) 3.86, 3.80, 4.06, 4.20 and 3.58 g/cm^3 respectively, the densities which were determined through the Archimedes method have been 5.26, 5.02, 5.48, 5.35 and 5.27 g/cm^3 respectively. The theoretical density which was determined from the lattice parameters of Bi,Pb(2223) structure, is approximately 6.3 g/cm^3 [22]. In this research, the density values, which were determined through the Archimedes method, reach 80–86% of the theoretical value. The pellets possess a highly porous microstructure with porosities in the 35–43% range. The denser structure of sample D in the SEM photographs agrees with the density values that were determined from geometrical dimensions.

4 Conclusions

The substitution of Zn for Ca in BiPbSrCaCuO ceramic superconductors effects the properties considerably. When ZnO is added to Bi–Pb 2223 systems at $x = 0.15$ substitution level, a liquid phase may be formed and this leads to the observation of a T_c of 92 K only in this sample. The presence of Zn might have improved the coupling of the grains with improvements in the weak links at the grain boundaries. The addition of ZnO decreased the normal-state resistances (180 K) significantly. The $Bi_{1.7}Pb_{0.3}Sr_2Ca_{1.85}Zn_{0.15}Cu_3O_y$ superconductor ceramic was observed to have the densest packed microstructure with plate-like grains and 4.2 g/cm^3 bulk density.

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