Effect of In_2O_3 on the grain connectivity and superconducting behavior of $\text{Bi}_2\text{Sr}_{2-x}\text{In}_x\text{CaCu}_2\text{O}_{8+d}$

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Abstract

The effect of In_2O_3 on grain connectivity and superconducting properties of Bi-2212 was investigated. Indium was intentionally doped on the Sr-site of BSCCO at doping levels from $x=0$ to $x=0.8$. Accessing the Sr lattice site in BSCCO provides useful control on the possible effect of indium on its superconducting behavior and microstructural properties. Results show that the superconductivity persists in BSCCO even at high indium concentration ($x=0.8$). However, secondary phases form at $x \geq 0.4$ indium concentration affecting normal resistivity, magnetic susceptibility response and superconducting transition temperature of BSCCO. Formation of secondary phases weakens the diamagnetic intergrain coupling. An apparent increase in the formation of micron-sized grains is related to the increased sinterability of BSCCO with indium doping. The enhanced sinterability of BSCCO with indium provides possibility of synthesizing thin films with reduced thermal heat treatment.

Keywords (74.72.h) Cuprate superconductors · (75.30Cr) Saturation moments and magnetic susceptibilities · (74.62.Dh) Effects of crystal defects, doping and substitution · (74.81.Bd) Granular, melt-textured, amorphous, and composite superconductors

1 Introduction

The granular features of ceramic superconductors such as grain size, connectivity and porosity significantly affect its superconducting and current-carrying ability. Efforts to improve grain structure and connectivity include doping and several fabrication processes such as hot pressing, melt growth and laser floating zone techniques [1–4]. Increasing the size of superconducting grains could reduce the grain boundary loss through which current flows. In particular, alkali metals lower the formation temperature of BSCCO resulting in nucleation at liquid phase that could result to larger grains. Optimized co-doping using alkali metal such as Na with Li, V, and K are reported to increase critical temperature and critical current density [5–9]. Other studies which used Gd, Nd and dilute rare-earth

doping are shown to repair grain boundaries or improve flux pinning that enhanced superconducting properties [10–13]. Addition of particle and nanoparticles such as Ag, Dy, Zr, Eu, Nb, Al and Ca-iridates improves grain connectivity [14–21].

The AC Magnetic Susceptibility $\chi'(T)$ of bulk BSCCO and YBCO are often characterized by the intra- and intergrain responses. The intragrain response corresponds to intrinsic diamagnetic shielding of the individual grains upon its transition to superconducting state, while the intergranular response represents the coupling of grains correlated with bulk diamagnetic shielding [22]. AC susceptibility measurements can therefore be a viable method to discern coupling and measure the efficiency of superconducting grain boundaries. The nanoparticle addition of BSCCO by Eu, Yb and Ag has been observed to result in

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a sharp $\chi'(T)$ transition corresponding to improved grain connection [23–25].

Indium which is commonly used as a low-melting fusible alloy can be used as flux in some ceramics [26]. Previous investigation of In-doping of BSCCO system revealed two interesting features: (1) decrease in the diamagnetic signal due to reduced superconducting volume at high indium concentration in the case of Pb-doped BSCCO and (2) increased superconducting volume translating to high superconducting transition temperature of Bi-2212 [27, 28]. However, the effect of indium in the sintering properties and granular characteristics of BSCCO has never been explored. In this work, In doping on Sr-site of BSCCO was performed to assess stability of Bi-2212 phase at wider range of indium concentration. The smaller ionic size of indium proved useful in confirming its substitution with strontium site, and its effects in the structure and granular property of BSCCO. The changes in the intergranular connection can be correlated to the electrical transport and magnetic susceptibility behavior of Bi-2212.

2 Methodology

Differential thermal analyses (DTA) of indium-doped BSCCO show reduced melting point of Bi-2212 phase with indium content. Taking this result as a guide, the sintering temperature was lowered with increasing indium additions. The indium-doped BSCCO bulk samples were prepared by solid-state sintering of Bi_2O_3 , SrCO_3 , In_2O_3 , CaCO_3 and CuO powders to produce $\text{Bi}_2\text{Sr}_{2-x}\text{In}_x\text{CaCu}_2\text{O}_{8+d}$ at stoichiometric ratios. The powders were ground for 1 h and pressed into a 15 mm-diameter pellet at 10 kPa for 30 min. For pure BSCCO samples, the powders were twice sintered 835 °C for 30 h in air with subsequent decrease by 2 °C as the indium doping concentration increases from $x=0.10$ to 0.80. To ensure material homogeneity, repeated intermediate grinding and pressing before sintering was performed.

The crystallinity, phase formation and crystal size of the samples were investigated using XRD with $\text{CuK}\alpha$ radiation of 1.54 Å (Shimadzu Maxima 7000, Japan). Scanning electron microscope together with energy X-ray dispersive spectrometer was used to analyze the microstructure and compositions of the films (Philips FESEM XL30, USA). Temperature-dependent resistivity measurements were taken using a four-point technique/or Van-der Pauw configuration with the samples placed in a cryo-refrigerator cooled down to 10 K. AC Susceptibility measurements were taken using home-made mutual inductance bridge AC susceptibility work station. The diamagnetic transition was

measured at an applied field of 1.8 mT at a frequency of 800 Hz. The magnetization results were calibrated by taking the background signals resulting from the emf produced by the coils of the mutual inductance bridge.

3 Results and discussion

Figure 1a shows the XRD patterns of bulk $\text{Bi}_2\text{Sr}_{2-x}\text{In}_x\text{CaCu}_2\text{O}_{8+d}$ ($x=0$ to 0.8). The Bi-2212 phase was indexed using the JCPDS 00-041-0317. Minor low- T_c phase of BSCCO, $\text{Bi}_2\text{Sr}_2\text{CuO}_{8+d}$ (Bi-2201) was also detected and indexed using JCPDS 00-042-0241. Other phases attributed to CaCO_3 (JCPDS 01-076-0606) and In_2O_3 (JCPDS 000-006-0416) were also found. The XRD patterns reveal that the indium-doped BSCCO crystallizes into orthorhombic structure which is predominantly 2212 phase. Diffraction patterns of higher doped samples $x=0.4$ to 0.8 reveal impurity phases of 2201, (006), (113), (115) and (0010) planes; CaCO_3 (130) and (111) planes; and In_2O_3 (222) and (431) planes. Moreover, the broadening of the peaks at approximately 35° and 60° is also attributed to (400) and (622) planes of In_2O_3 peaks coinciding with the much more intense peaks of Bi-2212. The peaks of 2212 corresponding to (002), (006) and (008) slightly shift toward the higher angles at indium doping of $x=0$ to 0.5. This result suggests shrinking of lattice to accommodate indium dopant which is ~ 0.2 Å smaller than strontium.

The change in lattice parameters with indium doping concentration is shown in Fig. 1b. The evaluated c -lattice constant of BSCCO decreases from ~ 30.81 to ~ 30.48 Å with indium doping $x=0$ to 0.3; from $x=0.3$ to 0.5, the c -lattice continuously decreases at small decrements from 30.48 to 30.45 Å. The c -lattice slightly increases from 30.45 to 30.56 Å for $x=0.6$ to 0.8. The a - and b - lattice parameters are nearly constant, approaching the literature values of ~ 5.40 Å. The shrinking of c -lattice confirms substitution of indium into strontium sites for small indium doping concentrations. Hence, the solubility limit of indium doping in strontium site is less than $x=0.40$ or 20% wherein the effect of indium doping in BSCCO crystal structure is prominent. At higher indium content such as, $x=0.6$ to 0.8, the increasing c -axis values suggest that the additional indium is no longer a substitute to strontium and may appear as secondary-phase products. Correspondingly, at high indium content, In_2O_3 and CaCO_3 peaks appear together with the Bi-2201 as secondary phases.

SEM–EDS elemental maps of indium-doped BSCCO at low ($x=0.1$) and high ($x=0.8$) doping concentration are shown in Fig. 2. The color maps indicate the distribution of Bi, Sr, In, Ca, Cu, and O detected, alongside the SEM image

Fig. 1 **a** X-ray diffraction pattern of bulk $\text{Bi}_2\text{Sr}_{2-x}\text{In}_x\text{CaCu}_2\text{O}_{8+d}$ for $x=0$ to 0.8 indexed against (hkl) JCPDS 00-041-0317 of $\text{Bi}_2\text{Sr}_2\text{CaCuO}_{8+d}$ (2212), asterisk for $\text{Bi}_2\text{Sr}_2\text{CuO}_{8+d}$ (2201) with JCPDS 00-042-0241, triangle for CaCO_3 with JCPDS 01-076-0606 and open circles for In_2O_3 with JCPDS 00-006-0415, **b** lattice parameters of bulk $\text{Bi}_2\text{Sr}_{2-x}\text{In}_x\text{CaCu}_2\text{O}_{8+d}$ for $x=0$ to 0.8

on the left. At $x=0.1$, a homogeneous elemental distribution of Bi, Sr, In, Ca, Cu, O was observed. At higher indium doping concentration $x=0.8$, high concentration of indium was detected on the lower part (white arrows). An inhomogeneous distribution of indium at $x=0.8$ indicates the possibility of indium segregation at the grain boundaries. This confirms the XRD results of indium peaks at higher doping concentrations, indicating that some indium was not incorporated in the 2212 crystal but instead was lodged in the intergranular spaces. Impurities (non Bi-2212 phase) could be formed due to the uneven distribution of Cu, Bi, Sr at $x=0.8$.

Figure 3 shows the SEM micrograph cross section of bulk $\text{Bi}_2\text{Sr}_{2-x}\text{In}_x\text{Ca}_2\text{CuO}_{8+d}$ ($x=0$ to 0.80) at high

magnification. A plate-like morphology with randomly oriented grains was observed consisting with the microstructural feature of superconducting BSCCO. At lower doping concentration $x=0.1$, a smaller average grain size of $\sim 1.3 \mu\text{m}$ wide is formed, while higher doping of $x=0.8$ resulted to an average size of $\sim 4.2 \mu\text{m}$. At higher indium doping, stacking of plate-like grain also became more evident. The plates also appear to have plasticized or melted in samples with higher indium doping, $x=0.6$ to 0.8. The melting indicates lowering of melting temperature of BSCCO because of high indium content. Melting assists in the merging of smaller grains of BSCCO into larger blocks of grains. This result confirms that addition of indium improved the sinterability of BSCCO. In-doping

Fig. 2 Energy dispersive X-ray spectroscopy of bulk $\text{Bi}_2\text{Sr}_{2-x}\text{In}_x\text{CaCu}_2\text{O}_{8+d}$ for representative samples **a** $x=0.1$ and **b** 0.8. Left: SEM image of the sample. Right: color map areal distribution of Bi, Sr, Ca, In, Cu and O. The white arrow points to the high concentration of In in $x=0.8$

affects sintering properties of Bi-2212 that resulted to the formation of large and stacked grains.

Figure 4a shows the temperature dependence of the resistivity of indium-doped BSCCO. All samples are superconducting with apparent broad transitions up to $x=0.8$. It is interesting to note that at $x=0$ to 0.7, samples show metallic behavior while further increase in $x=0.8$ approached an insulating state at room temperature. Two resistive transitions were attributed to Bi-2212 and Bi-2201. The higher T_c representing Bi-2212 and the lower drop corresponds to the low- T_c Bi-2201 phase.

Figure 4b shows the normal state resistivity of the sample. At $x=0$ to 0.5, the resistivity increases by two orders of magnitude from ~ 1 to ~ 100 m Ω -cm for high indium doping concentration ($x=0.6$ to 0.8). The formation of secondary phases such as Bi-2201, In_2O_3 and CaCO_3 phases may be the reason for the high normal state resistivity. The

secondary phases and impurities increase the resistance along grains which percolates supercurrent paths resulting in broadening of superconducting transition temperature.

Figure 5 shows the temperature-dependent in-phase AC susceptibility measurements of indium-doped BSCCO at $x=0$ to 0.5 and for $x=0.6$ to 0.8. The samples with $x=0$ to 0.5 show a diamagnetic transition followed by another hump at a lower temperature. At higher doping levels, $x=0.6$ to 0.8, only one transition was observed. The diamagnetic transitions are rather broad and persist even up to $x=0.8$ or 40% indium doping concentration.

The $\chi'(T)$ of bulk granular BSCCO has two responses: the higher temperature diamagnetic transition within individual grains—the intragranular response; and the lower temperature intergranular response coming from the coupling of the neighboring grains (22).

Fig. 3 Scanning electron micrograph of freshly fracture bulk $\text{Bi}_2\text{Sr}_{2-x}\text{In}_x\text{CaCu}_2\text{O}_{8+d}$ for $x=0$ to 0.8 at $\times 12,500$ magnification

XRD results reveal that samples $x=0$ to 0.5 are predominantly Bi-2212 phase, while SEM images showed randomly oriented grains. As the temperature is lowered, the bulk granular Bi-2212 makes the transition from normal to superconducting state. Superconductivity accompanied by magnetic field expulsion or diamagnetic shielding will occur in the Bi-2212 grains first—represented by the intragranular response. As the temperature is further reduced, coupling of between Bi-2212 grains will occur—represented by the intergranular response at lower temperature. The two responses on the AC susceptibility measurements therefore represent as intra- and intergranular responses of the grainy Bi-2212 bulk samples ($x=0$ to 0.5).

At higher doping level $x=0.6$ to 0.8 , SEM-EDS, XRD and resistivity suggest large amount of impurities with at least 3 orders of magnitude jump in the resistivity values. Meanwhile, the AC susceptibility measurements of these ($x=0.6$ to 0.8) bulk samples showed only intragranular hump with diminished or insignificant intergranular response. The diminished intergrain response suggests that the grains are decoupled with respect to diamagnetism. As the temperature is lowered for these samples, remaining Bi-2212 grains was able to make the transition from normal to superconducting state as represented by intragranular response. However, due to enormous amount of impurities

in the sample, the intergranular coupling between the neighboring Bi-2212 grains is very weak thus diminishing the AC susceptibility intergranular response, which led to us conclude that very high amount of indium could lead to diamagnetic decoupling of Bi-2212 grains. This result positively agrees with (1) X-ray measurements showing increased impurities (Bi-2201, In_2O_3 and CaCO_3) at high indium content $x=0.6$ to 0.8 ; (2) SEM-EDS showing segregated indium at $x=0.8$ and (3) two order of magnitude increase in normal state resistivity at $x=0.6$ to 0.8 indicating increased resistivity at these doping levels. Impurities embedded in Bi-2212 grains act as resistive links; thus at $x=0.6$ to 0.8 , the superconducting grains are decoupled.

The diamagnetic and resistive transition temperatures for each doping concentration are shown in Fig. 6. Both transitions follow the same trend, with the highest T_c achieved for $x=0.3$. The T_{conset} of ≥ 70 K verifies that all samples are predominantly Bi-2212 phase.

Results show that indium lowers the melting point of Bi-2212. Increasing indium content produces larger and stacked grains. Indium doping is more evident at doping levels $x \leq 0.4$ (20%); while doping higher concentrations results in impurities. Secondary phases and impurities add to electrical resistance and block the percolation path of the supercurrent which results in broadening of

Fig. 4 **a** Resistivity versus temperature measurement of bulk $\text{Bi}_2\text{Sr}_{2-x}\text{In}_x\text{CaCu}_2\text{O}_{8+d}$ for $x=0$ to 0.8. For $x=0.6$ to 0.8, the values were multiplied by 0.05, 0.03 and 0.01, respectively. **b** Normal state resistivity versus indium doping level of bulk $\text{Bi}_2\text{Sr}_{2-x}\text{In}_x\text{CaCu}_2\text{O}_{8+d}$ for $x=0$ to 0.8 measured at 120 K

the superconducting transitions. Further doping at $x=0.6$ to 0.8 dramatically increases normal state resistivity. At this stage, the enormous amount of resistivity from impurities does not only broaden the superconducting transitions but also results to decoupling of grains.

Superconductivity—zero electrical resistance and diamagnetism persist at $x=0.8$, even with the removal of 40% Sr in favor of In. High amounts of indium weaken the inter-grain coupling but do not eliminate the superconductivity of the bulk material. Indeed, Bi-2212 is stable in the presence of indium.

4 Conclusion

Indium-doped Bi-2212 exhibited broad diamagnetic and resistive transitions in all doping levels. It is noteworthy that indium could increase grain sizes and substitute to Sr even if the melting point of In_2O_3 ($\sim 1900^\circ\text{C}$) far exceeds the processing temperature of Bi-2212 ($\sim 835^\circ\text{C}$). Melting point lowering of Bi-2212 due to indium promotes the mobility of the material to produce larger grains. Partial melting with indium could be promising as Bi-2212 persists despite the large amount

Fig. 5 In-phase AC Magnetic susceptibility versus temperature measurement of bulk $\text{Bi}_2\text{Sr}_{2-x}\text{In}_x\text{CaCu}_2\text{O}_{8+d}$ for **a** $x=0.1$ to 0.5 (inset $x=0$), **b** $x=0.6$ to 0.8 . Samples $x=0$ to 0.5 have two diamagnetic response corresponding to the intra- and intergranular transitions, while $x=0.6$ to 0.8 only has one transition, the intragranular transition indicating that the grains were decoupled

Fig. 6 Resistive (closed circles) and diamagnetic (open circles) transition temperatures of bulk $\text{Bi}_2\text{Sr}_{2-x}\text{In}_x\text{CaCu}_2\text{O}_{8+d}$ for $x=0$ to 0.8

of impurities and un-substituted indium. This indicates that indium does not destroy and can co-exist with Bi-2212. Moreover, the enhanced sinterability of BSCCO with indium provides possibility of synthesizing thin films with reduced thermal heat treatment.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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