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Characterization of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ ceramic superconductor prepared via coprecipitation method at different sintering time

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Abstract The Bi(Pb)-2223 superconductor has been prepared via coprecipitation (COP) method from solutions of metal acetates and 2-propanol solution of oxalic acid at low temperature (0–2 °C). The metal oxalates powder was subjected to precalcination of 12 h at 730 °C, followed by 24 h calcination at 845 °C. The pelletized powder was sintered for 24, 48 and 100 h at 850 °C. The dominance of high-T_C phase was observed for all samples as evidenced in the single step transition of (R–T) curves. The $T_{C(R = 0)}$ for samples sintered at 24, 48 and 100 h were 102, 102 and 104 K, respectively. XRD data showed the tetragonal structure for all samples followed by the enhancement of the 2223 phase as sintering time increased. Ac magnetic susceptibility measurements showed the improvement of the grain connectivity as sintering time increased. SEM micrographs showed large flaky grains of ~7 μm in size and randomly distributed, which belong to 2223 phase. The degree of grains alignment increased as the sintering time increased.

Introduction

It is widely known that Bi(Pb)-2223 high temperature superconductor merits great attention owing to its several inherent advantages such as higher critical temperature (~110 K), atmospheric stability, ability to be rolled into long wires or tapes, and its weak superconductivity dependence upon oxygen stoichiometry [1]. Soon after the discovery of high temperature ceramic superconductors great effort has been focused on the processing techniques. The solid state reaction is one of the most common techniques employed to produce superconducting ceramics where the starting materials are metal oxides, carbonates, or other salts, which are mixed, homogenized and heated at a given temperature [2]. However, this method has many disadvantages such as large particle size and long heating duration and sometimes several intermittent grindings are required. Conventional solid state methods are therefore laborious, time intensive and have a tendency towards producing a contaminated product [3]. Wet chemical methods such as coprecipitation [4, 5] sol–gel [6–8] freeze-drying [9, 10] and spray drying [11] have been previously employed to overcome this problem. The powders obtained by the coprecipitation technique have a smaller grain size and are of higher purity and homogeneity than the powders produced by the solid state reaction method. This is due to the initial mixture of cations on an atomic scale in solution so as to enhance the reaction during heat treatment and the resulting powder, which is more homogenous. Using metal nitrates, metal hydroxides or metal oxides in the oxalate coprecipitation require pH adjustment for the solutions by sodium hydroxide, and several washings in order to eliminate residual sodium from the coprecipitation, thus complicating the preparation procedure for superconducting material.

In this paper we describe the preparation of oxalate precursor by using metal acetate starting powders which are used to make Bi(Pb)-2223 superconductor with high yield at different sintering time. The starting solution was

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prepared without controlling the pH or applying washing step to the precipitate. We carried out a systematic investigation of oxalate coprecipitation processes, using metal acetates and oxalic acid as starting materials with 2-propanol and deionized water as a solvent. Results of DC electrical resistance-temperature measurements, AC susceptibility, XRD and SEM are presented.

Experimental

The coprecipitated powders with nominal composition of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta$ were synthesized by mixing $Bi(CH_3COO)_3$, $Sr(CH_3COO)_2$, $Pb(CH_3COO)_2 \cdot 3H_2O$ $Ca(CH_3COO)_2 \cdot H_2O$ and $Cu(CH_3COO)_2$ (purity > 99%) to form solution (A). The oxalic acid was dissolved in water:isopropanol (1:1.5) to have a concentration of 0.5 M (solution (B)). Solution (A) was added to the stirred solution (B) in an ice bath and a uniform, stable, blue suspension was obtained. The slurry was filtered after 5 min of reaction followed by the drying stage at 80 °C for 8 h. The dry powder, which is slightly aggregated with particle size of 0.1–0.6 μm, was subjected to precalcination of 12 h at 730 °C in air to remove the remaining volatile materials. The calcined powder was reground in a marble mortar for 10 min and heated at 845 °C in air for 24 h to ensure the elimination of the 2201 phase [5]. The powders were reground and pressed into pellets of ~12.5-mm diameter and ~2 mm thickness. The pellets were sintered at 850 °C for the duration of 24, 48 and 100 h and slowly cooled to room temperature at 120 °C per hour. The samples were labeled A, B and C, respectively. X-ray powder diffraction with CuK_α radiation was performed using Phillips PW1830 diffractometer at 40 kV and 30 mA with a step of 0.02° over the 2θ range 4–60°. Resistivity measurements of the samples were carried out using the four-point probe technique with silver paint contacts. The cryogenic system used was a Closed Cycle Helium Cryostat. Ac susceptibility measurements were carried out using Lakeshore AC susceptometer model 7000. The amplitudes of the ac fields were varied between 8 A/m and 800 A/m at a fixed frequency of 125 Hz. Scanning electron microscope (SEM) micrographs of fractured surface of the samples were recorded using a JEOL 6400.

Results and discussion

Normalized resistance at room temperature as a function of temperature for the samples A, B and C are shown in Fig. 1. All samples displayed a normal metallic behaviour with single step feature. The offset temperature, $T_{C(R=0)}$ and onset temperature, $T_{C\text{-onset}}$ were observed at (102 K, 110 K) for both A and B samples. For the sample C, $T_{C(R=0)}$ and $T_{C\text{-onset}}$ were obtained at 104 K and 112 K, respectively. The widening of $\Delta T = 8$ K implies that these samples have small traces of low T_C phase and hence it is still strongly dominated by the 2223 phase.

Figure 2 shows the results of XRD patterns for samples A, B and C. Almost all diffraction peaks can be indexed by using a tetragonal lattice cell of Bi(Pb)-2223 phase. The measured lattice parameters are $a = 5.406 \pm 0.004$ Å, $c = 37.050 \pm 0.014$ Å and the density of lattice $d = 3.137$ g/cm^3 for all samples with an estimated ±0.004

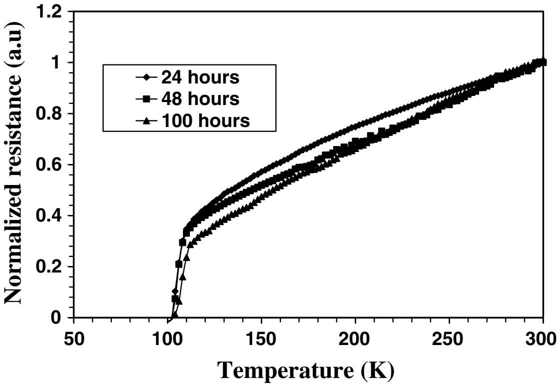

Fig. 1 Dc electrical resistance as a function of temperature for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta$ samples at different sintering time

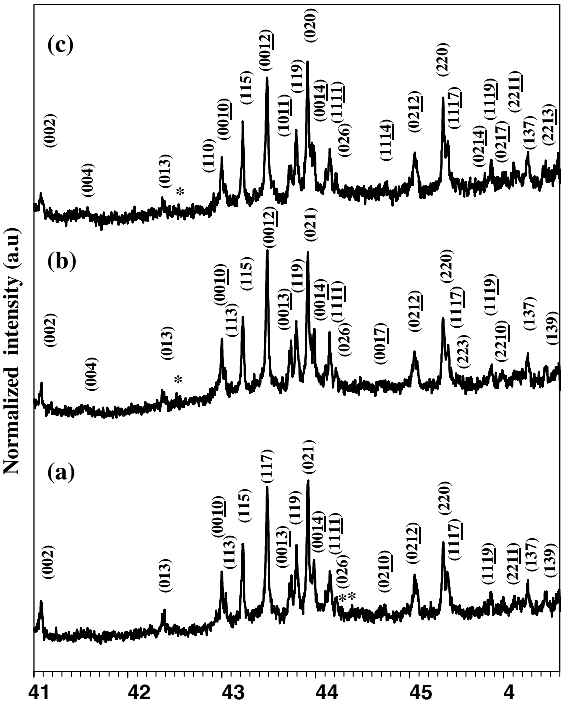

Fig. 2 XRD analysis of BSCCO samples sintered for (**a**) 24 h, (**b**) 48 h and (**c**) 100 h, showed (hkl) for 2223 phase and (*) for 2212 phase

precision. The volume fractions of high-T_C and low-T_C phase can be estimated from the intensities of high-T_C, low-T_C phase peaks and other peaks observed, as used in Ref. [12, 13], namely, the Eqs. (1, 2)

$$\text{Bi}-2223(\%) = \frac{\sum I_{2223}}{\sum I_{2223} + \sum I_{2212} + \sum I_{\text{others}}} \times 100\% \tag{1}$$

$$\text{Bi}-2212(\%) = \frac{\sum I_{2212}}{\sum I_{2223} + \sum I_{2212} + \sum I_{\text{others}}} \times 100\% \tag{2}$$

where I is the peak intensity of the present phases. The proportions of Bi-2223/Bi-2212 (%) phase in the phase mixture were estimated to be 97/3, 97.5/2.5 and 98.7/1.3%, for samples A, B and C, respectively.

Figure 3(a–c) show the temperature variation of, $\chi = \chi' + i\ \chi''$, for pure samples, sintered for 24, 48 and 100 h. The curves of real part (χ') which provide information on the diamagnetic behaviour and an imaginary part (χ'') that displays the features of coupling effect of the grains in the superconductor. $T_{\text{C-onset}}$ was obtained at 108 K for all samples. The χ'–T curves displayed two-step features due to the weak coupling behaviour of the samples. The strong dependence of χ' on the ac field strength is shown by the decreasing of shielded volume and decreasing of the $T^{2\text{nd}}_{\text{C-onset}}$ as the field strength increases. This is due to the magnetic flux penetrating the sample surface when the screening current required to exclude the flux decreases. The phase lock-in temperature, T_{cj} was observed at 105.5, 106.1 and 106.7 K for samples sintered at 24, 48 and 100 h, respectively. This revealed that above this temperature the grains de-coupled because of the thermally activated phase slipping and it is just slightly below the onset temperature, $T_{\text{C-onset}}$ [14]. By determining the phase locking temperature associated with the onset of the lower transition temperature and using the Ambegaokar–Baratoff equation [15], the maximum Josephson's current I_o passing through the grain boundaries can be calculated by using the following Eq. (3):

$$I_o = 1.57 \times 10^{-8} \times \frac{T_{\text{C-onset}}}{T_{\text{C-onset}} - T_{\text{Cj}}} \tag{3}$$

Taking the appropriate values for $T_{\text{C-onset}}$ and the T_{Cj} gives $I_o(0) \approx 73.8$, 96.4 and 138.7 μA for the samples sintered at 850 °C for 24, 48 and 100 h, respectively. These values are much higher than that of the sample prepared via conventional method (sintered for 150 h, $I_o(0) \approx 55.9$ μA [16]), indicating stronger coupling between the grains due to the submicron sized particles and high homogeneity of the starting powders.

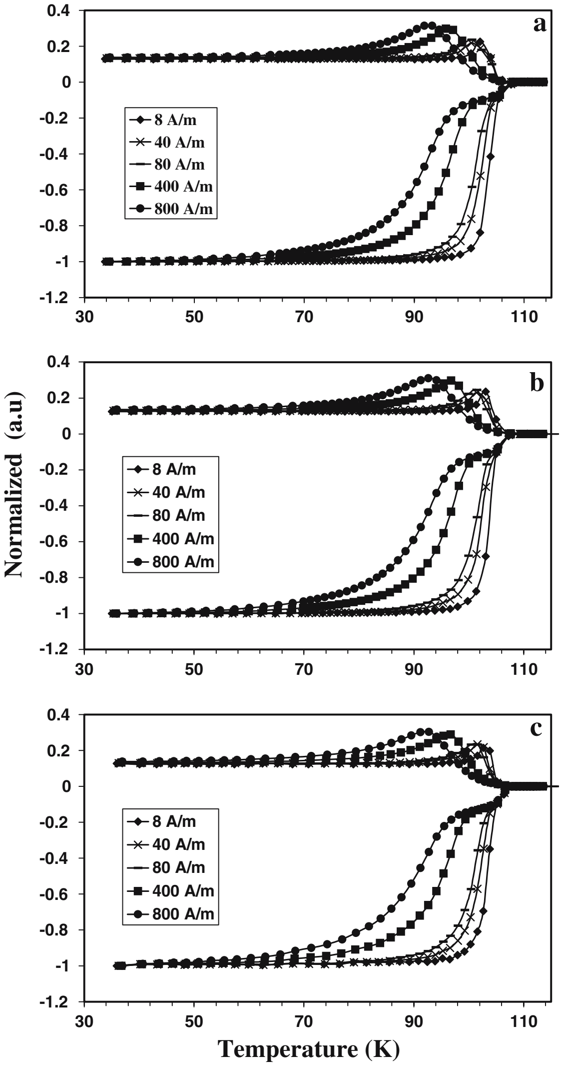

Fig. 3 AC susceptibility of pure $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta$ samples sintered for (**a**) 24 h, (**b**) 48 h and (**c**) 100 h

The imaginary component, χ'', shows there is no intrinsic peak (indicates the ac losses that are associated with intragranular vortices) in all the pure samples. The intergranular coupling peak, T_P, which is associated with intergranular (matrix) critical current density, J_{cm} decreases as the magnetic field increases (Fig. 4). This implies that hysteresis loss occurs at the grain boundaries. The coupling peak was shifted towards lower temperature as the magnitude of the applied magnetic field increases. The values of T_P were improved as the sintering time increased implying that the granularity of the samples has improved as more 2223 phase was formed as observed by X-ray results.

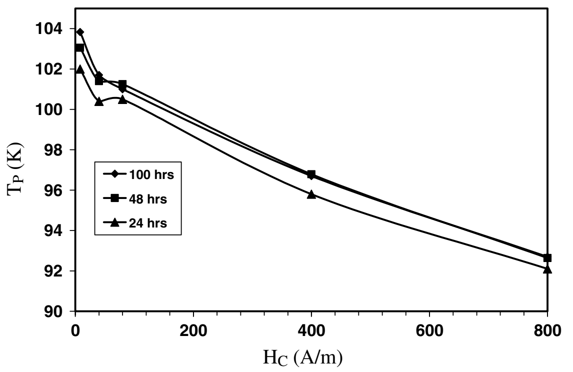

Fig. 4 Applied field as a function of the coupling peak temperature at different sintering times

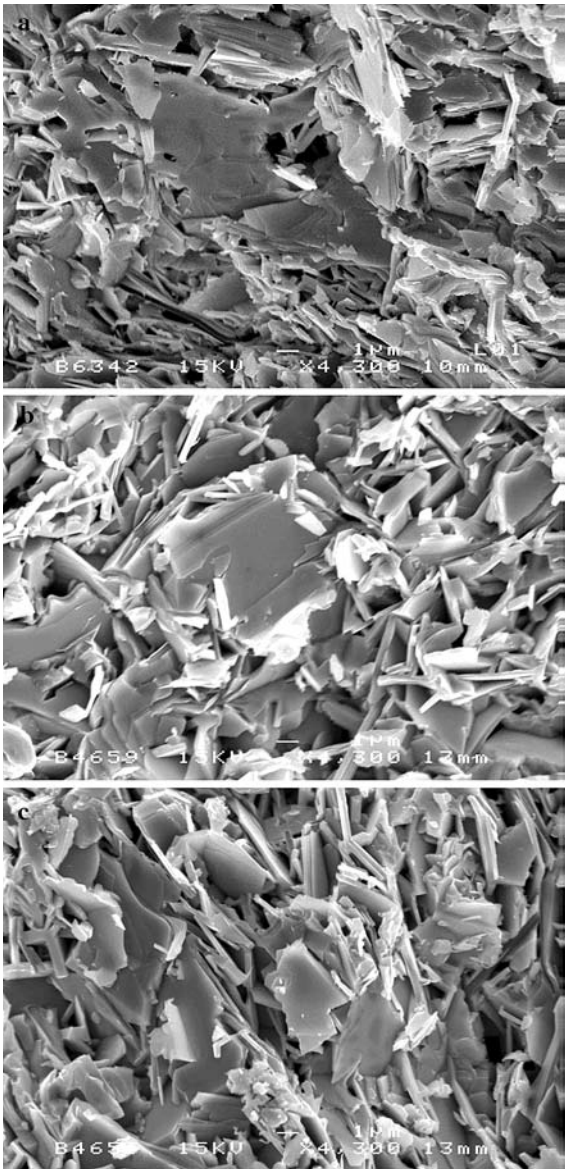

Fig. 5 SEM micrographs of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta$ samples sintered for (**a**) 24 h, (**b**) 48 h and (**c**) 100 h

SEM micrographs for the samples A, B and C displayed compacted layers of thin flaky plate-like grains with random distribution (Fig. 5a–c). The average grain size is 7 µm, approximately. However, the grains became well aligned at 100 h sintering as compared to the other samples, and thus the connectivity between the grains was enhanced.

Conclusions

Bi(Pb)-2223 superconducting ceramic has been successfully prepared via coprecipitation method using metal acetate precursor without using any pH controller or washing to the precipitate. XRD data showed a high production of the Bi-2223 for all samples ($V2223_{phase} \approx$ 97–99%). The calculated lattice parameters showed that all samples are nearly similar, where $a \cong 5.406$ Å, $c \cong 37.050$ Å. Electrical resistivity studies displayed the metallic behaviour for all samples with a slight improvement in the $T_{C(R\,=\,0)}$ for longer sintering time. AC magnetic susceptibility measurements showed an improvement in the grain connectivity as sintering time increases due to the submicron size of the starting powders. The typical features of the grains of 2223 phase were observed via SEM micrographs. The grain size for all samples is ≅7 µm with better grain alignment for the sample with higher sintering time.

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