Preparation and characterization of glassy and superconducting (Bi, Pb, Sb)–Sr–Ca–Cu–O systems

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Abstract. Superconducting compounds with nominal compositions $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_{3.4}\text{O}_x$ and $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ have been synthesized by ceramic and glass routes and characterized by X-ray diffraction, electrical resistivity and dielectric constant measurements. The zero-electrical resistance temperatures are about 70 K. The dielectric constant of the glasses at room temperature is around 30.

Keywords. (Bi, Pb, Sb)–Sr–Ca–Cu superconductors; high temperature superconducting glass ceramics; melt-quench method; dielectric constant.

1. Introduction

Following the initial work of Michel *et al* (1987) and Maeda *et al* (1988), a number of studies have reported high T_c superconductivity in Bi–Sr–Ca–Cu oxides. However, the amount of high T_c 2223 phase is very sensitive to the preparation conditions. As a result, under normal conditions, it is difficult to obtain superconductors with a zero-resistance transition temperature (T_{CRO}) higher than 85 K in this system. Sunshine *et al* (1988) discovered that Pb substitution for Bi stabilizes the 2223 phase and raises the T_{CRO} above 100 K. Hongbao *et al* (1989) reported that the substitution of Sb for Bi in the Pb-doped compound gives a T_{CRO} of about 132 K. Recently Chandrachood *et al* (1989) reported that the substitution of Sb for Bi in the Pb-free compound leads to superconductivity at 132 K.

In this paper, we describe the preparation of (Bi, Pb, Sb)–Sr–Ca–Cu–O superconductors by both ceramic and glass routes. Characterization of the samples by X-ray diffraction (XRD), differential thermal analysis (DTA), non-resonant microwave absorption and electrical resistivity measurements is also reported here.

2. Experimental

Appropriate amounts of high purity (99.99%) powder reagents Bi_2O_3 , PbO , Sb_2O_3 , SrCO_3 , CaCO_3 and CuO were well mixed and ground in acetone medium carried in an agate mortar. The powder mixture was calcined in oxygen or air at 810–840°C for 15–24 h. It was then reground and pressed into disc-shaped pellets with 10 mm diameter and 2–3 mm thickness at a pressure of 6–8 ton/cm². In the ceramic route, the pellets were heat-treated in air at 840–860°C for 24 h with intermittent grinding. It was again reground and the pellets finally sintered in air at 870°C for 24 h, then cooled to 840°C and were kept there for about 72 h, in the case of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_{3.4}\text{O}_x$ (sample 1) and at 890°C for 15 h, in the case of $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (sample 5), followed by furnace cooling. In the glass route, the dense chunks of pre reacted materials were melted in an alumina or platinum crucible at 1100°C for 15 min and the melt was

rapidly quenched (10^2 – 10^3 °C/s) by sandwiching it between two polished copper plates, resulting in an opaque black sheet of about 0.5–1.0 mm thick (samples 2 and 6). For crystallization, the above dense glass plates were annealed in air at 840 °C for 15 h, in the case of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_{3.4}\text{O}_x$ (sample 2a) and at 890 °C for 15 h in the case of $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (sample 6a), followed by furnace cooling.

Room temperature XRD was carried out with a Seifert diffractometer using CuK_α radiation. DTA for the melt-quenched sample was made at 5 °C/min. Microwave absorption of the sample was recorded using a Varian E-109 X-band EPR spectrometer operating at 9.39 GHz. Through-zero-field detection was achieved by using a pair of current-carrying Helmholtz coils producing an auxiliary field in a sense opposite to that of the electromagnet. Electrical resistivity was measured with a four-probe Van der Pauw and Montgomery technique in a APD closed-cycle refrigeration system (12–300 K range). The temperature was measured with a calibrated Si diode with an uncertainty of ± 0.05 K. Leads were attached onto a rectangular sample with air/light bulb-dried silver paste. Voltage was measured with an accuracy of 0.01 μV (181 Keithley nanovoltmeter), using a reversible DC current of 1–5 mA (Knick precision current/voltage source). Dielectric constant (capacitance) was measured using a micrometer cell (so constructed to avoid the need for edge correction) on the glassy samples as a function of frequency (1 kHz–10 MHz) with a signal strength of 1 V_{rms} (HP 4192 A).

3. Results and discussion

In the present study Pb was first substituted for Bi with the nominal composition $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_{3.4}\text{O}_x$. This composition was chosen to see the effect of Ca and Cu-rich sample. Later Sb was substituted for Bi with the nominal composition $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$, to see the effect of Sb^{+3} on the large ion site (Bi, Sr, Ca). The polycrystalline material obtained by glass crystallization has several advantages over the ceramic counterpart: (i) the glass-derived material has a much denser matrix; (ii) it is much more homogeneous and could be a candidate for a high-current carrier; (iii) since the starting material is a very uniform glass, the microstructure and the high T_c phase are much easier to control and obtain. Finally it could solve some of the technological problems faced by the ceramic counterpart.

Figure 1 shows the XRD pattern of sample 1 which contains both 85 and 110 K phases. Non-resonant microwave absorption is obtained (figure 2) in this sample at 77 K. Figure 3 shows its electrical resistivity. It initially behaved semiconductor-like up to 74 K and then showed a metallic behaviour with a $T_{\text{CRO}} = 40$ K. Sample 1 was further annealed at 400 °C for 24 h, followed by air quenching (sample 1a). There was no detectable change in the XRD patterns of samples 1 and 1a. Sample 1a now

Figure 1. XRD pattern for the sintered (840 °C, 72 h) $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_{3.4}\text{O}_x$ sample.

Figure 2. Non-resonant microwave absorption signals of samples with nominal compositions: ceramic $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_3\text{O}_x$ (1), crystallized glass $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_3\text{O}_x$ (2a) and ceramic $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (5) at 77 K as a function of magnetic field H .

Figure 3. Temperature dependence of the electrical resistance of sintered (840°C , 72 h) $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_3\text{O}_x$ (1) and further annealed (400°C , 24 h) and air-quenched (1a) samples.

Figure 4. DTA curve of melt-quenched sample of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_{3.4}\text{O}_x$.

Figure 5. XRD patterns for the melt-quenched samples with nominal compositions: $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_{3.4}\text{O}_x$ (2) and $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (6).

dramatically behaved metal-like with a deviation from the linear behaviour which starts at 127 K, followed by a T_c onset (T_{c0}) about 92 K with a $T_{\text{CRO}} = 74$ K. This is, in general, contrary to the behaviour observed in $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ system which calls for further investigation. Figure 4 shows the DTA curve of the melt-quenched sample of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_{3.4}\text{O}_x$ (sample 2). The kink toward the endothermic direction at 382°C is the glass transition temperature (T_g), the sharp exothermic peak at 443°C is the crystallization temperature (T_x). From T_g and the XRD pattern (figure 5) we conclude that the rapidly quenched sample is almost “glass”. Sample 2 was heat-treated for crystallization in air at 840°C for 15 h, followed by furnace-cooling (sample 2a). The temperature dependence of the resistance of this as-grown sample is seen in figure 6. It initially behaved like a semiconductor which later turned metal-like at 110 K with a T_{c0} of 85 K followed by a $T_{\text{CRO}} = 70.5$ K. The room temperature resistance of sample 2a with a few layers removed (sample 2b) was higher than the as-grown sample 2a. The difference is also clearly seen from the XRD pattern (figure 7). This indicates that the annealing time was very short and calls for much longer time for the possible growth of 110 K high T_c phase. Superconductivity in sample 5 was ensured by the non-resonant microwave absorption at 77 K. X-ray measurement reveals that this sample contains both 2212 and 2223 phases (figure 7). Figure 8 shows its resistance. Deviation from the

Figure 6. Temperature dependence of the electrical resistance of crystallized $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_{3.4}\text{O}_x$ glass.

Figure 7. XRD patterns of samples with nominal compositions: annealed (840°C , 15 h) $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_{3.4}\text{O}_x$ [as-grown (2a), few layers removed (2b)] and sintered (890°C , 15 hr) $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (5).

linear metallic behaviour indeed starts at 130 K with a sharp drop at 115 K followed by a T_{c0} of 85 K with a $T_{CR0} = 70$ K. This is in contrast to the behaviour observed by Chandrachud *et al* (1989). Our preliminary study on this system via the crystallized glass (sample 6a) did not show any sign of high T_c superconductivity. We believe that the sintering temperature (890°C) is too high and needs to be reduced to $860\text{--}880^\circ\text{C}$ to induce possible superconductivity.

Figure 8. Temperature dependence of the electrical resistance of sintered $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ sample (5).

Silver paste (air-dried) was applied onto the samples as electrodes to measure the dielectric constant of glasses. The real part (ϵ'_r) of the complex dielectric constant was calculated from $\epsilon'_r = (\Delta C_p)t/A_s\epsilon_0 + 1$ where ΔC_p is the difference in the capacitance with zero and without the sample between the electrodes, t the thickness of the sample, A_s the area of the sample and ϵ_0 the permittivity of free space. We found that for glasses (2,6) of the above systems ϵ'_r varies from 40 at 1 kHz to 20 at 10 MHz. This little dispersion in dielectric constant with frequency (at room temperature) dies out at low temperatures and approaches a common value around 10 at 77 K. Also, no non-resonant microwave absorption was found at 77 K in these samples (2,6). The resistivities of our quenched glass samples were about 5×10^6 ohm-cm at room temperature.

4. Conclusions

The exact composition responsible for the 110 K or a still higher temperature phase is not clear but it exists in a certain narrow composition with a particular sintering temperature (varies with composition), much longer sintering time etc. Additional annealing in air at 400°C followed by quenching to room temperature, seems to improve the situation. In contrast to the results of Chandrachood *et al* (1989) we find no evidence for the existence of any zero-resistance transition at 132 K.

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