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Superconducting Properties of BiPbSrCsCuO and BiSrCaCuO Glass-Ceramics

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In this work we study the main differences between the superconducting properties of the $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ and $(\text{Bi}_{0.8}\text{Pb}_{0.2})_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ glass-ceramics. The $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ and $(\text{Bi}_{0.8}\text{Pb}_{0.2})_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ glass-ceramics prepared in the same conditions contain similar amounts of the superconducting 2212 phase, however their superconducting and normal-state electrical properties differ significantly. The main reason which makes BiSrCaCuO glass-ceramics worse superconductor than BiPbSrCaCuO is its microstructure.

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1. Introduction

Oxide $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ and $(\text{Bi}_{0.8}\text{Pb}_{0.2})_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ glasses, annealed above 470°C , crystallise. The crystalline phases forming during annealing are, among others, oxide superconductors: $(\text{Bi,Pb})_2\text{Sr}_2\text{CuO}_x$ (2201 with $T_c = 10$ K), $(\text{Bi,Pb})_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (2212, $T_c = 85$ K), and $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (2223, $T_c = 105$ K) [1]. Glass-ceramic are granular materials which usually show a double superconducting transition. At higher temperature isolated grains transit into the superconducting state, while at lower one the grains couple into a long-range ordered state [2]. In this work we study the main differences between the superconducting properties, especially transition temperatures of the $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ and $(\text{Bi}_{0.8}\text{Pb}_{0.2})_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ glass-ceramics.

2. Experimental

The $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ and $(\text{Bi}_{0.8}\text{Pb}_{0.2})_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ glasses were prepared from nitrates and oxides. The substrates, after calcination at 820°C for 10 h, were

melted in a platinum crucible at 1250°C and quenched. The glass was cut into bars ($2 \times 1 \times 8 \text{ mm}^3$) and polished before further annealing. Glass-ceramic samples were produced by annealing at 820°C, 840°C, and 850°C. Short time annealing varied from 1 to 32 minutes. Some samples were also annealed for 66 hours. The samples were checked by X-ray diffraction and SEM methods.

Measurements of resistivity as a function of temperature were made by a DC technique in four-terminal configuration at a temperature range of 3–300 K.

3. Results and discussion

Examples of temperature dependence of resistivity of the annealed samples are shown in Fig. 1. In order to discuss in details the superconducting transition in both materials the temperature derivative of resistivity has been analysed (Fig. 2). The temperature dependence of the derivative reveals strong granularity of the materials. The double maxima in $d\rho/dT$ show that the superconducting transition occurs in two steps. The differences between both materials are strik-

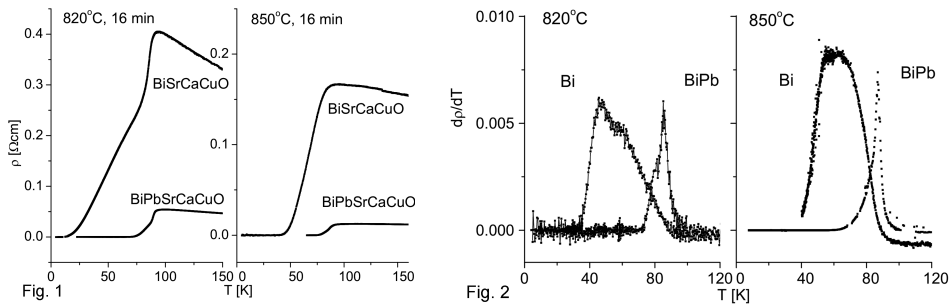


Fig. 1. Temperature dependence of resistivity of the samples annealed at 820°C and 850°C for 16 minutes.

Fig. 2. Temperature derivative of the resistivity versus temperature of the samples annealed for 8 minutes at 820°C and 850°C.

ing. Except for the onset transition temperature BiSrCaCuO has all characteristic temperatures lower than those of BiPbSrCaCuO. The pairing transition is located around 61 K and 65 K for BiSrCaCuO annealed at 820 and 850°C, respectively, while in the case of BiPbSrCaCuO it is about 86 K. The coherence transition temperature is shifted towards lower temperatures, but the difference between pairing and coherence transition temperatures is larger in BiSrCaCuO than in BiPbSrCaCuO ($\Delta T_c \cong 13 \text{ K}$ and 6 K, respectively). The results obtained for all the studied samples are collected in Table.

Generally speaking, electrical properties of both glass-ceramics differ significantly. BiSrCaCuO in comparison to BiPbSrCaCuO has a larger resistivity and larger value of temperature coefficient of resistivity (TCR). Even for a long annealing (66 h) the value of TCR does not become positive, while in the case of

TABLE

Electrical properties of the BiSrCaCuO and BiPbSrCaCuO glass-ceramics.

Annealing conditions		T_{onset} [K]		T_1 [K]		T_2 [K]		TCR [$10^{-4} \Omega \text{ cm/K}$]		ρ (300 K) [$\Omega \text{ cm}$]	
[$^{\circ}\text{C}$]	[min]	Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb
850 $^{\circ}\text{C}$	2	86		80		69	< 3	-7.3	-35	1.96	0.53
	8	92	91.8	87	67	82	55	-1	-6	0.035	0.16
	16	98	92.8	89	85.7	82	55.4	-1.04	-9	0.033	0.19
	32	92.2	90	87.3	85	82.6	63.6	-0.8	-3.9	0.031	0.11
820 $^{\circ}\text{C}$	8	92	92	85.7	60.7	79.5	46.2	-0.6	-2.3	0.04	0.13
	16	98	91	85.2	63.1	79.8	53	-0.11	-4.7	0.01	0.156
	32	92	91	85.6	70.6	83.3	56.5	-0.24	-2.9	0.03	0.11
840 $^{\circ}\text{C}$	66 h	100	99	91.4	83	-	-	+0.06	-0.5	0.014	0.052

the lead-containing samples it may be positive after about 1 hour of annealing. Also regardless the annealing conditions, the lead-containing glass has significantly better superconducting properties.

The reasons of large differences between the two materials have been discussed before but no convincing conclusion has been reached [1, 3]. For instance, it has been proposed that in the BiPbSrCaCuO glass-ceramics Ca_2PbO_4 forms and enhances the oxygen diffusion through the glass [1]. Our studies show that Ca_2PbO_4 being present on the surface only does not take part in the oxygen diffusion in the bulk of BiPbSrCaCuO [4]. What is more, the relative mass change, which reflects the amount of oxygen incorporated into the material during the crystallisation, is larger in the BiSrCaCuO than in the BiPbSrCaCuO [5]. So that, the difference between the rate of oxygen diffusion into both materials does not seem to be responsible for different superconducting properties. In order to find the reason of these differences we have conducted thorough studies the evolution of the BiSrCaCuO and the BiPbSrCaCuO microstructure and phase composition during annealing [5, 6]. The examples of XRD and SEM results are shown in Figs. 3 and 4. XRD spectra show that BiSrCaCuO glass-ceramic does not contain a smaller amount of the 2212 superconductor than BiPbSrCaCuO [5, 6]. However, it can be seen in Fig. 3 that the amount of the amorphous phase is larger in BiSrCaCuO than in BiPbSrCaCuO (the bump between 20 and 40 degrees). On the other hand, the crystallites of the 2212 phase (Fig. 4) are significantly smaller and ordered in a different way than those in the material containing lead. Smaller crystallites signify the larger number of grain boundaries. Simultaneously, the presence of amorphous and other phases, which accumulate between the 2212 crystallites (on the grain boundaries), weakens the links between the grains. Even on the surface of the sample, where there is little foreign phases, the 2212 crystallites without lead seem to be worse connected than those containing lead.

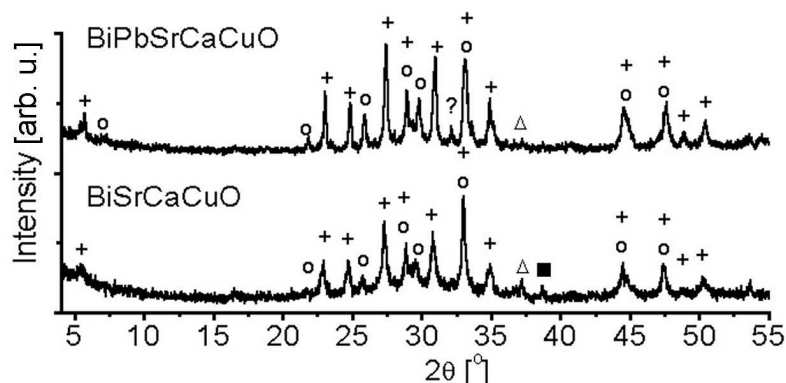


Fig. 3. XRD patterns of samples annealed for 8 minutes at 850°C. ○ — 2201, + — 2212, ■ — CuO, Δ — CaO, ? — undefined phases.

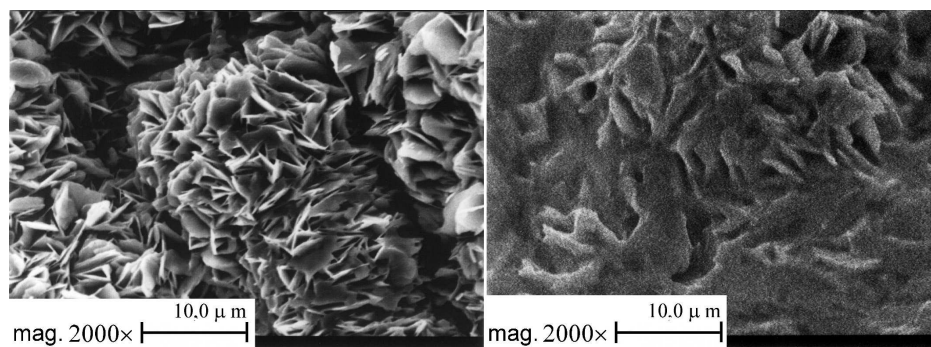


Fig. 4. SEM images of surface of the glass-ceramics samples annealed at 850°C for 8 minutes, BiSrCaCuO (left), BiPbSrCaCuO (right).

Summing up, the main reason which makes BiSrCaCuO glass-ceramics worse superconductor than BiPbSrCaCuO is the poor quality of the links between the grains. Bad connections between the crystallites explain well high normal state resistivity, temperature coefficient of resistivity, and low coherence transition temperature. It does not, however explain low pairing transition temperature, since it does not depend either on the grain boundaries or on the grain dimensions. It is possible that the 2212 phase forming in the BiSrCaCuO material is of low quality (for instance, it may be more defected etc.). It requires further studies to solve this problem.

4. Conclusions

The $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ and $(\text{Bi}_{0.8}\text{Pb}_{0.2})_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ glass-ceramics prepared in the same conditions apparently contain similar amounts of the superconducting 2212 phase, however their superconducting and normal-state electrical properties differ significantly. The main reason which makes BiSrCaCuO glass-

-ceramics worse superconductor than BiPbSrCaCuO is its microstructure. In comparison with BiPbSrCaCuO it is composed of smaller crystallites poorly linked between one another, which causes a decrease in the coherence transition temperature.

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