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Conductivity and Superconductivity of $(Bi,Pb)_4Sr_3Ca_3Cu_4O_x$ Glass-Ceramics

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(Bi,Pb)–Sr – Ca–Cu–O glasses, annealed in proper conditions, transform into a granular metal and superconductor. As a result of annealing oxide superconductors belonging to the bismuth family $(Bi,Pb)_2Sr_2CuO_x$, $(Bi,Pb)_2Sr_2CaCu_2O_x$, and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ crystallize. (Bi,Pb)–Sr–Ca–Cu–O glass-ceramic samples were obtained by annealing the amorphous solid at temperatures between 500°C and 870°C. Their microstructure was studied with scanning electron microscopy, atomic force microscopy, and X-ray diffraction. The temperature dependence of resistivity in annealed samples was studied in a temperature range from 3 K to 300 K. In this work we present the influence of the microstructure on the electrical properties of the granular and disordered material composed of the 2201 and 2212 grains embedded in the nonmetallic matrix.

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1. Introduction

The (Bi,Pb)–Sr–Ca–Cu–O material obtained by the solid-state crystallization method, depending on the synthesis condition, is either a granular or disordered metal. The metallic phases, which form as a result of crystallization are the oxide superconductors belonging to bismuth family, that is $(Bi,Pb)_2Sr_2CuO_x$ (2201 with $T_c = 10$ K), $(Bi,Pb)_2Sr_2CaCu_2O_x$ (2212, $T_c = 85$ K), and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (2223, $T_c = 105$ K) [1]. In the first seconds of the crystallization process the material may be considered as a system of oval grains of 2212 and 2201 phase embedded in the insulating matrix, while the further annealing leads to the formation of plate-like or oval crystallites weakly connected one with another. The electrical properties of such an inhomogeneous material differ significantly from that of a typical metal [2]. They depend strongly on both the fraction of the metallic or superconducting phase and type of microstructure of the crystallized material.

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This work emphasizes the relation between microstructure of the $(Bi,Pb)_4Sr_3Ca_3Cu_4O_x$ disordered materials obtained by the method of solid-state crystallization and their normal-state and superconducting properties.

2. Experimental

The samples were produced by the solid-state crystallization. First, the samples of $(Bi_{0.8}Pb_{0.2})_4Sr_3Ca_3Cu_4O_x$ glass were prepared from reagent grade: $Bi(NO_3) \cdot 5H_2O$, PbO, CuO, $Sr(NO_3)_2$, and $CaCO_3$. The substrates were mixed in the (Bi,Pb):Sr:Ca:Cu ratio 4:3:3:4 and calcinated at 820°C for 10 h. Then, they were melted in a platinum crucible at high temperature (1250°C and 1350°C), kept in the high temperature for about 10 min, and quenched. The glass was cut into bars of similar dimensions ($2 \times 1 \times 8$ mm^3) and polished before a further thermal treatment.

The crystallization was carried out in a tube furnace at various temperatures between 650°C and 850°C. The samples were put either into already hot furnace or were heated with the rate of 200°C/h and then annealed for the proper time. The annealing time varied from 4 min to 290 h.

The samples microstructure was qualitatively studied with atomic force microscopy (AFM) and scanning electron microscopy (SEM) methods. In order to study further the microstructural differences between the samples containing relatively small crystallites, X-ray diffraction (XRD) analysis of the crystallite dimensions was performed. The estimations were based on the Scherrer formula: $C = k\lambda/[(B_{\mathrm{e}} - B_{\mathrm{t}})\cos\theta]$, where C is an average diameter of the crystalline grain, k is a constant usually assumed to be 0.9, λ is the X-ray wavelength, B_{e} indicates the measured width of a peak profile, while B_{t} is the ideal, non-broadened width of a peak and θ is the diffraction angle. The reflections corresponding to the $(113)_{2201}$ and $(115)_{2212}$ were analyzed. The value of B_{t} was estimated on the basis of the measurements performed for the sample crystallized for 290 h and independently, on the reference sample of polycrystalline Si with large crystalline grains. The accuracy of the Scherrer analysis has been estimated to be about 50%.

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

3. Results and discussion

Normal-state and superconducting properties of the (Bi,Pb)–Sr–Ca–Cu–O materials obtained by the solid-state crystallization depend on the crystallization conditions. As a result of crystallization the material first becomes a granular metal or a superconductor. Then, it gradually develops into a disordered polycrystalline material with good superconducting properties. The changes occur through the crystallization of the 2212 and 2201 phases and the microstructure evolution. There are two important microstructural factors that influence the

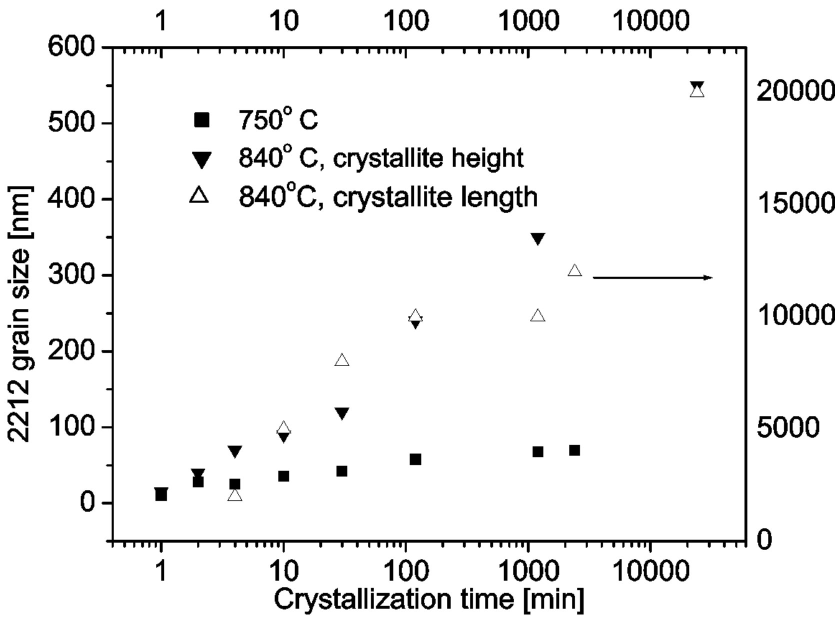

Fig. 1. Estimated dimensions of the crystallites as a function of crystallization time. The estimations of the grain height were performed on the basis of the XRD data (full symbols) while the length of the plate-like crystallites was estimated from SEM (empty symbols) analysis.

electronic conduction in the glass-ceramic materials. They are the type of the microstructure and the size of the crystallites. The type of microstructure depends on the temperature and time of annealing. The samples annealed at 650–750°C are composed of crystallites of rather irregular, oval shapes [3]. During annealing their radius increases from about 10 nm to 300 nm, but their shape remains the same. Different evolution of microstructure occurs in the case of the samples annealed at temperatures above 800°C. Crystallites forming at the beginning of the process (up to 2–4 min) are oval and they grow up to about 100 nm. Further annealing leads to the growth of plate-like crystallites [3]. The plates are 2212 crystallites with the c axis parallel to the height of the plates. The samples consisting of plate-like crystallites are much more porous than these built of oval grains. Both types of the crystallites gradually increase their size during the annealing process, however the growth is faster in the case of the plate-like crystallites. It is illustrated in Fig. 1. The results of the estimations of dimensions of the crystallites performed on the basis of the XRD and SEM analysis are also collected in Table.

Structural disorder influences strongly such material properties like normal state resistivity, temperature coefficient of resistivity, and the width of the transition into the superconducting state [2]. The results of the measurements performed

TABLE

Average sizes of the crystallites (performed on the basis of the XRD and SEM analysis), room temperature resistivity, temperature coefficient of resistivity, and the width of the superconducting transition, of the glass-ceramic material annealed at 750°C and 840°C.

Time [min]	2201 grain size (113) [nm]	2212 grain size (115) [nm]	2212 plate size (001) [nm] (SEM)	ρ(300 K) [Ω cm]	$\Delta\rho/\Delta T$ [10^{-3} Ω cm/K]	ΔT_c [K]
Crystallization at 750°C						
1	25	10	–	21	–230	–
2	43	28	–	3	–20	74
4	45	25	–	0.8	–4	60
10	45	36	–	0.1	–0.2	15
30	50	42	–	0.02	–0.02	8
120	70	58	–			
1200	70	68	–			
2400	85	70	–	0.01	0.009	9
Crystallization at 840°C						
1	50	15	–	6	–50	–
2	60	40	–	1.4	–25	68
4	56	70	2000	0.1	–0.1	9
10	50	90	5000			
30	65	120	8000	0.02	–0.01	5
120	60	240	10000			
1200	50	350	10000	0.009	0.03	3
24000	43	550	20000	0.008	0.04	3

in the glass-ceramic samples are shown in Table and Figs. 2 and 3. Figures 2 and 3 present the dependence of room temperature resistivity, temperature coefficient of resistivity, and the width of the superconducting transition on the crystallization time, respectively. It is impossible to distinguish the influence of microstructure from that of phase composition on the electrical properties of glass-ceramics. However, it may be observed that in the case of glass-ceramics with both types of microstructure, if the crystallization is long enough, it is possible to obtain the material with low resistivity, linear temperature dependence of resistivity, positive temperature coefficient of resistivity, and good superconducting properties. Nevertheless, materials annealed at higher temperatures (e.g. 840°C) containing larger crystallites are always more conductive and the transition into the superconducting state is more narrow in comparison with the materials annealed at lower temperature (e.g. 750°C). One of possible reasons for this is that larger crystal-

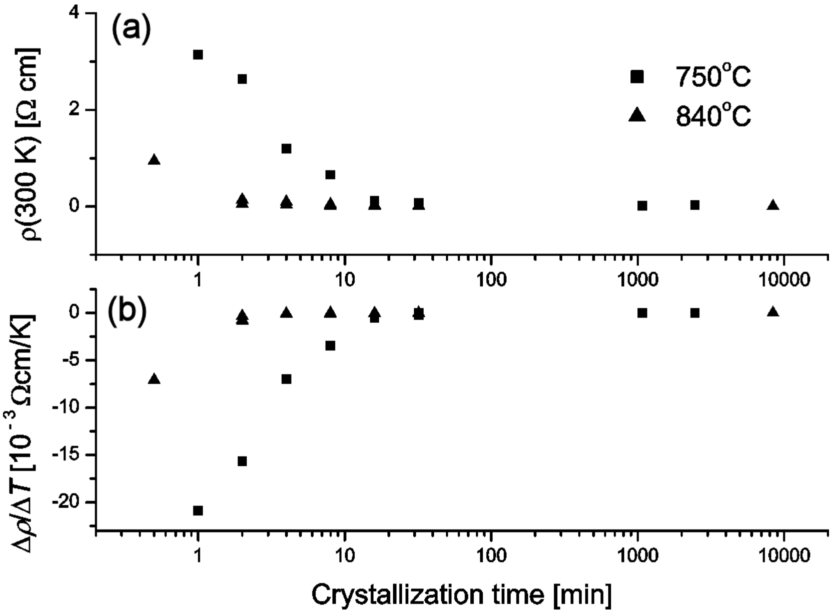

Fig. 2. The dependence of room temperature resistivity (a) and temperature coefficient of resistivity on the crystallization time (b).

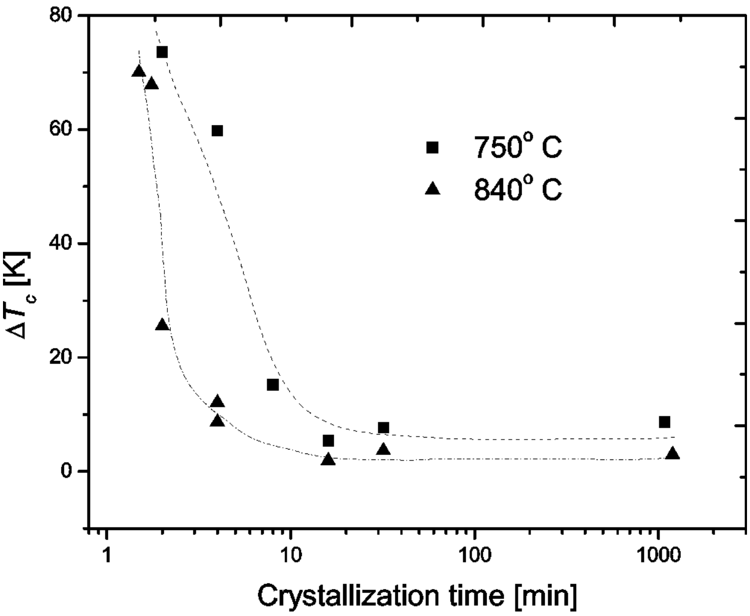

Fig. 3. The dependence of the width of the superconducting transition on the crystallization time.

lites signify less grain boundary defects and the smaller number of links between the grains. A relatively larger porosity of samples annealed at higher temperature seems to be less important.

In order to study the influence of the microstructure itself on the electrical properties of glass-ceramics the samples with the same phase composition but composed of the crystallites of different average sizes, were compared. Figure 4 shows an example of temperature dependence of resistivity measured in two samples. One was crystallized in quasi-isothermal conditions (840°C, 32 min), that is, it was put into already hot furnace (heating rate about 80°C/s), while the other sample was heated up slowly (0.055°C/s) and then it was annealed in the same conditions as the first one. The sample, which was heated up slowly consisted of smaller crystallites than those heated quickly. The shape of the crystallites was the same (plate-like) but both the length and height of the plates in the sample heated slowly was about 80% of these corresponding to the sample heated quickly. The heating rate influences both the nature of nucleation process and the activation energy of crystallization and therefore it influences the microstructure of material [4]. It can be seen from Fig. 1 that the sample heated slowly has a significantly larger resistivity and worse superconducting properties in comparison with the other one. Taking into consideration that the differences between the mi-

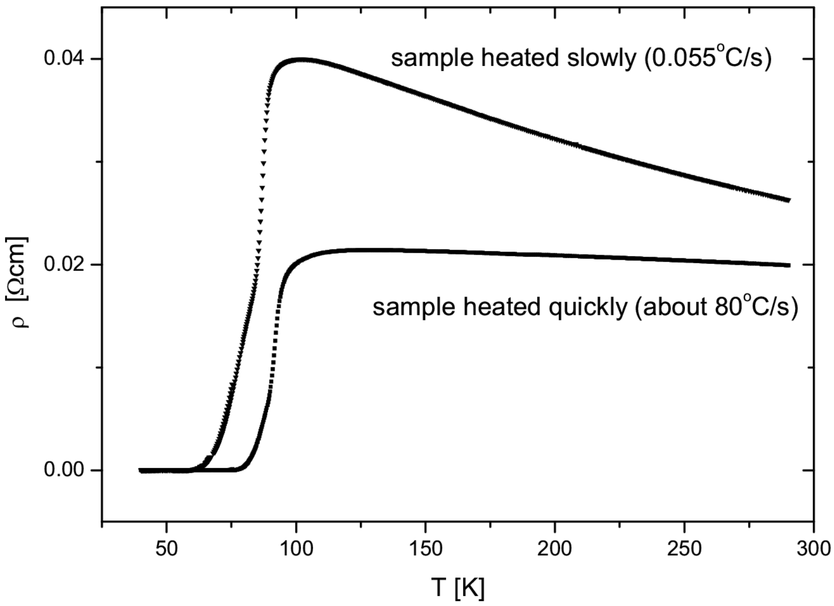

Fig. 4. Temperature dependence of resistivity measured in two samples. One was crystallized in quasi-isothermal conditions (heating rate about 80°C/s and annealing at 840°C, 32 min), while the other sample was heated up slowly (0.055°C/s, and annealing at 840°C, 32 min).

crostructure of these two samples are not large, it shows that the microstructure of glass-ceramic materials is a very important factor determining their transport properties.

4. Conclusions

In the (Bi,Pb)–Sr–Ca–Cu–O system, materials of various electrical and superconducting properties may be produced by a solid-state crystallization of the amorphous material. Materials obtained by this method have very interesting properties and they belong to a group of materials which may be considered as a system of superconducting grains embedded in a non-superconducting matrix.

Microstructure of the glass-ceramic material seems to determine the normal--state and superconducting properties. The samples with two types of the microstructure were studied. In all the cases the materials with plate-like crystallites had a lower resistivity and better superconducting properties. Moreover, the size of the crystallites has been shown to be an important factor determining the electrical properties of the material.

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