Vol. **106** (2004) *ACTA PHYSICA POLONICA A* No. 5

Proceedings of the School Superconductivity and Other Phenomena in Perovskites, Warsaw 2004

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

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In the (Bi,Pb)-Sr-Ca-Cu-O system, materials of various electrical and superconducting properties may be produced by a glass-ceramic method. Phase composition, structure, microstructure and also electrical properties of the material change as a result of heat treatment. Depending on the heat treatment conditions, either a superconductor with the critical temperature between 8 and 105 K or material without a superconducting transition may be obtained. The properties of the material change so much because during annealing three oxide superconductors belonging to the bismuth family are formed. $(Bi_{0.8}Pb_{0.2})_4Sr_3Ca_3Cu_4O_x$ glass was prepared by a standard technique of quenching homogenized and melted substrates. The glass-ceramic samples were obtained by annealing of the glass beneath melting temperature. Structure and microstructure of glass-ceramic samples were studied with scanning electron microscopy and X-ray diffraction method. Superconducting properties were studied by means of electrical conductivity and magnetization measurements. In this paper we present the influence of the phase composition, structure and microstructure on the electrical conductivity in the normal state and the superconducting properties of $(Bi,Pb)_4Sr_3Ca_3Cu_4O_x$ glass-ceramics.

PACS numbers: 74.72.Hs, 72.80.Ng

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1. Introduction

In this paper we present electrical properties, structure, and microstructure of $(Bi,Pb)_4Sr_3Ca_3Cu_4O_x$ glass-ceramics. Glass-ceramic technology is a method of producing crystalline or partly crystalline materials through the recrystallization of glass. Its main potential advantage is that it allows forming the material into a desired shape without any special difficulties. Preparation of the material proceeds in two steps. First, a mixture of raw materials is melted at high temperature and quenched to form glass. Afterwards the glass is reheated to crystallize. The crystallized products are called glass-ceramics. Materials in a (Bi,Pb)-Sr-Ca-Cu-O system quenched from a melt easily form an amorphous solid. As a result of annealing 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) crystallize forming a granular metal and superconductor. Granular metals (superconductors) are materials containing metallic or superconducting grains embedded in an insulating matrix. Studies of this kind of materials are of great interest because of their unusual electrical properties caused by the interplay of the Coulomb effects, electron tunnelling and various aspects of disorder. In this work we applied the above method to $(Bi_{0.8}Pb_{0.2})_4Sr_3Ca_3Cu_4O_x$ glass. We present how the electrical and superconducting properties of material change in the course of annealing.

2. Experimental

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 1250°C, kept in the high temperature for about 10 minutes, and quenched. The glass was cut into bars of similar dimensions ($2 \times 1 \times 8$ mm^3) and polished before further thermal treatment.

In order to produce glass-ceramic samples, annealing was carried out in a tube furnace at various temperatures between 700°C and 865°C. The samples were put into already hot furnace and after proper time they were quenched. Short time annealing varied from 1 to 32 minutes. Some samples were also annealed for 43 hours. The samples were checked by X-ray diffraction and scanning electron microscopy (SEM) methods.

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

The magnetic measurements were performed in the temperature range 4.2–120 K at magnetic field up to 16 kOe using a PAR 4500 vibrating sample magnetometer (VSM). Temperature dependence of magnetization was measured using zero field cooling (ZFC) and FC procedure, whereas $M(H)$ dependence was measured after ZFC.

3. Results and discussion

3.1. Structure and properties of $(Bi_{0.8}Pb_{0.2})_4Sr_3Ca_3Cu_4O_x$ glass

$(Bi_{0.8}Pb_{0.2})_4Sr_3Ca_3Cu_4O_x$ material quenched from the melt gives a good quality glass with a glass transition temperature about 470°C [1]. Amorphous structure and homogeneity of the glass was confirmed by X-ray diffraction (XRD) and atomic force microscopy (AFM) measurements.

The structure of Bi-Sr-Ca-Cu-O glasses was studied by Khaled et al. [2]. Both Bi and Cu cations are considered as glass formers and it has been shown that a glass network is created by Bi^{3+} and Cu^{1+} ions, with Bi ions coordinated by 6 and Cu ions by 2 oxygen atoms. The remaining cations (Ca, Sr) are distributed in the surrounding environment.

The results of AC conductivity measurements show that the electrical conductivity is of mixed electronic and ionic character [3]. Relatively low activation energy of ionic transport (0.72 eV) implies that ions can move easily through the material. High ionic mobility observed in AC conductivity measurements as well as relatively low glass transition temperature are the symptoms, which indicate that the amorphous material may crystallize easily when annealed at proper temperature. Electronic conductivity of the glass is very low and it increases with the temperature increase [1].

3.2. Phase composition of $(Bi_{0.8}Pb_{0.2})_4Sr_3Ca_3Cu_4O_x$ glass-ceramic

The XRD analysis showed that the heat treatment causes a very rapid crystallization process. This is illustrated in Fig. 1, where XRD spectra recorded

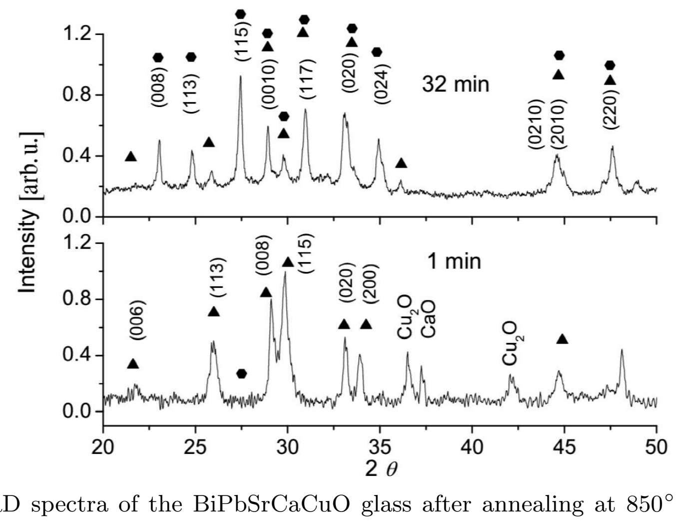

Fig. 1. XRD spectra of the BiPbSrCaCuO glass after annealing at 850°C for 1 and 32 minutes (full triangle signifies 2201, full hexagon — 2212 phase). Miller indices mark the reflexes indexed within 2212 and 2201 phase in the upper and lower part, respectively.

for the samples annealed at 850°C for 1 and 32 minutes are presented. In the first minute of annealing well-resolved diffraction reflexes attributed to $(Bi,Pb)_2Sr_2CuO_x$ (2201) and other oxides like Cu_2O and CaO, can be seen, while after 32 minutes the maxima characteristic of 2212 and 2201 phases dominate the spectra.

Quantitative analysis of diffraction patterns performed by the Rietveld profile refinement allowed us both to determine lattice parameters of the main crystalline phases (2201, 2212, Cu_2O and CaO) and to estimate their approximate weight fractions [4]. Amount of all the total amount of the crystalline phases change from about 10% to 70% after 1 and 32 minutes of annealing, respectively. The cell parameters of 2201 phase did not change significantly with the annealing time and it was found to be: $a = 5.388(2)$ Å, $b = 5.316(2)$ Å, and $c = 24.419(7)$ Å. In the case of 2212 phase average cell parameters were $a = 5.372(1)$ Å, $b = 5.411(1)$ Å, and $c = 30.761(5)$ Å. The 2212 phase in the samples annealed for very short time (1–2 minutes) had c parameter slightly shorter than the average, which indicates oxygen deficiency. The plots of amount of 2212 and 2201 versus time are presented in Fig. 2. It can be seen very clearly that the kinetics of crystallization at lower and higher annealing temperature is different. It reflects different mechanisms of nucleation and growth of crystalline phases at both temperatures [4].

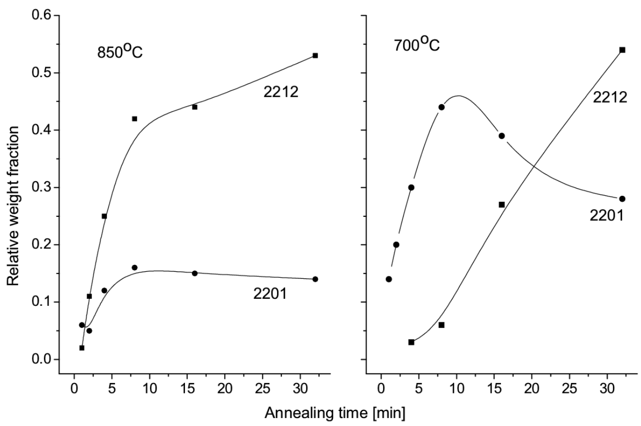

Fig. 2. Proportion of high-T_c phases (2212 and 2201) in the glass ceramics forming during annealing at 700 and 850°C as a function of time.

3.3. *Microstructure of* $(Bi_{0.8}Pb_{0.2})_4Sr_3Ca_3Cu_4O_x$ *glass-ceramic*

Examples of SEM images of the material annealed at 750 and 850°C are presented in Fig. 3. The microstructure of the glass-ceramics during the annealing depends on the temperature and time of the thermal treatment. It can be seen that the surface of the sample annealed at 750°C is composed of crystallites of

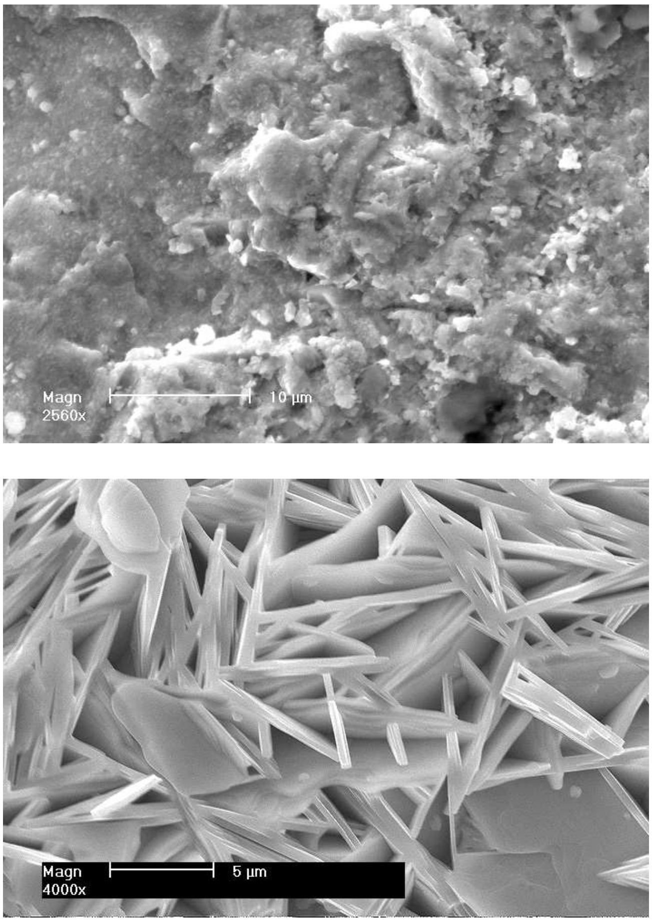

Fig. 3. Examples of SEM images of the material annealed for 32 minutes at 750°C (upper part) and 850°C (lower part).

rather irregular, oval shapes, while that of the sample annealed at 850°C contains plate-like crystallites. Also different types of evolution of microstructure occur in the case of the samples annealed at higher and lower temperatures. During the annealing at lower temperature the shape of the crystal grains remains the same (oval) and only their radius and number increase. At the beginning of crystallization at 850°C, crystallites are oval, but in about fourth minute of annealing a qualitative change occurs [4]. The oval grains disappear while plate-like ones form. Further annealing leads to the growth of their dimensions. It can be also seen that the grains are partly ordered in such a way that their heights are parallel to the sample surface. Crystallization at 865°C proceeds in a similar way as at 850°C but more rapidly. Isolated regions of plate-like grains form already in the first minute of annealing. On the other hand, long-time annealing results in a porous sample where large crystallites are not well connected between each other.

3.4. Normal-state electrical properties of $(Bi_{0.8}Pb_{0.2})_4Sr_3Ca_3Cu_4O_x$ glass-ceramic

The electrical properties of the material change continuously as its composition and microstructure change as the result of heat treatment. Both the normal state and superconducting properties depend on the temperature and time of annealing. All the observed types of characteristics are presented in Fig. 4. In the samples annealed for only a short time the conductivity is thermally activated and no superconducting transition down to 2 K can be seen (Fig. 4a). Longer time and/or higher temperature cause the 2212 grains to grow and the activation energy of the conductivity to decrease (Fig. 4b). Simultaneously, a transition to the superconducting state starts to be observed in the $\rho(T)$ plots. Finally, as the proportion of 2212 and 2223 phases becomes sufficiently large for the metallic pathways to be established the material undergoes a metal–insulator transition to a metallic state (Fig. 4c).

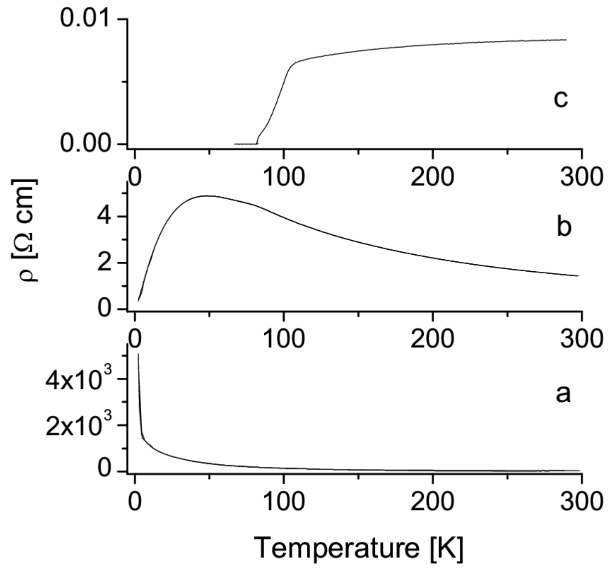

Fig. 4. All the observed types of $\rho(T)$ dependencies observed in glass-ceramic samples: (a) non-superconducting, with the conductivity increasing with the temperature increase, (b) superconducting, with the conductivity increasing with the temperature increase, (c) superconducting, with the conductivity decreasing with the temperature increase.

First, we discuss the properties of the materials annealed only for a short time, with the conductivity increasing with the temperature increase, which do not have a transition to superconducting state on the $\rho(T)$ curve. In this case, the glass ceramics is a granular metal on the dielectric side of the metal–isolator transition. It is a system of crystalline, metallic granules embedded in the dielectric matrix. Electrical conductivity of granular metals is often described by a relation

$$\rho(\mathrm{T}) = \rho_0 \mathrm{e}^{(T_0/T)^n}.$$

Such temperature dependence was observed in several granular metals and models of electrical conductivity were constructed [5, 6]. In the case of (Bi,Pb)-Sr-Ca--Cu-O glass ceramics annealed for time up to 1.5 minute at 830−865°C and to 4 minutes at 700−750°C such an exponential temperature dependence of resistivity was observed at low temperatures. Examples of the results are presented in

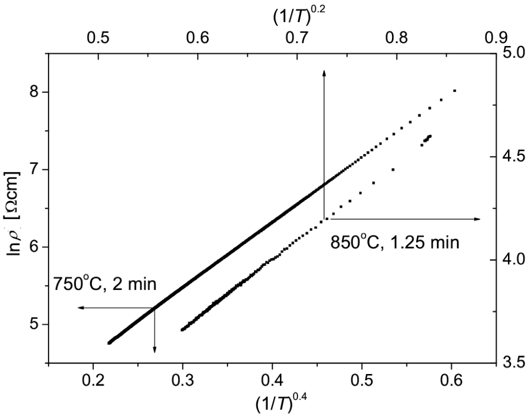

Fig. 5. Resistivity of samples annealed at 750°C for 2 minutes and 850°C for 1.25 minute plotted as a function of $T^{-0.4}$ and $T^{-0.2}$ respectively.

Fig. 5. The exponent n is usually in the range from 0.2 to 1 and depends on the geometry of the conductivity and the details of the density of states

$$n = \frac{p+1}{d+p+1},$$

where d is the dimensionality and p is the exponent, which describes the density of states about the Fermi level, $g(\varepsilon) = g_p|\varepsilon|^p$ [5]. With the value of p index for $(Bi,Pb)_2Sr_2CaCu_2O_x$ equal to 1 [7], dimensionality $d = 3$, we obtain the expected n equal to 0.4. Indeed, in the case of low annealing temperatures n is about 0.4 (for the samples annealed for 2 minutes at 700 and 750°C it is 0.39 and 0.36, respectively). However, for higher annealing temperatures n is about 0.2 (for the sample annealed for 1 minute at 850 and 860°C as well as for 1.5 minute at 840°C n is 0.19, 0.20, and 0.21, respectively). Magnetization measurements show that the samples annealed at about 850°C for a short time transit into superconducting state ($T_\mathrm{c} \cong 90$ K), so that in low temperature they contain isolated granules, which are in the superconducting state. On the other hand, the samples annealed about 700°C do not contain a superconducting phase. We believe that this is a reason why the samples annealed at higher temperature do not fit into a picture of electron hopping between metallic granules embedded in the dielectric matrix. So far various types of behaviour was observed in granular superconductors [8, 9]. For instance a very interesting behaviour of "super-isolator" was found by Gerber et al. [8]. They observed that the resistivity of a granular metal below critical temperature was much higher than in the normal state. Measurements of magnetoresistivity in strong magnetic fields are necessary to verify whether this phenomenon occurs in the case of glass-ceramic superconductors.

The other group of glass-ceramic materials comprises the materials, which have a transition to superconducting state on the $\rho(T)$ curve. They may be considered as strongly disordered metals. Their normal state electrical properties have much in common with these of other known disordered metals [10]. They have large residual resistivity and large and usually negative temperature coefficient of resistivity (TCR). Values of ρ_0 and TCR are correlated with each other and they both decrease during annealing. Finally, TCR becomes positive. The change of the TCR sign from negative to positive occurs about $\rho_0 \approx 0.01\ \Omega$ cm, which corresponds to the Mott minimum conductivity.

3.5. Superconducting properties of $(Bi_{0.8}Pb_{0.2})_4Sr_3Ca_3Cu_4O_x$ *glass-ceramic*

Superconducting properties of glass-ceramics depend strongly on the annealing conditions. Figure 6 presents annealing temperature dependence of critical temperature and intragranular critical current for the samples annealed for 32 minutes. It can be seen that the best superconducting properties are achieved at annealing temperature between 840 and 850°C. Indeed, first isolated superconducting grains form already in the first minute of annealing at this temperature. Also the first superconducting paths in the glass-ceramic samples annealed around this temperature form very quickly. Resistive superconducting transition can be

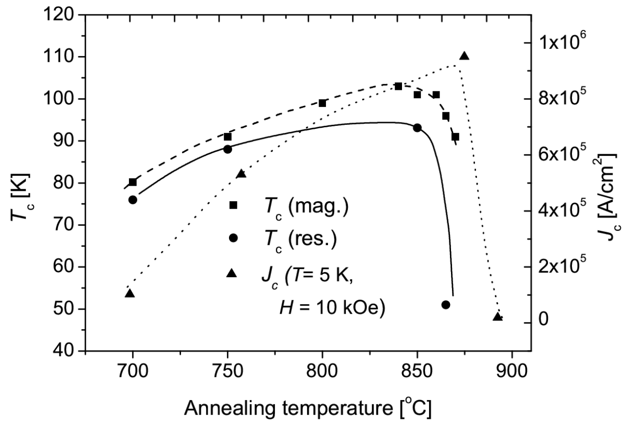

Fig. 6. Critical temperature and intragranular critical current of the samples annealed for 32 minutes plotted as a function of annealing temperature. Critical current was determined at the temperature and magnetic field of 5 K and 10 kOe, respectively.

observed already after 90 s at 820−870°C. After 1.5 minutes of annealing the onset of superconductivity ($T_{\mathrm{conset}} = 25$ K) is observed [4]. Then, during the next few minutes (about 8) critical temperatures increases quickly. After that, the dynamics of changes slows down, but a gradual improvement of the parameters characterizing the superconducting properties is observed. In view of the structural and microstructural changes, we believe that the first, rapid increase in critical temperature reflects the increase in the amount of 2212 phase in the material, while the grain size growth causing better connectivity between them is responsible for the second, slower part of the process. Similarly as critical temperature also the intragranular critical current grows significantly with annealing time. Long crystallization time (43 h) increased critical current density from the value of 8.4×10^5 for 32 min to 2.5×10^6 A/cm^2 at the temperature of 5 K and the field of 10 kOe.

4. Conclusions

In the (Bi,Pb)-Sr-Ca-Cu-O system, materials of various electrical and superconducting properties may be produced by a glass-ceramic method. Materials obtained by this method have very interesting properties and they constitute a new group of granular metals and superconductors. Depending on the heat treatment conditions, either a superconductor with the critical temperature between 8 and 105 K or material without a superconducting transition may be obtained. Both similarities and differences can be observed between glass-ceramic granular superconductors and conventional ones.

Glass-ceramic technology is a good method of obtaining BiSrCaCuO superconductors. Especially, $(Bi,Pb)_2Sr_2CaCu_2O_x$ phase forms well by this method. Best superconducting properties can be achieved at the temperatures of annealing about 840−850°C.

References

[1] Y. Abe, *Superconducting Glass-Ceramics in Bi-Sr-Ca-Cu-O: Fabrication and its Applications*, World Scientific, River Edge, NJ 1997.

[2] J. Khaled, R. Watanabe, R. Sato, T. Komatsu, *J. Non-Cryst. Solids* **222**, 175 (1997).

[3] R.J. Barczyński, M. Gazda, L. Murawski, *Solid State Ionics* **157**, 299 (2003).

[4] M. Gazda, *Physica C* **411**, 170 (2004).

[5] C.J. Adkins, *J. Phys.* **1**, 1253 (1989).

[6] B. Abeles, Ping Sheng, M.D. Coutts, Y. Arie, *Adv. Phys.* **24**, 407 (1975).

[7] May Chiao, R.W. Hill, Ch. Lupien, L. Taillefer, P. Lambert, R. Gagnon, P. Fournier, *Phys. Rev. B* **62**, 3554 (2000).

[8] A. Gerber, A. Milner, G. Deutscher, M. Karpovsky, A. Gladkikh, *Phys. Rev. Lett.* **78**, 4277 (1997).

[9] K.B. Efetov, A. Tschersich, *Phys. Rev. B* **67**, 174205 (2003).

[10] P.A. Lee, T.V. Ramakrishnan, *Rev. Mod. Phys.* **57**, 287 (1985).