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(Bi,Pb)–Sr–Ca–Cu–O glass-ceramics – superconductor and granular metal

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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. As a result of heat treatment, amorphous material partially crystallizes. It causes an increase in the size and/or the number of conducting grains and a decrease in the width of the insulating barriers between them. The resistivity of the samples containing small, weakly coupled grains in the normal state follows the exponential temperature dependence of resistivity, while in the samples with larger intergrain conductivities the dependence is logarithmic. Still stronger connections between the grains lead to linear or almost linear $\rho(T)$. The granular character of the $(Bi,Pb)_4Sr_3Ca_3Cu_4O_x$ materials also influences their superconducting properties.

Keywords: bi-based cuprates; mobility edges; hopping transport; granular, melt-textured, amorphous, and composite superconductors.

1. Introduction

Granular materials are composed of conducting or superconducting grains embedded in an insulating or semiconducting matrix. The size of the grains may be between a few and a few hundreds nanometres. Granular metals and superconductors have been studied for many years and several physical mechanisms of the electronic transport phenomena have been proposed [*e.g.*, 1–6]. They are very interesting materials thanks to their unusual electrical properties caused by the presence of various effects competing with one another. These are Coulomb effects, electron tunnelling and Josephson coupling between the granules in the superconducting state. Additionally, various aspects of disorder also influence the material properties.

Properties of granular materials are determined by the tunnelling conductivity between the neighbouring grains and the relations between energies characteristic of the system [7]. The tunnelling conductivity is described as a dimensionless conductance g expressed in the units of quantum conductance $e^2/\hbar$. The energy scale is determined by the inter grain coupling energy V_L, the Coulomb charging energy E_C,

the splitting between the electronic levels δ at the Fermi level in the single grain and in the case of the grains in the superconducting state by the Josephson coupling energy E_J.

When the conductance between the grains in the normal state is low ($g < 1$), granular material is in the dielectric regime and electrical conductivity occurs through thermally activated tunnelling of electrons between grains [1]. Moreover, the Coulomb effects may be very important in this case. The temperature dependence of the resistivity of such materials usually follows the exponential relation:

$$\rho(T) = \rho_0 \exp\left(\frac{T_0}{T}\right)^n \tag{1}$$

where the n exponent is in the range $0.2 \le n \le 1$ and depends on the geometry of the conductivity and on the details of the density of states of the granular material. In low temperatures, n close to 0.5 has been often observed [3].

When the conductivity between the metallic grains is larger ($g > 1$), the granular material is in the metallic regime and Coulomb interaction between the grains may be neglected. Nevertheless, because the intergrain conductivity is still much smaller than the intragrain one, the material may be considered as a granular material in the metallic regime. In this case, as it was shown by EFETOV *et al*. [8], conductivity follows the logarithmic relation:

$$\sigma(T) = \sigma_0(1 - \alpha \ln T) \tag{2}$$

where

$$\alpha = (2\pi dg)^{-1} \tag{3}$$

depends on the tunnelling conductivity of the grains g and dimensionality of the system d. Dimensionality d is considered as a half of the coordination number of the grains. This relation is valid if $T \gg g\delta$, where δ is the mean energy level spacing in a single grain [8]. Recently, a logarithmic temperature dependence of either resistivity or conductivity has been observed in several granular materials [*e.g.*, 5].

In the case of granular metals with $g \gg 1$, the material may be considered as a strongly disordered metal. Its temperature dependence of resistivity is determined mainly by the disorder and it differs significantly from that of a typical metal. Phenomenological Mooij model describes well many disordered conductors [9]. The approximate equation for $\rho(T)$ is the following:

$$\rho(T) = \rho_0 + A(\rho_{0c} - \rho_0)T \tag{4}$$

where ρ_0 is the residual resistivity, ρ_{0c} is the value of residual resistivity for which the temperature coefficient of resistivity changes sign from negative to positive and A is a coefficient describing the temperature dependent part of resistivity [10].

(Bi,Pb)–Sr–Ca–Cu–O materials obtained by solid state crystallization provide the opportunity to study the whole variety of electrical properties characteristic of granular and disordered materials. They may be considered as a 3D system of grains of a metallic phase embedded in the insulating matrix. The insulating or semiconducting matrix in which metallic grains are located is composed both of amorphous material and crystalline non-metallic phases [11]. 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), and $(Bi,Pb)_2Sr_2CaCu_2O_x$ (2212, T_c = 85 K). In the presented work, electrical properties of $(Bi,Pb)_4Sr_3Ca_3Cu_4O_x$ granular materials obtained by solid state crystallization are presented.

2. Experimental

The samples were produced by the solid state crystallisation. 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 1250 °C, kept in the high temperature for about 10 minutes, and quenched. The glass was cut into bars of similar dimensions ($2\times1\times8$ mm^3) and polished before further thermal treatment.

The crystallisation was carried out in a tube furnace at temperatures between 500 °C and 870 °C. The samples were put into an already hot furnace and after proper time they were quenched. The heat treatment conditions affect the amount of metallic phases and the granule radius. Generally speaking, the higher temperature and longer annealing time, the larger amounts of metallic phases distributed in the form of the larger granules are present in the sample [11]. The samples were checked by X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM) methods.

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

3. Results and discussion

The evolution of room temperature conductance as a function of the amount of the 2212 phase in the sample crystallized at 850 °C is shown in Figure 1. Changes of the microstructure are also shown. As a consequence of solid state crystallization, initially amorphous material partially crystallizes. The amount of the 2212 phase monotonically increases and simultaneously electrical conductance of the material increases. The increase in the amount of the 2212 phase is tantamount to the increase in the size and/or the number of conducting grains and the decrease in the width of the insulating barriers between them. Simultaneously, coupling between the grains becomes stronger and, as a result, the electrical properties of the material change.

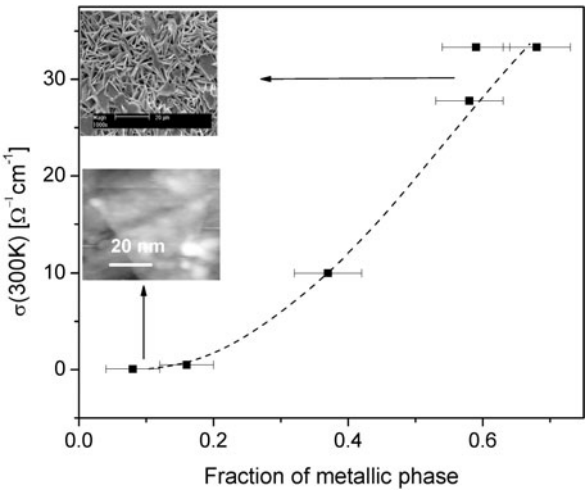

Fig. 1. The evolution of room temperature conductance as a function of the amount of the 2212 phase in the sample crystallized at 850 °C. The evolution of the sample microstructure is also shown.

It is not possible in a granular system obtained by the solid state crystallization to calculate the exact value of the tunnelling conductance g and to determine the electrical properties of the granular system in which the grains are in the normal state. Nevertheless, rough estimations basing on the knowledge of room temperature resistivity and average grain dimensions have been performed ($R = \rho l/S$). It has been also assumed that the distance between neighbouring grains is approximately 2 nm. The results are shown in the Table. It can be seen that g depends strongly on the conditions of crystallization. For the samples annealed at the same temperature it increases with the crystallization time, which means that the connectivity between the grains improves. Samples annealed for longer times may be considered as strongly disordered metals. Figures 2–4 show the temperature dependence of resistivity of the samples crystallized in different conditions and therefore, having different electrical properties. Figure 2 shows the results obtained for the materials with small grains very weakly connected with one another ($g \ll 1$), while Figs. 3 and 4 display the data for $g \geq 1$ and $g \gg 1$, respectively. The data shown in the figures illustrate three models of electronic transport in granular materials. The mechanism of conductivity changes along with the changes in the intergrain conductivity. Selected parameters characteristic of particular mechanisms of conductivity are also collected in the Table.

Detailed analysis of the physical parameters describing temperature dependence of resistivity in (Bi,Pb)SrCaCuO granular system of the small granules in the normal state has been performed elsewhere [12]. In this case tunnelling conductivity between granules is small ($g \ll 1$) and temperature dependence of resistivity follows the exponential law (Fig. 2). The electronic transport in this group of materials occurs by the variable range hopping either with or without Coulomb interactions.

T a b l e. Microstructural and electrical properties of the studied samples: d is the average diameter of the $(Bi,Pb)_2Sr_2CuO_x$ or $(Bi,Pb)_2Sr_2CaCu_2O_y$ metallic granules; ρ(300 K) is the resistivity at room temperature, g is the intergrain dimensionless conductance, α and A are parameters describing logarithmic or linear temperature dependence of resistivity, respectively.

Sample description	ρ(300 K) [Ωcm]	Average grain dimension [nm]	Grain shape	d	g	Characteristic parameter	Type of $\rho(T)$ dependence
500 °C, 1 h	10±1	8–10	oval	3	0.01	$n = 0.38$	exponential
500 °C, 2 h	3.4±0.3	21–25	oval	3	0.1	$n = 0.26$	
650 °C, 4 min	1.6±0.1	10–27	oval	3	0.1	$n = 0.17$	
750 °C, 2 min	21±0.2	10–15	oval	3	0.1	$n = 0.37$	
800 °C, 2 min	6.6±0.2	30–40	oval	3	1	$\alpha = 0.156$	logarithmic
840 °C, 2 min	0.25±0.05	30–40	oval	3	1–10	$\alpha = 0.156$	
850 °C, 2 min	0.45±0.05	30–40	oval	3	1–10	$\alpha = 0.156$	
750 °C, 8 min	0.09±0.01	100	oval	3	> 10	$\alpha = 0.134$	
750 °C, 32 min	0.06±0.01	100	oval	3	> 10	$\alpha = 0.134$	
800 °C, 8 min	0.05±0.01	1000	plate	2	> 100	$\alpha = 0.128$	
850 °C, 32 min	0.03±0.005	5000	plate	2	> 100	$\alpha = 0.128$	
820 °C, 16 min	0.01±0.001	5000	plate	2	> 100	$\alpha = 0.1$	
750 °C, 20 h	0.01±0.001	300	oval	3	≫100	$A = 1\times10^{-3}$ K^{-1}	linear
820 °C, 8 min	0.04±0.005	1000	plate	2	≫100	$A = 1.9\times10^{-3}$ K^{-1}	
840 °C, 16 min	0.02±0.002	7000	plate	2	≫100	$A = 1.8\times10^{-3}$ K^{-1}	
840 °C, 140 h	0.008±0.001	15000	plate	2	≫100	$A = 1\times10^{-3}$ K^{-1}	

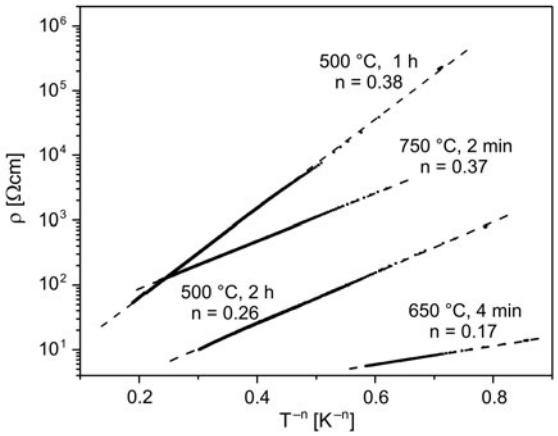

Fig. 2. Resistivity of the samples annealed at temperature between 500 °C and 750 °C plotted as a function of T^{-n}.

The Coulomb interactions determine the conductivity in the case of the material containing granules of about 10 nm [12]. Exponential dependence $\rho(T) \propto \exp[(T_0/T)^n]$ is also observed in the case of materials containing small granules of the superconducting phase (*e.g.*, in Fig. 2 in the case of the sample annealed at 650 °C for 4 minutes). However, values of the exponent n are lower than those typical of granular metals (about 0.17). Such low exponents signify that the temperature dependence of resistivity becomes less steep and the material becomes close to the insulator-superconductor transition.

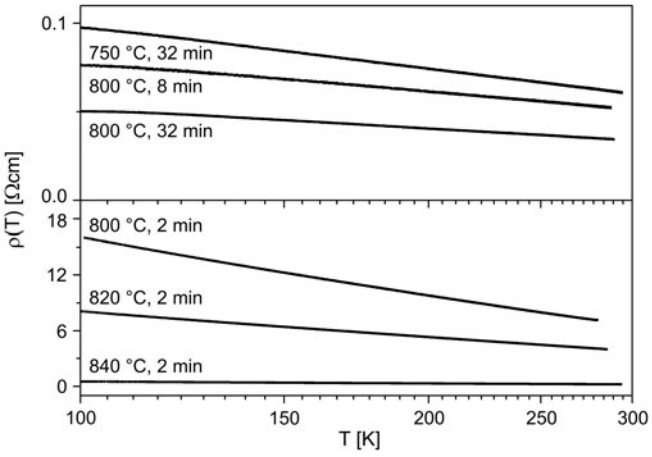

Fig. 3. Temperature dependence of resistivity of the granular samples in the metallic regime. The samples were annealed at temperature between 750 °C and 850 °C.

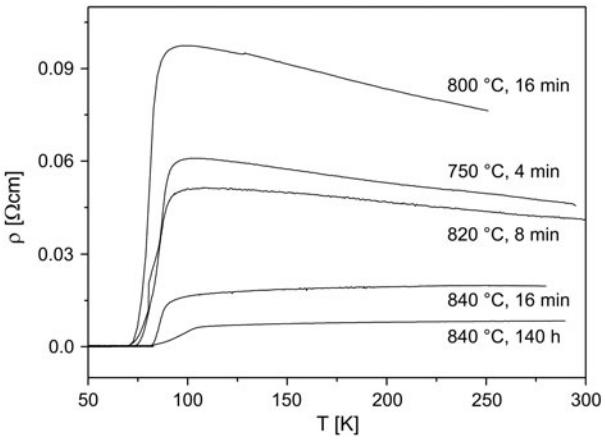

Fig. 4. Temperature dependence of resistivity of the samples with linear or almost linear temperature dependence of resistivity.

The temperature dependence of resistivity in (Bi,Pb)SrCaCuO granular system with larger granules (about 30 nm and larger) and with higher conductivity between them ($g > 1$) above the superconducting critical temperature is described well by the logarithmic law. Parameters describing the logarithmic temperature dependence of resistivity are collected in the Table. It can be seen that the α parameter tends to decrease with the increase in g, in qualitative agreement with the relation (3). It should be noted that the theory predicts the logarithmic temperature dependence of conductivity, not resistivity. Such dependences may be treated as similar in narrow temperature intervals [8]. Nevertheless, the results shown in this work indicate that the logarithmic temperature dependence of resistivity is fulfilled even in such a disordered granular system like a (Bi,Pb)SrCaCuO obtained by solid state crystallization.

In the case of $g \gg 1$ $\rho(T)$, dependence is either linear or almost linear, as it is shown in Fig. 4. The (Bi,Pb)–Sr–Ca–Cu–O materials crystallized in solid state, similarly to other disordered metals, exhibit both negative and positive slopes of the $\rho(T)$ plots. First, such a temperature dependence of resistivity was phenomenologically described by MOOIJ [9]. However, a microscopic model of electronic conduction leading to such a $\rho(T)$ law has not been elaborated yet.

Granular character of the studied materials manifests itself also in their superconducting properties. A granular material transits into the superconducting state in a two-step process [13]. First, at temperature T_1 the so-called pairing transition occurs, that is, most of the isolated granules transit into the superconducting state. The second step, the coherence transition, appears at temperature T_2 when the grains couple into a long-range ordered state. Such two-step transition is usually expressed as two maxima on the plot of temperature derivative of the resistivity. It is

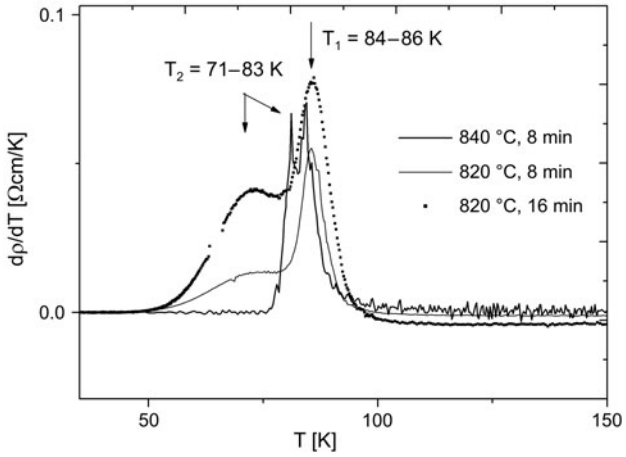

Fig. 5. Temperature dependence of temperature derivative of resistivity for the samples annealed at similar temperatures for different time intervals.

illustrated in Fig. 5, which shows the results obtained for three samples crystallized in different conditions. It can be seen that pairing transition temperature is almost the same in all the samples, while the coherence transition temperature differs significantly between them.

Coupling between the grains being in the normal state and between the superconducting grains are two distinct phenomena. However they are influenced by the same micro structural factors, that is, the quality and quantity of the boundaries between the grains. Therefore, along with the decreasing normal state resistivity and temperature coefficient of resistivity, the superconducting coherence transition temperature increases. It is observed experimentally as the correlation between the normal state electrical properties and critical temperature. For example, in the studied materials a correlation between temperature coefficient of resistivity and the coherence transition temperature has been observed [14].

4. Conclusions

The electrical properties of $(Bi,Pb)_4Sr_3Ca_3Cu_4O_x$ granular materials have been studied.

The resistivity of the samples containing small, weakly coupled grains in the normal state follows the exponential dependence on temperature $\rho(T) \propto \exp[(T/T_0)^n]$. The granular samples with larger inter grain tunnelling conductivities exhibit a very interesting logarithmic temperature dependence of resistivity. In the case of $g \gg 1$ $\rho(T)$, the dependence is either linear or almost linear, similarly to other disordered metals.

Granular character of the $(Bi,Pb)_4Sr_3Ca_3Cu_4O_x$ materials influences also their superconducting properties, especially the coherence transition temperature.

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