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Some properties of honeycomb-type $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ superconductors

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Abstract

A Bi-based superconductor of nominal composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ was prepared using Bi_2O_3, PbO, $SrCO_3$, CaO and CuO powders and liquid ammonium nitrate as solvent and homogenizer. For comparison, another superconductor with nominal composition $Bi_{1.8}Pb_{0.2}Sr_2Ca_2Cu_3O_x$ was obtained using the same method and conditions. It was observed that the ceramic has a honeycomb granular structure, a transition temperature of 110 K, an increased thermal expansion coefficient (8.7×10^{-6} K^{-1}) and a fourfold higher critical current density (25 A cm^{-2}). The volume of the sample increased during annealing (for 100 h at 845 °C). The phases existing in this new type superconductor were determined. The composition and temperature dependences of phase transition characteristics, resistivity and inductance changes were investigated. The height of the energy barrier separating the metastable local superconducting phase and the normal metallic phase was found to be 0.34 eV in the temperature interval 110 K$<T<$130 K from $\rho(T)$ measurements.

Keywords: Superconductors; Expansion; Honeycomb-type structure

1. Introduction

Investigation of high-temperature superconducting ceramics containing Bi and having the general composition $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ has been continuing. Mainly three superconducting phases ($n=1$, 2 and 3) have been considered. The phase with $T_c=110$ K and $n=3$ has been discussed extensively [1–10]. In this phase, small amounts of other oxides exist together with phases having superconducting properties [4,5].

It has been possible to increase the amount of the $T_c=110$ K phase in samples by replacing some of Bi in the superconducting compound $Bi_2Sr_2Ca_2Cu_3O_y$ by lead [6,7]. This increase has been obtained in samples prepared by using dry ceramic technology [2,7] and also in samples produced using a technology in which the nominal compound suffered a melting stage [4,8,9]. For that purpose a ceramic superconductor having the nominal composition 2234 containing lead was produced. Thus it was possible to increase further the amount of the $T_c=110$ K phase and the critical current density J_c [4,10].

We have not encountered any work aimed at producing high-T_c superconductors with a low and controllable critical current density which may be required in some areas of electronics. However, a new superconductor having these characteristics and the nominal composition $Bi_{1.8}Pb_{0.2}Sr_2Ca_2Cu_3O_x$ has been reported recently [11]. This paper compares the properties of that new honeycomb-type superconductor with one of another nominal composition, $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$. For this purpose, the granular structure, phase ratios, thermal expansion coefficients, critical current densities, resistivity and inductance changes were examined. The effect of Pb, Ca and Cu on the above-mentioned properties is also discussed.

2. Experimental methods

Bi_2O_3, PbO, $SrCO_3$, CaO and CuO powders were weighed in proportions suitable for the nominal compositions $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ and $Bi_{1.8}Pb_{0.2}Sr_2Ca_2Cu_3O_x$. These constituents were dissolved in liquid ammonium nitrate at 180 °C to obtain a chemically homogeneous mixture. By slowly increasing the temperature to 750 °C the ammonium nitrate was removed from the mixture as H_2O and N_2O. Details of the calcination process and preparation of pellets were

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given previously [11]. The phase composition of samples were determined by using the X-ray powder diffraction method employing Cu Kα radiation. Thermal expansion properties were measured using a Linseis L75 dilatometer in the temperature range 300–1000 K. Electrical resistivities of samples were measured using the four-probe method, the contact material being indium. Magnetic properties in the interval 10–300 K were determined using an inductance meter at 1 kHz with a closed-circuit cryogenerator under 10^{-3} Torr (1 Torr = 133.3 Pa). The value of the critical current was associated with a 5 μV potential drop across the two inner electrodes held approximately 3 mm apart at 77 K.

3. Results and discussion

Substantial changes (30–40%) occurred in the volumes of samples obtained from powders containing complex oxides. These complex oxides were formed and well homogenized during a fast exothermic reaction of the starting oxide powders. Samples having the same nominal composition and preparation conditions but produced from mechanically mixed powders showed only about a 5% volume increase. Dilatometric measurements indicated that the enlargement of samples and the formation of a new granular structure started at about 600 °C and accelerated as the temperature increased (Fig. 1). This process was essentially completed in the first 8–10 h of annealing at 845 °C. The following hours of annealing changed the phase ratios and affected the electrical and magnetic properties of the samples.

Fig. 2 is a photograph of the fractional surface of a sample having nominal composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ and a honeycomb structure acquired during annealing. The white spots exhibit some linear and curved positions. This sort of arrangement is an indication of the honeycomb-type structure in low density ($d \approx 3.0$ g cm^{-3}) ceramics. The large, bright areas which do not have regular shapes are thought to be due to mainly alloys containing Ca and Cu. In fact, SEM studies [12] of Bi-based superconductors produced by mechanical mixing showed that the small, bright, circular spots located randomly on the surface are alloys of Cu, Ca and Sr, whereas the large, bright spots which do not have regular shapes contain mainly lead.

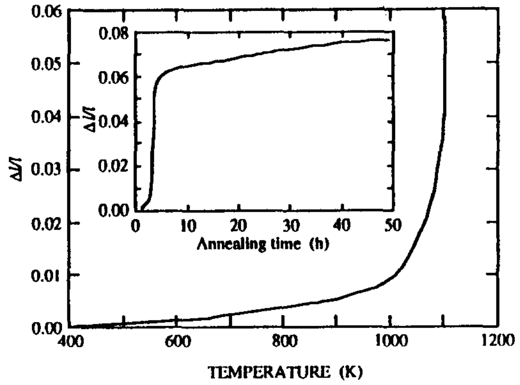

Fig. 1. Expansion of annealed sample of nominal composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ versus temperature. The inset shows the time variation of expansion at 845 °C.

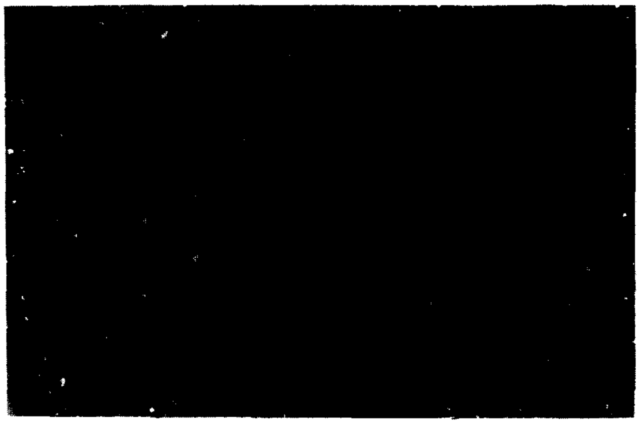

Fig. 2. Enlarged photograph of the fractional surface of a honeycomb-type sample having nominal composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$.

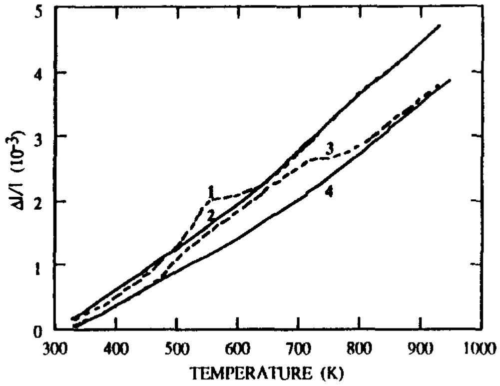

Fig. 3. Dependence of expansion of samples having honeycomb structure and nominal composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ (1, 2) and $Bi_{1.8}Pb_{0.2}Sr_2Ca_2Cu_3O_x$ (3, 4) on temperature during the first (1, 3) and the second (2, 4) heating.

Thermal expansion of samples in which a honeycomb structure was formed shows a behaviour similar to that of samples prepared by conventional powder methods (Fig. 3). During the first heating cycle, an anomalous variation was observed in the region of 600–800 K (curves 1 and 3 in Fig. 3). This may be due to the sample's history since it disappeared in the following cycles. At higher temperatures, $\Delta l(T)/l(300\ K)$ varied almost linearly in all cycles. The effect of the sample composition on the expansion coefficient can be seen in Fig. 3. Values of the expansion coefficients corresponding to the lower and upper linear temperature regions are 6.6×10^{-6} and 8.7×10^{-6} K^{-1} respectively for the sample of nominal composition 2234. These and other related parameters are given in Table 1. These values are of the same order of magnitude as

Table 1
Characteristics of honeycomb-structure superconductors having nominal compositions $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ and (1) $Bi_{1.8}Pb_{0.2}Sr_2Ca_2Cu_3O_x$ (2) which were annealed at 845 °C for 100 h

Sample	$\Delta V/V$* (%)	β (10^{-6} K^{-1})	T_c (K)	ρ_o (mΩ cm)	α (10^{-2} mΩ cm K^{-1})	ΔE (eV)	J_c (a cm^{-2})
1	28	6.6; 8.7	110	1.8	2.3	0.34	25
2	36	5.2; 7.7	110	1.6	2.0	0.16	6.1

* Volume of sample prior to annealing.

those for metals such as Mo, Ta and Cr. This temperature–expansion–composition relationship should be explained by the effect of temperature on the lattice parameters a and c. In fact, X-ray analysis showed that lattice parameters depend on temperature in a similar way [13,14].

Curves (1, 2) of resistivity $\rho(T)$ and curves (3, 4) of the variation of inductance

$$\frac{\Delta L\ (T)}{L\ (300\ K)}$$

for $Bi_{1.8}Pb_{0.2}Sr_2Ca_2Cu_3O_x$ and $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ ceramic samples annealed at 845 °C for 100 h are given in Fig. 4. By using the point of the $\rho(T)$ curve where $d\rho/dT$ is a maximum, we can deduce that the 2223 superconducting phase having critical temperature $T_c = 110$ K had formed in both samples. The existence of resistivity in the region $T < 110$ K indicates that other phases are also present in samples in different amounts. This point can be more clearly seen in the curves of inductance variation. The form of the steps in curve 4 shows that the majority of the sample of nominal composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ is in the 2223 phase. The difference between phase ratios is seen in the X-ray diffraction (XRD) pattern.

The XRD pattern for the honeycomb superconductor with nominal composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ is shown in Fig. 5. Peaks corresponding to phases 2223 and 2212 are indicated by the letters H and L, respectively. It can be concluded that the dominant phase in the sample is 2223. Some weak peaks observed in this pattern are thought to belong to 2201 superconducting phase, Ca_2CuO_3 and Ca_2PbO_4. The intensity of the (00*10*) peak belonging to the phase H of the $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ sample is comparable to that of the peak (00*12*) which belongs to both H and L. According to the intensities of the peaks labelled (008) and (00*10*), the volume ratio of the high-T_c phase is estimated to be about 86%. Nearly the same result was obtained for the sample $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ using a method [15] where the heights of the steps in the inductance curves were utilized. Although there is an increase in lattice parameter c from 30.8 Å (2212) to 37.1 Å (2223) [2], this is not the only reason for the volume increase of about 30–40% that occurred on annealing during the first 8–10 h for our samples. Dilatometric measurements indicated that this large increase in volume during annealing is related to the formation of the honeycomb structure. This is supported by the generally systematic arrangement of white spots in Fig. 2.

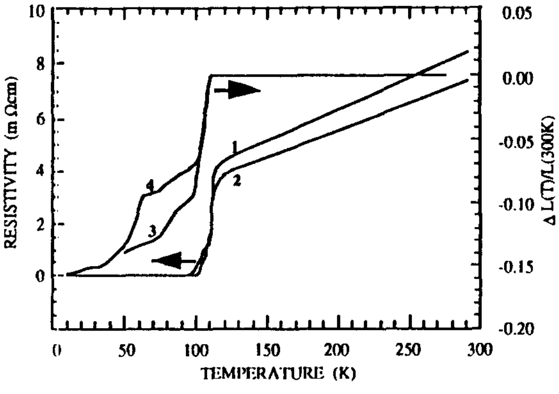

Fig. 4. Temperature dependences of variations in resistivity (1, 2) and inductance (3, 4) for samples having nominal compositions $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ (1, 3) and $Bi_{1.8}Pb_{0.2}Sr_2Ca_2Cu_3O_x$ (2, 4), both annealed at 845 °C for 100 h.

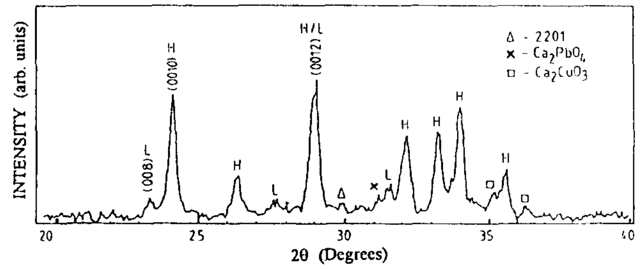

Fig. 5. X-ray diffraction plot of honeycomb sample having nominal composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ which was annealed at 845 °C for 100 h.

Fig. 4. indicates that it is possible to divide the temperature interval 10–300 K into three regions where the sample has different electrical properties [11]. These are the superconducting region $T < T_c$, the transition region $T_c < T < T_c + \Delta T_F$ and the region $T > T_c + \Delta T_F$ which has a normal metallic behaviour. Here $\Delta T_F = 20$ K. In the second region, the effect of the Flicker noise of superconduction dimension parameter on resistivity can be observed. For this reason the resistivity deviates from linear behaviour and forms a tail. We can assume that an energy barrier ΔE separates the local metastable

superconducting cluster from the normal state of the system. The probability of the existence of local clusters increases as the temperature decreases according to $\exp(\Delta E/kT)$. This affects the resistivity values. Above the proximity of T_c, the variation of resistivity behaves as $\Delta\rho(T) \propto \exp(\Delta E/kT)$ as shown in Fig. 6. Here $\Delta\rho = \rho_n(T)\text{-}\rho(T)$, where $\rho_n(T)$ is the resistivity of the normal state obtained by extrapolation. ΔE values calculated for samples having nominal composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ and $Bi_{1.8}Pb_{0.2}Sr_2Ca_2Cu_3O_x$ annealed under the same conditions are given in Table 1. The values of ΔE are found to vary by almost 100% from one composition to the other.

In the last region, $T > 130$ K, $\rho(T)$ is observed to have normal metallic behaviour (Fig. 4, curves 1 and 2). This region is characterized by the equation $\rho(T) = \rho_o + \alpha T$, where ρ_o is the extrapolated resistivity at absolute zero and α is the slope of the straight portion of the resistivity curve. Table 1 shows how the parameters such as ρ_o, α and especially J_c changed with the sample's nominal composition. It can be seen that the critical current density measured at 77 K increased from 6.1 to 25 A cm^{-2}. It can be argued that this is a result of a different ratio of superconducting phases H and L. Comparison of the results for honeycomb-type superconductors shows once again that the abundance (up to certain limits) of Ca and Cu ions increases the amount of high-T_c phase 2223.

The fact that lead present in samples enhances the 2223 phase and its stabilization is explained in different ways [7,13]. One is that Pb causes certain regions of samples to melt at lower temperatures, thus making it homogeneous during the process of ceramic production [16,17]. Another explanation is that due to the presence of lead ions the low-temperature phase loses its stability at 850 °C and is transformed into a high-temperature phase [17]. Another assumption is that Pb substitution at the Bi sites produces depletion of the excess oxygen, thereby improving the metallicity of the Bi–O layer [7]. We can say that in our procedure the homogenizing effect of lead is not needed because the sample was synthesized from a mixture highly homogenized in liquid ammonium nitrate. When speaking about lead addition is should be remembered that lead changes the diffusion mobility of Bi^{3+} ions in ceramics.

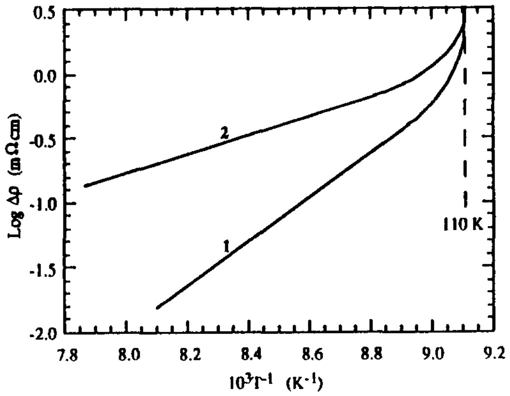

Fig. 6. Temperature dependences of $\Delta\rho = \rho_n(T)\text{-}\rho(T)$ for honeycomb samples having nominal compositions $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ (1) and $Bi_{1.8}Pb_{0.2}Sr_2Ca_2Cu_3O_x$ (2) in the Flicker-noise region ($110 < T < 130$ K).

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