Isolation of the 110 K superconducting phase of Bi-Pb-Sr-Ca-Cu-O compounds

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We have prepared 90% single-phase bulk samples of the 110 K superconducting phase of the Bi-Sr-Ca-Cu-O compounds with different Pb amounts. Critical superconducting temperatures (zero resistance) of up to 109 K were measured in the bulk samples. X-ray powder diffraction patterns of the almost isolated 110 K phase are presented. Computer-simulated diffractograms were obtained, which are in general agreement with the measured ones. A discussion of the role of Pb in the stability of the 110 K phase in this compound is presented.

The discovery of high T_c in Bi[1,2] and Tl[3] based compounds has attracted the attention of many research groups. A few months after their discovery, the existence of three different phases in these compounds became evident. All three have orthorhombic structures but different c lattice parameters, which are increased by the introduction of additional layers of Cu-O and Ca atoms. These additional layers lead to an improvement of the critical superconducting transition temperatures.[4]

In the particular case of the Bi-based compounds, the three phases have been called the 22, 80, and 110 K phases, since drastic drops in the resistance versus temperature curves are observed at approximately those temperatures. The first two phases were quickly isolated and their structure determined,[1,5] but for the 110 K phase additional work was needed.

Tarascon *et al.*[6] were able to isolate a small crystal of the 110 K phase and $T_c = 107$ K was measured. However, in the bulk material, a mixture of two phases was always detected. Kuwahara *et al.*[7] measured zero resistance at 108 K in bulk material after a prolonged heat treatment at about 400 °C, which induced the formation of the 110 K phase from the 80 K one. Again in this case, a clear mixture of both phases was observed in their x-ray powder spectra. More recently, bulk superconductivity at 106 K in approximately 60% isolated 110 K phase was reported,[8] but no complete isolation was attained. In this work we present new measurements in the bulk samples of Bi-based compounds with up to 90% of the isolated 110 K phase, as observed in x-ray powder diffractograms.

The samples were prepared starting from powders of Bi_2O_3, $CaCO_3$, $SrCO_3$, and CuO. Pb was added to the samples in the form of PbO or Pb subacetate. The powders were mixed and compressed into pellets, fired at 800 °C for 16 h, sintered at 860 °C for very long periods of time, and quenched in air at room temperature. A part of each pellet was used to measure resistance versus temperature curves, using the four-point contact technique and a closed cycle refrigerator. The measurements of the resistance and temperature were realized with a Barras–Provence bridge, whose sensitivity is $10^{-7}\ \Omega$, and a thermocouple of Au-Fe-Constantan calibrated to a precision of ± 0.01 K, respectively. Another part of the pellet was used to obtain the x-ray powder diffraction patterns, with Cu $K\alpha$ radiation.

In this letter we report the four most relevant samples from different batches of a wide range of the stoichiometries that we studied. Table I shows the nominal composition of the samples, the time of heat treatment at 860 °C, the T_c (zero resistance), and the percentage of the 110 K phase in the samples. From Table I it follows that no clear relationship exists between the percentage of the 110 K phase observed in the x-ray diffractograms and T_c. This lack of consistency in our observations could be due to inhomogeneities in the distribution of the 110 K phase in the bulk pellets, which lead to preferential percolation during the resistance measurements as will be discussed later.

Figure 1 shows the resistance versus temperature curves of samples 2 and 4 in Table I. Onset temperatures of about 117 K can be deduced from these curves. It is interesting to note that these high onset and critical temperatures can, in general, only be obtained in bulk material when lead is added in amounts of 0.3–0.6 in the nominal composition. Attempts to prepare samples with higher Pb content resulted in multiphase products, as observed by x-ray diffraction patterns, and a decrease of the critical temperature.

In Figs. 2(b)–2(d) we compare different x-ray powder diffractograms with increasing proportions of the 110 K phase. Three peaks of the 80 K phase are arrowed in these figures, following the decrease in volume fraction of the 80 K phase in the samples. Those three arrowed peaks correspond to the (002), (115), and (117) reflections of the orthorhombic structure of the 80 K phase. The relative volume frac-

TABLE I. Sample preparation and characteristics. From left to right: the compound stoichiometry, the sintering time at 860 °C (in days), the zero resistance critical temperature of the superconducting transition (in K), and the percentage of 110 K phase in each compound.

No.	Compound	Time at 860 °C (days)	T_c ($R = 0$) (K)	% of 110 K phase
1	$Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_y$	18	106	50
2	$Bi_{1.8}Pb_{0.6}Sr_2Ca_2Cu_3O_y$	21	108	90
3	$Bi_{1.8}Pb_{0.6}Sr_2Ca_2Cu_3O_y$	24	108.7	85
4	$Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_y$	26	109.1	70

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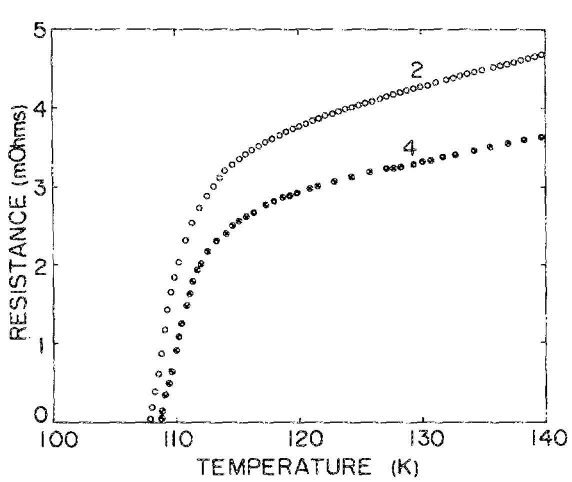

FIG. 1. Resistance vs temperature characteristics of samples 2 and 4, whose compositions are shown in Table I. For sample 4, T_c ($R = 0$) is 109.1 K.

tions of the 80 and 110 K phases were estimated by comparing the intensities of the (002) peaks in both structures and also the (115) and (117) peaks in the 80 and 110 K structures, respectively (which corespond to the highest intensity peaks in these structures). From these estimations, a percentage of isolation of the 110 K phase was obtained and it is shown in Figs. 2(b)–2(d) for each x-ray spectrum. Careful grinding of the samples and the utilization of a rotating specimen holder were expected to decrease preferential orientation of the powder particles during the x-ray measurements. The remaining texture effects can be reasonably supposed to be alike for both phases in the x-ray powder samples. Then, the determination of the volume fraction of the 110 K phase in the samples is not expected to be appreciably affected by such texture effects.

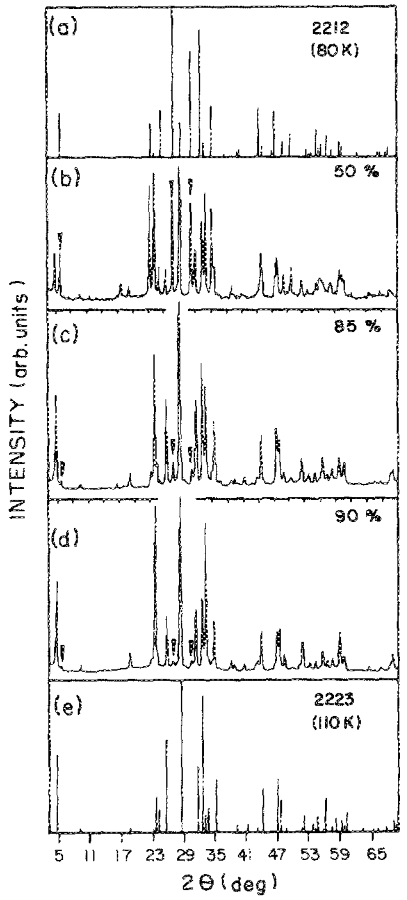

FIG. 2. X-ray powder diffractograms. (a) and (e) show the computer-generated spectra of the 80 and 110 K phases, respectively, using the space group *Fmmm*. (b)–(d) show the increasing proportion of the 110 K phase, which for (d) is about 90%. The arrows show the evolution of some peaks of the 80 K remaining phase.

Figures 2(a) and 2(e) are computer-generated powder diffractograms of the 80 and 110 K phases, respectively, obtained by using the Lazy–Pulverix program.[9] In both cases the *Fmmm* space group and the Debye–Waller parameters given by Sunshine *et al.*[10] for the 80 K phase were considered. The measured lattice parameters were $a = 5.41$ Å $\pm$ 0.005 Å, $b = 5.42$ Å $\pm$ 0.005 Å for both phases, and $c = 30.90$ Å $\pm$ 0.005 Å and $c = 37.18$ Å $\pm$ 0.005 Å for the 80 and 110 K phases, respectively. These were determined by comparing d values with quartz as an internal standard. The a, b lattice parameters appear to be somewhat surprising since they are quite close to those measured for the 80 K phase (without Pb) by Sunshine *et al.*[10] This result will become clarified with the discussion about the role of Pb atoms in the structure that we will present later. In Fig. 2(e), it can be seen that the general features of the 110 K phase powder diffraction pattern are well reproduced.

A remaining problem to be solved in the Bi-based compounds is the difficulty in preparing the 110 K single-phase material. This difficulty must be related to the inherent instability of the structure, partially due to the enormous difference between the c axis and the a and b axes ($c \simeq 7a$), which is reflected in the high degree of disorder between the different layers of Cu-O, Sr-O, Bi-O, and Ca, as reported by several authors.[11,12] Moreover, the solid-state reaction is accomplished at temperatures quite close to the melting point of the compound ($\simeq$870 °C) where a high ionic mobility is expected and, therefore, a high degree of disorder occurs in the different layers. It is interesting to note that these kinds of arguments can be used to understand why in Tl-based compounds the high T_c phase can be prepared more easily than in Bi compounds, since in the former the c axis is smaller and the solid-state reaction is performed at temperatures far enough from the melting point. Also, in the Bi compounds the four Cu-O layered structure has not been observed in large proportions so far as it has been in Tl-based ones.[13] The improvement of the percolative characteristic at higher temperatures in the Bi compound when lead is added must be related to different types of physical processes. One may be associated with some changes in the kinetics of the solid-state reaction, which is obviously speeded up. This became evident in our experiments when attempts to prepare samples of $Bi_2Sr_2Ca_2Cu_3O_y$ without lead were tried for the same periods of time, with no impovements in T_c. The thermodynamical stability also is changed, as we observed in samples with and without lead impurities. In the former case the 110 K phase is obtained when the material is quenched in air from the sintering temperature to room temperature. This is in contrast with samples without lead where the quenched material never gives higher percolative resistance transition temperatures. These samples have to be slowly cooled and annealed at about 400 °C by a period of time, in order to accomplish the solid-state reaction and allow the 110 K phase to grow at expenses of the 80 K phase.[7] This treatment leads to the correct stacking ordering of the 110 K phase.

Nobumasa *et al.*,[14] using high-resolution analytical electron microscopy, find that Pb atoms are located in the Bi-O layers. According to this experimental fact, our conclusion is that Pb atoms are easily incorporated into the structure due to their similar outer electronic configuration. Note that the resulting configuration of $6s^2 6p^0$ is the same for Bi in a $+3$ oxidation state and for Pb in $+2$ state.

Another important characteristic of the Bi-based compound is the large separation between the basal Bi-O bilayers, which is about 3.1 Å. This fact is reflected in two different aspects. First, the weak bonding energy between basal Bi-O bilayers[15,16] gives to the compound a mica-like character and affects the stability of such a long structure, producing big amounts of structural defects and increasing the intrinsic resistivity in the *c* direction, as was observed by Martin *et al.*[17] Second, the introduction of Pb to the structure as a substitutional impurity in Bi sites increases the strength of the bonding between the Bi-O bilayers and improves the stability of the structure, which, in turn, leads to an increase in the connectivity between unit cells and in the percolative characteristic of the 110 K phase. This last effect explains why in the Bi compound, Pb increases the density of current[18] by decreasing the resistivity along the *c* direction.[17] This last observation obviously eliminates the possibility that Pb atoms act as a flux or form an amorphous phase between Bi-O layers, because in that case lead oxide would be insulating and, therefore, it should reduce the connectivity along the *c* direction.

Moreover, assuming that Bi in a $+3$ valence state is substituted by Pb in a $+2$ valence state, an increase in the hole density at the Cu-O planes can be expected. Hybertsen and Mattheiss[19] indicate that Bi-O planes dope the Cu-O planes with additional holes; that is, that electrons are transferred from the Cu-O planes to the Bi-O planes. Therefore, Pb in a $+2$ valence state promotes the electron transfer to the Bi(Pb)-O planes, as proposed by Richert and Allen.[20] This fact could explain why in Pb-added Bi compounds, the observed onset temperatures are slightly higher than those in the same compound without Pb.

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