

Influence of lead on the formation of the 110-K superconducting phase in the Bi-Sr-Ca-Cu-O compounds

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The fraction of the 110-K phase in the Bi-Sr-Ca-Cu-O compound is rapidly increased if small amounts of Pb are incorporated in the compound. The maximum $T_c(R=0)$ of 106 K was obtained after a sintering treatment of several days at 860°C. Computer-generated powder diffraction patterns showed, when compared to the measured ones, the possibility for Pb to occupy Ca or Bi sites.

The discovery of superconductivity at 20 K in Bi-based compounds by Raveau and co-workers,¹ about 110 K by the group of Maeda, Tanaka, Fukitoki, and Asano,² together with the $T_c=125$ K measured in Tl-based compounds by Parkin *et al.*³ has generated a lot of research activity on this new family of high- T_c superconductors.⁴⁻⁸

The structural differences between this new family of compounds and the rare-earth 1:2:3 compounds, offered us an incomparable opportunity to test the relative importance of some structural features in both types of systems. On one hand, Bi- and Tl-based compounds have very similar crystallographic structure, on the other hand, the 1:2:3 compound presents subtle differences. For instance, Tl and Bi compounds have only one type of Cu-O configuration, the Cu-O₂ planes, while in the 1:2:3 compounds two Cu-O configurations exist, the Cu-O₂ planes and the Cu-O chains. The relevance of the Cu-O₂ planes in high- T_c superconductivity is then put forward by this difference. Furthermore, a correlation between the number of Cu-O₂ planes and T_c , has been suggested by several authors.^{9,10}

In this work we focused on the preparation methods which enhance the formation of the 110-K phase in Bi-based compounds. It is clear that this type of study is important at the present time since, until now, it has become somewhat difficult to prepare an isolated phase. This difficulty could be related to the kinetics of the reaction,¹¹ or to the thermodynamical equilibrium of phases in the compound, as proposed by Kuwahara *et al.*¹² In this paper, we report some experimental results concerning the preparation and structural characteristics of Bi-based compounds and some improvements in T_c attained by the introduction of small quantities of Pb in the samples. Similar studies, using Pb additions to the Bi-Sr-Ca-Cu-O compounds have been mentioned in the work of Sunshine *et al.*⁶ However, to our knowledge, no details of the Pb content and its influence have been reported.

Pellets of different compositions were prepared starting from powders of Bi₂O₃, CaCO₃, SrCO₃, and CuO. For the addition of Pb, two starting powders were used PbO and Pb(C₂H₃O₂)₂·2Pb(OH) (lead subacetate). The powders were mixed, compressed into pellets, fired at 800°C for 16 h, and sintered in air at temperatures be-

tween 860°C and 865°C for different periods of time and quenched to room temperature.

A part of each pellet was used to measure the resistance versus temperature characteristic, from room temperature to 10 K, using the four-point contact technique. Another part of the pellets was used to obtain x-ray powder diffraction patterns, with Cu K α radiation and a secondary monochromator.

The lattice parameters were measured for the 80- and 110-K structures and were determined to be $a=5.41$ Å, $b=5.42$ Å for both structures and $c=30.9$ Å and $c=37.0$ Å, respectively. The unit cell of the 110-K phase was constructed by adding extra Cu and Ca layers to the 80-K structure, as suggested by several authors.^{9,12} The 80- and 110-K structures are presented in Fig. 1. X-ray powder diffraction patterns were simulated by using the Lazy-Pulverix program,¹³ with the values reported by Sunshine *et al.* for the Debye-Waller coefficients.⁶

Different diffractograms were simulated for several reported space groups and atom combinations within the 2:2:1:2 (80-K) and the 2:2:2:3 (110-K) structures, and were compared with the experimental ones. Figure 2 shows a x-ray spectra of the 2:2:1:2 (80-K) phase and three computer simulated spectra, obtained by using the *Fmmm* (Refs. 6 and 8), *Cccm* (Ref. 14), and *Immm* space groups, respectively. It is clear from Fig. 2 that the best choice for the space group is *Fmmm*, and it was used in all the generated diffractograms presented in this work.

Table I shows the nominal composition of the samples, the preparation temperatures and times, the critical temperature $T_c(R=0)$ and the different phases detected in each sample. From this table one can observe that all the compounds consist of 80- and 110-K phases. We can note the absence of the 20-K phase in our samples, probably due to the instability of this phase at high temperature¹² inhibit due to the quenching procedure in the sample preparation process. In particular sample 1 in Table I, with a total of six Copper atoms in its nominal composition, was also found to contain both the 80- and 110-K phases, although the x-ray pattern showed that the 80-K phase was highly majoritary. Two drops in the resistance versus temperature curve were observed for sample 1 at onset temperatures of 110 and 80 K, as shown in Fig. 3 (curve 1). Sample 2, with Cu₂, corresponds to the average

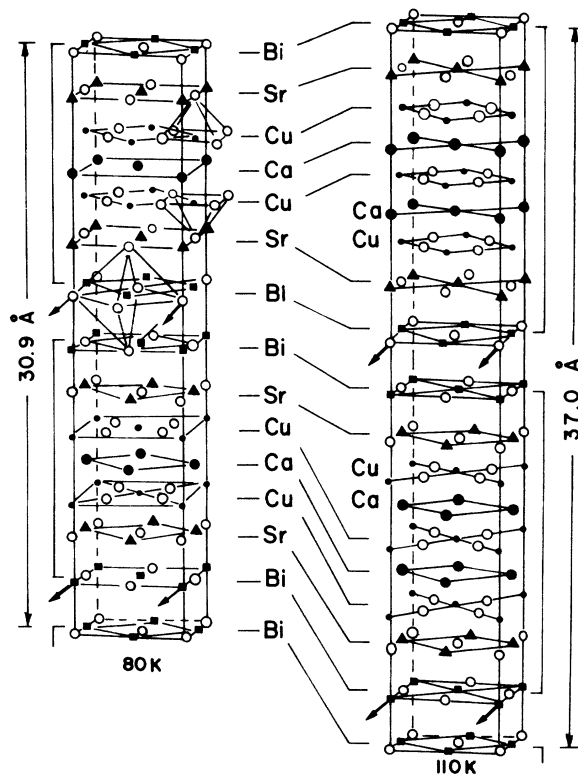


FIG. 1. Crystallographic structures for Bi-Sr-Ca-Cu-O. System on the left is the 80-K compound and system on the right is the 110-K compound.

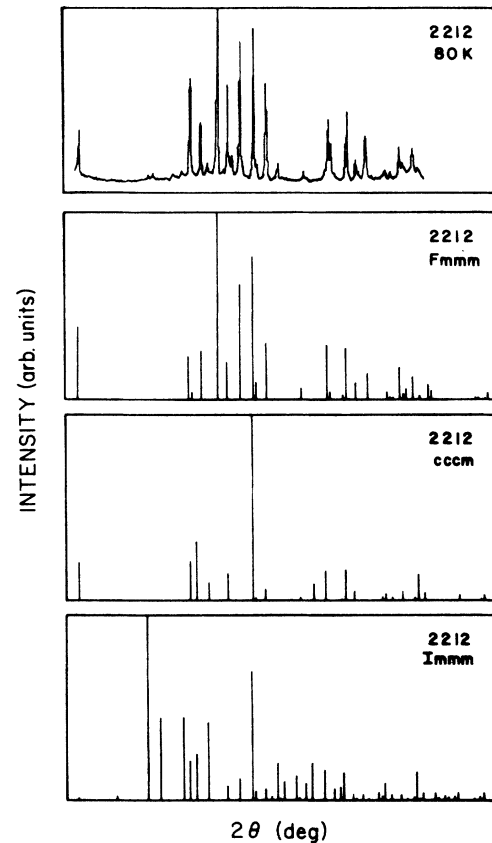


FIG. 2. X-ray spectra of the 2:2:1:2 phase ($T_c = 80$ K) and three computer-generated spectra using the space groups *Fmmm*, *Cccm*, and *Immm*.

composition measured by Hazen *et al.*⁵ for the 80-K phase; its resistance versus temperature curve is shown in Fig. 3 (curve 2). The series of samples 3, 4, and 5, with Cu_3 , showed an increase in T_c for decreasing quantities of Bi and increasing quantities of Ca. On the other hand, the series of samples 6, 7, and 8, with Cu_3 , showed also an increase in T_c for decreasing quantities of Bi and increasing quantities of Pb. The resistance versus temperature curve of sample 7 is shown in Fig. 3 (curve 3). Finally,

samples 9 and 10, with Cu_3 , show the small influence of Pb on T_c when we increase the content of this impurity from 0.3 to 0.6 in the compound with approximated stoichiometry 2:2:2:3. The resistance versus temperature curve for sample 10 is shown in Fig. 3 (curve 4).

It is important to note that very long times of reaction

TABLE I. Sample preparation and characteristics. From left to right: the compound stoichiometry, transition temperature T_c , sintering temperature in °C, sintering time in hours, and the phases and precipitates found by x-ray analysis.

No.	Compound	T_c (K)	Sintering		Phases ^a
			Temp. (°C)	Time (h)	
1	$Bi_2Sr_2Ca_2Cu_6O_y$	68	860	12	H+A+C
2	$Bi_{2.15}Sr_{1.68}Ca_{1.17}Cu_2O_y$	70	880	32	H+P+C
3	$Bi_{2.4}Sr_2Ca_{1.6}Cu_3O_y$	24	850	43	H+P+C
4	$Bi_{2.2}Sr_2Ca_{1.8}Cu_3O_y$	30	850	43	H+P+C
5	$Bi_2Sr_2Ca_2Cu_3O_y$	76	865	72	H+A+P
6	$Bi_{1.95}Sr_2Ca_2Cu_3Pb_{0.05}O_y$	58	860	192	H+A+P
7	$Bi_{1.8}Sr_2Ca_2Cu_3Pb_{0.2}O_y$	95	860	192	H+A+P
8a	$Bi_{1.7}Sr_2Ca_2Cu_3Pb_{0.3}O_y$	99	860	192	H+A
8b	$Bi_{1.7}Sr_2Ca_2Cu_3Pb_{0.3}O_y$	106	860	192	H+A
9	$Bi_{1.9}Sr_2Ca_2Cu_3Pb_{0.3}O_y$	104	860	192	H+A
10	$Bi_{1.8}Sr_2Ca_2Cu_3Pb_{0.6}O_y$	104	865	240	H+A

^aH = 80-K and A = 110-K phases; P = Ca-Bi and C = CuO precipitates.

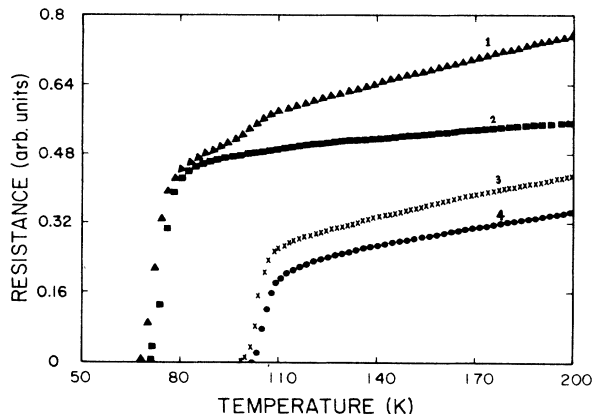


FIG. 3. Resistance vs temperature characteristic of some composition shown in Table I. (1) $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_6\text{O}_y$, (2) $\text{Bi}_{2.15}\text{Sr}_{1.68}\text{Ca}_{1.17}\text{Cu}_2\text{O}_y$, (3) $\text{Bi}_{1.8}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{Pb}_{0.2}\text{O}_y$, and (4) $\text{Bi}_{1.8}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{Pb}_{0.6}\text{O}_y$.

are needed to obtain the highest superconducting transition temperatures. The dependence of T_c with the reaction time is well illustrated in the series of resistance versus temperature curves of Fig. 4, which corresponds to sample 10 in Table I after 3 days (curve *a*) ($T_c = 95$ K), 6 days (curve *b*) ($T_c = 99$ K), and 10 days (curve *c*) ($T_c = 104$ K) of reaction treatment at 865°C . Also in Fig. 4 we show sample 8b which showed the highest transition temperature of $T_c = 106$ K (curve *d*).

In all the samples with Pb addition, a mixture of the 80 and 110 K was detected in the x-ray powder diffractograms. We identified these two phases in the samples by comparing the spectra with computer generated diffractograms of the 80- and 110-K phases. Figure 5 shows the x-ray powder diffractogram of sample 10 in Table I (center), compared with computer simulated diffractograms of the 2:2:1:2-80-K phase (up) and the 2:2:2:3-110-K phase (down). The inset in Fig. 5 shows the evolution of the relative intensity of the (002)

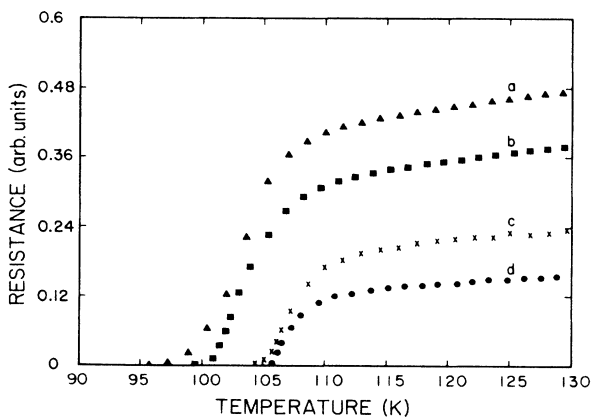


FIG. 4. Resistance vs temperature characteristic of the composition $\text{Bi}_{1.8}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{Pb}_{0.6}\text{O}_y$ with different sintering times at (a) 3 days, (b) 6 days, and (c) 10 days at 865°C . Also shown is the sample with composition $\text{Bi}_{1.7}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{Pb}_{0.3}\text{O}_y$ that has $T_c = 106$ K after 10 days of sintering time at 860°C (curve *d*).

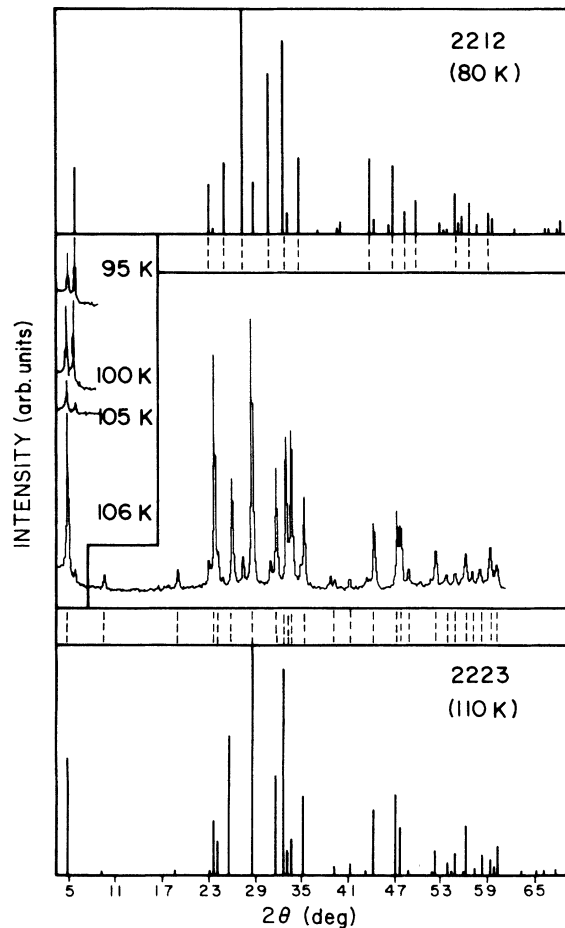


FIG. 5. X-ray powder diffractogram of sample $\text{Bi}_{1.8}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{Pb}_{0.6}\text{O}_y$ compared with simulated diffractograms of the 80- and 110-K phases.

reflections of both structures for increasing reaction times at 865°C .

The preparation procedure used to obtain the different samples in this work differs from the one reported by Kuwahara *et al.*¹² This difference could be due to some drastic changes in the reaction mechanisms and kinetics associated with the introduction of Pb to the samples. Since, for instance, sample 5 with a 2:2:2:3 stoichiometry, but without Pb addition, presents a T_c value of only 76 K. This is due to the high majority proportion of the 80-K phase in the compound. This sample and other samples without Pb were reacted for longer times, and no significant improvement in T_c was observed. This is in agreement with the conclusions by Kuwahara *et al.*¹² who proposed an equilibrium phase diagram for the Bi-based compounds. According to these authors, the 110-K phase (and also the 20-K phase) is not stable at high temperatures where the reaction takes place, thus, a long treatment at about 400°C is needed in order to decompose the 80-K phase into the 110-K phase. It seems, therefore, that in our case, the addition of Pb modifies the general characteristics of the reaction at high temperatures, allowing us to increase the volume fraction of the 110-K phase.

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