Superconductivity above 100 K by Pr substitution in the two-copper-layer Bi-Pb-Sr-Ca-Cu-O system

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The effect of Pr substitution on superconducting and transport properties has been studied in the Bi-Pb-Sr-Ca-Cu-O system. We obtain samples with structure similar to the 80-K phase for $T_c(R=0)$ up to 102 K. In particular, the highest T_c (102 K) is obtained with the nominal composition $Bi_{1.7}Pb_{0.3}Sr_{1.8}Pr_{0.2}Ca_2Cu_3O_{10+y}$, showing an 80-K single phase. We believe that the variation of T_c is determined by changes in the hole density in the $Cu-O_2$ planes due to the substitution of Pr into Sr sites.

Since the discovery of the Bi- and Tl-based superconductors, a great deal of effort has been directed towards the preparation of the three main superconducting phases.[1,2] It has been found that this goal is very difficult to achieve in the Bi compounds, especially for the 80-K (2:2:1:2) and 110-K (2:2:2:3) phases. Even though the addition of Pb has proved to stabilize the 110-K phase,[3] a 110-K single-phase sample has not yet been obtained. On the other hand, a truly 80-K single-phase bulk sample has neither been obtained[4] nor isolated.

Several reports have shown that changes in the hole concentration of the $Cu-O_2$ planes (which are responsible for superconductivity in the copper-oxide high-T_c compounds) are possible by substitution of cations with different chemical balance.[5–14] We present here experimental results demonstrating that the introduction of Pr into Sr sites provides an alternative method for changing the hole concentration and obtaining 80-K single-phase samples with higher critical temperatures.

Samples were prepared using the conventional method of solid-state reaction. Prior to weighting, the reagents (Bi_2O_3, PbO, $SrCO_3$, Pr_6O_{11}, $CaCO_3$, and CuO) were dried at 500 °C, synthesized in air at 810 °C for 16 h, then reground, pressed into pellets, sintered at 860 °C for 7 d, and quenched in air to room temperature. After the reaction, polycrystalline samples were oxygen annealed under 1 atm of pressure of pure oxygen for 5 h at 800 °C. The completeness of reaction and the phase purity of the samples were checked by the x-ray powder-diffraction method using a SIEMENS D-500 diffractometer and Cu $K\alpha_1$ radiation. This system is able to detect up to a minimum of 3% of impurities according to our measurements. For accurate d-spacing measurements, SiO_2 (α quartz) was added as an internal standard.

The electrical resistance versus temperature curves were measured for all specimens using the four-point contact technique and a close-cycle refrigerator. For the resistance measurements, we used a Barras-Provence bridge, whose sensitivity is $10^{-7}\Omega$. The temperature was sensed with a thermocouple of Au-Fe-Constantan cali-

brated to a precision of ± 0.01 K.

By studying the $Bi_{1.7}Pb_{0.3}Sr_2Pr_{0.5}Cu_3O_{8+y}$ composition without Ca, only the 20-K single phase becomes observable in the x-ray pattern; transport measurements only give the 20-K onset temperature. The addition of Ca to the sample results in an 80-K single-phase superconductor with a transition temperature of about 75 K. This is an evidence that Ca atoms are necessary to obtain the 80-K phase.

Table I shows the composition x, the T_c (zero resistance), and the phases obtained by x-ray diffractograms for samples with the composition $Bi_{1.7}Pb_{0.3}Sr_{2-x}Pr_x Ca_2Cu_3O_{10+y}$ which were annealed in air and in oxygen atmosphere. The increase of T_c when $x=0.00$ and 0.05 is due to the presence of the 110-K phase as an impurity in the samples which became observable even in the x-ray powder-diffraction pattern. We noticed that when the x values increase, T_c increases too. However, the maximum transition temperature was obtained at $x=0.20$, the sample has $T_c(R=0)=102$ K and 100% of the 80-K phase. The maximum Pr substitution that we have found that exhibits superconductivity is

TABLE I. Sample characteristics. From left to right: the composition x, atmosphere conditions, transition temperature T_c (K), and phases observed by x-ray powder diffraction. The heat treatment is described in the text. The asterisks indicate the $H = 80$-K phase $A = 110$-K phase.

| Composition x | $Bi_{1.7}Pb_{0.3}Sr_{2-x}Pr_x Ca_2Cu_3O_{10+y}$ | | | |
| | In air atmosphere | | In oxygen atmosphere | |
	T_c (K)	Phases*	T_c (K)	Phases*
0.00	100.0	$H + A$	96.0	$H + A$
0.05	95.0	$H + A$	94.0	$H + A$
0.18	75.8	H	70.0	H
0.20	102.0	H	65.0	H
0.22	75.3	H	58.0	H
0.30	71.6	H	45.0	H
0.40	52.0	H	38.0	H

$x = 0.40$. For $x = 0.50$ the resistance measurements show semiconductor-like behavior. We found that the best compositions concerning the superconducting properties were those shown in Table I.

We considered the 80-K phase (2:2:1:2) to be isostructural with the phase observed in the system with Pr substituted because all peaks can be indexed using an orthorhombic unit cell.

In Figs. 1 and 2 we compare the x-ray powder diffractograms of $Bi_{1.7}Pb_{0.3}Sr_{2-x}Pr_xCa_2Cu_3O_{10+y}$ samples prepared in air and in an oxygen atmosphere. The asterisks show the reflections of the 80-K phase which correspond to an orthorhombic unit cell, followed by the decrease in the volume fraction of the 110-K phase with arrows on the (002), (0010), and (115) reflections and the absolute disappearance of this phase when $x = 0.20$ (in fact, this is observed from $x = 0.18$, but the corresponding x-ray-diffraction pattern is not shown in the figures). The only differences observed in the x-ray powder diffractogram data of the samples prepared in air and in

the oxygen atmosphere, were the intensity changes, that are also depending on preferential orientation or texturing effects.[8] However, it should be pointed out that T_c decreases considerably after annealing in the oxygen atmosphere. This decreasing may be associated with several factors, one of those is related to changes in the oxidation state of Pr. This statement is supported by the fact that in our samples with the composition $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_{10-d}$, but without Pr, oxygen annealing produces increasing transition temperatures from $T_c = 103$ to 106 K. Therefore, we can rule out that those changes in the oxidation states of Bi and Pb decreases T_c, instead they must be related to changes in the Pr oxidation state (Pr occupying Sr sites) that, in turn, changes the coordination number, and then reduces the hole density in the $Cu-O_2$ planes, as will be clarified later.

We indicate in Table II the observed powder-diffraction pattern of the $Bi_{1.7}Pb_{0.3}Sr_{1.8}Pr_{0.2}Ca_2Cu_3O_{10+y}$ composition; it can be indexed satisfactorily as an orthorhombic unit cell whose lattice parameters are

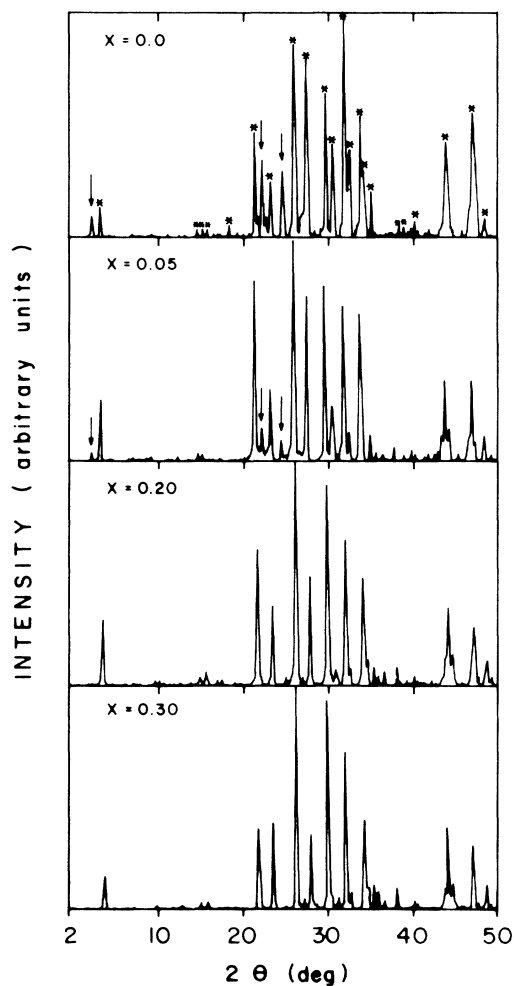FIG. 1. X-ray diffractograms of samples annealed in air with the composition $Bi_{1.7}Pb_{0.3}Sr_{2-x}Pr_xCa_2Cu_3O_{10+y}$ for $x = 0.00$, 0.05, 0.20, and 0.30. The asterisks (*) show the peaks of the orthorhombic unit cell of the 80-K single phase. The arrows show the 110-K phase.
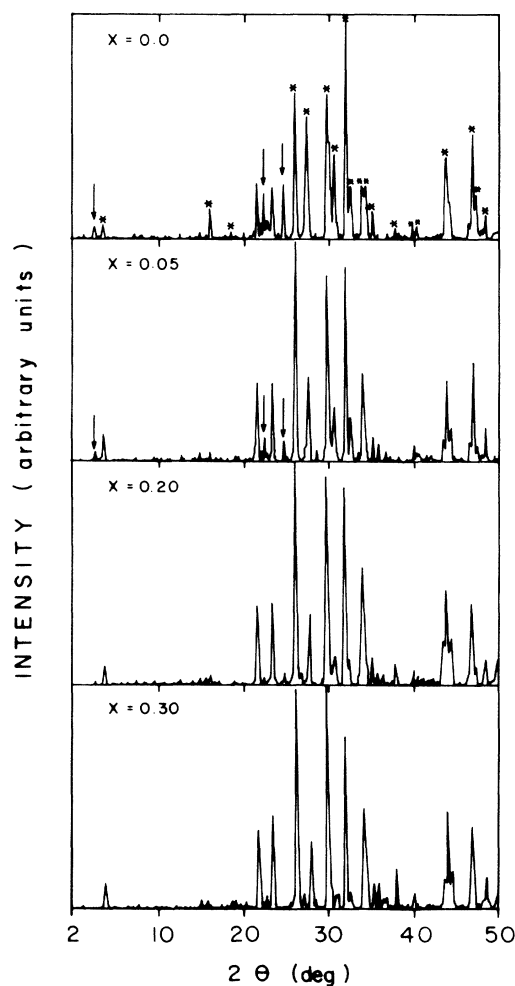

FIG. 2. X-ray powder diffractograms of samples annealed in oxygen with the composition $Bi_{1.7}Pb_{0.3}Sr_{2-x}Pr_xCa_2Cu_3O_{10+y}$ for $x = 0.00$, 0.05, 0.20, and 0.30. The asterisks (*) show the 80-K phase and the arrows the 110-K phase.

TABLE II. Powder-diffraction pattern for the $Bi_{1.7}Pb_{0.3}Sr_{1.8}Pr_{0.2}Ca_2Cu_3O_{10+y}$ composition.

d (obs)	I/I_0	h	k	l	h	k	l
15.4867	42.5	0	0	2			
5.1039	15.4	0	0	6			
3.8433	65.5	0	0	8			
3.5857	43.0	1	1	3			
3.2461	100.0	1	1	5			
3.0707	56.5	0	0	10			
2.8809	96.8	1	1	7			
2.7047	70.5	0	2	0			
2.7000	68.0	2	0	0			
2.6573	<1	0	2	2			
2.5555	50.2	0	0	12			
2.1994	<1	2	0	8			
2.0288	41.0	2	0	10,	0	2	10
2.0085	<1	1	1	3			
1.9119	32.6	2	2	0			
1.8582	19.7	2	0	12			
1.8036	26.9	1	1	15			
1.7054	<1	2	2	8			
1.6432	19.4	3	1	5,	1	3	5
1.6326	<1	2	2	10			
1.5943	22.8	3	1	7,	1	3	7
1.5764	<1	0	2	16			
1.5318	20.7	2	2	12			
1.3530	<1	1	3	13			

$a = 5.398 \pm 0.001$ Å, $b = 5.409 \pm 0.001$ Å, and $c = 30.69 \pm 0.01$ Å.

Measurements of the lattice parameters of polycrystalline samples prepared in air and in the oxygen atmosphere are shown in Figs. 3 and 4. An interesting feature that is observed in the a and b parameters is the tendency of the crystalline structure in reducing the orthorhombic distortion with oxygen annealing, increasing the a parameter toward b, this fact could be interpreted as an indication of the oxygen uptake, due to the conversion of Pr^{3+} to Pr^{4+}. Also, it is worth observing a rather smooth c-axis decrease with increasing x composition. This behavior also provides the characterization of the partial range of solid solution that is expected to occur since the atomic radius of Pr is smaller than Sr. We propose a complex solid solution mechanism where a cation of lower charge substitutes for one of higher charge and at the same time the charge balance may be maintained by creating anion vacancies. The formula may be written as $Bi_{1.7}Pb_{0.3}Sr_{2-x}Pr_xCa_2Cu_3O_{10+y}$: $0.18 < x < 0.40$. The solid solution cannot be considered from $x = 0.00$ or 0.05 because some 110-K phase remains as impurity in the sample. When $x \geq 0.5$ the c parameter increases, that is why we do not consider that the system exhibits complete solid solubility. The behavior of the lattice parameters when the polycrystalline samples were oxygen annealed
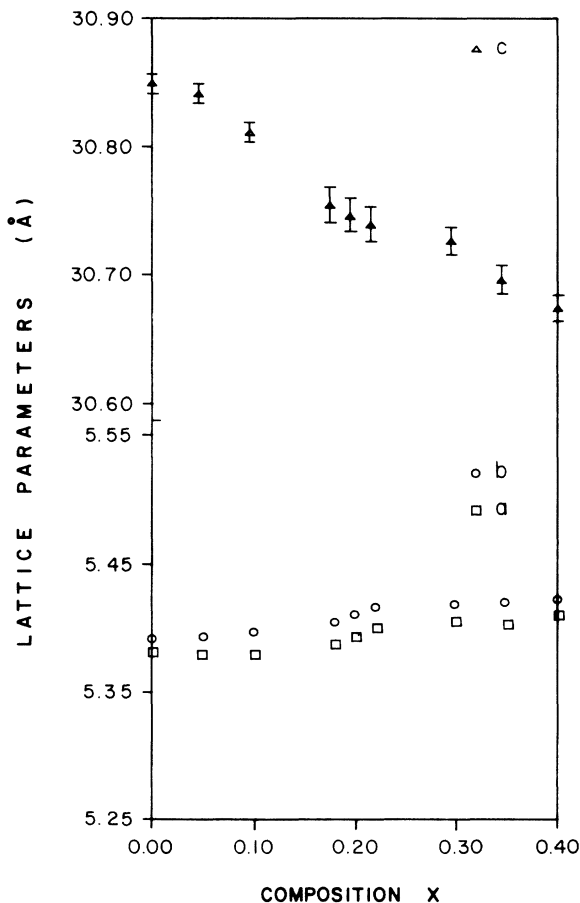

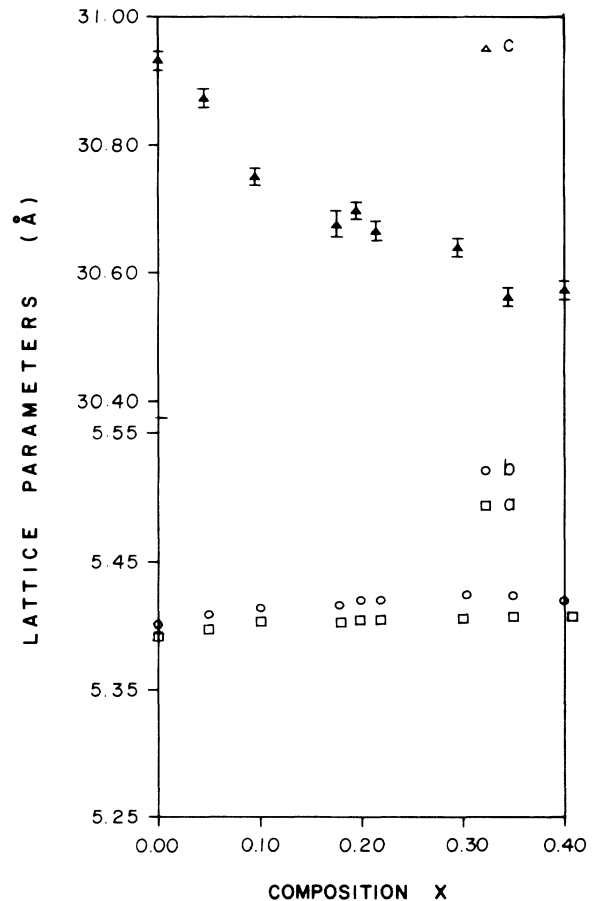FIG. 3. Lattice parameter data for the solid solution annealed in air.

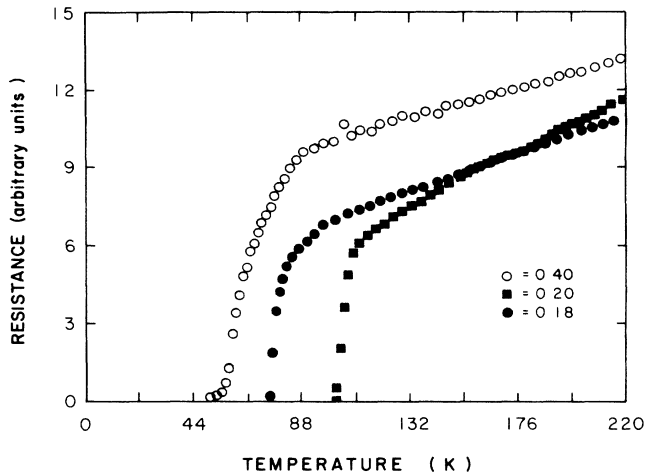FIG. 4. Lattice parameter data for the solid solution annealed in oxygen atmosphere.

FIG. 5. A series of resistance vs temperature curves of different composition of $Bi_{1.7}Pb_{0.3}Sr_{2-x}Pr_xCa_2Cu_3O_{10+y}$ when $x = 0.18$, 0.20, and 0.4 annealed in air.

FIG. 6. Resistance vs temperature curves for samples of $Bi_{1.7}Pb_{0.3}Sr_{2-x}Pr_xCa_2Cu_3O_{10+y}$ with $x = 0.18$, 0.20, and 0.4 annealed in oxygen.

have essentially the same behavior as the samples which were not oxygen annealed.

Figures 5 and 6 show a series of resistance versus temperature curves with $x = 0.05$, 0.18, 0.20, and 0.40. It is observed in these curves that T_c increases with increasing Pr content but arrives to a maximum at $x = 0.20$ ($T_c = 102$ K) and then decreases. Besides, the width of the superconducting transition becomes broader after oxygen annealing and with increasing Pr content. It seems that the optimum hole concentration in our system is achieved when $x = 0.20$.

The behavior of the ratio of resistances at room temperature, (R_T/R_{300K}), for various samples, should also be pointed out. We observed that the magnitude of that ratio goes up with increasing O_2 content. We may assume, accordingly, that the hole concentration is decreasing or is inhibited due to the fact that the O_2 favors only one kind of valence state of praseodymium atoms, which must be according to our early assumption in a formal valence state close to Pr^{4+}, therefore altering the crystal structure and then the electronic density of states in such a way that no improvement in the superconducting properties is obtained as occurs in $Pr_1Ba_2Cu_3O_{7-\delta}$.

Some conclusions can now be drawn based on the results we presented here. It appears that the role of Pr in our system is much like that of Y in the 1:2:3 compound when substituted by a rare earth with larger ionic radii, this is, to increase the internal pressure within the unit cell and therefore, favoring the hole pumping from Cu(I) chains to the Cu(II) planes, producing an enhancement in T_c. On the other hand, in this Pr-doped compound it seems that the internal pressure produces an optimum value for the hole concentration at around $x = 0.20$ ($T_c = 102$ K). After that critical value, the internal pressure follows increasing, according to the trend observed in the c parameter (see Figs. 3 and 4), and the critical temperature diminishing up to a value of $x = 0.40$, above which there is a semiconducting-like behavior. It is interesting to point out that the critical temperature versus
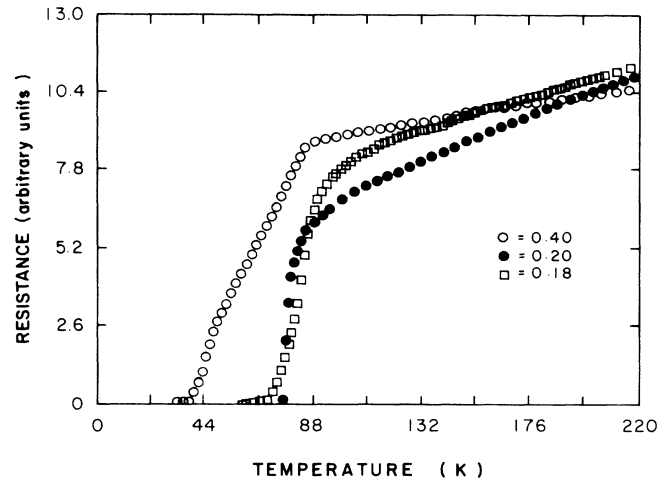
hole concentration follows the tendency already observed by Torrance et al.[15]

Last, our preparation method has proved to be very efficient in order to get 80-K single-phase samples more easily and in a shorter reaction time. Some efforts have been made by some other authors[4,13,14,16] to obtain 80-K single-phase polycrystalline samples but some extra peaks belonging to an unidentified phase are always present, and the preparation process requires considerably longer reaction times. The addition of Pr to the Bi-Pb-Sr-Ca-Cu-O system provides a useful method for achieving 80-K single-phase samples in 7 d of reaction at 860 °C under air atmosphere and higher critical temperatures. In this paper, we also showed that the phase formation is enhanced by including an excess concentration of calcium and copper atoms in the starting stoichiometry. This excess very probably acts as a flux, initiating the formation of the basic blocks of the crystalline structure, in a similar way to the methods used to grow single crystals in these perovskite materials,[17] where an excess of copper is frequently used and forms an amorphous phase, which surrounds the crystals. In our case, it surrounds the microcrystals in the pellet. This is the reason why we start with a stoichiometry, and at the end of the process we finish with a single phase of the other stoichiometry. However, some of the thermodynamical processes that occur in the formation of these ceramics deserve more study, and, in particular, the formation of the equilibrium phase diagram, which may give information about the solid solution regime.

ACKNOWLEDGMENTS

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