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Composition-Induced Superconductivity (up to 55 K) in the System $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$

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We demonstrate a compositionally induced superconductor-to-semiconductor transition in the system $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$. Superconducting behavior is observed over the composition range $0.1 \leq x \leq 0.6$. Samples with $0.1 \leq x \leq 0.3$ are multiphasic, but the superconducting transition temperature is a maximum (55 K) over this range of compositions. The sample having $x = 0.5$ gives rise to an acceptable phase purity, a superconducting transition temperature of 45 K, and the maximum superconducting (Meissner) volume fraction (20.2%). A superconductor-to-semiconductor transition occurs at $x = 0.7$. © 1991 Academic Press, Inc.

1. Introduction

Recently, a new family of lead-based cuprate superconductors, $(Pb_{0.5}M_{0.5})$ Sr_2 $(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$ [M = Sr (*1*) and Ca (*2, 3*)] has been discovered with a maximum T_c of 80 K. The parent compound is isostructural with the thallium-based 1212 phase, e.g., $(Tl,Pb)Sr_2(Ca,Y)Cu_2O_{7-\delta}$ (*4*), but contains (Pb,M)O layers rather than (Tl,Pb)O layers. Its structure is derived from the general formulation $(ACuO_{3-x})_m$ $(AO)_n$, and consists of double pyramidal copper layers (m = 2) intergrown with double rock-salt type layers (n = 2). Moreover, the presence of the $6s^2$ lone pair on Pb^{2+} in this new system results in the stabilization of oxygen-deficient layers $(SrO_{1-\delta/2})$ surrounded by the $(Pb_{0.5}M_{0.5}O)$ layers. Therefore, we felt it appropriate to explore another possible candidate for substitution, namely Cu^{2+}, in the Pb-based 1212 compound. However, Subramanian *et al.* (*5*) and Lee *et al.* (*6*) have previously reported nonsuperconducting phases of $(Pb_{0.7}Cu_{0.3})$ $Sr_2(Ca_{0.15}Y_{0.85})O_{6.8}$ and $(Pb_{0.71}Cu_{0.29})Sr_2$ $(Ca_{0.27}Y_{0.73})Cu_2O_7$, respectively, in the (Pb,Cu)-based 1212 material. Subsequently, Ono *et al.* (*7*) observed superconductivity at 17 K in a liquid nitrogen-quenched bulk sample of $(Pb_{0.63}Cu_{0.35})Sr_2(Ca_{0.35}Y_{0.65})$ Cu_2O_7, and Bush *et al.* (*8*) found superconductivity at 40 K in a single crystal having a chemical composition $(Pb_{0.75}Cu_{0.25})Sr_2$ $(Ca_{0.46}Y_{0.54})Cu_2O_y$. Soon after, Maeda *et al.* (*9*) pointed out that a sample having a nomi-

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nal chemical composition of $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.6}Y_{0.4})Cu_2O_{7-\delta}$ exhibits an onset superconductivity (as measured by resistivity) at 52 K when the material was prepared in an oxidizing atmosphere and was subsequently quenched into liquid nitrogen. Tang *et al.* (*10*) have also stated that a sample of nominal composition $(Pb_{0.5}Cu_{0.5})Sr_2(Ca_{0.4}Y_{0.6})Cu_2O_{6.99}$ becomes superconducting below 67 K when the material is prepared at high pressure of oxygen (100 ~ 200 bar).

Here, we demonstrate a compositionally induced superconductor-to-semiconductor transition in this new series $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$.

2. Experimental

In this work, we have attempted to maintain the Pb concentration at a constant value, and have varied the Ca/Y ratio. High-purity powders of $SrCO_3$, $CaCO_3$, Y_2O_3, and CuO were weighed in appropriate proportions to form the nominal compositions $Sr_2(Ca_{1-x}Y_x)Cu_{2.25}O_y$ with $x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$, and 0.9. The mixed powders were calcined at 970°C for 12 hr in air. The precursor powders were then mixed with PbO to form the compositions of $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$. The resulting mixtures were ground and pressed into a pellet (10 mm in diameter and 3 mm in thickness) under a pressure of 5 ton/cm^2. The pellets were sealed in gold foil (to prevent the loss of lead at elevated temperatures) and were then sintered at 970°C for 3 h in flowing oxygen. After this time, the furnace was cooled to room temperature at a rate of 2°C/min. Enclosure of pellets in gold foil is absolutely necessary for the synthesis of superconducting materials.

X-ray diffraction (XRD) analyses were performed using a Philips-PW1710 X-ray diffractometer with Cu$K\alpha$ radiation. Lattice parameters were determined by a least-squares-refinement program from XRD patterns. Chemical compositions of the specimens were examined by energy dispersive X-ray spectrometry (EDS) from a JEM-200CX electron microscope operating at 200 kV. Molybdenum specimen grids were used and background spectra were obtained to ensure that no copper signals were detected from the sample-free area.

Bar-shaped samples (1.5 × 2 × 10 mm) were cut from the sintered pellets for standard four point probe electrical resistivity measurements. The electrical contacts to the sample were made by fine copper wires with a conductive silver paint; the applied current was 1 mA. The temperature was recorded using a calibrated silicon diode sensor located close to the sample. Magnetization data were obtained using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design).

3. Results and Discussion

In Fig. 1 we show the powder XRD patterns of the series $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$ samples with nominal x values of 0.2 ~ 0.8. At $x = 0.2$ sample, the majority phase (marked by ×) can be indexed on the basis of a hexagonal unit cell [11] with lattice constants $a \simeq 10.11$ Å and $c \simeq 7.11$ Å, and the minority phase (marked by ●) can be fitted by a tetragonal unit cell with $a \sim 3.8$ Å and $c \sim 11.9$ Å, corresponding to the so-called 1212 phase (*1–10*). We find that this hexagonal phase is semiconducting. An increase in nominal yttrium concentration in the series $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$ decreases the amount of the hexagonal phase and increases the concentration of the tetragonal phase. From the peak intensity ratio, $[I(200)/I(200) + I'(110)]$, where $I(200)$ and $I'(110)$ are derived from the intensity of the tetragonal phase at $2\Theta = 47.5°$ and the hexagonal phase at $2\Theta = 17.5°$, respectively, we obtain a semiquantitative estimate of the relative amount of the 1212 phase for various yttrium to calcium ratios, as shown in Fig. 4a.

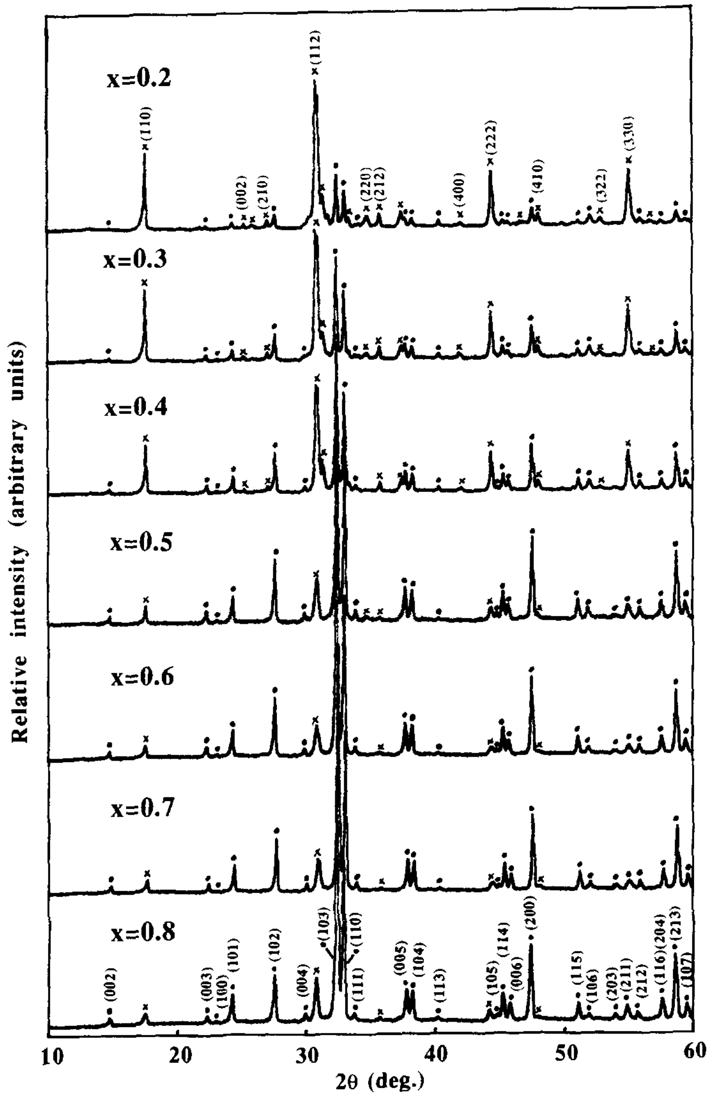

FIG. 1. Powder XRD patterns of the series $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$ samples with nominal x values of 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8.

Moreover, we observe a contraction in the *c* lattice parameter for the tetragonal phase from 11.8758(16) Å for $x = 0.3$ to 11.8337(9) Å for $x = 0.8$, and an expansion in the *a* lattice parameter from 3.8159(4) Å for $x = 0.3$ to 3.8228(2) Å for $x = 0.8$. The reduction in the *c* lattice parameter probably arises from substitution of the smaller Y^{3+} ion (0.93 Å), as compared with Ca^{2+} ion (0.99 Å). The expansion in the *a* lattice parameter can be attributed to a decrease in the average copper oxidation state, leading to longer Cu–O distances within the copper oxygen sheets. A similar effect has been observed in $Bi_2Sr_2(Ca_{1-x}Y_x)Cu_2O_{8+\delta}$ (*12*) and $(Tl_{0.5}Pb_{0.5})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$ (*4*).

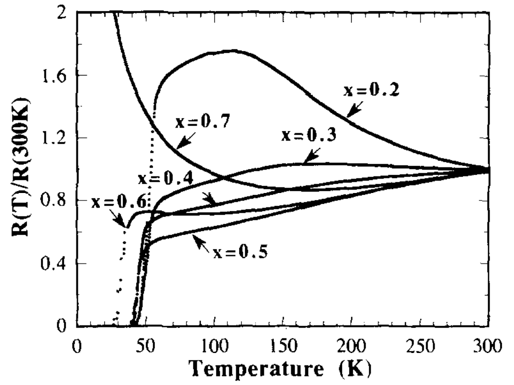

FIG. 2. Temperature dependence of the normalized resistance of the $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$ samples with nominal x values of 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7.

The elemental compositions of 25 individual microcrystals were determined on samples having nominal composition $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7-\delta}$. From these studies, the majority phase in the sample was determined to be $[Pb_{0.75(1)}Cu_{0.25}]Sr_{1.99(7)}[Ca_{0.49(1)}Y_{0.51(2)}]Cu_2O_{7-\delta}$.

In Fig. 2 we show the temperature dependence of the normalized resistance of the $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$ samples with nominal x values of 0.2 ~ 0.7. Although the $x = 0.2$ sample appears to exhibit semiconducting behavior in its normal state, it nevertheless has the highest superconducting transition temperature of the entire series, with $T_{c(onset)} = 60$ K, $T_{c(midpoint)} = 54$ K, and $T_{c(zero)} = 42$ K. Samples with nominal compositions in the region of $0.3 \leq x \leq 0.6$ exhibit metallic behavior in their normal state and a decrease in $T_{c(midpoint)}$ from 52 to 32 K. Samples with $x \geq 0.7$ are semiconducting. In Fig. 4b we show the variation in T_c with x in $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$.

In Fig. 3 we show the temperature dependence of the low field magnetization (5 Oe, field-cooled) of the powder samples having nominal compositions $x = 0.1 \sim 0.6$ in $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$. The onset of diamagnetism appears at a temperature of 55 K for samples $x = 0.1$, 0.2, and 0.3. However, for $x \geq 0.3$, the onset diamagnetic signal moves to low temperatures as x

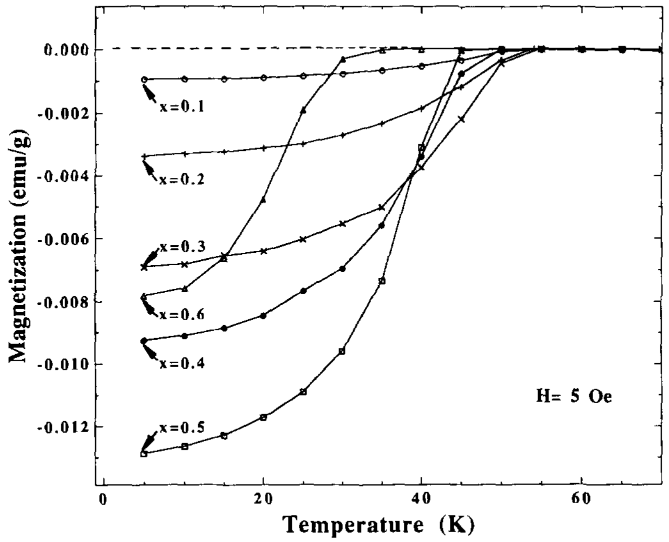

FIG. 3. Temperature dependence of the low field magnetization (5 Oe, field-cooled) of the powder samples having nominal compositions $x = 0.1$, 0.2, 0.3, 0.4, 0.5, and 0.6 in $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$.

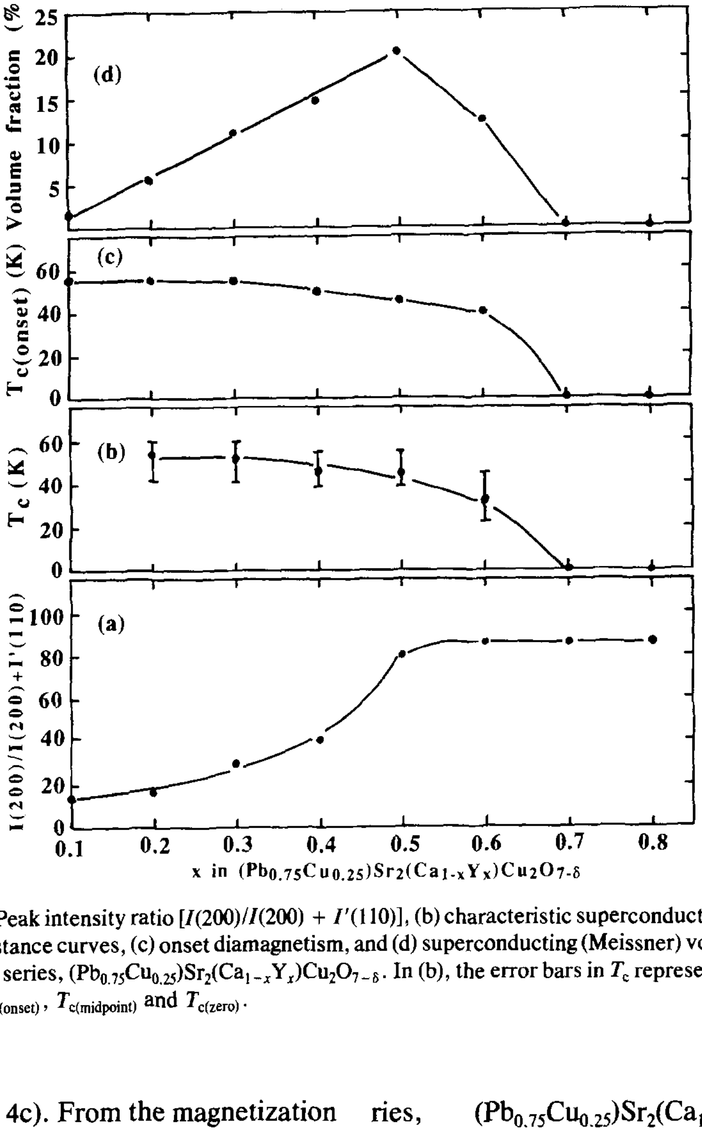

FIG. 4. (a) Peak intensity ratio [$I(200)/I(200) + I'(110)$], (b) characteristic superconducting properties from the resistance curves, (c) onset diamagnetism, and (d) superconducting (Meissner) volume fraction for the entire series, $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$. In (b), the error bars in T_c represent the limiting values for $T_{c(onset)}$, $T_{c(midpoint)}$ and $T_{c(zero)}$.

increases (Fig. 4c). From the magnetization data we estimate the superconducting (Meissner) volume fractions; the maximum value, 20.2% of $-1/4\pi$ at 5 K, is found for the $x = 0.5$ sample (Fig. 4d). This result reveals that bulk superconductivity is found in the $x = 0.5$ sample.

In Fig. 4 we summarize (a) the peak intensity ratio [$I(200)/I(200) + I'(110)$], (b) the characteristic superconducting properties from the resistivity curves, (c) the onset diamagnetism, and (d) the superconducting (Meissner) volume fraction for the entire series, $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$. From the peak intensity ratio [$I(200)/I(200) + I'(110)$] (Fig. 4a), we see that for samples with $x \geq 0.5$ the 1212 tetragonal phase is, by far, the majority phase. Based on these data, and the characteristic superconducting properties (Figs. 4b and 4c), one can propose that a higher (nominal) calcium content in the Pb-based 1212 compound results in a higher superconducting transition temperature. It seems likely that the substitution of Y^{3+} for Ca^{2+} in the system $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$ decreases the hole concentration in the CuO_2 sheets, probably via the removal of holes from the $\sigma^*_{x^2-y^2}$ orbital (*13*). The experimental support for this view derives from the observation of an increase in the *a* lattice parameter with yttrium concentration. When $x \geq 0.7$, a transition to semiconducting behavior is observed. The potential variability of the Y/Ca ratio may be one reason for the apparent disparity in results from different laboratorities (*5–10*). Once again, the hole carrier density appears to play an important role in determining superconductivity.

The composition-induced change in electronic properties of the title series is reminiscent of those observed in the system $(Tl_{0.5}Pb_{0.5})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$ (*4*). Here the partial substitution of Y^{3+} into Ca^{2+} sites results in a decrease in hole concentration and superconductivity with a maximum T_c (110 K) for $x = 0.2$. The $(Tl_{0.5}Pb_{0.5})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$ system has a complete homogeneity range between Ca^{2+} and Y^{3+} substitutions. In contrast, the present study suggests that the $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$ system will only tolerate ca. 50% substitution of Ca^{2+} into the Y^{3+} sites. This situation is reminiscent of that in $YBa_2Cu_3O_{6.2}$ [with one Cu–O chain corresponding to the (Pb,Cu)O layer in the 1212 system] and $YBa_2Cu_4O_8$ [with two Cu–O chains corresponding to the (Pb,Cu)O layer in the 1212 system]; in these systems, one finds a maximum solubility range of Ca substitution into the Y sites of ca. 25% (*14*) and 10% (*15*), respectively. In general, the Bi- and Tl-based superconductors possess the Cu–O sheets which are nearly planar, compared with the buckled Cu–O planes in Y-123 superconductor. This would lead one to propose that in the Bi-2212 structure [for example $Bi_2Sr_2YCu_2O_{8+\delta}$ (*12*)] and in the Tl-1212 structure, [for example $(Tl_{0.5}Pb_{0.5})Sr_2YCu_2O_{7-\delta}$ (*4*)] the Y^{3+} layer can accommodate more easily the larger Ca^{2+} ion, as compared with the Pb-1212 systems [for example $(Pb_{0.75}Cu_{0.25})Sr_2YCu_2O_{7-\delta}$]. Interestingly, the multiphasic samples with $0.1 \leq x \leq 0.3$ have the largest T_c, even though the volume fraction of superconductor drops rapidly with increasing (nominal) calcium content. It may be possible for the (low volume fraction) superconducting phase to accumulate a high concentration of calcium within the crystallites.

In summary, we have demonstrated the compositionally induced superconductor-to-semiconductor transition in $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$. Here the Y/Ca ratio appears to play an important role in determining the hole concentration and the superconductivity in this new lead-based cuprate material.

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