

Superconducting lead cuprates $(\text{Pb}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{1-y}\text{Ba}_y)_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_w$

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The effects of Ba substitution for Sr and Ca substitution for Y on superconducting properties of lead cuprates, $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_7$ (the "1:2:1:2" phase), are investigated. The parent material of these cuprates, i.e., $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_7$, is found to have few charge carriers and, therefore, does not exhibit superconductivity at a temperature above 4.2 K. A sample in which Sr is substituted by Ba has a small amount of holes but yet does not exhibit superconductivity above 4.2 K. A sample in which both Sr and Y are substituted, respectively, by Ba and Ca contains more holes than the one in which only Ba substitution for Sr is made. This sample exhibits superconductivity with the superconducting onset temperature as high as 25 K. For superconducting lead cuprates of the 1:2:1:2 phase, the charge carriers are found to be holes according to Hall-coefficient measurements. The Ba substitution for Sr is found to contribute to the increase in hole concentration through two different mechanisms: (1) It extends the solubility limit of Ca in the Y sites when the $[\text{Pb}]/[\text{Cu}]$ ratio is fixed in the $(\text{Pb,Cu})\text{O}$ rocksalt-type plane; (2) it changes the valency from $2+$ to $1+$ of a portion of the Cu ions in the $(\text{Pb,Cu})\text{O}$ plane.

INTRODUCTION

Superconducting lead cuprates (with T_c 's near 70 K) have been found by Cava *et al.*¹ in the $(\text{Pb}_2\text{Cu})\text{Sr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_8$ system (the "3:2:1:2" phase). The crystallographic structure of the 3:2:1:2 phase is slightly different from the "2:2:1:2" structure known for the Bi- or Tl-based superconducting cuprates.²⁻⁴ That is, in the 3:2:1:2 structure, there exists an additional Cu layer sandwiched between two rocksalt-type layers (consisting of PbO units).

Lee, Swinnea, and Steinfink⁵ and Subramanian *et al.*⁶ found other lead cuprates, $(\text{Pb,Cu})\text{Sr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_7$, of the same crystallographic structure as that of superconducting $\text{TlBa}_2\text{CaCu}_2\text{O}_7$,⁴ i.e., the 1:2:1:2 structure, and reported that none of these oxides exhibited superconductivity. The 1:2:1:2 phase characteristically contains $(\text{Pb,Cu})\text{O}$ (rocksalt-type) layers and (Y,Ca) layers instead of TlO (rocksalt-type) layers and Ca layers of the Tl-based 1:2:1:2 structure, respectively. Rouillon *et al.*⁷ reported that a Pb-based cuprate $(\text{Pb}_{0.5}\text{Sr}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$ of the 1:2:1:2 phase was superconducting. The present authors reported⁸ previously that the Pb-based 1:2:1:2 cuprates synthesized from starting compositions of $\text{Pb}(\text{Sr,Ca,Y})_3\text{Cu}_2\text{O}_z$ exhibited superconductivity with T_c^{on} 's (superconductivity onset temperatures) around 30 K. They also reported that a Ba-containing Pb-based 1:2:1:2 compound $(\text{Pb,Cu})(\text{Sr,Ba})_2(\text{Y,Ca})\text{Cu}_2\text{O}_7$ exhibited superconductivity with T_c^{on} of near 60 K (Ref. 9) and that Ba-free Pb-based 1:2:1:2 compounds $(\text{Pb,Cu})\text{Sr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_z$ exhibited superconductivity with T_c^{on} 's up to 52 K.¹⁰ However, these superconducting Pb-based 1:2:1:2 compounds have not yet been well characterized. In the present study, a variety of $(\text{Pb}_{0.5}\text{Cu}_{0.5})(\text{Sr,Ba})_2(\text{Y,Ca})\text{Cu}_2\text{O}_w$ samples were synthesized and investigated in terms of the oxygen content, Hall coefficient, and magnetic susceptibility.

EXPERIMENTAL PROCEDURE

The samples used in the present study were prepared by a solid-state reaction method using high-purity (>99.9%) powders of PbO , SrCO_3 , BaCO_3 , Y_2O_3 , CaCO_3 , and CuO . These powders were mixed to nominal compositions of $(\text{Pb}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{1-y}\text{Ba}_y)_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_w$ ($x=0, 0.05, 0.1, 0.15, \text{ and } 0.2$; $y=0 \text{ and } 0.2$) by means of planetary ball milling using ethanol as the solvent. The mixed powders were pelletized and then calcined at 850°C for 10 h in air. The calcined pellets were ground, pelletized, and then calcined again at 1000°C for 1 h in O_2 -gas flow. These pellets were reground and pressed into $3 \times 1.5 \times 20\text{-mm}^3$ parallelepiped bars. The bars were sintered at 1020°C for 1 h in O_2 -gas flow and furnace cooled to room temperature. The samples were again heat treated at 500°C for 5 h in O_2 -gas flow and cooled down to room temperature at a rate of 50°C/h.

The samples were characterized by x-ray diffractometry (XRD) equipped with a graphite monochromator using $\text{Cu } K\alpha$ radiation. Electrical resistivity and dc magnetic susceptibility were measured in terms of temperature by a conventional four-probe method and superconducting-quantum-interference-device (SQUID) magnetometry, respectively. Oxygen contents were determined by means of a Coulometric titration technique.¹¹ Hall coefficients were measured in magnetic fields in the range between -6 and 6 T at temperatures ranging from 30 to 300 K. Polished surfaces of the samples were observed and analyzed by backscattered-electron microscopy and electron-probe energy-dispersive x-ray analysis (EDX), respectively.

RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show schematic representations of the crystallographic structures of lead cuprates of the

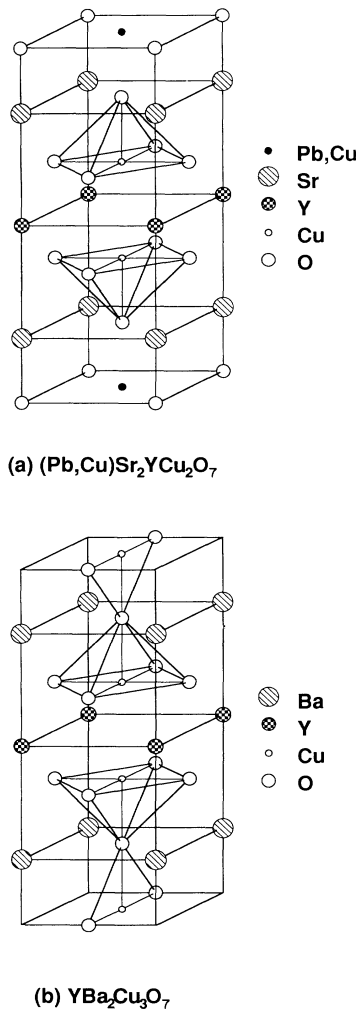


FIG. 1. Schematic representation of crystallographic structures of the (a) 1:2:1:2 phase and (b) 1:2:3 phase.

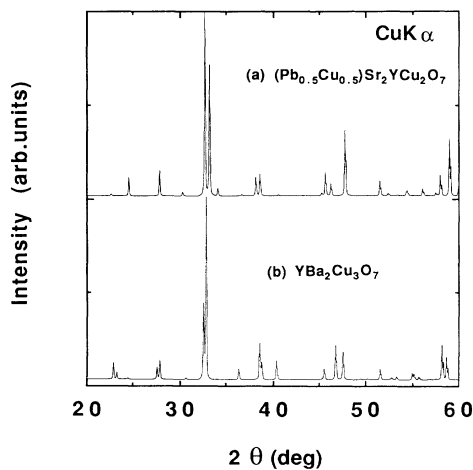


FIG. 2. Simulated powder XRD patterns for (a) $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_7$ with the 1:2:1:2 phase and (b) $\text{YBa}_2\text{Cu}_3\text{O}_7$ with the 1:2:3 phase.

1:2:1:2 and 1:2:3 (or $\text{YBa}_2\text{Cu}_3\text{O}_7$) structures, respectively. These crystallographic structures are similar to, but slightly different from, each other. In the former structure, there are (Pb,Cu)O planes of a rocksalt configuration instead of Cu-O chains of an oxygen-deficient perovskite configuration of the latter structure. $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$ are distinguishable from each other by XRD because the 1:2:1:2 structure has Pb and Sr for half of the Cu atoms in the chain sites and for Ba in the 1:2:3 structure, respectively. Figure 2 shows simulated XRD patterns for the two compounds (a) $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_7$ and (b) $\text{YBa}_2\text{Cu}_3\text{O}_7$.

Figures 3(a) and 3(b) show XRD patterns of the sam-

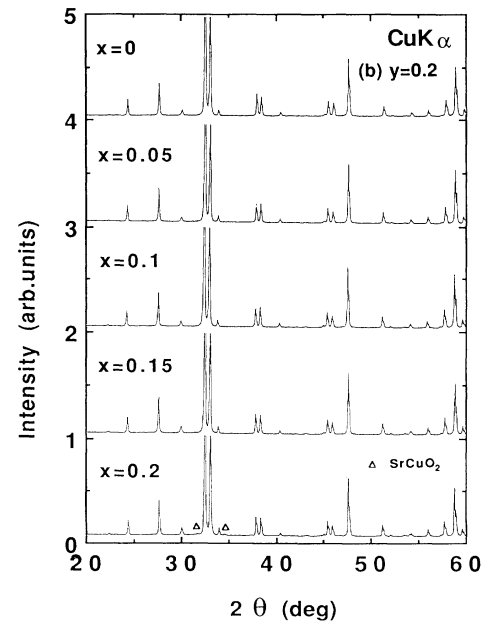
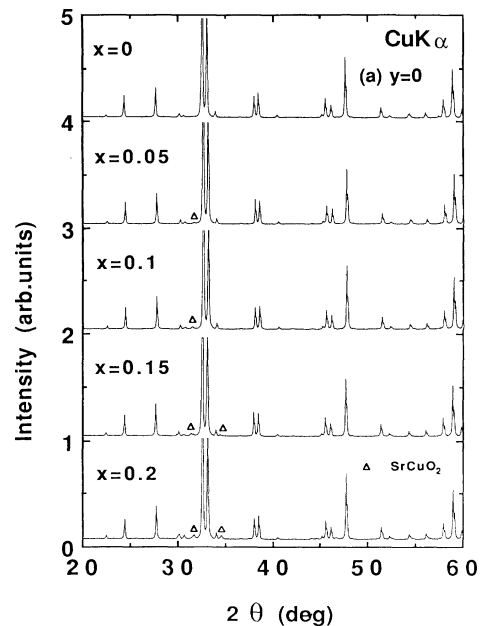


FIG. 3. XRD patterns for $(\text{Pb}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{1-y}\text{Ba}_y)_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_w$ samples with $x=0-0.2$ and (a) $y=0$ and (b) $y=0.2$.

ples of $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_w$ ($y=0$) and $(\text{Pb}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{0.8}\text{Ba}_{0.2})_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_w$ ($y=0.2$) for different amounts of Ca dopant x . All the samples were found to contain the 1:2:1:2 phase as the main phase, but no evidence for the 1:2:3 phase was obtained. Among the Ba-free ($y=0$) samples, only the Ca-free sample, i.e., $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_w$, was single phase. The samples with nominal compositions of $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_w$ ($x \geq 0.05$) contained a secondary phase of $(\text{Sr,Ca})\text{CuO}_2$ as identified by both XRD and EDX. We reported¹⁰ previously that the chemical compositions of the Ba-free, Pb-based 1:2:1:2 compounds were given by the formula $(\text{Pb}_{(1+x)/2}\text{Cu}_{(1-x)/2})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_z$ ($x=0-0.35$). However, among the Ba-doped samples of $(\text{Pb}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{0.8}\text{Ba}_{0.2})_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_w$, with a fixed $[\text{Pb}]/[\text{Cu}]$ ratio in the $(\text{Pb,Cu})\text{O}$ plane, those with x up to 0.15 were single phase of the 1:2:1:2 type. As shown in Fig. 4, the lattice constant a decreases and c increases with increasing Ca content, x . Therefore, it is strongly suggested that the Ba substitution for Sr has worked to extend the solubility of Ca in the Y sites when the $[\text{Pb}]/[\text{Cu}]$ ratio is fixed to 1:1 in the $(\text{Pb,Cu})\text{O}$ plane.

The temperature dependences of the electrical resistivity for Ba-free ($y=0$) and Ba-doped ($y=0.2$) samples with various Ca contents x are shown in Figs. 5(a) and 5(b). When $y=0$ the electrical resistivity data for all the samples were similar in magnitude and did not exhibit superconductivity. When $y=0.2$, as x increased, the electrical resistivity at room temperature decreased and the

temperature dependence of electrical resistivity changed from a semiconductor type to a metallic one. The samples with Ca content x not less than 0.1 exhibit superconductivity. The results of XRD and electric resistivity measurements may be interpreted as follows. In the Ba-free ($y=0$) samples, the 1:2:1:2 phase contained Ca less than the nominal compositions of the samples, and the actual chemical compositions of the 1:2:1:2 phase were rather close to that of the Ca-free compound $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_w$. On the other hand, in the Ba-doped ($y=0.2$) samples, the 1:2:1:2 phase contained Ca as much as the nominal composition if $x \leq 0.15$ and the dependence of resistivity on temperature varied for samples with different Ca contents.

In order to investigate the effects of Ba and Ca substitution for Sr and Y, the oxygen content, Hall coefficient, and magnetic susceptibility were measured. The following three single-phase samples *A*, *B*, and *C* were prepared for these measurements:

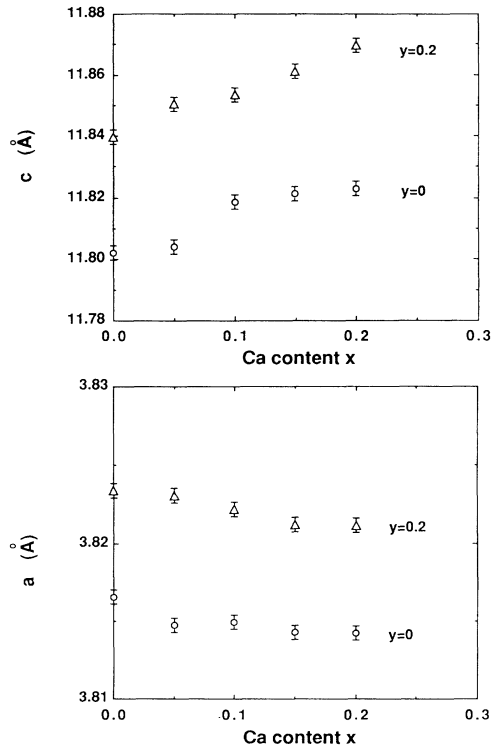
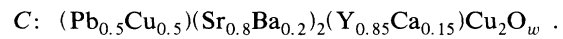
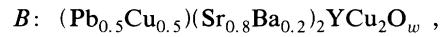
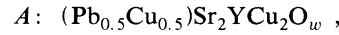


FIG. 4. Lattice constants for $(\text{Pb}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{1-y}\text{Ba}_y)_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_w$ samples with $x=0-0.2$ and $y=0$ and 0.2

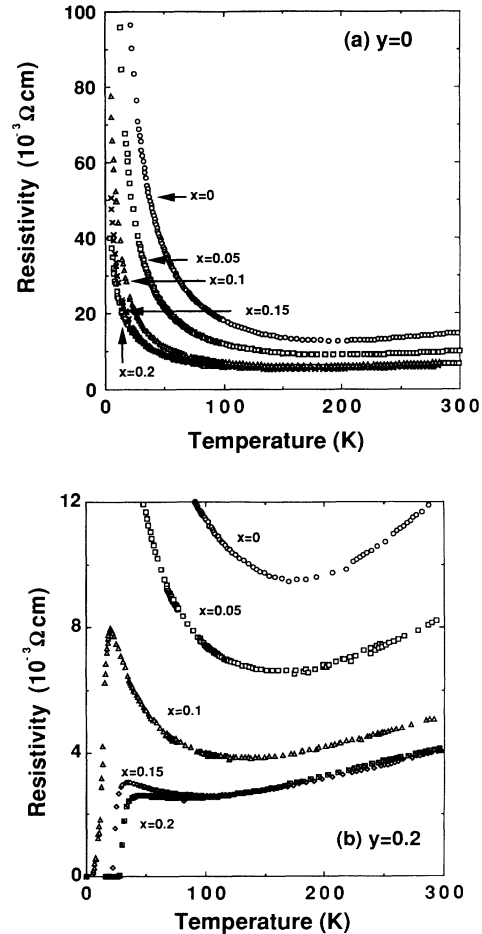


FIG. 5. Temperature dependence of electrical resistivity for $(\text{Pb}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{1-y}\text{Ba}_y)_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_w$ samples with $x=0-0.2$ and (a) $y=0$ and (b) $y=0.2$.

It was observed by backscattered-electron microscopy that all the three samples were nearly single phase. The amount of impurity phases in the three samples was estimated to be less than 1 vol%. Using XRD and EDX, the secondary impurity phases were identified to be SrCuO_2 and BaPbO_3 .

Figure 6 shows the temperature dependence of electrical resistivity of samples *A*, *B*, and *C*. It is found that sample *C* is a superconductor with superconducting onset temperature of 25 K. Figure 7 shows the temperature dependence of magnetic susceptibility of sample *C*. The data were obtained for the field-cooling mode using a magnetic field of 5 Oe. It is found that the superconductivity of sample *C* is of a bulk nature because the magnitude of diamagnetic susceptibility at 5 K corresponds to 11% of the perfect diamagnetism. The magnitude of electrical resistivity at room temperature decreases in following order: samples *A*, *B*, and *C*. Sample *B* was obtained by substituting Ba^{2+} for Sr^{2+} in sample *A* (the parent material). Usually, substitution of an ion by another kind of ion of the same valency does not affect the electrical resistivity (or carrier density). However, the Ba^{2+} substitution for Sr^{2+} in this case apparently decreased the electrical resistivity. The reason for this is discussed below.

The oxygen contents of all the three samples were determined by a Coulometric titration technique. All the samples have the same value for the average oxygen content, i.e., $w=6.98$, which is nearly equal to the stoichiometric value of 7. This implies that the oxygen content was not affected by both Ba substitution for Sr and Ca substitution for Y.

Figure 8 shows the temperature dependence of the Hall coefficient measured in the temperature range between 30 and 300 K. The Hall coefficient is positive and increases as the temperature decreases, but the temperature dependence is rather weak, as observed for a Bi-based 2:2:1:2 cuprate.¹² Assuming a single-band model, the effective number of holes per CuO_2 in the CuO_2 plane was estimated from the Hall coefficient at room temperature. The es-

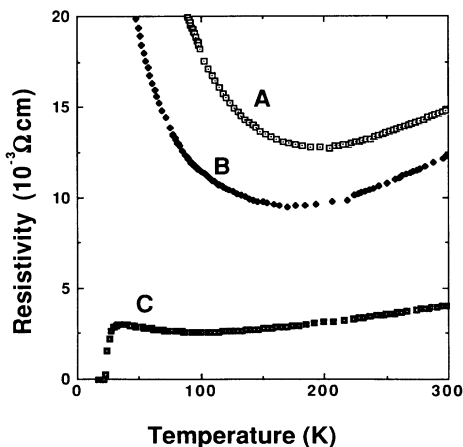


FIG. 6. Temperature dependence of electrical resistivity for $(\text{Pb}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{1-y}\text{Ba}_y)_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_w$ samples: *A*, with $x=0$ and $y=0$; *B*, with $x=0$ and $y=0.2$; and *C*, with $x=0.15$ and $y=0.2$.

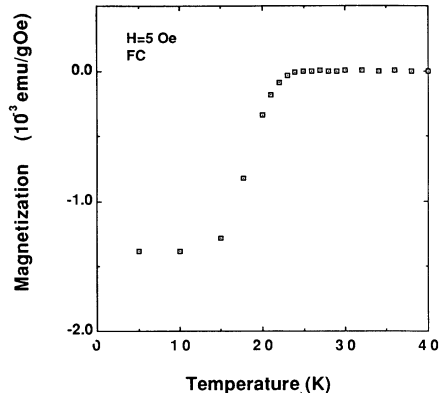


FIG. 7. Temperature dependence of magnetic susceptibility for a $(\text{Pb}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{1-y}\text{Ba}_y)_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_w$ sample with $x=0.15$, $y=0.2$, i.e., sample *C*.

timated numbers for samples *A*, *B*, and *C* were 0.04, 0.12, and 0.27, respectively. It is found from the measured oxygen contents and hole concentrations that the valency of Pb ions for the 1:2:1:2 compounds is a close 4+, unlike the valency of 2+ for the Pb-based 3:2:1:2 compounds. The difference in the valency of Pb ions between the 1:2:1:2 and 3:2:1:2 compounds may be caused by different atmospheres during the synthesis. The 1:2:1:2 compounds were synthesized in an oxidizing atmosphere, i.e., 1 atm O_2 gas. This oxygen partial pressure is 100 times larger than that used for the synthesis of 3:2:1:2 compounds.¹ The magnitude of the hole density at room temperature increased in the following order: samples *A*, *B*, and *C*. This implies that both Ba substitution for Sr and Ca substitution for Y introduced holes. When Y^{3+} ions were substituted by Ca^{2+} ions in sample *C*, the hole concentration (at room temperature) increased by 0.15 per unit cell (see Table II) in accordance with the amount of the substitution, i.e., 0.15 per unit cell. Even when Sr was substituted by Ba in sample *B*, the oxygen content remained constant, being equal to 7. However, the electrical resistivity decreased in accordance with the increase in the hole concentration. This means that a cer-

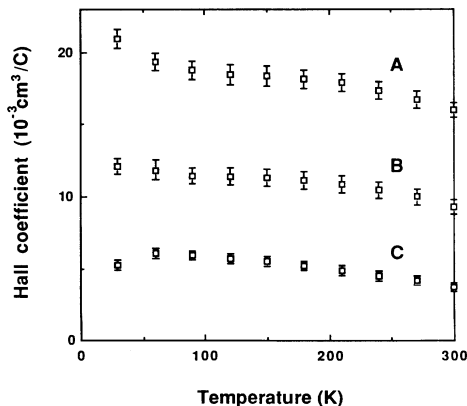


FIG. 8. Temperature dependence of the Hall coefficients for $(\text{Pb}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{1-y}\text{Ba}_y)_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_w$ samples with *A*, $x=0$ and $y=0$; *B*, $x=0$ and $y=0.2$; and *C*, $x=0.15$ and $y=0.2$.

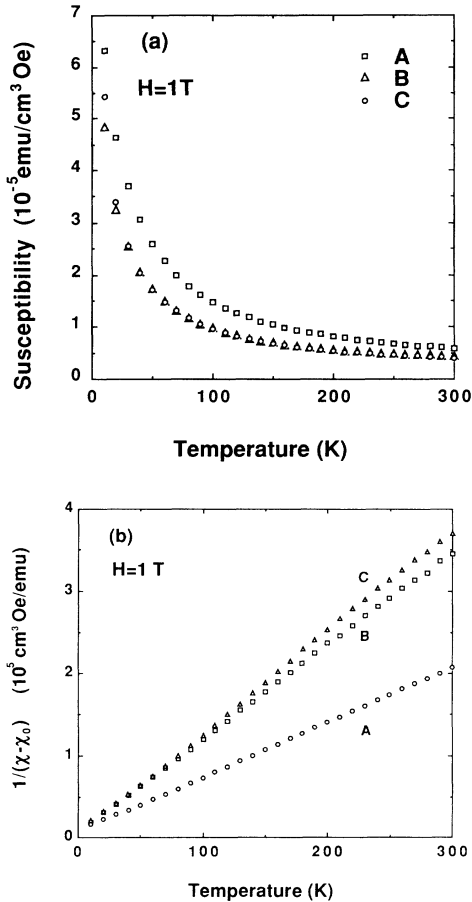


FIG. 9. Temperature dependence of (a) paramagnetic susceptibility χ and (b) $1/(\chi - \chi_0)$ for $(\text{Pb}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{1-y}\text{Ba}_y)_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_w$ samples with *A*, $x = 0$ and $y = 0$; *B*, $x = 0$ and $y = 0.2$; and *C*, $x = 0.15$ and $y = 0.2$.

tain mechanism worked to create holes in sample *B* when Sr was substituted by Ba. In order to elucidate the mechanism for hole creation, the magnetic susceptibility (which would exclusively reflect the localized magnetic moment of Cu^{2+}) was measured with respect to temperature.

Figure 9(a) shows the temperature dependences of the magnetic susceptibility (χ) for the three samples *A*, *B*, and *C*, measured in a magnetic field of 1 T. For all the three samples, the susceptibility increased with decreasing temperature; i.e., the three samples were paramagnet-

ic. Figure 9(b) shows the plots of $1/(\chi - \chi_0)$ vs T , where χ_0 was determined such that $1/(\chi - \chi_0)$ became linear with respect to temperature. Some localized magnetic moments must exist in all the three samples because every set of the plotted data points shows a linear relation. The Curie constant C , the Curie temperature Θ , Pauli paramagnetic susceptibility χ_0 , and the density of Cu^{2+} ($s = \frac{1}{2}$) per unit cell, $N(\text{Cu}^{2+})$, were estimated assuming that the observed Curie paramagnetism was due to only localized spin angular moment of Cu^{2+} ($s = \frac{1}{2}$) and using the equations

$$\chi = C/(T - \Theta) + \chi_0$$

and

$$N(\text{Cu}^{2+}) = 3k_B C / (1.73^2 \mu_B^2 V) \quad (\text{per unit cell}),$$

where k_B is the Boltzmann constant, μ_B the Bohr magneton, and V the unit-cell volume calculated from the lattice constants. The obtained constants are summarized in Table I. It is seen in this table that even sample *C*, which is superconducting, has a relatively large Curie constant. Both superconducting $(\text{La,Sr})_2\text{CuO}_4$ and $\text{Bi}_2\text{Sr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_{8+y}$ are known to contain Cu ions only in the CuO_2 planes which contribute to the electrical conduction as well as to the occurrence of superconductivity. For these compounds the normal-state magnetic susceptibilities are nearly independent of the temperature.^{13,14} Therefore, we supposed that the observed magnetic moment was caused by Cu^{2+} ions in the $(\text{Pb,Cu})\text{O}$ rocksalt-type planes. From Table I it is seen that sample *B* contains Cu^{2+} ions fewer than sample *A*. As previously noted, when Sr^{2+} was substituted by Ba^{2+} , the electrical resistivity decreased in accordance with the increase in the hole concentration, while the oxygen content of the sample remained constant. This fact may be interpreted as follows. The Ba substitution for Sr in the Pb-based 1:2:1:2 compounds changes the valency of part of Cu ions in the $(\text{Pb,Cu})\text{O}$ planes from 2+ to 1+, and therefore the resultant excess positive charge (holes) is transferred to the CuO_2 planes to increase the hole concentration in the planes. On the other hand, the Ca substitution for Y does not affect the valency of Cu ions in the $(\text{Pb,Cu})\text{O}$ planes because the distance between the Y and Cu sites in the $(\text{Pb,Cu})\text{O}$ plane is relatively long.

In Table II the following quantities for samples *A*, *B*, and *C* are summarized: Pb content $1 - z$; Ba content y ; Ca content x ; O content w ; hole density per unit cell, n_H

TABLE I. Magnetic parameters of samples *A*, *B*, and *C*.

| Sample | C^a (emu K/cm ³ Oe) | χ_0^b (emu/cm ³ Oe) | Θ^c (K) | $N(\text{Cu}^{2+})^d$ (per unit cell) |
|----------|-------------------------------------|--|-------------------|--|
| <i>A</i> | 1.5×10^{-3} | 1.1×10^{-6} | 10.7 | 0.41 |
| <i>B</i> | 8.8×10^{-4} | 1.2×10^{-6} | -5.5 | 0.24 |
| <i>C</i> | 8.1×10^{-4} | 1.7×10^{-6} | -3.0 | 0.22 |

^aCurie constant.

^bPauli paramagnetic susceptibility.

^cCurie temperature.

^d Cu^{2+} concentration estimated with an assumption that the paramagnetism is caused by Cu^{2+} ($s = \frac{1}{2}$) only.

TABLE II. Chemical composition ($1-z$), y , x , and w ; hole density n_H ; Cu^{2+} density $N(\text{Cu}^{2+})$; and T_c^{on} .

| Sample | Pb content ($1-z$) | Ba content y | Ca content x | O content w^b | n_H^a (per unit cell) | $N(\text{Cu}^{2+})$ (per unit cell) | T_c^{on} (K) |
|--------|-------------------------|-------------------|-------------------|--------------------|----------------------------|--|--------------------------|
| (A) | 0.5 | 0 | 0 | 6.98 | 0.04 | 0.41 | |
| (B) | 0.5 | 0.2 | 0 | 6.98 | 0.12 | 0.24 | |
| (C) | 0.5 | 0.2 | 0.15 | 6.98 | 0.27 | 0.22 | 25 |

^aEstimated from the Hall coefficient at room temperature.

^bDetermined by a Coulometric titration technique.

(calculated from the measured Hall coefficient at room temperature); Cu^{2+} ($s = \frac{1}{2}$) density per unit cell, $N(\text{Cu}^{2+})$ (calculated from the magnetic-susceptibility data); and the superconducting onset temperature T_c^{on} .

CONCLUSION

Ba-containing Pb-based 1:2:1:2 (single-phase) superconducting compounds were synthesized and characterized. It was revealed that the Pb-based 1:2:1:2 superconductors had holes as charge carriers (i.e., p type) according to the Hall measurement. The parent material $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_w$ contained few holes, but was fully oxidized, i.e., $w = 7$. Therefore, it was found that the valency of Pb ions in the Pb-based 1:2:1:2 compounds was $4+$, unlike Pb^{2+} ions in the Pb-based 3:2:1:2 compounds. The oxygen contents were found not to be affected by both Ba substitution for Sr and Ca substitu-

tion for Y, being nearly equal to the stoichiometric value of 7. The Ca^{2+} substitution for Y^{3+} introduced holes to the CuO_2 plane in accordance with the decrease in the cation valency. The Ba^{2+} substitution for Sr^{2+} was effective for introducing holes through two independent mechanisms: (1) It extended the solubility limit of Ca ions in the Y sites for a fixed $[\text{Pb}]/[\text{Cu}]$ ratio in the (Pb,Cu)O plane, and (2) it changed the valency of some of Cu ions in the (Pb,Cu)O plane from $2+$ to $1+$ such that the induced excess positive charge (holes) was transferred to the CuO_2 plane.

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