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Optimization of Superconducting Transition Temperature in $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7+\delta}$ by Postannealing

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We demonstrate systematic studies of the optimization of the superconducting transition temperature in $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7+\delta}$ by annealing in an oxygen atmosphere. As-sintered samples with a superconducting midpoint transition temperature, $T_{c(\mathrm{midpoint})}$, of 18 K were prepared by solid state reaction at 1000°C for 1 hr in oxygen and then quenched in air. Subsequently, the samples were annealed in the temperature range between 700 and 1000°C for 12 hr in oxygen and then rapidly quenched in air. The ultimate $T_{c(\mathrm{midpoint})}$ increased from 30 to 48 K with an increase in the annealing temperatures from 700 to 800°C, but a further increase in the annealing temperature of the samples from 800 to 1000°C resulted in a decrease in $T_{c(\mathrm{midpoint})}$. Based on our studies, we believe that the optimum $T_{c(\mathrm{midpoint})}$ of 48 K arises from the removal of excess oxygen in the insulating slabs of (Pb,Cu)O in $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7+\delta}$ and this leads the material to approach an optimum hole concentration.

1. Introduction

The discovery of nonsuperconductors in the Pb-based 1212 compounds, $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.15}Y_{0.85})Cu_2O_{6.8}$ and $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.27}Y_{0.73})Cu_2O_7$, by Subramanian *et al.* (*1*) and Lee *et al.* (*2*), respectively, has led to widespread research aimed at inducing superconductivity in these phases. The structure of $(Pb,Cu)Sr_2(Ca,Y)Cu_2O_{7\pm\delta}$ resembles that of $YBa_2Cu_3O_{7-\delta}$: the (Pb,Cu)O layers replacing the CuO chains, Sr atoms replacing Ba atoms, and Ca or Y atoms replacing Y atoms. The compounds are generally prepared in oxidized conditions and it is believed that the valencies of Pb and Cu in $(Pb_{0.7}Cu_{0.3})Sr_2YCu_2O_{7+\delta}$ are 4+ and 2+, respectively. Assuming that $\delta = 0$ in $(Pb_{0.7}Cu_{0.3})Sr_2YCu_2O_{7+\delta}$, the Cu valency is 1.8+, which suggests that an increase in Cu valency up to 2.1+ ~ 2.2+ (i.e., an increase the hole concentration) may induce or increase the superconducting transition temperature, T_c. This hypothesis was confirmed by Liu *et al.* (*3*), who wrapped the samples in gold foil (to control the oxygen partial pressure during the heat treatment) and sintered in oxygen. These

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authors (*3*) reported that the cation ratio of Ca/Y between two conducting layers of CuO_2 in $(Pb_{0.75}Cu_{0.25})Sr_2(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$ is a crucial factor in controlling the superconductivity. More Ca^{2+} ion substitution into Y^{3+} sites led to an increase in hole concentration and T_c; the maximum solubility of Ca^{2+} ions in Y^{3+} sites is about 50% (i.e., $x = 0.5$). However, preparation of these compounds under alternative sintering conditions (for example, firing the sample in oxygen without encapsulation in gold foil) resulted in materials which had the optimum Ca and Y ratio but were still not superconducting after sintering. The possible reason was explained by Maeda *et al.* (*4, 5*), who pointed out that the superconducting transition of the Pb-1212 compound is markedly suppressed by excess oxygen situated in the insulating (Pb,Cu)O slabs. Many workers have applied a postannealing of as-sintered samples in air or oxygen (*4–7*), or a high pressure of oxygen (*8, 9*), to optimize the oxygen content in the (Pb,Cu)O layers and induce or improve the superconductivity in the Pb-1212 compound. Clearly, therefore, it is important to know the detailed relationships among the annealing temperature, oxygen content, and T_c in this newly discovered Pb-based 1212 material. In this paper, we demonstrate a systematic study of annealing the samples in oxygen to approach the optimum superconducting transition temperature in $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7+\delta}$.

2. Experimental

The samples were synthesized initially by solid state reaction. High-purity (>99.9%) powders of PbO, $SrCO_3$, $CaCO_3$, Y_2O_3, and CuO were weighed in the appropriate proportions to form the nominal composition $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7+\delta}$. The mixed powders were calcined at 800°C for 5 hr in air, pulverized, and pressed into pellets (10 mm in diameter and 2 mm in thickness). They were then sintered at 1000°C for 1 hr in oxygen and rapidly quenched in air. The as-sintered samples were subsequently annealed in the temperature range between 700 and 1000°C for 12 hr in oxygen and again quenched in air. The weight loss between the as-sintered and the annealed samples was measured.

Powder X-ray diffraction (XRD) analyses were performed using a Philips PW1710 X-ray diffractometer with Cu$K\alpha$ radiation. Bar-shaped samples ($1.5 \times 2 \times 10$ mm) were cut from the sintered pellets; these were then used 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. A Lake Shore 7000 ac susceptometer with a frequency of 333.3 Hz and a magnetic field of 1 Oe was used to measure the susceptibility of the samples.

3. Results and Discussion

In Fig. 1 we show powder XRD patterns of the $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7+\delta}$ samples annealed at the temperatures of (a) 700°C, (b) 800°C, (c) 900°C, (d) 930°C, (e) 950°C, and (f) 970°C. Almost all the peaks can be indexed on a tetragonal phase (marked by "●") with lattice constants $a \sim 3.8$ Å and $c \sim 11.9$ Å, except a small amount of hexagonal impurity phase (marked by "×") and an unidentified impurity phase (marked by "△"). Moreover, we observed a contraction of 0.04% in the a lattice parameter and an expansion in the c lattice parameter of 0.15% for samples annealed from 700 to 970°C, which may correspond to an oxygen loss during the high temperature annealing process. Adachi *et al.* (*7*) observed an orthorhombic phase in the sample annealed at 700°C in oxygen which they assumed to be caused by an oxygen content

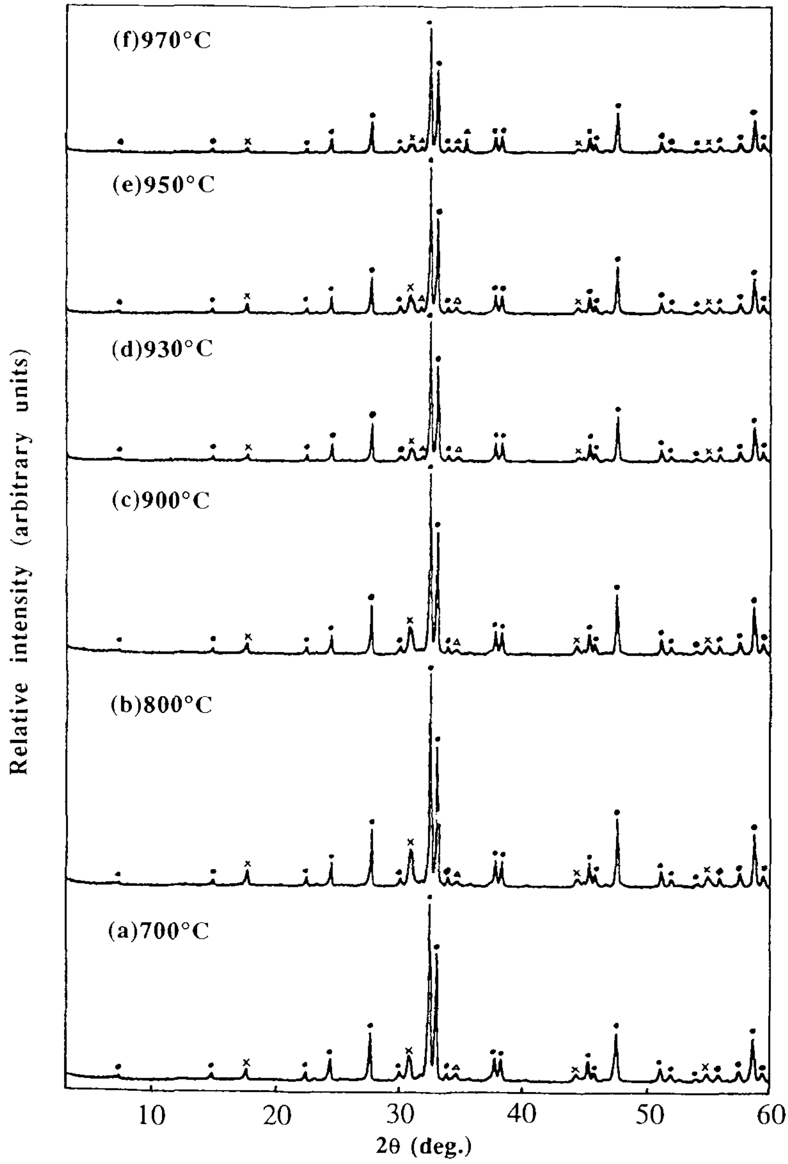

FIG. 1. Powder XRD patterns of the $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7-\delta}$ samples annealed at the temperatures of (a) 700°C, (b) 800°C, (c) 900°C, (d) 930°C, (e) 950°C, and (f) 970°C. A tetragonal superconducting phase labeled by "●," an impurity hexagonal phase labeled by "×," and an unidentified impurity phase labeled by "△" are also shown.

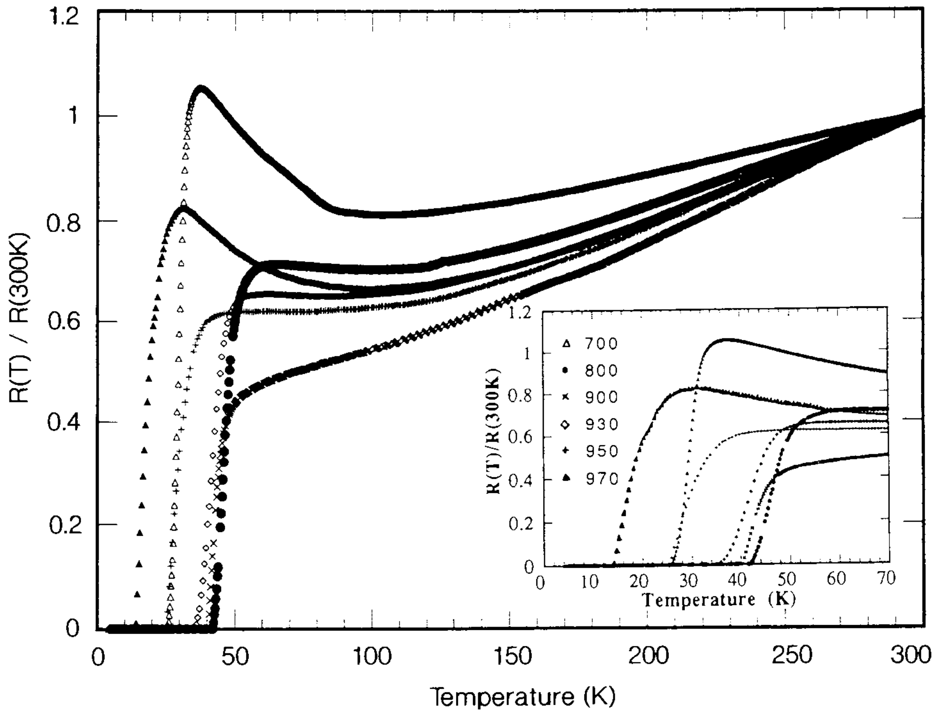

FIG. 2. Temperature dependence of the normalized resistance of the $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7+\delta}$ samples annealed at the temperatures of 700, 800, 900, 930, 950, and 970°C.

different from that of the tetragonal phase. However, when we used the same annealing condition, we failed to find any phase transformation, as shown in Fig. 1a.

The as-sintered sample has a semiconducting behavior in the normal state and superconducting transition temperatures of $T_{c(onset)}$ = 38 K, $T_{c(midpoint)}$ = 29 K, and $T_{c(zero)}$ = 8 K. In Fig. 2 we show the temperature dependence of the normalized resistance of the $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7+\delta}$ samples annealed at the temperatures of 700, 800, 900, 930, 950, and 970°C. When the samples were annealed from 700 to 970°C, maximum T_c was attained at an annealing temperature of 800°C and more metallic behavior in the normal state in the annealing temperature range of 800 to 950°C.

In Fig. 3 we summarize the characteristic superconducting properties (derived from Fig. 2) for the $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7+\delta}$ samples annealed at the temperatures of 700, 800, 900, 930, 950, and 970°C. The superconducting midpoint transition temperature, $T_{c(midpoint)}$, increases from 30 to 48 K for the samples annealed at 700 and 800°C, respectively. However, an increase in the annealing temperatures from 800 to 970°C decreases the $T_{c(midpoint)}$ from 48 to 21 K, respectively. Based on our studies, superconducting transition temperatures of $T_{c(onset)}$ = 60 K, $T_{c(midpoint)}$ = 48 K, and $T_{c(zero)}$ = 41.7 K were established when the sample was annealed at 800°C in oxygen.

In Fig. 4 we show the temperature dependence of the normalized relative susceptibility [taking the limiting, low temperature (5

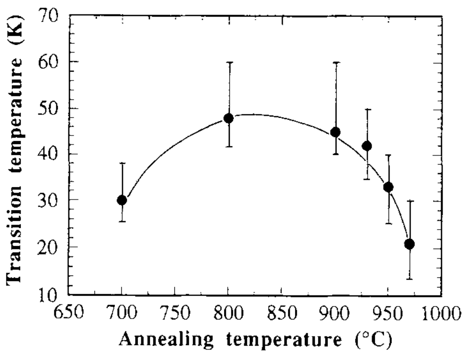

FIG. 3. Summarization of the characteristic superconducting properties (derived from Fig. 2) for the $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7+\delta}$ samples annealed at the temperatures of 700, 800, 900, 930, 950, and 970°C.

K) value as − 1 for the sample annealed at 800°C] of the powdered $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7+\delta}$ samples annealed at the temperatures of 700, 800, 900, 930, and 950°C. For samples annealed at 800, 900, and 930°C, the diamagnetic onset temperature appeared to be around 50 K, whereas for the samples annealed at 700 and 950°C, it occurred around 30 K. All the diamagnetic onset temperatures of the samples are consistent with the $T_{c(midpoint)}$ values measured by electrical resistance (Figs. 2 and 3). Moreover, the transition width of all the samples is broadened (see Fig. 4), which may be correlated with probable inhomogeneity of the oxygen content in the annealed samples.

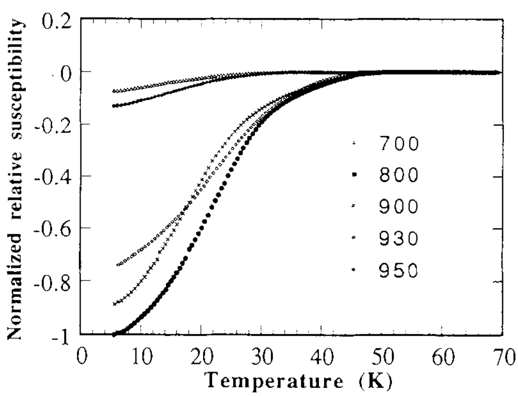

FIG. 4. Temperature dependence of the normalized relative susceptibility [taking the limiting, low temperature (5 K) value as − 1 for the sample annealed at 800°C] of the powdered $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7+\delta}$ samples annealed at the temperatures of 700, 800, 900, 930, and 950°C.

In Fig. 5 we show the dependence of the weight loss before and after annealing on the annealing temperature of the $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7+\delta}$ samples. A gradual weight loss was observed between 700 and 900°C in all cases. If we assume all the weight loss from oxygen, the above weight loss corresponds to a value of $y = 0.1$ for $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7+\delta-y}$. This small amount of oxygen loss results in an increase in $T_{c(midpoint)}$ from 18 K for the as-sintered sample to 48 K for the sample annealed at 800°C. These results are in agreement with the report from Maeda *et al.* (*4*, *5*). When the annealing temperature was raised above 900°C in our samples, a large weight loss was found (Fig. 5), which may correspond to loss of both oxygen and lead from the samples.

Maeda *et al.* (*5*) pointed out that excess oxygen in the $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})$

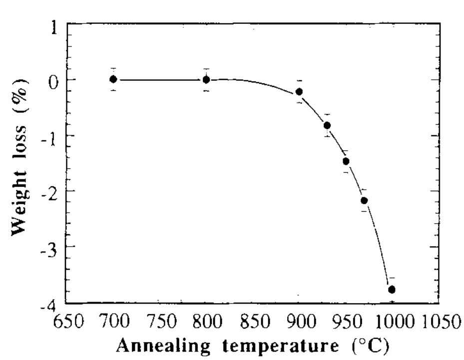

FIG. 5. Dependence of the weight loss before and after annealing on the annealing temperature of the $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7+\delta}$ samples.

$Cu_2O_{7+\delta}$ compound possibly occupied a $2f$ site on a (Pb,Cu)O layer based on their TOF neutron powder diffraction data. This $2f$ site oxygen corresponds to the chain site oxygen in $YBa_2Cu_3O_{7-\delta}$. The excess oxygen in the as-sintered $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7+\delta}$ material appears to act as a hole-trap which leads to a decrease in hole concentration in the conducting CuO_2 plane and therefore suppresses the superconductivity. Based on our studies, we believe that annealing as-sintered samples at 800 ~ 900°C in oxygen is an effective method to remove the excess oxygen (0.1 oxygen per formular unit) and improve the superconducting properties.

Acknowledgments

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