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Impact of Pr doping on superconductivity in $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$

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A systematic study on the nature of Pr doping in $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ ($0.2\leqslant x\leqslant 0.6$) has been made on films grown by laser ablation. These films are a metastable Bi-2212 phase which has not yet been grown in this doping range by other methods. The film with $x=0.2$ shows the highest zero-resistance temperature (T_{cz}) of about 65 K. T_{cz} of the films decreases with increasing Pr content yielding a metal-to-insulator transition for $x>0.5$. By analyzing x-ray photoelectron spectra we show that Pr is trivalent. From this we are able to demonstrate that the variation of T_{cz} with doping is predominantly due to hole filling induced by the trivalent Pr.

I. INTRODUCTION

Most materials of the $LnBa_2Cu_3O_7$ system (Ln: lanthanide and Y) exhibit superconductivity at about 90 K, and the value of the critical temperature (T_c) does not change dramatically[1,2] with the change of the element Ln. One exception to this behavior is insulating $PrBa_2Cu_3O_7$, and some experimental results indicate that valence of Pr in $PrBa_2Cu_3O_7$ is trivalent, while others indicate tetravalent (Refs. 3 and 4). To explain its nonsuperconductivity, many models have been proposed: (i) hole filling due to Pr^{4+} ion,[4] (ii) replacement of Ba site with Pr^{3+} (Ref. 5) and (iii) localization of holes by hybridization of Pr $4f$ and O $2p$ orbitals.[4,6] Among them, the model of hybridization has been widely accepted, though Blackstead *et al.* pointed out that the model cannot explain the difference in Pr content y, at which superconductivity disappears, and $|dT_c/dy|$ between $Y_{1-y}Pr_yBa_2Cu_3O_7$ and $Y_{1-y}Pr_yBa_2Cu_4O_8$ systems.[7]

Recently, however, bulk superconductivity has been observed in the single crystal of $PrBa_2Cu_3O_7$ prepared by the traveling-solvent floating-zone (TSFZ) method.[8–10] The results showed: Superconductivity of the sample was very sensitive to the growth condition, the valence of Pr was trivalent in the sample, and the lattice parameter c of the sample was longer than the nonsuperconducting sample. Further, in the $LnBa_2Cu_3O_7$ system (Ln: lanthanide and Y), only the superconducting $PrBa_2Cu_3O_7$ compound showed large T_c enhancement under a high pressure;[9–11] the maximum increase of T_c was by about 50 K and the value of T_c was 105 K. However, neither the reason for the difference between the superconducting and nonsuperconducting $PrBa_2Cu_3O_7$ compounds nor the reason why only the superconducting $PrBa_2Cu_3O_7$ compound has large pressure effect on T_c among the materials of the $LnBa_2Cu_3O_7$ system has yet been understood. Therefore it is interesting to investigate other superconductors containing Pr and to compare them with the $PrBa_2Cu_3O_7$ compound.

The Bi-2212 phase in the Bi-Pr-Ca-Cu-O system is a superconductor containing Pr prepared by solid-state reaction. The crystal structure of the compound was reported to be similar to the Bi-2212 phase of $Bi_2Sr_2CaCu_2O_{8+\delta}$, and the sample of $Bi_2Pr_{0.5}Ca_{2.5}Cu_2O_{8+\delta}$ (Ref. 12) showed the highest zero resistivity temperature (T_{cz}) of 45 K among the materials of the $Bi_2Ln_xCa_{3-x}Cu_2O_{8+\delta}$ systems[12–17] (Ln=La, Pr, Nd, Sm, Eu, and Gd). However, in the $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ system, an almost single phase sample could be obtained only for the limited composition of $x=0.5$, and other samples were of the multiphase. On the other hand, the thin-film preparation method allows one to make metastable Bi-2212 phase that cannot be synthesized by solid-state reaction. For example, an almost single Bi-2212 phase sample in the bulk $Bi_2La_xCa_{3-x}Cu_2O_{8+\delta}$ system was only $x=0.5$ (Ref. 12), while thin-film preparation method has been able to make the Bi-2212 phase with a wide composition range,[18] $0.2\leqslant x\leqslant 0.7$.

We have prepared the Bi-2212 films with the wide composition range of Pr, and have investigated the role of Pr for superconductivity in the $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ system. In this paper, we report on the preparation and physical properties of Bi-2212 thin films of this system.

II. EXPERIMENT

The films were synthesized by the laser ablation method using $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ compound targets. First, pellets for the target were prepared by solid-state reaction. High purity powders of Bi_2O_3, Pr_6O_{11}, $CaCO_3$, and CuO were mixed to a nominal composition of $Bi_2Pr_xCa_{3-x}Cu_2O_8$ and pressed to pellets, which were heated at 820 °C for 10 h in air. The pellets for the target were reground, pressed, and sintered at 820 °C for 10 h in air again. The targets were placed in a high-vacuum chamber at a base pressure of 1.0×10^{-7} Torr and ablated by a pulsed KrF excimer laser ($\lambda=248$ nm, $\tau=23$ ns, 100 mJ/pulse) in 0.02 Torr oxygen

TABLE I. Pr content x of the target materials, film composition determined by SEM-EDS, substrate temperature, annealing temperature in O_2, lattice parameter c, T_{cs}, $T_{c\mathrm{mid}}$, T_{cz}, and T_{cm} of the $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ films.

Pr(x)	Film composition (SEM-EDS)	Deposition temp.	O_2 temp.	c (Å)	T_{cs} (K)	$T_{c\mathrm{mid}}$ (K)	T_{cz} (K)	T_{cm} (K)
0.2	$Bi_{1.79}Pr_{0.20}Ca_{2.64}Cu_{1.59}$	600 °C	760 °C	30.02	80.0	72.5	65.0	75.0
0.3	$Bi_{1.65}Pr_{0.30}Ca_{2.53}Cu_{1.71}$	630 °C	790 °C	29.97	77.0	67.0	57.0	70.0
0.4	$Bi_{1.79}Pr_{0.40}Ca_{2.82}Cu_{1.77}$	650 °C	790 °C	29.95	55.0	37.5	20.0	51.0
0.5	$Bi_{1.91}Pr_{0.50}Ca_{2.43}Cu_{1.81}$	670 °C	820 °C	29.92	45.0	30.0	15.0	
0.6	$Bi_{1.57}Pr_{0.60}Ca_{2.09}Cu_{1.56}$	670 °C	820 °C	29.94				

flow. The energy density of the laser at the target was 1.0 J/cm^2, and the pulse repetition rate was 4.0 Hz. The ablated materials were deposited on the MgO (100) substrate placed at a distance of 3.0 cm from the target in the chamber. The thickness of the films was 1.5 μm, and the deposition rate of the films was 3.0 Å per laser shot.

For the $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ films, the substrate temperatures were monitored by an optical pyrometer and were kept at 600–670 °C. After the deposition, O_2 annealing treatment was performed under 1 atm O_2 flow for 30 min at the temperature of 760–820 °C. The substrate and annealing temperatures of the films are summarized in Table I.

X-ray-diffraction patterns were obtained with a diffractometer using Cu$K\alpha$ radiation. The temperature dependence of electrical resistivity (ρ vs T) was measured by the dc four-probe method. The temperature dependence of magnetization (M vs T) was measured with a dc superconducting quantum interference device (SQUID) magnetometer. The composition of the films was analyzed by scanning electron microscopy–x-ray energy dispersion spectroscopy (SEM-EDS). The x-ray photoelectron spectroscopy (XPS) measurement was performed using Mg$K\alpha$ radiation.

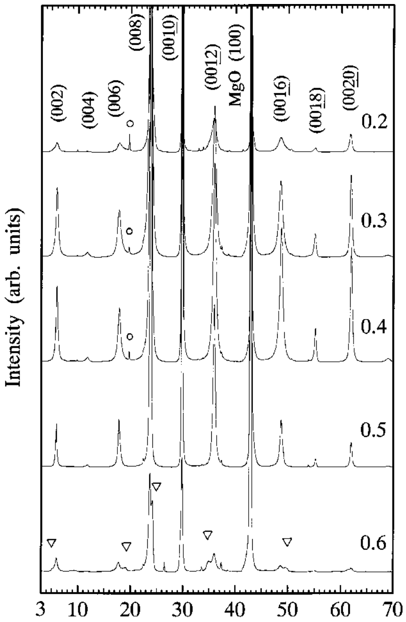

FIG. 1. X-ray-diffraction patterns of $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ films with $0.2 \leqslant x \leqslant 0.6$. Circles, impurity phase of Bi-Ca-O compound; triangles, Bi-2223 phase in the Bi-Pr-Ca-Cu-O system.

III. RESULTS

X-ray-diffraction patterns of the Bi-2212 thin films in the $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ system $(0.2 \leqslant x \leqslant 0.6)$ are shown in Fig. 1. From the figure, we can see that most of the diffraction peaks can be attributed to the c-axis oriented Bi-2212 phase. However, the impurity phase of Bi-Ca-O is mixed to a larger extent for smaller Pr content x. Though results for the films with $x < 0.2$ are not shown in the figure, these films have been found to be of the multiphase consisting of the Bi-2212 phase, Bi-Ca-O and other unknown impurity phases. The result indicates that Pr is necessary to stabilize the 2212 structure.

On the other hand, the film with $x = 0.6$ contains Bi-2212 and Bi-2223 phases of the Bi-Pr-Ca-Cu-O system together with unknown phases. The fact that the film contains the Bi-2223 phase shows the existence of the Bi-2223 phase in the Bi-Pr-Ca-Cu-O system. The detailed result of the Bi-2223 phase will be published elsewhere.[19] When x exceeds 0.6, the samples become of the mixed phase consisting of the present Bi-2212 phase, the Bi-2201 phase of the Bi-Pr-Ca-Cu-O system[20] and impurity phases. These results indicate that the composition range of Pr to stabilize the 2212 structure is $0.2 \leqslant x \leqslant 0.6$. This result is in contrast to the bulk Bi-2212 phase of $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$, as only for $x = 0.5$ an almost single phase was obtained.[12] From these results, we can emphasize that the present thin-film processing method is one of the most useful methods to prepare new metastable phases.

M vs T for the Bi-2212 films in the $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ system is shown in Fig. 2. The measurement was performed on heating after cooling within a magnetic field of 200 G, which was applied parallel to the c axis of the film. In the

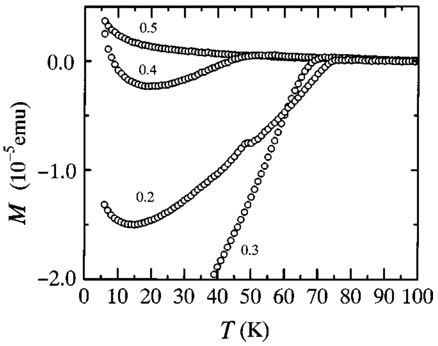

FIG. 2. M vs T of the $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ films with $0.2 \leqslant x \leqslant 0.5$.

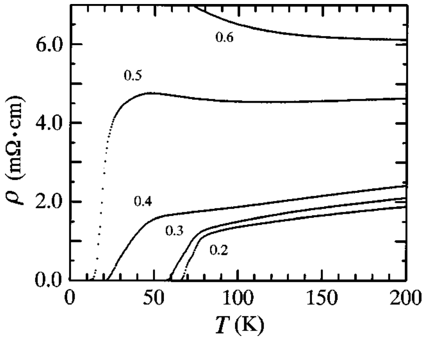

FIG. 3. ρ vs T of the $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ films $(0.2 \leqslant x \leqslant 0.6)$.

figure, the film with $x=0.2$ shows the highest starting temperature of diamagnetic signal (T_{cm}), and its value decreases with increasing Pr content x. The film with $x=0.5$ does not show the diamagnetic signal. The T_{cm} value of each film is shown in Table I. The result indicates that the $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ film changes from a superconductor to a nonsuperconductor with increasing x.

ρ vs T for the Bi-2212 films in the $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ system is shown in Fig. 3. From the figure, we can see that the film with $x=0.2$ shows the highest zero resistivity temperature (T_{cz}) at 65 K in the system. This value is higher by 20 K than that of the bulk sample.[12] Moreover, the starting temperature of resistivity drop (T_{cs}), the middle temperature between T_{cs} and T_{cz} ($T_{c\mathrm{mid}}$) and T_{cz} of the films decreased with increasing Pr content x. When x exceeded 0.5, metal-insulator transition occurred and the film with $x=0.6$ showed semiconductorlike temperature dependence with no trace of resistivity drop.

From the magnetic and resistivity measurements of the $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ films, it is clear that T_c of the film decreases with increasing Pr content x, and the film changes from a superconductor to an insulator. From the results mentioned in the previous section, we have found that T_c's of Bi-2212 films in the $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ system decrease with increasing Pr content x. In order to clarify the origin of this decrease in T_c, we need to address the valence of Pr. From the experimental results described below, we are able to show that Pr is trivalent.

Figure 4 shows XPS spectra in the binding-energy range of 100 to 140 eV for the $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ films $(0.2 \leqslant x \leqslant 0.6)$ as well as the bulk compounds Pr_6O_{11} and Pr_2CuO_4. In the case of the Pr_6O_{11} compound, the peak of Pr $4d$ is observed at the binding energy of about 115 eV; and an additional structure denoted by $4f$,[1] at the energy of about 126 eV. The former shows the existence of Pr^{3+}, and the latter, the existence of Pr^{4+} (Ref. 3). Since the valence of Pr is trivalent in the Pr_2CuO_4 compound, the peak of Pr $4d$ (115 eV) is observed without the $4f$ (Ref. 3) peak. On the other hand, in the $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ system, the peaks of Pr $4d$ and Cu $3s$ are present[3] at 115 and 121 eV and the peak intensity of Pr $4d$ increases with increasing Pr content x. However, the $4f$ (Ref. 3) peak which shows the existence of Pr^{4+} is absent. The Pr $4d$ spectra of the films is similar to the Pr_2CuO_4 compound than the Pr_6O_{11} compound though there is a shoulder on the low-energy side of the Pr $4d$ peak. From the result, we conclude that the valence of Pr is trivalent in the films.

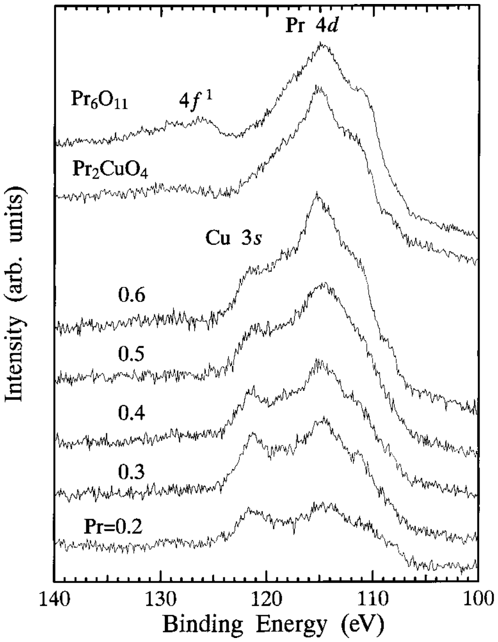

FIG. 4. XPS spectra for the $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ films $(0.2 \leqslant x \leqslant 0.6)$ and the reference samples of Pr_6O_{11} and Pr_2CuO_4 compounds.

Finally, we discuss the role of Pr^{3+} for superconductivity in the system. In Fig. 5, the variations, with Pr content x and hole concentration p, of $T_{c\mathrm{mid}}$ in the $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ system are shown (closed triangles). The data of the $Bi_2Sr_2Pr_xCa_{1-x}Cu_2O_{8+\delta}$ (open triangles) is cited from Ref. 21 for comparison. The hole concentration p of the systems has been calculated by the formula

$$p=0.3-x/2 \tag{1}$$

by assuming the following experimental facts of the $Bi_2Sr_2Pr_xCa_{1-x}Cu_2O_{8+\delta}$ system: (i) the oxygen content of the system is a constant independently of Pr content x, (ii) Pr is trivalent, (iii) one Pr^{3+} atom substituted for a Ca^{2+} atom diminishes one hole, and (iv) the hole concentration p in

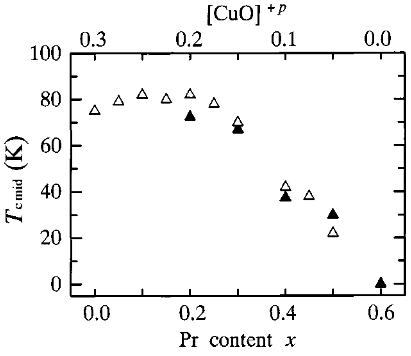

FIG. 5. Variations of $T_{c\mathrm{mid}}$ in the $Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}$ system with $0.2 \leqslant x \leqslant 0.6$ as a function of Pr content x and hole concentration p (closed triangle). The data of the $Bi_2Sr_2Pr_xCa_{1-x}Cu_2O_{8+\delta}$ system (open triangle) (Ref. 21) are given for comparison. The hole concentration p of the systems was calculated by the formula $p=0.3-x/2$ (see the text).

$[\mathrm{CuO}]^{+p}$ is 0.3 for $x=0.0$. As shown in the figure, the two systems show the parabolalike correlation of $T_{c\mathrm{mid}}$ with p, that is, $T_{c\mathrm{mid}}$ increases with increasing hole concentration p, takes on a maximum at $p=0.2$ and then decreases. Therefore the decrease of T_c in the system is interpreted in terms of hole filling due to the substitution of Pr^{3+} for Ca^{2+}.

IV. CONCLUSION

We have synthesized Bi-2212 thin films of the $\mathrm{Bi_2Pr_xCa_{3-x}Cu_2O_{8+\delta}}$ system prepared by the laser ablation method. For this system, the Bi-2212 films were obtained in a wide composition range, $0.2 \leqslant x \leqslant 0.6$. The films in this composition range were of the metastable Bi-2212 phase that have not been produced by solid-state reaction except the film with $x=0.5$. The film with $x=0.2$ showed the highest values of T_{cm} and T_{cz} at about 75 and 65 K in the system. The value of T_{cz} was higher by about 20 K than that previously reported for the bulk Bi-2212 sample. Further, T_c of the films decreased with increasing Pr content x, and metal-insulator transition occurred when x exceeded 0.5. The variation of T_c was explained in terms of hole filling due to the replacement of Ca^{2+} with Pr^{3+}.

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