Phase separation and oxygen variation in Pr-doped $Bi_2Sr_2CaCu_2O_{8+\delta}$

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The structural and electrical properties of $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ have been investigated as a function of x. Powder-x-ray-diffraction patterns indicate that this system forms a continuous solid solution. It is found that phase separation exists in this system. Two phases with different modulated periods appear as the Pr doping changes. At low doping levels, the short-period phase dominates, while at high doping levels the long-period phase dominates. The short-period phase and the long-period phase are thought to correspond to the poor-Pr- and rich-Pr-concentration phases, respectively. T_c was found to increase slightly for $x \leq 0.1$, decrease linearly for $0.1 \leq x \leq 0.4$, then to be depressed rapidly for $0.4 \leq x \leq 0.5$, and finally to disappear at $x=0.6$. The valence of Pr was inferred to be close to $+3$ from the measurement of the oxygen content and the comparison with other rare-earth-doped Bi-2212 systems. The variation of T_c was explained in terms of hole filling and phase separation.

It is known that substitution of most trivalent rare earths on the Y site in $YBa_2Cu_3O_{7-\delta}$ (Y-123) does not dramatically affect superconductivity. The variations in T_c are typically 1–2 K.[1] One exception to this behavior is $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, where T_c is depressed rapidly with increasing x and $T_c \to 0$ for $x_{cr} \approx 0.55$.[2-4] Moreover, unlike other $RBa_2Cu_3O_{7-\delta}$ compounds (R stands for trivalent rare earths), $PrBa_2Cu_3O_{7-\delta}$ is a semiconductor though it possesses an identical orthorhombic structure with $YBa_2Cu_3O_{7-\delta}$. This anomalous behavior of Pr has aroused much interest in studying $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ intensively to clarify the mechanism responsible for the nonsuperconductivity of $PrBa_2Cu_3O_{7-\delta}$.

The valence of Pr ions inferred from magnetic measurement,[5] Hall effect,[6] neutron diffraction,[7] and other studies[8,9] is greater than $+3$ and possibly close to $+4$, implying the depression of T_c as a result of hole filling in the CuO_2 sheets. On the other hand, spectroscopic measurements[10-12] suggest that there is substantial hybridization between the $4f$ electrons on the Pr site and the $2p$-$3d$ holes within the CuO_2 sheets. This hybridization may cause the electron (hole) pairs to break or to be localized, accounting for at least a portion of the depression of T_c with doping of Pr. Our recent studies[13] on $Pr_{0.2}Yb_{0.8-x}La_xBa_2Cu_3O_{7-\delta}$ support this argument. It has been found that the larger the radius of the rare earth

R^{3+}, the lower the required Pr^{3+} concentration, or rather the lower the critical concentration x_{cr} at which the T_c of $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ is depressed to zero. A linear correlation between the critical concentration of Pr and the radius of the rare earths has been found to exist.[13,14]

The Ca site in $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) has an identical crystallographic environment to the R site in R-123, both occupying the center of Cu-O octahedra. Experiments have indicated that R can substitute for Ca in Bi-2212 and the doped structure does not change fundamentally. R doping studies of $Bi_2Sr_2CaCu_2O_{8+\delta}$ have been extensively carried out. T_c was found to decrease with increasing R^{3+} with the critical concentration $x_{cr}=0.4$–0.6.[15-22] The critical concentration for Ce doping is about half that of other trivalent rare earths.[22,23] Similar results were also found in $Bi_2Sr_{2-x}R_xCaCu_2O_{8+\delta}$ ($R = $ Nd and Ce).[24] The filling of a $3d$ hole by an extra electron and the decrease of carriers in the CuO_2 sheets have been implicated in the depression of T_c with R doping[19,21,24] in these systems. No significant magnetic pair breaking was observed in the Pr- and Gd-doped systems. In addition, a dimensional changeover from two to three dimensions was observed in variable-range hoping in the Pr-,[22] Ce-,[22] Eu-,[20] Dy-,[20] and Tm-doped[20] Bi-2212 systems.

In this paper, we report our results of a systematic study of the properties of $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ as a

function of x. The structural features and electrical properties were analyzed within the framework of current understanding of Pr-doped Bi-2212.

$Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ samples with $x = 0.0$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 were prepared by solid-state reaction of appropriate mixtures of high-purity Pr_6O_{11}, Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO. The powders were mixed, ground, and fired at 800 °C for 12 h in air. Two or three additional firings for 24-h intervals with intermediate grinding were performed before the samples were pressed into pellets. The pellets were then calcined at 840–950 °C with increasing Pr doping levels.

Phase identification and measurement of lattice parameters were performed on a Rigaku automatic diffractometer using Cu $K\alpha$ radiation at room temperature. High-purity Si was added to the samples as an internal standard to correct the positions of the diffraction lines. The lattice parameters were then calculated using a standard least-squares method.

The electrical resistivity vs temperature was measured on rectangular bars cut from the sintered pellets employing the standard dc four-probe technique with silver paint contacts attached to the electric leads. Data were collected from 300 down to 4.3 K.

Powder-x-ray-diffraction patterns indicated that all samples are single phase and $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ forms a continuous solid solution over the entire compositional range of x. As an example, shown in Fig. 1 is the diffraction pattern for the sample with $x = 0.6$ and its indexed results. It has been reported that pure and Pr-doped Bi-2212 possess an orthorhombic structure with space group $Fmmm$ or $Amaa$.[22,25–27] Here we adopt $Fmmm$ with lattice parameters $a \approx b$ since the difference between a and b is so small that it is difficult to discern the split of the related diffraction lines in the powder-diffraction patterns. The variation of lattice parameters with x is depicted in Fig. 2. The c parameter decreases monotonically with x, while the a parameter slightly increases with x. The shrinkage in c can be attributed to the increase in oxygen content due to trivalent or tetravalent Pr ion substitution for divalent eight-coordinated Ca. The slight expansion in a suggests that the CuO_2 sheets accept
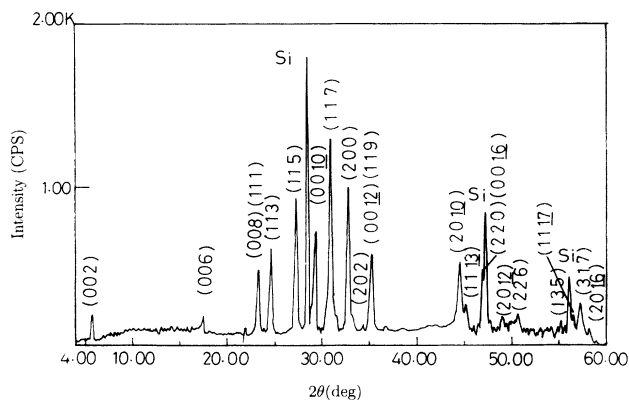

Pr dopant concentration x

FIG. 2. Variation of lattice parameters a and c vs dopant concentration of Pr. Standard deviation < 0.002 Å for a and < 0.01 Å for c.

electrons and consequently hole filling occurs. The hole concentration has been found to decrease with increased doping level of Pr in this system.[17]

In order to understand the details of the variation of the lattice parameters, we measured the oxygen content for all samples by iodometric titration. Spectral-purity CuO was used as a standard to correct the concentration of $Na_2S_2O_3 \cdot 5H_2O$. The measurement error is estimated to be less than 0.3%. Figure 3 shows the variation of oxygen content vs x for $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$. The oxygen content n increases almost linearly with x, the doping level of Pr. Fitting n vs x yields the equation $n = 8.19 + 0.34x$, where 8.19 corresponds to the oxygen content for pure Bi-2212, and 0.34 is the slope of the line. The line slope, 0.34, is less than 0.5, half of the difference of valence between Pr^{3+} and Ca^{2+} (assuming the valence of Pr is $+3$). This means that the structure cannot accommodate enough oxygen to neutralize the extra elec-

FIG. 1. X-ray-diffraction pattern of $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ for $x = 0.6$. High-purity Si was added as a standard to correct the position of diffraction lines.
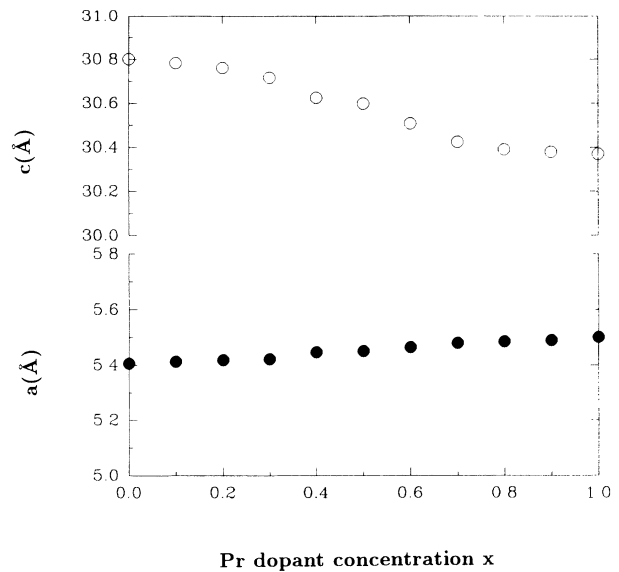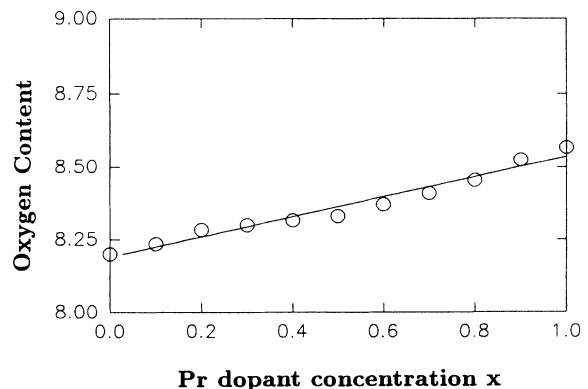

Pr dopant concentration x

FIG. 3. Variation of oxygen content of $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ vs dopant concentration of Pr, x.

trons introduced by the substitution. The remaining electrons will bring about the reduction of Cu in the CuO_2 sheets. In the present case, 0.32 $[=2(0.5 - 0.34)]$ Cu^{2+} ions will be reduced by the substitution of one Pr ion for one Ca ion. This value is approximately equal to that (0.34) for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$.[28] It is, therefore, reasonable to infer that the valence of Pr in $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ is close to $+3$ and the hole filling should be responsible, at least partially, for the depression of T_c in this system.

Shown in Fig. 4 are the variations of T_c vs x for $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$, where T_c is defined as the temperature at which the resistivity corresponds to 50% of the extrapolated normal-state value, while the transition width indicated by vertical bars is defined as the temperature difference between the 90% and 10% values. T_c slightly increases with $x \leq 0.1$, reaches maximum value at $x = 0.1$, and decreases almost linearly for $0.1 \leq x \leq 0.4$. Then there is an abrupt decrease in T_c for $0.4 \leq x \leq 0.5$. Superconductivity finally disappears for $x \leq 0.6$. On the other hand, the T_c(onset) remains almost unchanged for $0 \leq x \leq 0.4$, while $T_c(0)$ decreases with x in the same compositional region. Both T_c(onset) and $T_c(0)$ have a dramatic drop for $0.4 \leq x \leq 0.5$. Olivier et al.[29] found similar variations of T_c(onset) and $T_c(0)$ in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$. They thought that abrupt drops of T_c resulted from the existence of a compositional range of Y in samples at certain doping level of Y.

One striking feature in $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ shown by this study is the appearance of phase separation as the doping of Pr increases. Figures 5(a)–5(d) are electron-

diffraction patterns taken for compounds with $x = 0.2$, 0.6, and 1.0. All electron incidences parallel to the c axis. Superlattice spots showing a one-dimensional modulated structure as well as fundamental spots are observed for all samples. The period for the compound with $x = 0$ has been reported to be $4.8b$.[30,31] In this study, a modulated period for $x = 0.2$ is determined to be $4.5b$. As the doping level increases, this period decreases to $4.3b$ at $x = 0.6$ and disappears at $x = 1.0$. Meanwhile, another period of $8.5b$ appears at $x = 0.6$ and decreases to $8.0b$ for $x = 1.0$. A period of $8.3b$ is observed to exist predominantly at $x = 0.8$. Inoue et al.[31] also found a long modulated period $8b - 10b$ in the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ system. Considering that the volume of two structures with different periods varies in an opposite way with Pr doping, we have reason to think that these two periods correspond to two phases with different Pr concentration. At low doping levels, the short period dominates, while at high levels, the long period dominates. For the intermediate doping levels, the two periods coexist equally. This is understood to relate to the variations of T_c vs doping of Pr, where T_c(onset) is essentially unchanged and $T_c(0)$ decreases for $0.0 \leq x \leq 0.4$. Hence the short-period phase corresponds to the Pr-poor phase, which possesses high T_c; and the long-period phase corresponds to the Pr-rich phase, which possesses low T_c. The wide transitions of T_c suggest intergrowth of these two phases in grains. The abrupt change of T_c for $0.4 \leq x \leq 0.5$ suggests that the
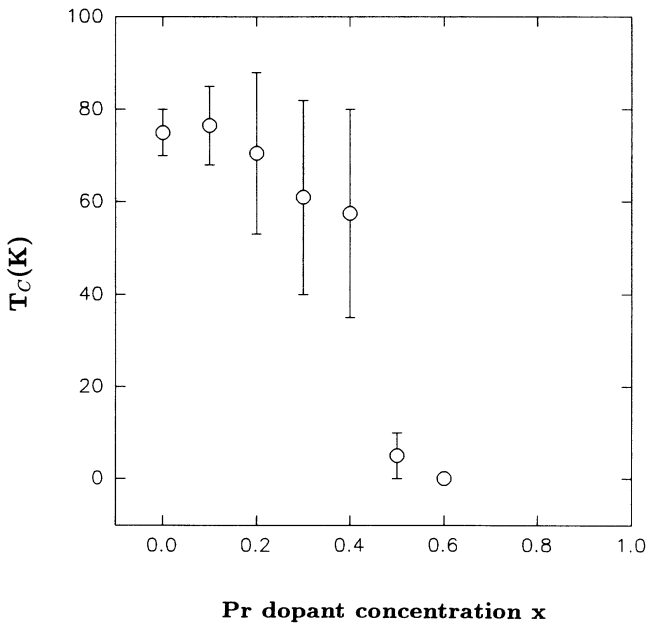

FIG. 4. Variation of T_c vs dopant concentration of Pr in $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$, where T_c is defined as the temperature at which the resistivity corresponds to 50% of the extrapolated normal-state value, while the transition width indicated by vertical bars is defined as the temperature difference between the 90% and 10% values.
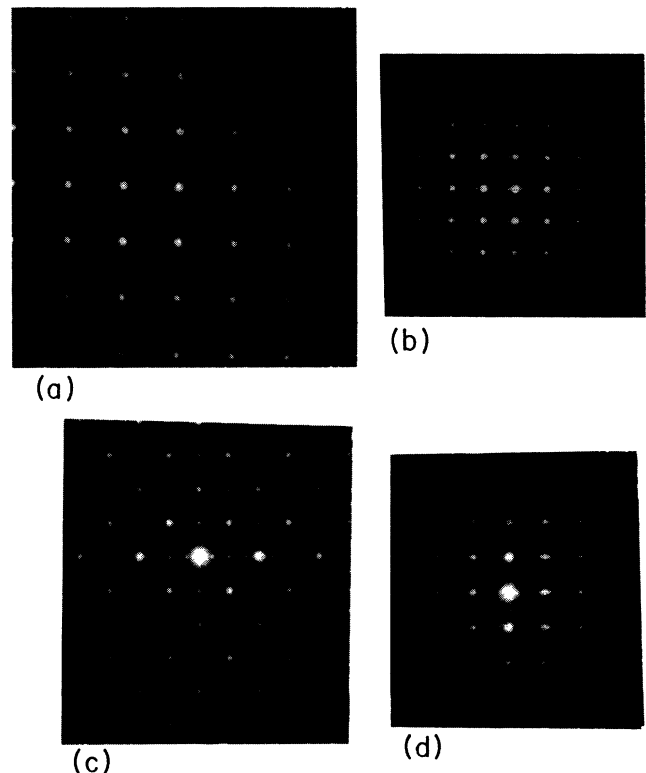

FIG. 5. Electron-diffraction pattern of $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ for (a) $x = 0.2$, (b) $x = 0.6$, (c) $x = 0.6$, and (d) $x = 1.0$. Electron incidence of all patterns is parallel to the c axis.

grains of the short-period phase may be poorly connected with each other and electrical transportation is controlled by the long-period phase.

In conclusion, studies of the structural and electrical properties and oxygen content of the $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ system indicate that the mechanism responsible for depression of T_c is mainly hole

filling, not magnetic pair breaking. There exists phase separation of two phases with different modulated periods in the presently studied system, which is thought to have effects on the electrical properties.

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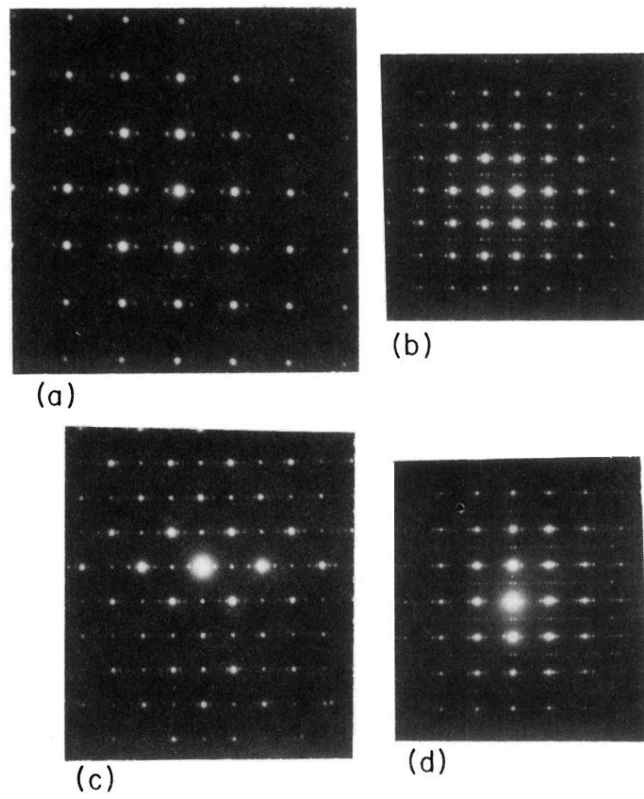
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