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Role of Pr in Eu-123 high T_c nanometer-sized superconductors

V.R. Huse, V.D. Mote, B.N. Dole*

Advanced Materials Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431004, India

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Abstract

Samples of $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ with compositions $x=0.0$, 0.1 and 0.3 were prepared by the solid state reaction route. The structural, electrical and microstructural properties were investigated by X-ray diffraction, Physical Property Measurement System (PPMS) and scanning electron microscopy (SEM) techniques respectively. The lattice parameters, oxygen deficiency, hole concentration in the CuO_2 plane, average charge on Cu–O plane were evaluated from X-ray diffraction data. From XRD data, it is observed that the lattice parameters and oxygen deficiency increase with increasing Pr concentration. It was also observed that the hole concentration in CuO_2 plane and average charge on Cu–O plane decrease with increasing Pr concentration. The electrical resistivity of all samples was measured in the temperature range 300 K to 4 K. It was found that the normalized transition temperature decreases with increasing Pr concentration. This may be due to reduction in hole concentration or average charge on Cu–O plane. From scanning electron microscopy images, it was observed that grain size increases with increasing Pr concentration. This increase may be the possible cause for suppression of T_c.

Keywords: B. Grain size; Lattice parameters; Oxygen content; Transition temperature; Hole concentration

1. Introduction

The discovery of superconducting oxides by Bednorz and Muller [1] predicted that higher transition temperature might be achievable in metallic oxides. Many researchers and theorists were working on the problem and tried to enhance the critical temperature of the system. After 1986, a great deal of efforts has been made to explain the mechanism responsible for the superconductivity in the new oxide high temperature superconductors. Compounds of the $RE_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ where RE is the rare earth elements except (Ce, Pr, Pm and Tb) form an important family of superconducting materials with the critical temperature near 90 K [2–7]. The reduction in T_c for $REBa_2Cu_3O_{7-\delta}$ series where RE = Y or other rare earth elements except (Ce, Pr, Pm and Tb) is strongly suppressed by the partial substitution of Pr for the RE element. The origin of disappearance of superconductivity due to Pr substitution has not been completely understood although many researchers have studied these problems.

In the present study we wish to throw some more light on Pr substituted Eu-123 series. This system has its own importance because the Pr is having higher magnetic moment as compared to Eu. The aim of the present work is to investigate the effect of Pr substitution at rare earth site of $EuBa_2Cu_3O_{7-\delta}$ series.

2. Experimental

Samples of $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ with compositions $x=0.0$, 0.1 and 0.3 were prepared by the solid state reaction route. The appropriate mixtures of high purity (Aldrich make 99.99%) Eu_2O_3, $BaCO_3$, Pr_6O_{11} and CuO were used. The powders were mixed thoroughly, ground for 3 h and calcined twice at 915 °C for 24 h with intermediate grinding for 3 h. The calcined samples again ground for 2 h for making pellets and finally sintered at 930 °C for 24 h. These pellets were annealed in oxygen

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*Corresponding author. Tel.: +91 240 2403385; fax: +91 240 2403335.
E-mail addresses: drbndole.phy@gmail.com, bndole@indiatimes.com (B.N. Dole).

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atmosphere for 24 h at 450 °C followed by slow cooling at 1 °C/min up to room temperature.

The structural parameters of samples were investigated from X-ray diffractometer (Model: PW-3710) employing CuK_α radiation ($\lambda = 0.1541$ nm). Resistivity measurement was performed on the rectangular specimens in the temperature range 300 K to 4 K using a Physical Property Measurement System (PPMS). The microstructural study was carried out using (Model: JSM-7600F) Scanning Electron Microscopy (SEM).

3. Result and discussion

3.1. XRD study

X-ray diffraction patterns were recorded at room temperature by X-ray diffractometer (Model PW-3710) using CuK_α radiation and only high intensity peaks are indexed as shown in Fig. 1. The peak intensity goes on decreasing with increasing Pr concentration. The X-ray diffraction of all samples revealed that they have the orthorhombic crystal structure with no evidence of impurity phases.

The lattice parameters, oxygen deficiency, hole concentration in CuO_2 plane, average charge on Cu–O chain were evaluated from X-ray diffraction data and tabulated in Table 1.

The lattice parameters of all samples were calculated using well known formula

$$d_{hkl} = \frac{1}{\sqrt{h^2/a^2 + k^2/b^2 + l^2/c^2}} \tag{1}$$

where a, b, c are the lattice parameters and (hkl) are the Miller indices.

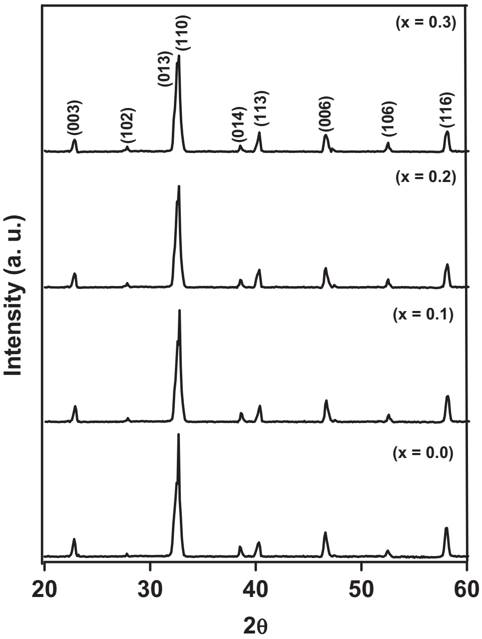

Fig. 1. XRD patterns of $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system.

Table 1
The lattice parameters, oxygen deficiency, hole concentration and average charge of $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system.

Pr conc. (x)	Lattice parameters (nm)			Oxygen deficiency (δ)	Hole concentration (P_{sh})	Average charge (p)
	a	b	c			
0.0	0.3835	0.3896	1.1683	0.09	0.20	0.27
0.1	0.3839	0.3899	1.1690	0.14	0.13	0.23
0.3	0.3843	0.3907	1.1693	0.17	0.02	0.22

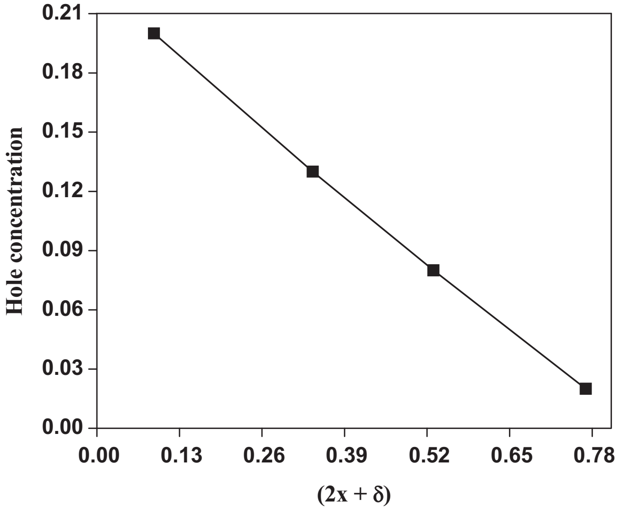

Fig. 2. Hole concentration vs ($2x+\delta$) of $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system.

It is interesting to note that the crystal structure remains nearly the same, i.e. orthorhombic for all samples with increasing Pr concentration.

It is well known that oxygen content is responsible for charged reservoir CuO_2 planes in a superconductor. A reduction in oxygen content which lowers the number of oxygen atoms in Cu–O chains in the unit cell. The oxygen content in the samples was calculated from X-ray diffraction data by the formula [8]

$$\int_{c/3\,=\,3.890}^{c_{\exp}/3} dc = 0.047 \times \int_0^{\delta} d\delta \tag{2}$$

The average oxygen content is found to be ≈ 6.87 for all samples with minimum value 6.83 and maximum value 6.91. It is observed that the oxygen content depends on the lattice parameter 'c' and almost independent for Pr content in the samples.

The hole concentration in the CuO_2 plane is calculated using the formula [9]

$$P_{\mathrm{sh}} = \left[\frac{0.5 - 2\delta - (Q_{\mathrm{Pr}} - 3)x}{2}\right] \tag{3}$$

where Q_{pr} is the valency of praseodymium atom.

The hole concentration in the (CuO_2) plane against ($2x+\delta$) is shown in Fig. 2.

The value of n (CuO_2) for optimum doping is 0.20, which is in good agreement with the reported literature [10,11]. The value of n (CuO_2) decreases with increasing x and δ and it has a linear dependence with $(2x+\delta)$. The decrement of hole concentration in the (CuO_2) plane is due to mixed valence state or 3+ valence state or 4+ valence state of Pr [12–14]. It implies that suppression of superconductivity results from a reduced number of carriers in the CuO_2 sheets. In our case Pr is in the 3+ valence state because T_c is suppressed monotonically and lattice parameters enhanced gradually, it is owing to ionic radius of Pr^{3+}(1.013 Å) is greater than ionic radius of Eu^{3+} (0.950 Å).

The superconducting properties of Pr substituted compounds are strongly dependent on structural changes that influence the Cu valence and thereby the number of holes in the CuO_2 planes [15] and on the oxygen defects ordering properties in the basal plane [16]. It has been well established that the holes are the superconducting carriers elements in p-type high T_c superconductors [17]. The average charge p per $[Cu–O]^{+p}$ unit is calculated using the formula [9]

$$p=\left[\frac{1-2\delta-(Q_{Pr}-3)x}{3}\right] \qquad (4)$$

It is observed that the average charge p per $[Cu–O]^{+p}$ unit decreases with increasing Pr content. This shows that charge on [Cu–O] chain depends upon the combined effect of Pr concentration as well as oxygen content present in the samples. From this one may conclude that for small p, all of this charge resides on the chains and these hole states are localized gives rise to an activated conductivity among the holes in the chains.

The plot of average charge against oxygen content is shown in Fig. 3.

It is observed that the charge (p) decreases with decreasing oxygen content in the samples. The reduction in oxygen content lowers the number of oxygen atoms in Cu–O chains in the unit cell. There is a tendency for the oxygen atom vacancies to occupy a single chain [18]. As the oxygen content reduces from $7-\delta=7$ to $7-\delta=6$, then the oxygen vacancies are introduced in the CuO chain [19–21] and oxygen atom completely vanishes from the chain at $7-\delta=6$. When $\delta=1$, then there are no chains hence, destroys superconductivity. In RE-123 compounds, the charge balance equation of the molecules for RE^{3+}, Ba^{2+} and $Cu^{(2+\delta)+}$ leads to $p=0.33$ at $7-\delta=7$, this excess amount of positive charges are responsible for superconductivity. When the oxygen content reduces from 7 to 6.5, one gets $p=0$ leading to the suppression of the superconductivity. We prove that the destruction of superconductivity by Pr substitution can be interpreted by means of increasing effective oxygen deficiency in the system.

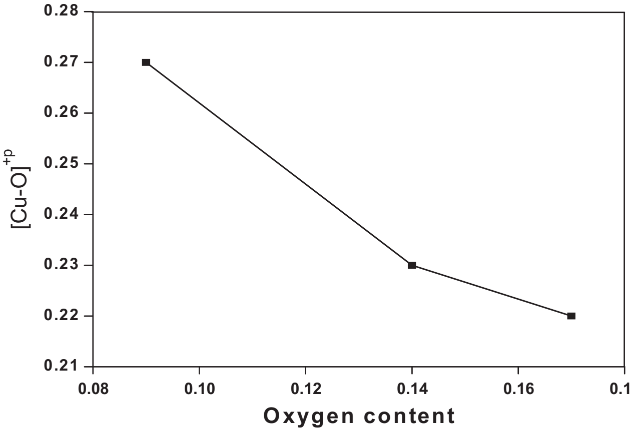

Fig. 3. Average charge against oxygen content of $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system.

3.2. Electrical resistivity measurements

The standard dc four probe technique was employed to measure electrical resistivity of the samples in the temperature range 300 K to 4 K using a Physical Property Measurement System (PPMS). The plot of temperature dependence resistivity $\rho(T)$ for the series of $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ with concentration $x=0.0$, 0.1 and 0.3 are shown in Fig. 4.

The transition temperature $T_{c(0)}$, $T_{c(onset)}$, ΔT_c and normalized T_c were determined using resistivity data and listed in Table 2.

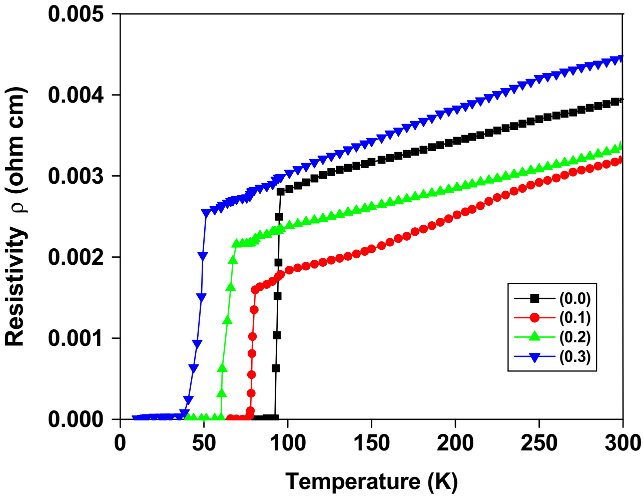

Fig. 4. The electrical resistivity vs temperature for $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system.

Table 2
Transition temperature, onset transition temperature, transition width and normalized transition temperature of $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system.

Conc. (x)	$T_{c(0)}$ (K)	$T_{c(onset)}$ (K)	ΔT_c (K)	$T_{c(x)}/T_{c(0)}$
0.0	92.3	95.7	2.6	1.00
0.1	77.4	80.6	3.2	0.84
0.3	38.4	51.3	12.9	0.42

It is noted that the normalized transition temperature decreases monotonically with increasing Pr concentration and it is linearly dependent on Pr concentration. The increment in resistivity with enhancing Pr concentration may be due to decrease in the amount of charge carriers and hole localization. The results of electrical resistivity also reveal that the considerably larger influence of the Pr substitution on superconducting transition temperature.

3.3. *Microstructural study*

Since the superconducting properties of the granular systems are highly sensitive to their microstructures. SEM analysis of all the samples was carried out to investigate the effect of Pr substitution on the microstructure of the Eu-123 system. The microstructures of the samples were studied by using scanning electron microscopy (Model JSM-7600F) technique. The rectangular samples were used and mounted on the sample holder. The SEM photographs of $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ with concentration $x=0.0$ and 0.3 are shown in Fig. 5(a) and (b).

The SEM photographs show that there are no secondary phases present in the grain boundaries. It was observed that the grain size of pure Eu-123 sample is 49.5 nm whereas Pr doped Eu-123 sample for $x=0.3$ is 58 nm. It clearly indicates that there is slightly enhancement in grain size. It has been noticed that the enhancement in grain size may affect the T_c of the Pr doped $EuBa_2Cu_3O_{7-\delta}$ samples. One can say that the grain size enhancement of the material may decrease T_c monotonically is one of the cause. The average grain size is normally 53.75 nm. From these photographs one may say that the substitution of Pr in Eu-123 system show a significant effect on the microstructure of the system owing to the enhancement in grain size.

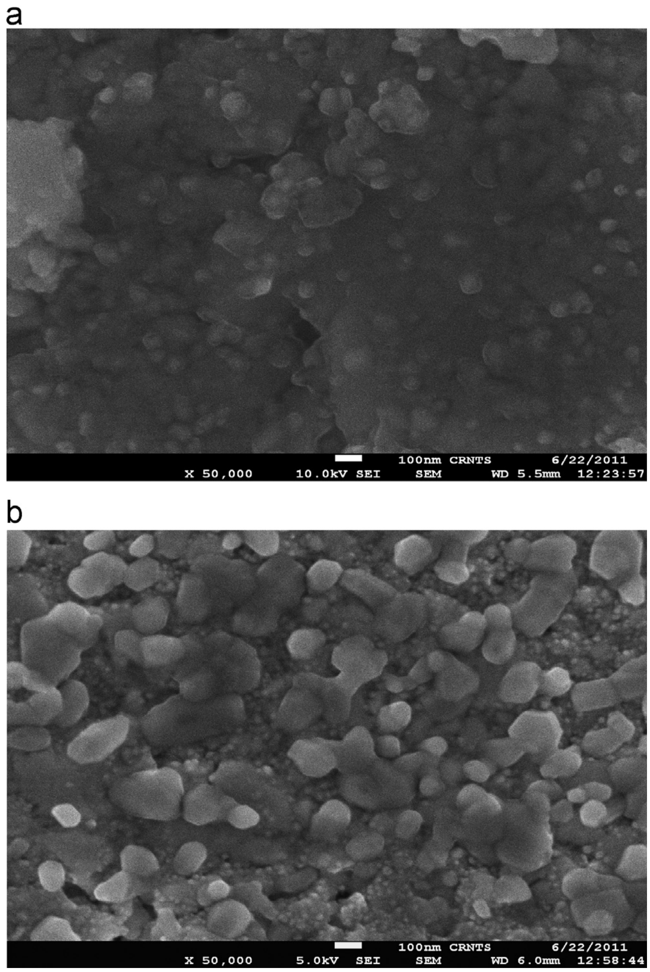

Fig. 5. (a) SEM photographs of $EuBa_2Cu_3O_{7-\delta}$ sample and (b) SEM photographs of $Eu_{0.7}Pr_{0.3}Ba_2Cu_3O_{7-\delta}$ sample.

It is reported by Tomckowicz et al. [22] that in $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system the superconductivity disappears at and above 0.4 concentrations, while Thampi et al. [23] reported that superconductivity disappears below 0.4 concentrations. In our case the T_c of the material decreases monotonically as Pr content increases it may be due to the enhancement of grain size.

4. Conclusions

X-ray diffraction data confirm that all samples are in single phase and having a pervoskite orthorhombic structure. It is observed that suppression of superconductivity results from a reduced number of carriers in the CuO_2 sheets. In our case Pr is in the 3+ valence state because T_c suppresses monotonically and lattice parameters enhances gradually, it is owing to ionic radius of Pr^{3+}(1.013 Å) is greater than the ionic radius of Eu^{3+} (0.950 Å). It is observed that the average charge p per $[Cu\text{–}O]^{+p}$ unit decreases with increasing Pr content. This shows that charge on [Cu–O] plane depends upon the combined effect of Pr concentration as well as oxygen content presents in the samples. The normalized transition temperature decreases with increasing Pr concentration. Results of electrical resistivity also reveal that the considerably larger influence of Pr substitution on superconducting transition temperature. From SEM photographs, grain size was observed in the range of 49.5–58 nm. From these observations we conclude that the transition temperature (T_c) is strongly dependent on oxygen content, hole localization as well as grain size.

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