

Synthesis, Structural and Magnetic Study of Pure and Pr Doped Eu-123 High T_c Superconductors

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ABSTRACT: Samples of $\text{Eu}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with compositions $x = 0.0, 0.1, 0.3$ and 0.5 were prepared by the solid state reaction route. The structural and magnetic properties were investigated by X-ray diffraction and SQUID techniques respectively. The lattice parameters, oxygen content, volume of unit cell, average charge on Cu-O plane were evaluated from X-ray diffraction data. From XRD data, it is observed that the average charge on Cu-O plane decrease with increasing Pr concentration. The Magnetic properties of all samples were measured in the temperature range 300K to 4K.

I. INTRODUCTION

In $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, it is found that the substitution of most magnetic rare earth element except (Ce, Pr, Pm and Tb) in the place of Y gives rise to superconductivity with nearly equal to the critical temperature $T_c = 90$ K [1-3] and have no significant effect on the superconductivity. The series of $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ where R = Y or another rare earth element except (Ce, Pr, Pm and Tb) are metallic and have an orthorhombic layered perovskite structure. But, however, the interesting exception is that the $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Pr-123) system which forms the same orthorhombic structure as (Y-123) and other rare earth compounds but it is an insulator instead of superconductor [4, 5]. The suppression effect of superconductivity in $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ series where R = Y or another rare earth element except (Ce, Pr, Pm and Tb) is strongly depressed by the partial substitution of Pr for the R element. There are some theoretical models such as hole filling [6-8], hole localization in CuO_2 plane [9-13] and magnetic pair breaking [14-16] have been explained the suppression of T_c and superconductor to insulator transition in these RE Pr-123 compounds. The experimental data shows that the occurrence of orthorhombic to tetragonal transition at critical value is due to the increase of oxygen deficiency in the CuO chains [17].

The origin of disappearance of superconductivity due to Pr substitution has not been completely understood although many researchers have studied these problems. In order to clarify the effect of Pr substitution in $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ we have characterized the samples by X-ray diffractometer and investigated the effect of Pr on structural and magnetic properties qualitatively in this paper.

II. EXPERIMENTAL

The samples of $\text{Eu}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ system with $x = 0.0, 0.1, 0.3$ and 0.5 were prepared by conventional solid state reaction technique. In this method, the appropriate amount of high purity (Aldrich make 99.99%) powders of Eu_2O_3 , Pr_6O_{11} , BaCO_3 and CuO were used in required proportion and homogeneously mixed and ground for 3 h with the help of agate mortar by pestle. After grinding these stoichiometric compositions were kept in alumina crucible [18] and calcined twice in a tubular furnace at a temperature 915°C for 24h with intermediate grinding for 3 h. After calcinations, the material was again ground for 3h to subdivide any aggregated products. The calcined material having black phase is observed. The powders were then palletized into the 12 mm diameter and sintered in closed tubular furnace at 930°C for 24 h. After sintering the samples were cooled at the rate 60°C/h upto 450°C and kept for 24 h and then samples cooled at room temperature at the rate 1°C/min . in oxygen atmosphere.

III. XRD STUDY

X - ray diffraction has been used to determine the phase present in the sample and to determine the lattice parameter for various concentrations. The 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 figure 1. The X - ray diffraction of all samples reveal that they have the orthorhombic P_{mmm} crystal structure with no evidence of impurity phases. This suggests that the preparation process was successful according to the stoichiometrical expectations and the material is in single phase form with homogeneous powder of finer particle size. The peak intensity goes on decreasing with enhancing Pr concentration.

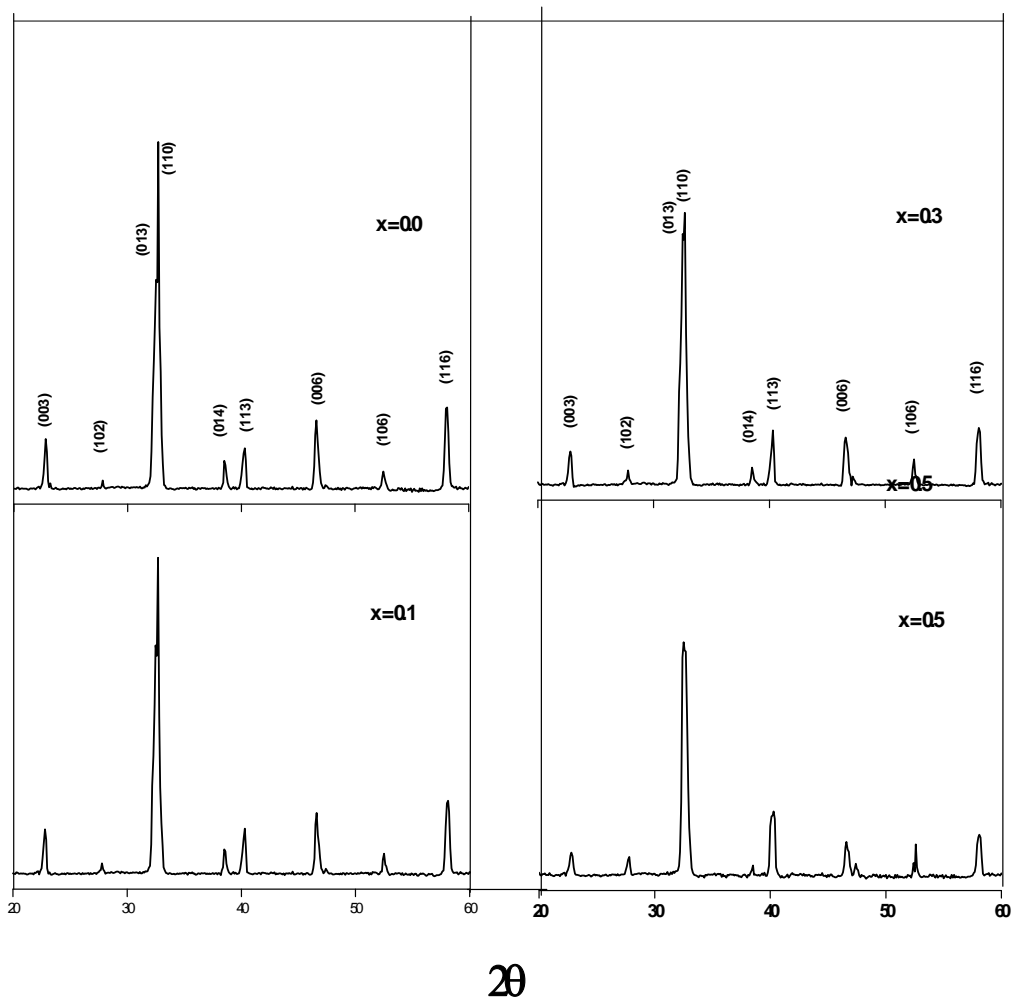


Figure 1. XRD patterns of sintered $\text{Eu}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ systems.

The structural data obtained from XRD patterns is tabulated in table 1.

Table 1: Lattice parameters, oxygen content, volume of unit cell and average charge of $\text{Eu}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with concentration $x = 0.0, 0.1, 0.3$ and 0.5 .

Pr conc. (x)	Lattice parameters in A°			Oxygen content ($7 - \delta$)	Volume of unit cell ($\text{A}^\circ)^3$	Average charge (p)
	a	b	c			
0.0	3.8359	3.8968	11.6832	6.91	174.6374	0.271
0.1	3.8399	3.8999	11.6902	6.86	175.0634	0.238
0.3	3.8430	3.9072	11.6933	6.83	175.5792	0.223
0.5	3.8510	3.9135	11.6965	6.81	176.2766	0.208

The oxygen content plays an important role in assigning the orthorhombic to tetragonal structure in the HTSC. An oxygen deficiency (δ) = 0.00 stoichiometry is only reached if samples are slowly cooled in oxygen atmosphere [19,20]. The oxygen deficiency, since the superconducting properties are strongly controlled by oxygen content and arrangement in EuPr-123 which in turns are controlled by annealing time, temperature, oxygen, partial pressure and cooling rate at the time of preparation. As the oxygen stoichiometry changes from $7 - \delta = 7$ to $7 - \delta = 6$, oxygen vacancies are introduced in the CuO chain [21]. There is a tendency for the oxygen atom vacancies to occupy a single chain resulting a structural phase transition from orthorhombic to tetragonal phase and hence destroys superconductivity.

Oxygen contents are well known to be charge reservoir in superconductor. Oxygen content reduction lowers the number of oxygen atom in Cu-O chains in the unit cell. The average oxygen content is found to be ≈ 6.85 for all samples with minimum value 6.81 and maximum value 6.91. It is observed that the oxygen content depend on the lattice parameter 'c' and almost independent for Pr content in the samples and hence the oxygen content remains almost constant for all x values.

The volume cell goes on increasing with increasing Pr concentration without any change in phase of the structure. It is observed that, this may be related to the ionic radii of Pr ion and Eu ion. The increment of volume cell with enhancing Pr content is consistent with the higher ionic radius of Pr compared to that of Eu. This shows that the substitution of Eu^{3+} ions by Pr^{3+} ions, since the ionic radius of Eu^{3+} & Pr^{3+} ion is 0.950 \AA , 1.013 \AA respectively and at the same time it is smaller than the radius of Ba^{2+} ion. These results are good agreement with the reported literature [22-24]. One may conclude that when oxygen content reduces in unit cell, the volume cell goes on increasing. This may be due to the lattice parameter 'c'. When the oxygen deficiency is more, it produces vacancies in the unit cell resulting the enhancement in lattice parameter 'c'.

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 [25] and on the oxygen defects ordering properties in the basal plane [26]. It has been well established that the holes are the superconducting elements in p - type high T_c superconductors [27]. A high T_c cuprate superconductors have a strong dependence of T_c on the hole content. The average charge p per $[\text{Cu-O}]^{+p}$ unit is calculated using the formula [28],

$$p = \left[\frac{1 - 2\delta - (Q_{\text{Pr}} - 3)x}{3} \right] \dots\dots\dots (5)$$

It is observed that, the copper valence is decreasing with increasing Pr content. This shows that charge on [Cu-O] plane is depend 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 giving rise to an activated conductivity among the holes in the chains. At $x \geq 0.4$, the $p > 0$, but it does not show superconductivity in the samples because it may be due to the holes in the sheets and the inter Ba – planes were insulating. This shows that all of the $[Cu-O]^{+p}$ charge or holes must then be in the inter Ba-plane. As the charge p increases at $x < 0.4$, the metallic conductivity and superconductivity occur. This may be due to that the increased charge begins to appear on the sheet which can sustain superconductivity. This shows that the charge in the inter Ba - plane cannot be increase beyond the threshold value, a point at which charge begins to appear on sheet which can sustain metallic conductivity and superconductivity, so that beyond threshold all of the increased charges come from sheet.

IV. MAGNETIC MEASUREMENT

The magnetic properties were performed on single crystal of $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ with compositions $x = 0.0, 0.1, 0.3$ and 0.5 in the temperature range $300\text{ K} - 4\text{ K}$. The rectangular bar of regular dimensions has cut from the superconducting samples using low speed diamond saw cut machine. The commercial SQUID magnetometer i.e. Magnetic Property Measurement System (MPMS) was used to measure the magnetic properties of the samples. The samples were cooled in field of 20 Oe and magnetic moment was measured in as the temperature was raised. The Curie – Weiss law temperature and effective magnetic moment μ_{eff} were derived by applying field of 3000 Oe on the sample by SQUID. The superconducting transition temperature T_c determined from magnetic measurement was taken as temperature at which onset of diamagnetism occurred. The zero field magnetization with temperature in a field of 20 Oe is shown in figure 2.

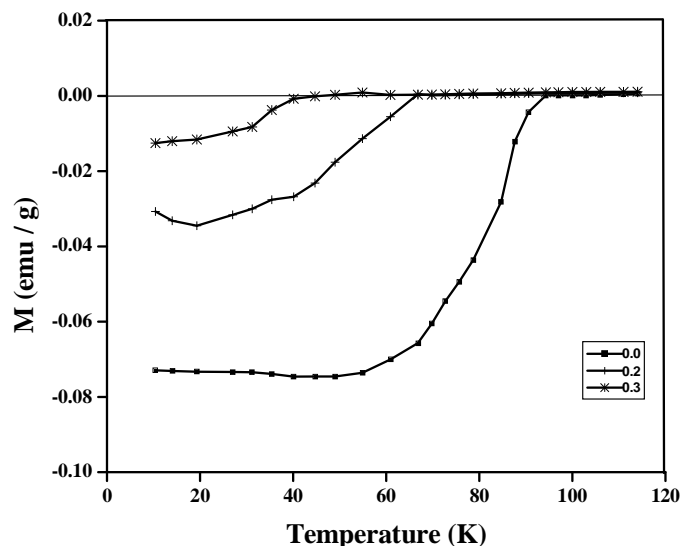


Figure 2. Magnetization vs Temperature

The transition temperature T_c obtained from dc susceptibility measurement is listed in table 2. It is observed that the transition temperature decreases with increasing Pr concentration. The superconductivity exist upto $x = 0.3$ and above this i.e. $x > 0.3$ annihilation so superconductivity occurs and superconductivity completely destroys at $x = 0.4$.

The typical temperature dependence of the dc susceptibility $\chi(T) = M(T)/H$ for $\text{Eu}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with compositions $x = 0.0, 0.1, 0.3$ and 0.5 is shown in figure 3. The inverse magnetic susceptibility χ^{-1} vs T is shown in figure 4.

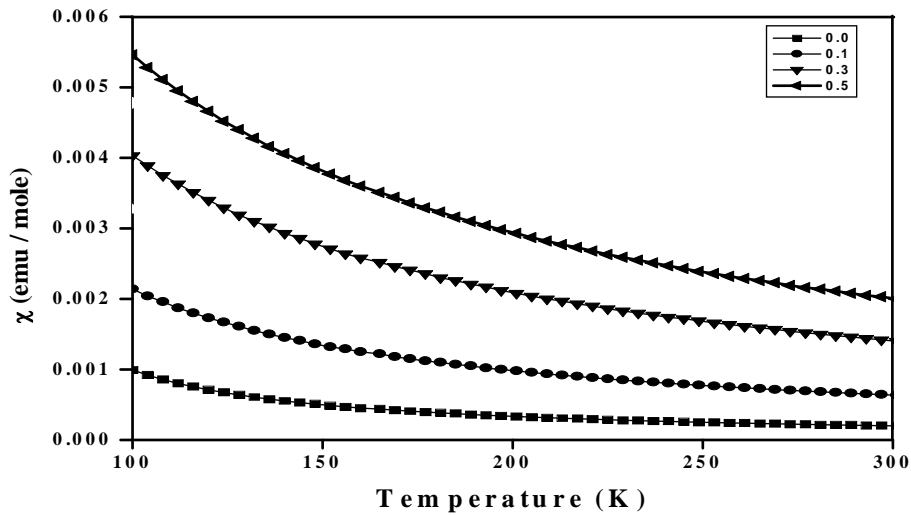


Figure 3. Magnetic susceptibility vs Temperature

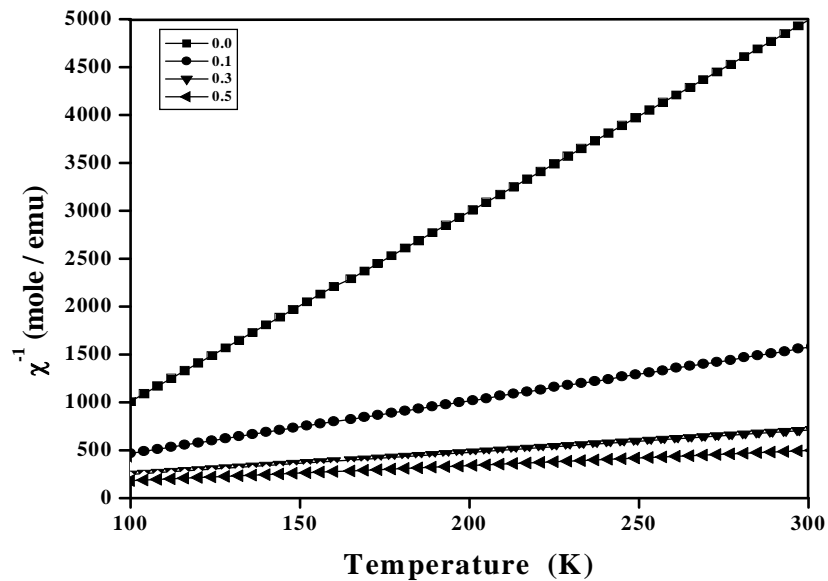


Figure 4. Inverse magnetic susceptibility vs Temperature

In this case, the magnetic susceptibility increases with increasing Pr concentration. The magnetic data for Pr doped EuPr-123 can be described quite well from inverse magnetic susceptibility by the sum of constant Pauli like contribution χ_o and Curie -Weiss contribution [29,30] i.e. The data obtained obey

$$\chi = \chi_o + \frac{C}{T - \theta} \quad \dots\dots\dots (1)$$

In which χ_o is Pauli-like susceptibility independent of temperature, θ be the Curie temperature and C is Curie-Weiss constant. The temperature independent susceptibility χ_o and Curie - Weiss temperature θ are only weakly concentration dependent. The Bohr magneton number is estimated by the formula [31],

$$\mu_{eff} = \sqrt{\frac{3K_B C}{N}} \quad \dots\dots\dots (2)$$

(Avagadro's number) = 6.02×10^{23} .

where, K_B (Boltzmann constant) = 1.38×10^{-16} erg/K and N

Table 2: $T_{c(onset)}$, Curie constant, Bohr magneton numbers, Curie temperature of $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ with compositions $x = 0.0, 0.1, 0.3$ and 0.5

Pr conc.	$T_{c(onset)}$ (K)	C (K emu/mole)	μ_{eff} (μ_B)	Θ (K)
0.0	94.3	0.05	0.63	50.8
0.1	78.7	0.18	1.20	15.7
0.3	49.0	0.43	1.86	-13.6
0.5	NS	0.63	2.25	-12.4

Using equation (1) and (2), the Curie constant and Bohr magneton number are obtained for Eu for each sample and listed in table 2. From table 2, it is observed that Bohr magneton numbers go on increasing with increasing Pr concentration. The sign of Curie temperature changes from positive to negative indicates that above critical temperature, the magnetic interaction in Pr substituted Eu-123 superconducting material changes from ferromagnetic to antiferromagnetic with increasing Pr concentration. This reflects that the magnetic interaction in Eu and Pr are probably different in nature.

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