



Role of Pr Substituted Eu-123 High T_c Cuprate Superconductors†

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The Pr substituted $\text{Eu}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ high purity samples with compositions $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5 were synthesized by ceramic route. The structural studies of all the samples were carried out by X-ray diffraction technique. The XRD studies of the samples show EuPr-123 system have an orthorhombic perovskite structure. The lattice parameters, volume of unit cell, oxygen deficiency, orthorhombicity, X-ray density and bulk density were evaluated using Rietveld refinement method. The lattice parameters, volume of unit cell and oxygen deficiency go on increasing while orthorhombicity, X-ray density and bulk density decrease as doping percentage of Pr increases. It may be due to the higher ionic radius or mixed valency or +3 or +4 valency state of praseodymium.

Key Words: Praseodymium, Eu-123, High T_c cuprate, Semiconductors, Volume cell, Orthorhombicity.

INTRODUCTION

The suppression effect of superconductivity by the introduction of Pr in the rare earth site in rare earth-123 high T_c cuprates have been widely investigated¹⁻³. It is found that substitution of rare earth elements except (Ce, Pr, Pm and Tb) in the place of rare earth (RE) in $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (rare earth-123) give rise superconductivity with nearly equal to the critical temperature $T_c = 90 \text{ K}^{4-5}$. The series of $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ where RE = Y or another rare earth elements except (Ce, Pr, Pm and Tb) are metallic and have an orthorhombic layered perovskite structure. But, the interesting exception is that the Pr-123 system, which forms the same orthorhombic structure as Y-123 and other rare earth compounds but it is an insulator instead of superconductor⁶⁻⁸. The suppression effect of superconductivity in $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ series where RE = Y or another rare earth elements except (Ce, Pr, Pm and Tb) is strongly depressed by the partial substitution of Pr for the rare earth element. There are some theoretical models such as hole filling⁹⁻¹¹, hole localization in CuO_2 plane¹²⁻¹⁶ and magnetic pair breaking¹⁷⁻¹⁹ have been explained the suppression of T_c and superconducting insulator transition in these RE Pr-123 compounds. The experimental data shows that the occurrence of orthorhombic-tetragonal transition at critical value is due to the increase of oxygen deficiency in the CuO chains²⁰. The origin of disappearance of superconductivity due to Pr substitution in EuBaCuO has not been well understood yet. We have undertaken a series of $\text{Eu}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with compositions ($x = 0.0, 0.1, 0.2, 0.3,$

0.4 and 0.5) to study at length. We wish to throw more light on Pr substituted EuBaCuO materials. This system has its own importance, because Pr plays significant role. Lattice parameters and other parameters are determined using X-ray diffraction data. Such investigations on Pr substituted EuBaCuO are reported in this paper laconically and qualitatively.

EXPERIMENTAL

The samples $\text{Eu}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with compositions $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5 were prepared by conventional solid state reaction route. The appropriate mixtures of high purity Eu_2O_3 , BaCO_3 , Pr_6O_{11} and CuO (Aldrich make 99.99 %) were used. The powders were mixed thoroughly, ground for 3 h and calcined twice at $915 \text{ }^\circ\text{C}$ for 24 h with intermediate grinding for 3 h. The calcined samples again ground for 2 h for making pellets and finally sintered at $930 \text{ }^\circ\text{C}$ for 24 h. These pellets were annealed in oxygen atmosphere for 24 h at $450 \text{ }^\circ\text{C}$ followed by slow cooling at $1 \text{ }^\circ\text{C}/\text{min}$ upto room temperature.

The structure of the samples were investigated using X-ray diffractometer (Model: PW-3710) employing CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$).

RESULTS AND DISCUSSION

The X-ray diffraction patterns were recorded at room temperature by X-ray diffractometer (Model: PW-3710) using CuK_α radiation. The X-ray diffraction study of all the samples reveals that they have orthorhombic perovskite structure with

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no evidence of impurity phases, suggesting 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 increasing Pr concentration. For all the Pr compositions X-ray diffraction patterns are corresponded to that of the orthorhombic structure. The lattice parameters 'a' and 'b' are increasing while the lattice parameter $c/3$ is slightly increasing and ranges from 3.8944 to 3.8992 Å with increasing Pr concentration as shown in Fig. 1.

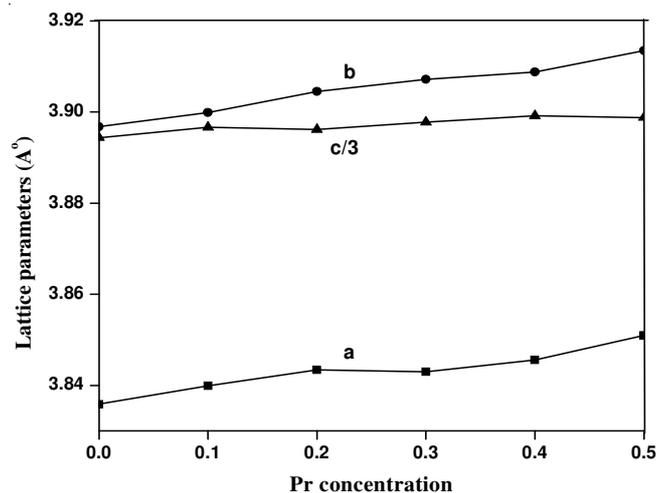


Fig. 1. Lattice parameter vs. Pr concentration

The oxygen content plays an important role in assigning the orthorhombic to tetragonal structure in the high TC superconductor. An oxygen deficiency (δ) = 0.00 stoichiometry is only reached if samples are slowly cooled in oxygen atmosphere²¹⁻²². The oxygen deficiency of samples is calculated from X-ray diffraction data using the formula given by Jung *et al.*²³. The average oxygen content is found \approx 6.85 for all the samples with minimum value 6.80 and maximum value 6.91. It is observed that oxygen deficiency increases with increasing Pr concentration (Fig. 2). It is well understood that oxygen content decreases as Pr content increases, samples turn into tetragonal phase and annihilation of superconductivity occurs. It may be owing to +3 valence state of Pr²⁴.

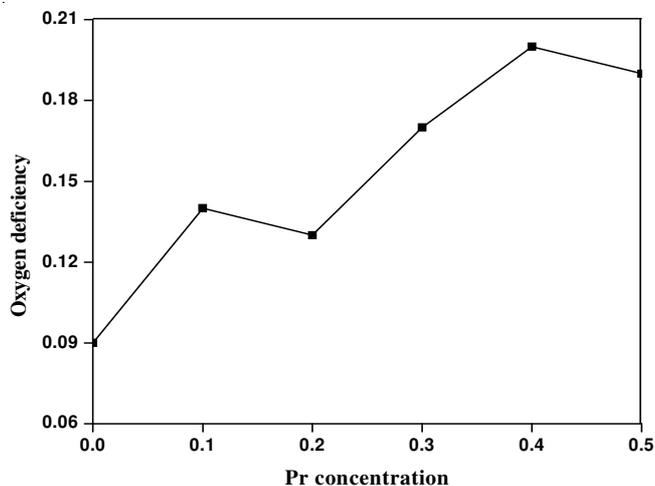


Fig. 2. Oxygen deficiency vs. Pr concentration

The volume cell goes on increasing with increasing Pr concentration is shown in Fig. 3.

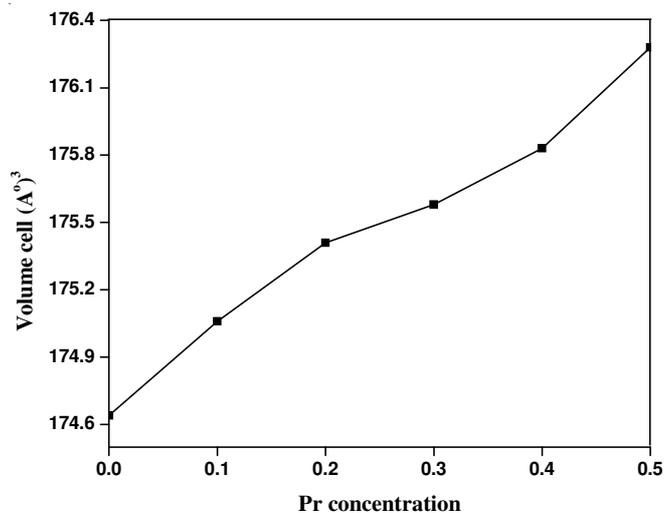


Fig. 3. Volume cell vs. Pr concentration

From Fig. 3, it is observed that, this may be related to the ionic radii of Pr ion and Eu ion. The increment of volume cell with increasing Pr content shows that the complete substitution of Eu³⁺ ions by Pr³⁺ ions, since the ionic radii of Eu³⁺ ions is 0.950 Å and Pr³⁺ ions is 1.013 Å. One may also conclude that when oxygen content reduces in unit cell, the volume cell goes on increasing and *vice versa*. This may be due to the lattice parameter 'c'. When the oxygen deficiency is less, the interaction between Cu and O is strong, this results the lattice parameter 'c' decreases. Due to this strong interaction, the unit cell is more compact and volume of the unit cell goes on decreasing order. When the oxygen deficiency is more, it means vacancies are more in the unit cell and therefore, the interaction between Cu and O is weak resulting the increment in lattice parameter 'c' and *vice versa*. Due to this the volume of the unit cell goes on increasing order.

The orthorhombic distortion in the samples is calculated using the formula given by previous authors^{25,26}. The orthorhombic distortion against Pr content is shown in Fig. 4.

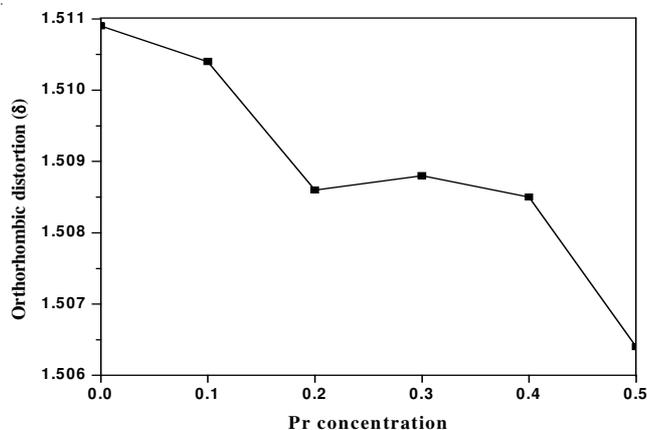


Fig. 4. Orthorhombic distortion vs. Pr concentration

It is clearly seen that, there is slight decrease in orthorhombicity with increasing Pr concentration. The

orthorhombic distortion slowly decreases from $x = 0.00$ to $x = 0.5$ with increasing x . The X-ray density is calculated from X-ray diffraction using the formula of Bell²⁷. The X-ray density plotted against Pr concentration is shown in Fig. 5.

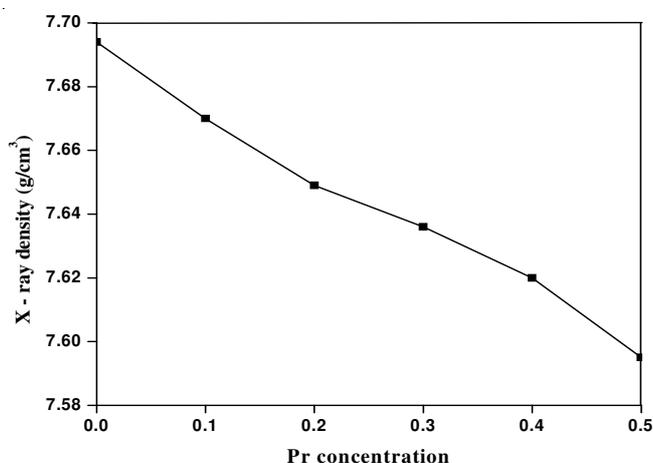


Fig. 5. X-ray density vs. Pr concentration

It is observed that X-ray density goes on decreasing with increasing Pr concentration. This may be due to the change in molecular weight which reflects the change in X-ray density. The molecular weight of the given system goes on decreasing with increasing Pr concentration resulting the decrease in X-ray density. This may be due to the ionic radii of Pr and Eu.

The bulk density plotted against Pr concentration is shown in Fig. 6.

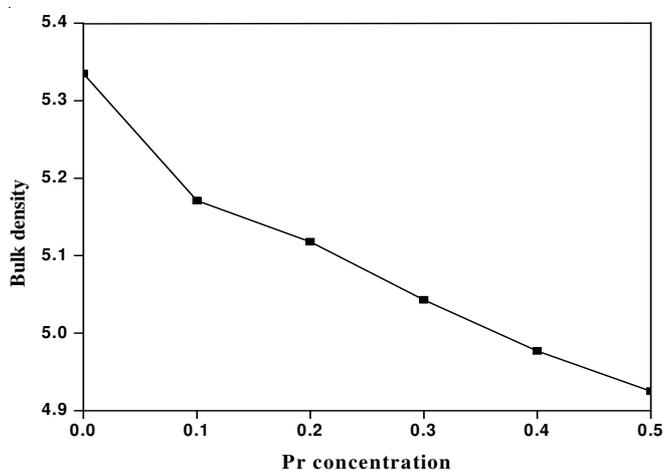


Fig. 6. Bulk density vs Pr concentration

The bulk density goes on decreasing with increasing Pr concentration. It may be due to the molecular weight and X-ray density. In this case the molecular weight goes on decreasing with increasing Pr concentration and thus the mass of the sample goes on decreasing. Also, due to the ionic radii of Pr is greater than that of Eu, the X-ray density goes on decreasing. Thus, due to both molecular weight and X-ray density, bulk density goes on decreasing as porosity increases.

Conclusion

The samples of $\text{Eu}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ were synthesized by ceramic route. The crystal structure was studied by X-ray diffraction technique. From XRD data, it is confirmed that all samples are in orthorhombic perovskite structure. It is found that the lattice parameters, volume of unit cell and oxygen deficiency increase with increasing Pr concentration. This may be due to the ionic radii of Pr^{3+} is greater than Eu^{3+} . The orthorhombicity, X-ray density and bulk density decrease as doping percentage of Pr increases. It is also observed that the oxygen deficiency depends on the lattice parameter 'c' and independent from the Pr content in the samples. It may be possible cause for changing the superconducting properties of the compound.

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