

## Metallic Behavior for Normal State Resistivity of $\text{PrBa}_{2-x}\text{R}_x\text{Cu}_3\text{O}_7$ Compounds

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**Abstract:** The present work investigates the effect of R substitution at the Ba site on structural and transport properties of  $\text{PrBa}_{2-x}\text{R}_x\text{Cu}_3\text{O}_7$  compound (R = Er, Gd, Nd, La & x = 0.00, 1.5). The samples are examined by using XRD, resistivity and Hall coefficient measurements. The results of XRD indicate that the structure of the samples with (x = 0 and R = Er, Gd, and La) are quasi-tetragonal, while the sample with R = Nd is orthorhombic. Further, some of undefined lines could be observed in the XRD patterns of (R = Er, Gd, Nd and La) as compared to Pr: 123 sample. Interestingly the substitution of R at the Ba site leads to unusual drop in the normal state resistivity as compared to Pr:123 compound. Similar behavior is recorded for the carrier concentration against R plot. These results suggested that the hole filling might be the key parameter controlling the absence of superconductivity of Pr: 123 compound.

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### 1. Introduction

The absence of superconductivity in Pr: 123 compounds have to date remained an important unsolved issue of high  $T_c$  superconductivity [1-5]. The researchers have mostly attributed the unusual behavior of Pr to its valence state. The obtained results using different techniques seem to be better explained based on the formed valence of Pr as trivalent [6-8]. While, some of studies like NMR and optical reflectivity support the tetravalent state for Pr [9-10]. The theorists who believe in the former prefer to explain the absence of superconductivity in the Pr: 123 compound in terms of A-G theory, where the superconducting pair breaking results from the magnetic moment of  $\text{Pr}^{3+}$ . Those having faith in the tetravalent state of Pr, however, ascribe the non-superconductivity of the Pr: 123 compounds to the hole filling effect [11]. In addition, the strong hybridization between (Pr-4f) and (O-2P) conduction band electrons and its sensitivity to the disorder leading to localization of holes, offers a possibility to understand the non-superconductivity of Pr: 123 compounds [12-13]. Furthermore, the STM studies based on YPr: 123 single crystals show an increase in the formation of oxygen vacancies in the Cu-O<sub>2</sub> planes, where superconductivity is believed to reside.

With more and more, experimental results appearing in the literature, the mystery of non-superconductivity in Pr: 123 compounds is becoming increasingly complicated. In order to examine further the above background, the effects of rare earth

elements R substitution at the Ba site on structural and normal state properties of  $\text{PrBa}_{2-x}\text{R}_x\text{Cu}_3\text{O}_7$  compound with various x and R will be investigated (R = Er, Gd, Nd, La & x = 0.00, 1.5).

### 2. Experimental Details

Samples of the series  $\text{PrBa}_{2-x}\text{R}_x\text{Cu}_3\text{O}_7$  (R = Er, Gd, Nd, La & x = 0.00, 1.5) are prepared by a solid-state reaction method. The ingredients  $\text{Pr}_6\text{O}_{11}$ ,  $\text{BaCO}_3$ ,  $\text{R}_2\text{O}_3$ , and CuO of 4 N Purity are thoroughly mixed in required proportions and calcined at 900 °C in air for a period of 24 hours. This exercise is repeated three times with intermediate grinding at each stage. The resulting powders are ground, mixed, palletized and annealed in flowing oxygen at 940 °C for a period of 24 hours and then the furnace is cooled to room temperature with an intervening annealing for 24 hours at 600 °C. The samples are characterized for phase purity by x-ray diffraction using  $\text{CuK}\alpha$  radiation. The electrical resistivity of the samples are measured by the standard four-probe technique in closed cycle refrigerator [cryomech compressor package with cryostat Model 810-1812212, USA] within the range of (10-300) K. Nanovoltmeter Keithley 2182, current source Keithley 6220 and temperature controller 9700 (0.001 K resolution) are used in this experiment. Finally, Hall coefficient measurements at room temperature are made using Ecopia HMS-2000 at a field of 0.57 T.

### 3. Results and Discussion

Figure 1 shows the room temperature x-ray diffraction patterns of  $\text{PrBa}_{2-x}\text{R}_x\text{Cu}_3\text{O}_7$  samples. As seen from this Figure, the samples with ( $R = \text{Er}$ ,  $\text{Gd}$ , and  $\text{La}$ ) are clearly quasi-tetragonal single phases as well as  $\text{Pr:123}$  sample. While the sample with  $R = \text{Nd}$  is clearly orthorhombic single phase, being evident from crystallographic splitting of (006), (200) and (116), (213).

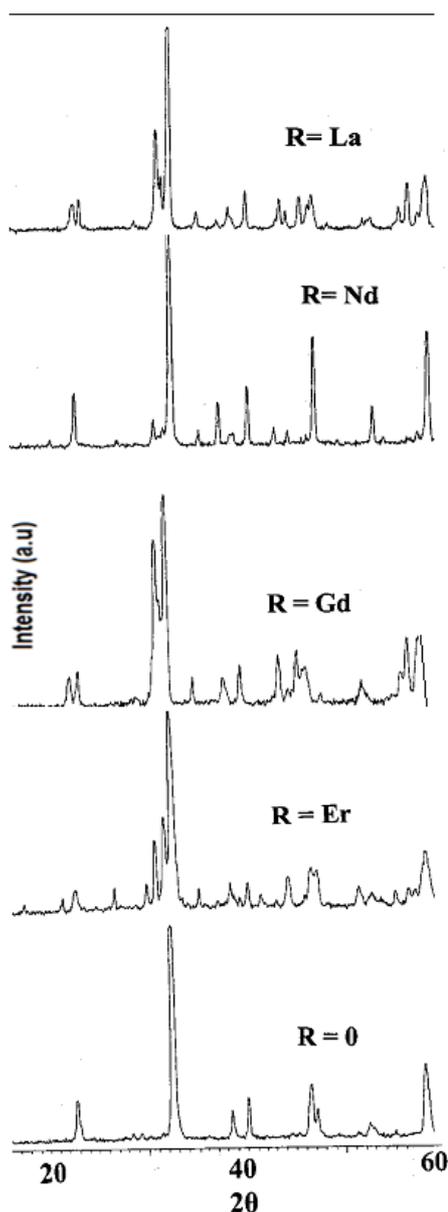


Figure 1 : XRD patterns of  $\text{PrBa}_{2-x}\text{R}_x\text{Cu}_3\text{O}_7$  samples

Further, some of undefined lines could be observed in the XRD patterns of ( $R = \text{Er}$ ,  $\text{Gd}$ , and  $\text{La}$ )

as compared to  $\text{Pr:123}$  sample. These lines are absent in the  $R = \text{Nd}$  sample.

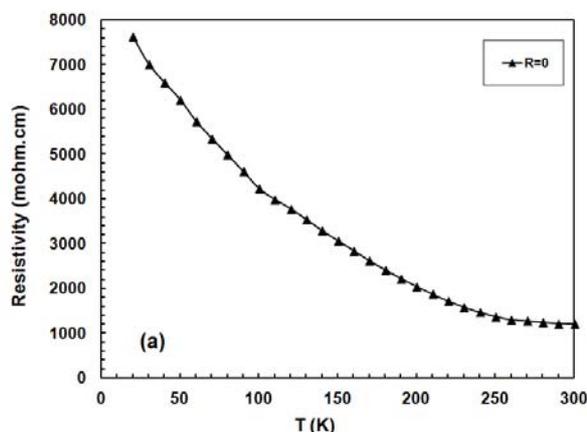


Figure 2 (a): Resistivity versus temperature for  $\text{Pr:123}$  sample

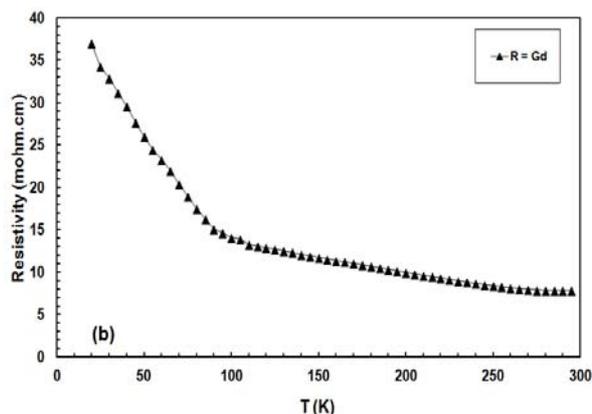


Figure 2 (b): Resistivity versus temperature for  $\text{PrBa}_{0.5}\text{Gd}_{1.5}\text{Cu}_3\text{O}_7$  sample

Figure 2 (a-c) shows the measured resistivity as a function of temperature for all considered samples. As evident from the Figure, the electrical resistivity turns with decreasing temperature to semi conducting behavior for  $\text{Pr:123}$  and  $\text{Gd}$  samples without any transition to superconducting state. The  $\text{Pr:123}$  sample shows a very higher sharp increase to semiconductor behavior as compared to the  $R = \text{Gd}$  sample. This behavior may be attributed to the magnetic moment of  $\text{Gd}$  as compared to  $R = \text{Er}$ ,  $\text{Nd}$  and  $\text{La}$  samples. Compared to  $\text{Pr:123}$  sample, a decrease in the resistivity values is observed for  $R = \text{Er}$ ,  $\text{Nd}$  and  $\text{La}$  samples. Figure 3 (a-b) shows the behavior of both normal state resistivity at  $T = 300 \text{ K}$  ( $\rho_{300}$ ), resistivity at  $T = 20 \text{ K}$  ( $\rho_{20}$ ), residual resistivity  $\rho_0$ , and  $d\rho/dT$  as a function of  $R$ . It is clear that the behavior of both of them is systematic with rare earth ionic size for  $R = \text{Er}$ ,  $\text{Nd}$  and  $\text{La}$  samples. While the same is different in case of  $\text{Pr:123}$  and  $R = \text{Gd}$  samples.  $d\rho/dT$  is found to

be negative for Pr:123 and R = Gd samples. Now, our question is why the considered samples remain non-superconductor. Of course, this is may be due some reasons, which will be discussed in the next section.

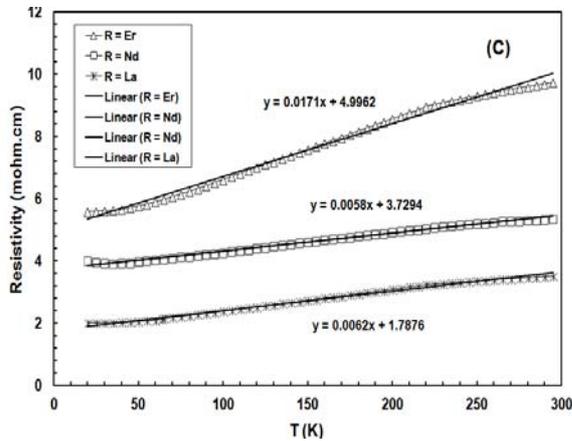


Figure 2 (c): Resistivity versus temperature for  $\text{PrBa}_{0.5}\text{R}_{1.5}\text{Cu}_3\text{O}_7$  samples

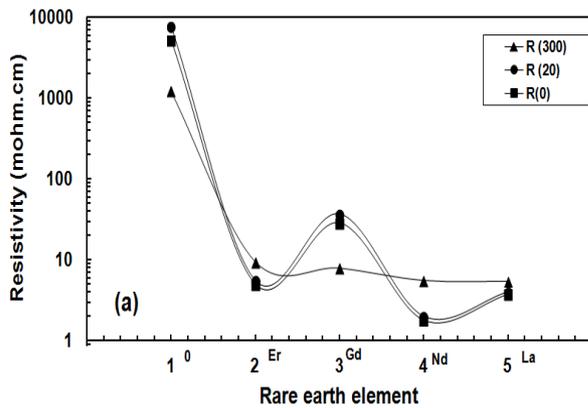


Figure 3 (a): Resistivity versus R for  $\text{PrBa}_{2-x}\text{R}_x\text{Cu}_3\text{O}_7$  samples

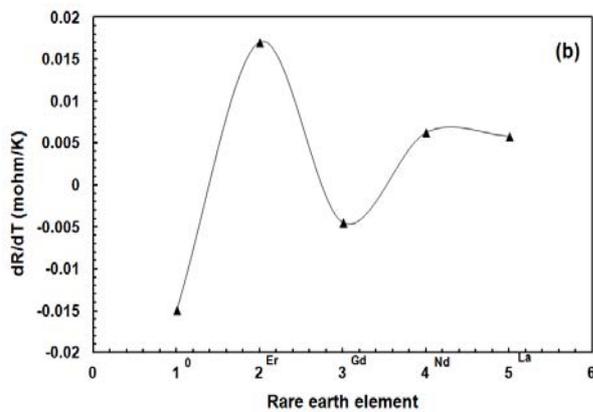


Figure 3 (b):  $dR/dT$  versus R for  $\text{PrBa}_{2-x}\text{R}_x\text{Cu}_3\text{O}_7$  samples

The Hall coefficient  $R_H$  dependence of R is illustrated in Figure 4 (a). It is clear that the sign of Hall coefficient is positive for all samples, which indicates P-type conduction. Also, the values of  $R_H$  are higher for R = Er, Nd and La samples as compared to Pr:123 and Gd samples. However, in such case the conduction band can be regarded as a parabolic behavior and the standard equation ( $n_H = 1/eR_H$ ) could be used to calculate the carrier concentration for these type of samples. The concentration of carriers shown in Figure 4 (b) is decreased against R for all samples, but it is higher for Gd sample. Anyhow, it has been reported that the effective Cu valence is decreasing with increasing the ionic radius of R in similar high  $T_c$  compounds. Decreasing Cu valence is only brought by the substitution of  $\text{R}^{3+}$  at  $\text{Ba}^{2+}$  site. This of course will cause a decrease in the concentration of holes in the Cu- $\text{O}_2$  planes, and consequently the net carriers will be decreased [5,14].

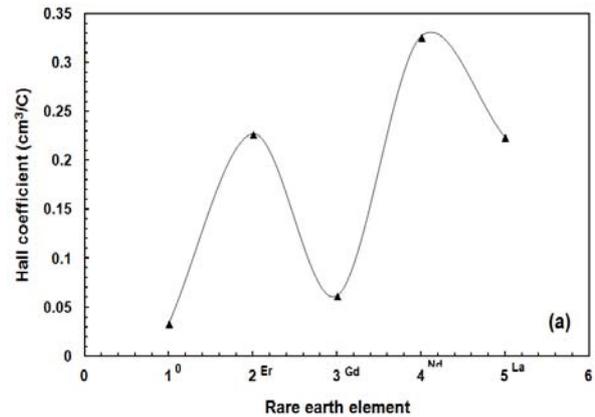


Figure 4 (a): Hall coefficient versus R for  $\text{PrBa}_{2-x}\text{R}_x\text{Cu}_3\text{O}_7$  samples

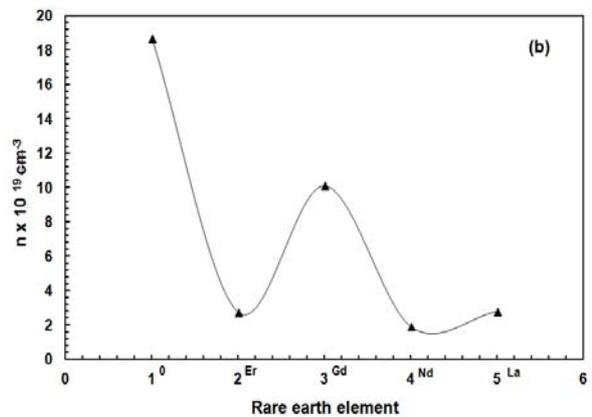


Figure 4 (b): Concentration of carriers versus R for  $\text{PrBa}_{2-x}\text{R}_x\text{Cu}_3\text{O}_7$  samples

On the other hand, it has been reported that the substitution of  $R^{3+}$  at  $Ba^{2+}$  site in  $R: 123$  superconductors can decrease the number of holes significantly when the doping concentration reaches the chemical concentration ( $n_{chem} = 2x/V$ ), where  $x$  is the doping content and  $V$  is the volume of unit cell. In the present case,  $V = 174.78 \times 10^{-24} \text{ cm}^3$  and  $x = 0.75$ . Then,  $n_{chem} = 4.29 \times 10^{21} \text{ cm}^{-3}$ , which is still higher than the values deduced from Hall measurements.

However, firstly we could obtain some undefined lines in some of the considered samples. This may be due to ability of Pr to substitute at Ba site and the vice is versa for rare earth element. If this is true, why these lines are absent in Pr:123 and Nd samples. Secondly, substitution of R decreased the concentration of carriers, and generally independent on the chosen R. This is right since the valance state of all substituted rare- earth elements is  $3^+$ . So, we do not expect any change in the carrier concentration with the chosen R. Thirdly, we do not expect any change in the oxygen deficient for all samples since the samples are prepared under the same conduction. But, we believe that the amount of oxygen may be decreases with R as a result of changing c-parameter, and consequently the number of hole carriers in the  $CuO_2$  planes is decreased, in agreement with the Hall data. Then, we believe that suppression of resistivity of Pr:123 by R substitution at Ba site is mainly controlled by the amount of oxygen deficient which can be consider the main factor for decreasing carrier concentration in the considered samples. Based on the above results, we suggest that the hole filling might be the key parameter controlling the absence of superconductivity of Pr: 123 compound.

### Conclusions

The structural and transport properties of  $PrBa_{2-x}R_xCu_3O_7$  compounds is reported. We have shown that the structure of the samples with (Er, Gd, and La) is quasi-tetragonal as well as undoped Pr:123, while the sample with  $R = Nd$  is orthorhombic. Further, the substitution of R at the Ba site leads to unusual drop in the normal state resistivity as compared to Pr:123 compound. Similar behavior could be reported for the concentration of carriers.

Our results show that the hole filling might be the key parameter controlling the absence of superconductivity in Pr: 123 compound.

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