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Structural and normal state properties of the $\text{PrBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-\delta}$ compound with $(0.00 \leq x \leq 1.00)$

A Sedky

Physics Department, Faculty of Science, Assiut University, Assiut 71516, Egypt

E-mail: sedky1@aun.eun.eg

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Abstract

The present work investigates the effect of La substitution at the Ba site on the structural and normal state properties of the $\text{PrBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-\delta}$ compound, with various x values ($0.00 \leq x \leq 1.00$). X-ray diffraction results indicate that the c lattice parameter decreases with increasing x for all samples. The samples with $x = 0.00$ and 0.25 are clearly quasi-tetragonal single phase, while the samples with $x = 0.50$, 0.75 and 1.00 are clearly orthorhombic single phase with a few small unreacted lines observed in the spectrum of the $x = 1.0$ sample. The effective Cu valence decreases linearly with increasing La content along with a small increase in the oxygen content. The EDX analysis reveals that the total amount of La and Ba remains constant with increasing La content. It is also found that the substitution of La at the Ba site leads to an unusual drop in the normal state resistivity as compared to the Pr:123 compound. We suggest that both the hole filling and oxygen disorder effects might be key parameters controlling superconductivity as well as the normal state properties of the Pr:123 compound. Our results are supported by a host of other considerations and experimental observations.

1. Introduction

In spite of numerous experimental studies [1–8] and many theoretical considerations [9–13], the absence of superconductivity in the isostructural single phase Pr:123 compound, formed by replacement of Y by Pr in the Y:123 superconductor, has to date remained an important unresolved issue of high temperature superconductivity. The researchers have mostly attributed the unusual behaviour of Pr to its valence state, which has to date remained a controversial and much debated issue. The results obtained using different techniques [14–16] seem to be better explained on the basis of the formal valence of Pr as trivalent. On the other hand, the studies of Ca substitution [17], Cu NMR [18] and the optical reflectivity [19] support the tetravalent state for Pr. The theorists who believe in the former prefer to explain the non-superconductivity of the Pr:123 compound in terms of the A–G theory, where the superconducting pair breaking results

from the magnetic moment of Pr(3+) [20]. Those having faith in the tetravalent state of Pr, however, ascribe the non-superconductivity of the Pr:123 compound to the hole filling effect [21].

The models based on anti-site disorder involving Pr occupying the Ba site (Pr/Ba) [22, 23] and/or *vice versa* (Ba/Pr) [24] have also been considered to explain the absence of superconductivity in the Pr:123 compound. However, the induced disorder might lead to carrier localization resulting in a destruction of superconductivity [24]. The model based on strong hybridization between (Pr 4f) states and (O 2p) conduction band electrons [24, 25] and its sensitivity to disorder leading to localization of holes, offers a possibility to understand the non-superconductivity of the Pr:123 compound.

Recently, the STM studies [26] show that the doping of Pr at the Y site in Y:123 single crystals produces an increase in the formation of rows of vacancies in Cu–O₂ planes, where superconductivity is believed to reside. More interestingly, with Pr substitution, these planes rapidly turns from metallic to quasi-insulating, while Cu–O chains remain metallic and unaffected throughout. However, as far as we know, three reports exist in the literature which claim superconductivity of the Pr:123 compound: one on laser ablated Pr_{0.5}Ca_{0.5}Ba₂Cu₃O_{7-δ} thin film [27], another on bulk Pr_{1-x}Ca_xSr₂Cu_{2.7}Mo_{0.3}O_{7-δ} [28] and one on the recently reported Pr:123 single crystal [29]. Unfortunately, none of these results have been confirmed until now. These results have been greeted with considerable criticism since the structure of the Pr:123 compound reveals an anomalously long *c* parameter, questioning whether this material is truly isostructural with superconducting R:123 material.

With more and more experimental results appearing in the literature, the mystery of non-superconducting the Pr:123 compound is becoming increasingly complicated. In order to examine further the above effects, we report interesting results on the effect of La substitution at the Ba site on the structural and normal state properties of PrBa_{2-x}La_xCu₃O_{7-δ} compound at different values of *x* (0.00 ≤ *x* ≤ 1.00). Our results show that both the hole filling and oxygen disorder effects might be key parameters controlling superconductivity as well as the normal state properties of the Pr:123 compound.

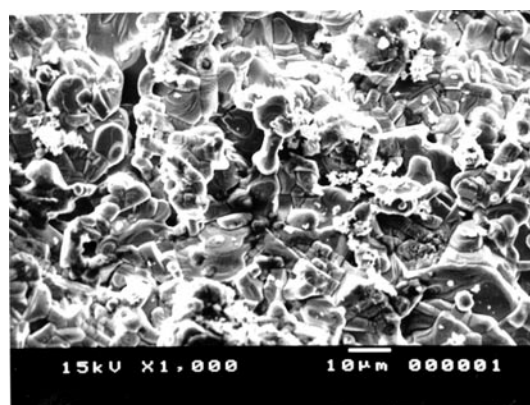
2. Experimental details

Samples of the series PrBa_{2-x}La_xCu₃O_{7-δ}, with *x* = 0.00, 0.25, 0.50, 0.75 and 1.00, were prepared by a solid state reaction method. The ingredients La₂O₃, Pr₆O₁₁, BaCO₃ and CuO of 4 N purity were thoroughly mixed in required proportions and calcined at 910 °C in air for a period of 24 hours. This exercise was repeated three times with intermediate grinding at each stage. The resulting powders were ground, mixed, palletized and annealed in flowing oxygen at 960 °C for a period of 24 hours and then furnace cooled to room temperature with an intervening annealing for 24 hours at 600 °C. The samples were then characterized by x-ray diffraction, scanning electron microscopy and EDX analysis. The resistivity measurements were obtained using the four-probe technique in a closed-cycle refrigerator. The oxygen content of the samples was determined by iodometry titration.

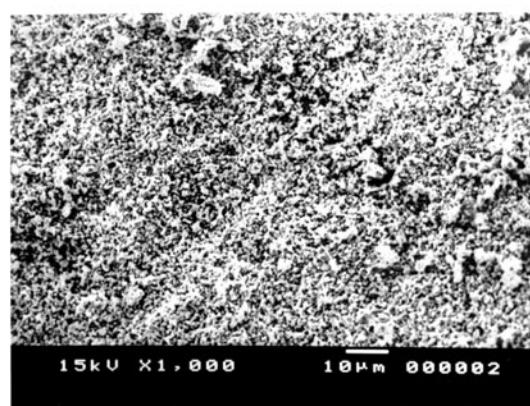
3. Results and discussion

3.1. Surface morphologies and surface composition

Figures 1(a) and (b) show SEM images of PrBa_{2-x}La_xCu₃O_{7-δ} samples, with *x* = 0.00 and *x* = 0.75. It is clear from the images that each sample had a clear grain boundary and a dense uniform structure. The average grain size seems to be decreasing slowly with increasing La content. Figure 2(b) shows the EDX analysis of the *x* = 1.00 sample, while figure 2(a)



(a)



(b)

Figure 1. SEM images of $\text{PrBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-\delta}$ sample surfaces with $x = 0.00$ and 0.75 . (a) $x = 0.00$; (b) $x = 0.75$.

shows the atomic composition ratio obtained from EDX analysis as a function of La content. It is found that the Ba atomic ratio decreases linearly with increasing La content and the total amount of (La + Ba) remains constant. Also, the total amount of Pr and Cu remains constant. These results suggest that La was only substituted at the Ba site without breaking the basic form of the 123 structure.

3.2. X-ray diffraction

Figure 3 shows the room temperature x-ray diffractograms of the $\text{PrBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-\delta}$ compound with $x = 0.00, 0.25, 0.50, 0.75$ and 1.00 . As seen from this figure, the samples with $x = 0.00$ and 0.25 are clearly quasi-tetragonal single phase while the samples with $x = 0.50, 0.75$ and 1.0 are clearly orthorhombic single phase, this being evident from crystallographic splitting of $[006]$, $[200]$ and $[116]$, $[213]$. Figure 4 shows the variation of lattice parameters and orthorhombic distortion, respectively for various x values of the $\text{PrBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-\delta}$ system. As seen from figures 3 and 4,

- (1) The c lattice parameter decreases with increasing La content for all samples, indicating probable substitution of smaller ionic radius $\text{La}(3+)$ (1.28 \AA) for the $\text{Ba}(2+)$ (1.52 \AA) in the system;

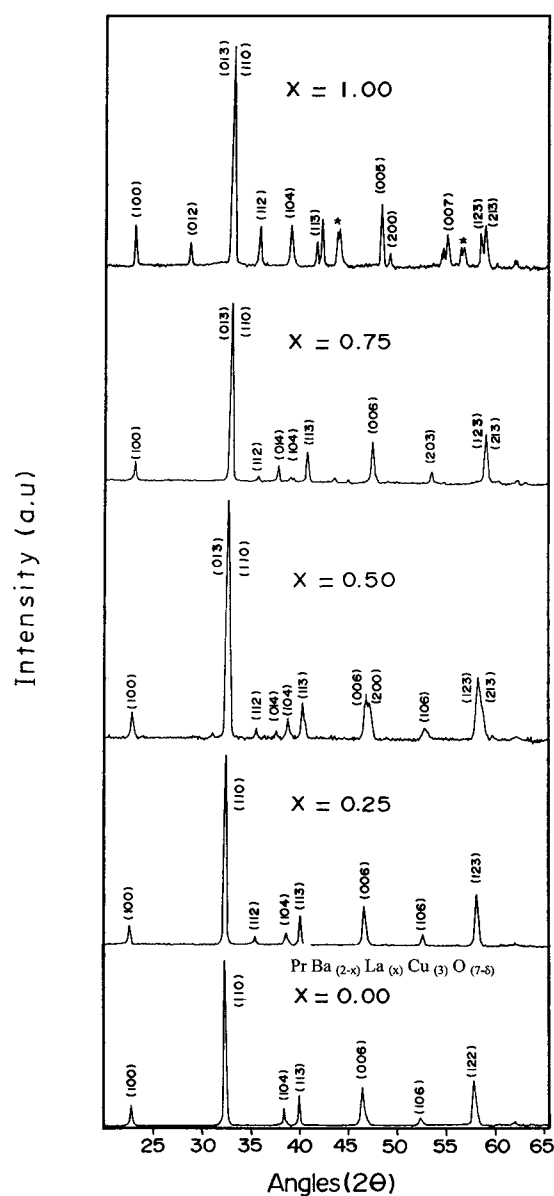


Figure 3. Room temperature x-ray diffractograms for various x values of the $\text{PrBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-\delta}$ compound.

3.3. Oxygen content and effective Cu valence

Figure 5 shows the variation of oxygen content and effective Cu valence for all samples. As seen from the figure that the effective Cu valence decreases linearly with increasing La content along with a small increase in the oxygen content. The decrease in the valency of Cu was brought by substitution of $\text{La}(3+)$ for $\text{Ba}(2+)$. This caused a decrease in the hole carrier concentration along with a small increase in the oxygen content. This is in good agreement with the reported data [30, 31].

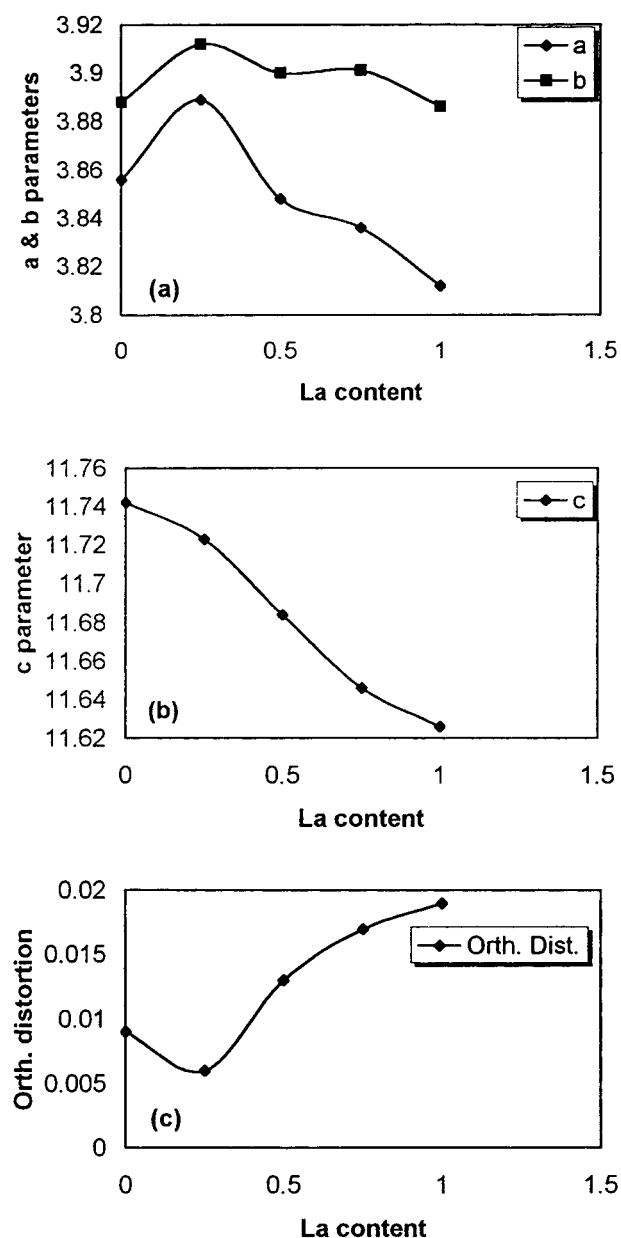


Figure 4. Lattice parameters and orthorhombic distortion, for various x values of the $\text{PrBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-\delta}$ compound.

3.4. Oxygen vacancies and hole carriers

Orthorhombic distortion in R:123 type superconductors is due to missing oxygen in Cu–O chains at the O(5) site. Any increase in the oxygen content beyond 7.0 fills them up and brings the system closer to a tetragonal structure by making O(1) and O(5) occupancies equal. The filling up of O(1) and O(5) of the the Pr:123 compound has an interesting consequence. All

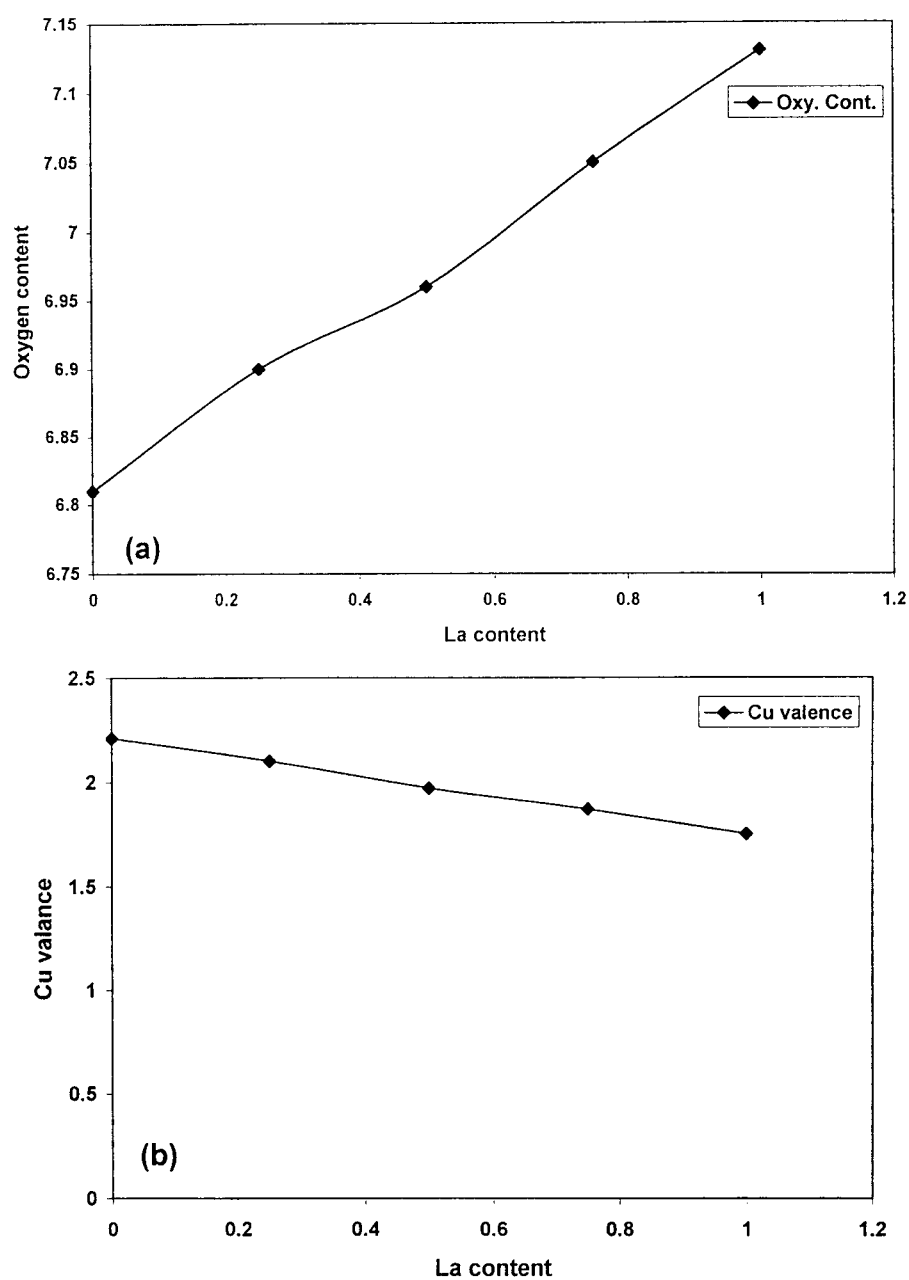


Figure 5. Oxygen content and effective Cu valence for various x values of the $\text{PrBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-\delta}$ compound.

the reported data [5, 26, 32] confirm that the oxygen content of the Pr:123 remains closer to 7.0. This implies that there is no fresh intake of oxygen but it is presumably transferred from some other parts of the unit cell. Since O(4) in the Ba–O plane is crucial to the formation of the R:123 structure without which the system will collapse, it is most unlikely that the oxygen is transferred from O(4) to the empty O(5) site. The O(2) and O(3) in Cu–O₂ planes are the

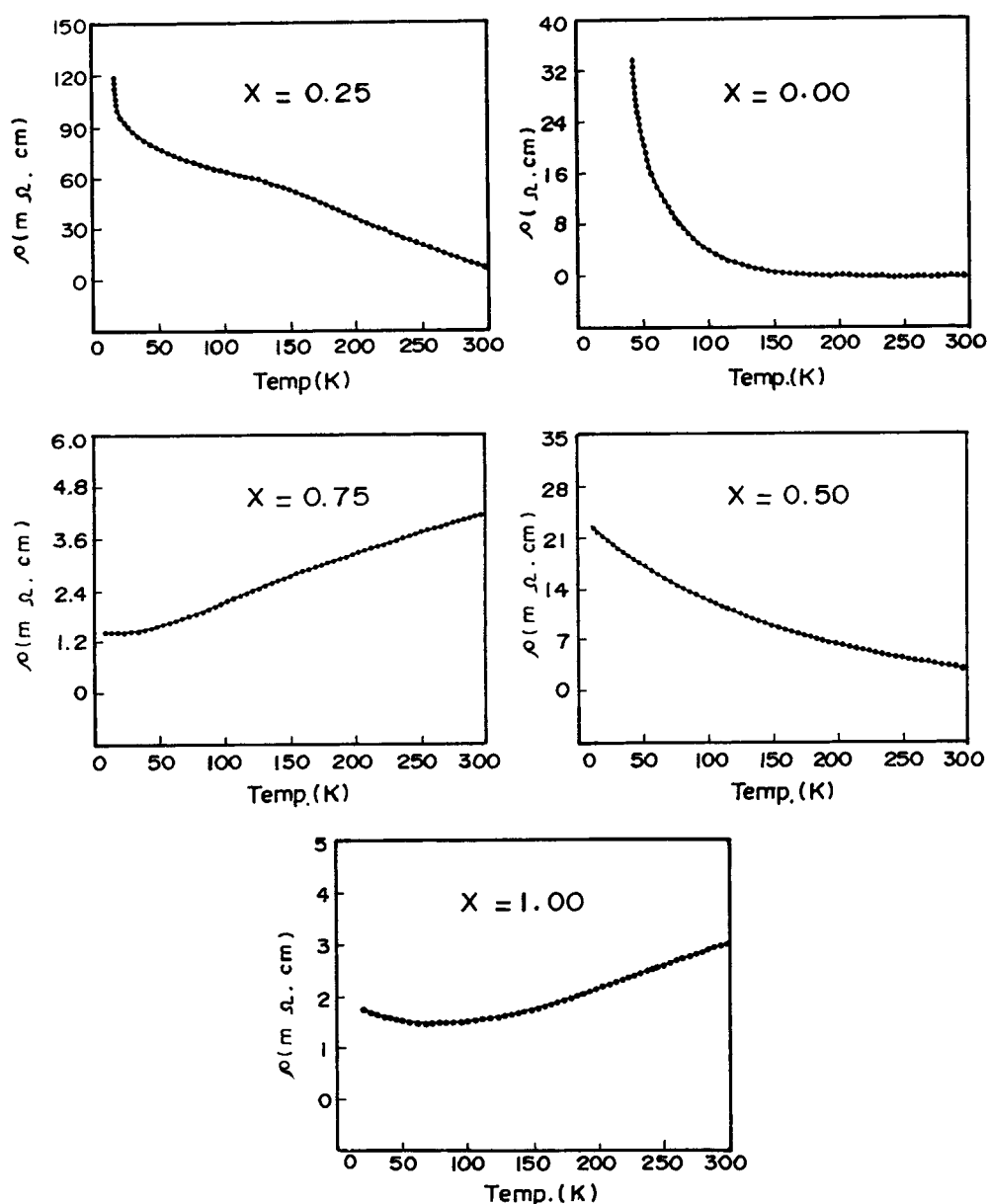


Figure 6. Resistivity versus temperature for various x values of the $\text{PrBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-\delta}$ compound.

only places where the oxygen might be depleted. We expect that the oxygen must be depleted from $\text{Cu}-\text{O}_2$ planes and goes to $\text{O}(5)$ in $\text{Cu}-\text{O}$ chains, and the system of Pr:123 becomes closer to quasi-tetragonal. This is in good agreement with the reported data [26]. On the other hand, the system is turned by La from tetragonal to orthorhombic structure. This is again reflect $\text{O}(5)$ vacancy with orthorhombic distortion similar to R:123 type superconductor. Now, our question is why the system remains non-superconducting. Of course this is due to decreasing

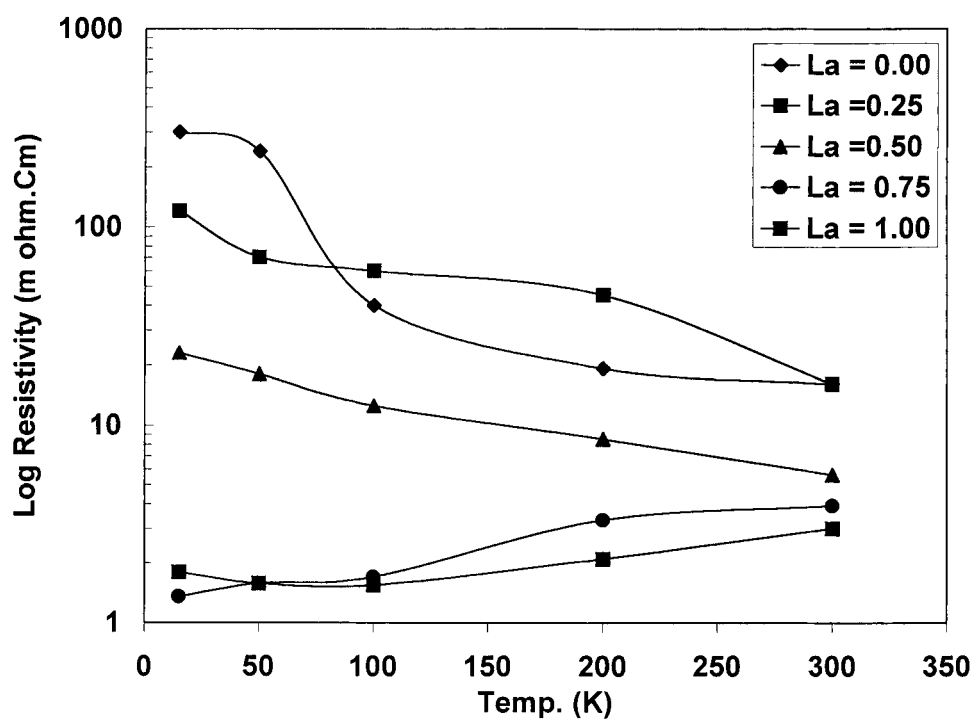


Figure 7. Log resistivity versus temperature for various x values of the $\text{PrBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-\delta}$ compound.

of the hole carriers. Therefore, we suggest that both the hole filling and oxygen disorder effects might be key parameters controlling the superconductivity of the the Pr:123 compound.

3.5. Resistivity

Figure 6 shows the resistivity versus temperature for all samples. The drop of resistivity with temperature at different values of La content for all samples is shown in figure 7. As is evident from these figures, a sharp drop in the resistivity values is observed with increasing La content. Interestingly, the normal state resistivity turns from semiconductor to metallic behaviour at $x = 0.75$ and 1.0 samples without any transition to the superconducting state.

4. Conclusion

The structural and normal state properties of the $\text{PrBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-\delta}$ compound, at different values of x , have been investigated. We have shown that the substitution of La at the Ba site leads to a drop in the normal state resistivity as compared to the Pr:123 compound. We suggest that both the hole filling and oxygen disorder effects might be key parameters controlling superconductivity as well as the normal state properties of the Pr:123 compound.

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