

Crystal structure and resistivity studies on $\text{PrBa}_{2-x}\text{Pr}_x\text{Cu}_3\text{O}_{7-y}$ oxide system

S K MALIK, C V TOMY, RAM PRASAD*, N C SONI* and K ADHIKARI*

Tata Institute of Fundamental Research, Bombay 400 005, India

*Bhabha Atomic Research Centre, Bombay 400 085, India

Abstract. The compound $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ is not superconducting while most other $\text{RBa}_2\text{Cu}_3\text{O}_{7-y}$ ($R = \text{rare earth}$) compounds exhibit superconductivity in the 90 K range. The system $\text{PrBa}_{2-x}\text{Pr}_x\text{Cu}_3\text{O}_{7-y}$ has been prepared to study the effect of excess Pr at the Ba site on the structure, resistivity and magnetic behaviour of this system. It is observed that single-phase compounds in the above series form for $x = 0.8$ —that is up to the composition $\text{Pr}_{1.8}\text{Ba}_{1.2}\text{Cu}_3\text{O}_{7-y}$. While stoichiometric $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ is orthorhombic, the compounds with excess Pr show tetragonal structure. Four-probe dc resistivity measurements show that all the single-phase compounds in the above series do not exhibit superconductivity and are semiconducting down to 12 K. Magnetic susceptibility measurements reveal deviation from Curie-Weiss behaviour starting at a characteristic temperature, which is taken to be the ordering temperature (T_N) of the Pr moments. Both T_N and overall resistivity decrease with increasing x and may have a common origin.

Keywords. $\text{PrBa}_{2-x}\text{Pr}_x\text{Cu}_3\text{O}_{7-y}$; structure; resistivity; magnetism.

1. Introduction

Among the family of $\text{RBa}_2\text{Cu}_3\text{O}_{7-y}$ ($R = \text{rare earth}$) oxide system, the compounds with Ce, Pr and Tb do not exhibit superconductivity although most other compounds are superconducting with T_c in the 90 K range (see, for instance, Murphy *et al* 1987). While the Pr compound is orthorhombic being isostructural to the superconducting $\text{RBa}_2\text{Cu}_3\text{O}_{7-y}$ compounds, Ce and Tb compounds do not even form in the same structure (Yang *et al* 1989). The non-formation of Ce and Tb compounds in the orthorhombic structure type and the absence of superconductivity in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ has been attributed to the capability of these ions to show a valence state of $4+$. The Pr compound is semiconducting down to very low temperatures. Moreover, it exhibits magnetic ordering of the Pr moments with Neel temperature (T_N) of about 17 K (Maple *et al* 1988; Li *et al* 1989), much higher than $T_N = 2.24$ K of the isostructural Gd compound (see, for instance, Dunlap *et al* 1987). The electronic specific heat coefficient, γ , of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ is also extremely large (Maple *et al* 1988; Jee *et al* 1989) suggesting the presence of $4f$ electronic states near the Fermi level. This is indeed confirmed by XPS measurements (Kang *et al* 1988). However, X-ray absorption edge studies reveal that the charge state of Pr is close to $3+$ (Neukirch *et al* 1988; Soderholm and Goodman 1989). Therefore, the absence of superconductivity in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ is thought to be due to strong hybridization between the Pr $4f$ electrons and the Cu-3d and O-2p electrons. This hybridization may also be responsible for the relatively high ordering temperature of Pr moment in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$, similar to the situation in CeRh_3B_2 which orders magnetically at 115 K (Dhar *et al* 1981).

It is known that rare earths can be partially substituted at the Ba site to give rise to compounds of the type $\text{R}\text{Ba}_{2-x}\text{R}_x\text{Cu}_3\text{O}_{7-y}$ (see for instance, Zhang *et al* 1987; Tomy *et al* 1988). The degree of substitution depends on the size of the rare earth ion involved and decreases with decreasing ionic radius. We have examined the system $\text{Pr}\text{Ba}_{2-x}\text{Pr}_x\text{Cu}_3\text{O}_{7-y}$ to study the effect of additional Pr on the structure, superconductivity and magnetism of this compound. We find that Pr can be introduced at the Ba site to the extent of $x=0.8$, i.e. up to the stoichiometry $\text{Pr}\text{Ba}_{1.2}\text{Pr}_{0.8}\text{Cu}_3\text{O}_{7-y}$, beyond which the samples are not single-phase. Magnetic susceptibility measurements reveal that the magnetic ordering temperature decreases with increasing x . Superconductivity is not observed in any of these Pr-rich compounds similar to the situation in stoichiometric $\text{Pr}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$. However, it is interesting to note that the decrease in magnetic ordering temperature is accompanied by a decrease in resistivity.

2. Experimental

The samples were prepared by the standard ceramic procedure. Stoichiometric amounts of Pr_2O_3 or Pr_6O_{11} , BaCO_3 and CuO were thoroughly mixed, pressed into pellets and sintered at 930°C for 24 h. The resulting material was powdered, compacted

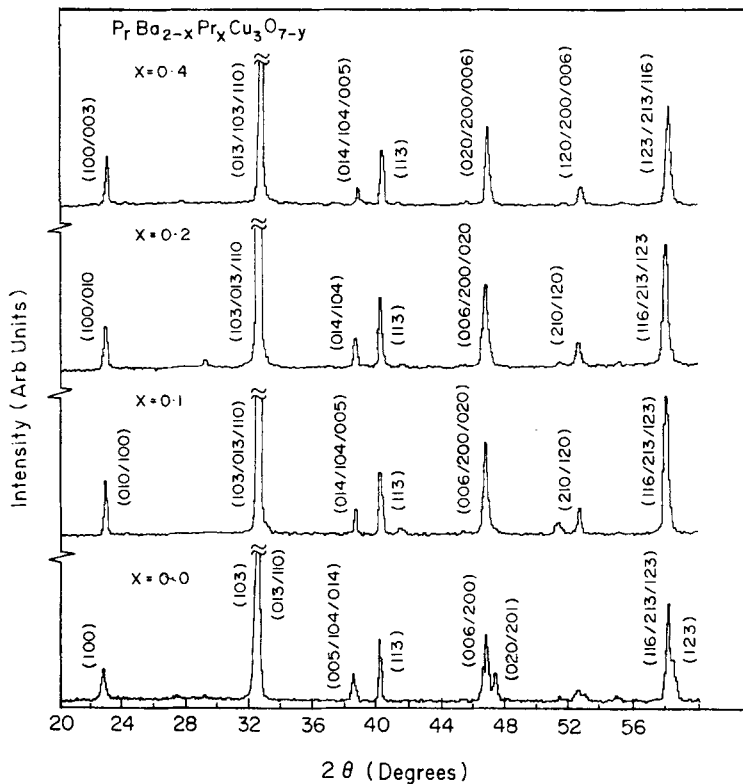


Figure 1. X-ray diffraction patterns of $\text{Pr}\text{Ba}_{2-x}\text{Pr}_x\text{Cu}_3\text{O}_{7-y}$ compounds with $x = 0.0, 0.1, 0.2$ and 0.4 .

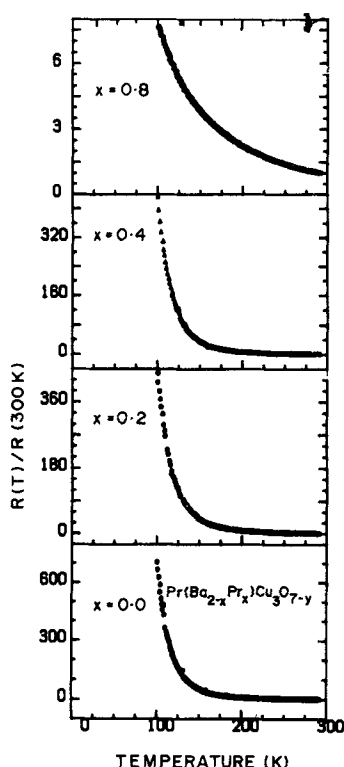


Figure 2. Normalized resistance vs temperature for $\text{PrBa}_{2-x}\text{Pr}_x\text{Cu}_3\text{O}_{7-y}$ compounds with $x = 0.0, 0.2, 0.4$ and 0.8 .

and reheated and this process was repeated twice with the final sintering being done in flowing oxygen atmosphere. Powder X-ray diffraction patterns were obtained on a Sieman's X-ray diffractometer equipped with CuK_α radiation. Electrical resistivity was measured using the four-probe dc method and a computer controlled data acquisition system. Temperature variation was achieved using a closed cycle refrigerator. Susceptibility was measured in the temperature range of 4.2–300 K using a set-up based on Faraday method.

3. Results and discussion

3.1 Structure

Powder X-ray diffraction patterns on some of the samples in the $\text{PrBa}_{2-x}\text{Pr}_x\text{Cu}_3\text{O}_{7-y}$ series with $x = 0.0, 0.1, 0.2$ and 0.4 are shown in figure 1. The X-ray patterns for samples with $x > 0.4$ are also similar to that of $x = 0.4$, except for a small shift in d values. As mentioned earlier, the stoichiometric $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ compound has the orthorhombic structure. In the $\text{PrBa}_{2-x}\text{Pr}_x\text{Cu}_3\text{O}_{7-y}$ series, as x or the Pr concentration increases, the observed X-ray patterns can be indexed on the basis of a tetragonal unit cell.

3.2 Resistivity

The results of four-probe dc resistivity measurements are shown in figure 2. All the compounds in the $\text{PrBa}_{2-x}\text{Pr}_x\text{Cu}_3\text{O}_{7-y}$ series exhibit semiconducting behaviour, similar to the behaviour observed in stoichiometric $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ compound. Thus, superconductivity is not observed in any of these compositions. However, the absolute resistivity seems to decrease with increasing x at all temperatures.

3.3 Susceptibility

Earlier magnetic susceptibility, heat capacity (Maple *et al* 1988), neutron diffraction and μSR (Li *et al* 1989; Cook *et al* 1990) studies have shown that stoichiometric $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ orders magnetically at a temperature of about 17 K. This magnetic ordering is thought to be due to the ordering of Pr moments. Neutron diffraction studies suggest a simple antiferromagnetic ordering with moments along the orthorhombic c axis. However, susceptibility does not reveal a peak at the Néel temperature, typical of antiferromagnetic systems, but instead shows only a change in slope compared to the behaviour expected from Curie–Weiss temperature dependence. This suggests that the magnetic ordering may not be simple antiferromagnetic

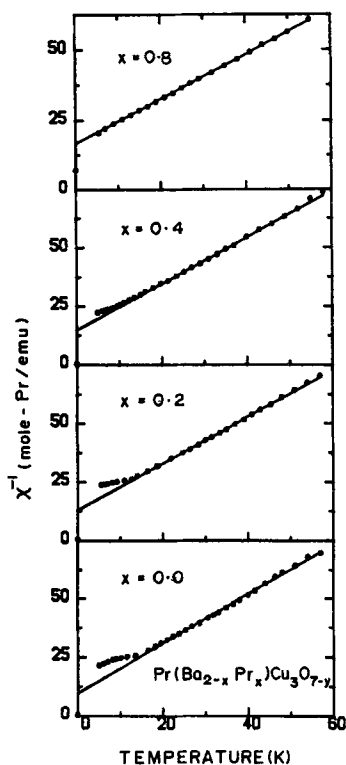


Figure 3. Inverse susceptibility vs temperature for $\text{PrBa}_{2-x}\text{Pr}_x\text{Cu}_3\text{O}_{7-y}$ compounds with $x = 0.0, 0.2, 0.4$ and 0.8 .

type as inferred from neutron diffraction measurements. If the temperature, where a change in slope in susceptibility occurs, is taken to be the magnetic ordering temperature, then our susceptibility measurements shown in figure 3 suggest that this ordering temperature decreases with increasing Pr concentration. The compound with $x = 0.8$ exhibits no deviation from Curie-Weiss behaviour down to 4.2 K, but may do so at lower temperatures.

It is noted that the decrease in ordering temperature is accompanied by a decrease in the overall resistivity and weakening of its temperature dependence. It is possible that both these effects have the same origin. As mentioned earlier, hybridization between Pr-4*f* electrons and Cu-3*d* and O-2*p* conduction electrons is thought to be responsible for the suppression of superconductivity and giving rise to magnetic ordering at 17 K. If the hybridization is reduced, it may result in lower ordering temperatures or no ordering of the Pr moments and therefore may, also lead to superconductivity. The changes in oxygen content with Pr concentration may also influence resistivity and magnetic behaviour. However, preliminary measurements yield quite similar values for oxygen contents for stoichiometric Pr compound (O_{7.05}) and $x = 0.8$ compound (O_{6.9}).

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