

X-ray absorption near-edge structure of $\text{Pr}_{1-x}\text{Ba}_{2+x}\text{Cu}_3\text{O}_7$ H. D. Yang^a, I. P. Hong^a, S. Chatterjee^a, P. Nachimuthu^b, J. M. Chen^b and J.-Y. Lin^c^aDepartment of Physics, National Sun Yat-Sen University, Kaohsiung 804, Taiwan, ROC^bSynchrotron Radiation Research Centre, No. 1, R&D Road VI, Hsinchu 300, Taiwan, ROC^cInstitute of Physics, National Chiao Tung University, Hsinchu 300, Taiwan, ROC

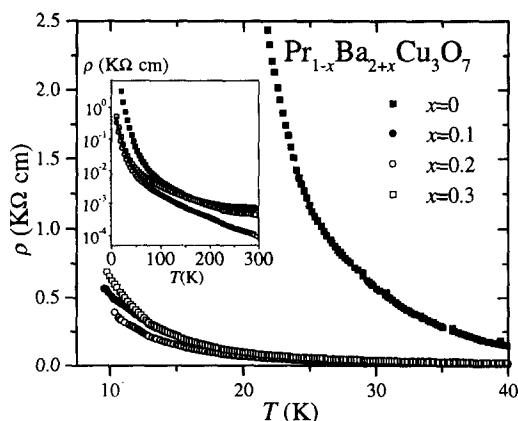
$\text{PrBa}_2\text{Cu}_3\text{O}_7$ (Pr123) has attracted much attention due to its non-superconductivity and other anomalies. The very recent reports on superconducting Pr123, instead of putting an end on this issue, virtually stimulate more controversies. One of the proposed explanations for the recently observed superconductivity in Pr123 is that the samples could be Ba-rich Pr123. To investigate this possibility, we have prepared $\text{Pr}_{1-x}\text{Ba}_{2+x}\text{Cu}_3\text{O}_7$ with $x=0$ to 0.3. It is found that resistivity of the samples becomes smaller with increasing x , together with elongation of the c -axis. O K -edge x-ray absorption structure indicates an increase in the carrier concentration with Ba doping. However, carriers are introduced in a peculiar way rather than simply added into CuO_2 planes.

There is a revived interest in $\text{PrBa}_2\text{Cu}_3\text{O}_7$ (Pr123) owing to the recently reported superconductivity in this compound [1]. Unlike other superconducting $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_7$ (R =rare earth), Pr123 was thought to be an exception that it is an insulator and not superconducting. Many efforts were made to explain the unique behavior of Pr123. Very recently, the superconducting Pr123 single crystals grown by traveling-solvent floating-zone (TSFZ) method, although still controversial, have raised at least two questions: 1) Why are these Pr123 samples made by

TSFZ superconducting, while others are not? 2) T_c of the TSFZ samples can be enhanced from 85 to 105 K under pressure. Is the mechanism of superconductivity in these samples the same as that in other R123? One of the proposed explanations for the superconductivity in Pr123 is that the samples could be Ba-rich Pr123. Moreover, the superconductivity in TSFZ Pr123 is generally believed to be associated with elongation of the c -axis. Further investigation of the magnetic susceptibility in superconducting Pr123 revealed a smaller effective moment than that in insulating Pr123 [2]. These make the studies of Ba-rich $\text{Pr}_{1-x}\text{Ba}_{2+x}\text{Cu}_3\text{O}_7$ interesting.

All polycrystalline $\text{Pr}_{1-x}\text{Ba}_{2+x}\text{Cu}_3\text{O}_7$ ($x=0$ to 0.3) samples were prepared by standard solid-state-reaction method. The structural analysis was carried out by powder x-ray diffraction using $\text{Cu } K\alpha$ radiation. Lattice parameters calculated by the method of least squares do show that the c -axis increases with the increase of Ba content.

Figure 1 shows the temperature variation of resistivity ρ of $\text{Pr}_{1-x}\text{Ba}_{2+x}\text{Cu}_3\text{O}_7$. All samples show insulating behavior down to the lowest temperature of measurement (10 K). But as the Ba content increases, the resistivity decreases up to $x=0.2$. This decrease of resistivity with an increase of Ba content may indicate that the increase in carrier concentration n as the substitution of Ba for Pr can

Figure 1. Resistivity for $\text{Pr}_{1-x}\text{Ba}_{2+x}\text{Cu}_3\text{O}_7$.

introduce more carriers in the samples. Therefore we

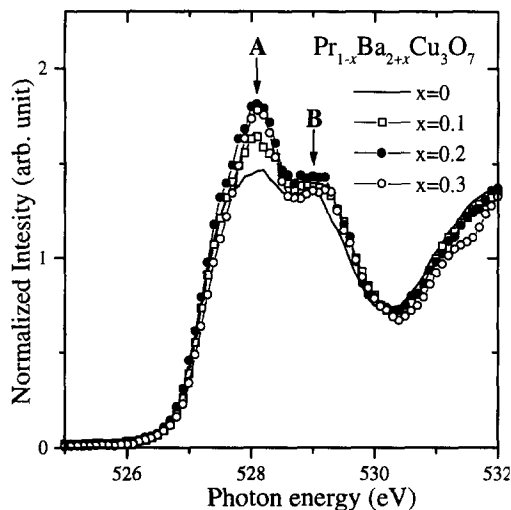


Figure 2. O *K*-edge X-ray fluorescence yield for $\text{Pr}_{1-x}\text{Ba}_{2+x}\text{Cu}_3\text{O}_7$.

may also speculate that the observed superconductivity in Pr123 single crystal grown by TSFZ may be in Ba rich $\text{PrBa}_2\text{Cu}_3\text{O}_7$ single crystal. For $x > 0.2$, ρ is close to that of $x=0$ at high T and is slightly larger than that of $x=0.2$ at low T . This behavior could be attributed to more disorders in $x=0.3$ sample.

To investigate the possible carrier doping in $\text{Pr}_{1-x}\text{Ba}_{2+x}\text{Cu}_3\text{O}_7$, we have also studied the O *K*-edge X-ray absorption near-edge structure (XANES) in these samples. X-ray absorption spectra were recorded by fluorescence yield mode which is a bulk-sensitive technique. XANES is a powerful tool to investigate the unoccupied (hole) electronic states in complex materials [3]. In particular, XANES can give information about n on specific sites. Results of O *K*-edge XANES of $\text{Pr}_{1-x}\text{Ba}_{2+x}\text{Cu}_3\text{O}_7$ are shown in Fig. 2. These spectra are normalized to the values from 600 to 620 eV, and the self-absorption correction has been made. The spectrum of the stoichiometric $x=0$ sample is similar to that in the literatures, with a suppressed peak A at 528.2 eV which indicates a hole-depleted CuO_2 plane and a significant peak B at 529.2 eV which is associated with the upper Hubbard band (UHB). Peak A grows

with increasing x up to $x=0.2$, which indicates an increase of n in the samples. For $x=0.3$, no further growth of peak A was observed which is consistent with the resistivity data. This might be due to either the saturation of carrier doping or incomplete substitution of Ba compared with the nominal composition. The similarity of the trend between the decrease of ρ and the growth of peak A is suggestive that the remarkable decrease in ρ with increasing x is the manifest of the increase of n in the samples. Therefore the substitution of Ba for Pr may benefit occurrence of superconductivity in Pr123. However, the preliminary analysis of XANES indicates that the value of n in $x=0.2$ sample has been close to that of superconducting R123. Thus, merely increasing n may not be sufficient to lead to superconductivity. Furthermore, it is not clear whether the doped holes go to Zhang-Rice (ZR) band which is associated with CuO_2 planes and mainly responsible for superconductivity in other R123. Presumably, an increase in XANES contribution from ZR band would be accompanied by a decreasing optical weight of UHB, in contrast to the persistent peak B with increasing x in Fig. 2. It is possible that the doped carriers reside in the Fehrenbacher-Rice (FR) band which is formed through Pr-O hybridization rather than ZR band [4,5].

In summary, the ρ decreases with the increase of Ba content in $\text{Pr}_{1-x}\text{Ba}_{2+x}\text{Cu}_3\text{O}_7$. The XANES study in this system clearly indicates that the substitution of Ba for Pr introduces holes in the samples. But it is not clear where these doped holes reside. We have speculated that these doped holes may reside in the FR band which is formed through Pr-O hybridization.

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REFERENCES

- [1] Z. Zou, J. Ye, K. Oka, and Y. Nishihara, *Phys. Rev. Lett.* **80** (1998) 1074.
- [2] V. N. Narozhnyi and S.-L. Drechsler, *Phys. Rev. Lett.* **82** (1999) 461.
- [3] J. M. Chen, R. S. Liu, J. G. Lin, C. Y. Huang, and J. C. Ho, *Phys. Rev. B* **55** (1997) 14586.
- [4] R. Fehrenbacher and T. M. Rice, *Phys. Rev. Lett.* **70** (1993) 3471.
- [5] A. I. Liechtenstein and I. I. Mazin, *Phys. Rev. Lett.* **74** (1995) 1000.