

Distribution of Pr ions in $Y(\text{Ba}_{1-x_n}\text{Pr}_{x_n})_2\text{Cu}_3\text{O}_y$

Dong Han Ha*, Kyu Won Lee, Jin-Tae Kim, Yong Ki Park and Jong-Chul Park

**Korea Research Institute of Standards and Science, P.O. Box 102, Yusong, Taejeon 305-606, Korea*

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Abstract

Distribution of Pr ions between Y- and Ba-site of the $Y(\text{Ba}_{1-x_n}\text{Pr}_{x_n})_2\text{Cu}_3\text{O}_y$ ($0 \leq x_n \leq 0.3$, x_n : nominal composition) material prepared by the solid state reaction method was studied. Although the samples have narrow superconducting transition, tiny peaks of Y_2BaCuO_5 impurity phase are included in the x-ray diffraction patterns suggesting that some of the Pr ions are entered into the Y-site. The distribution of Pr ions between Y- and Ba-site was determined by measuring the mass fraction of YBCO and Y_2BaCuO_5 phase for each sample through the Rietveld analysis of the x-ray diffraction data. About 60 % of Pr ions occupy the Y-site regardless of the Pr content. Various superconducting parameters such as the oxygen content and the hole concentration etc. are compared before and after the impurity correction.

Keywords: YBCO, Substitution, Impurity correction, Rietveld method, Hole concentration

I. Introduction

Among the rare earth elements, Pr is one of the most interesting ions in that the superconductivity of $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_y$ (R: rare earth element) deteriorates rapidly with Pr doping [1]. There have been many results describing the loss of superconductivity in the $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_y$ system. The substitution of Y by Pr is reported to suppress T_c by reducing the hole concentration on the CuO_2 plane due to the tetravalent Pr ions or by localizing the mobile holes but not hole filling [2-4]. Recently, Merz et al. suggested that the suppression of superconductivity is due to the change of character of the oxygen holes from P_σ to P_π [5].

Blackstead et al. [6,7], however, ascribed the depression of T_c with Pr doping to the breaking of Cooper pairs in chain layers by the unintended Ba-site Pr^{3+} . Large rare earth elements like La, Ce, Pr and Nd can be substituted into both R- and Ba-site of $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_y$ materials. Reports on the bulk superconductivity of $\text{Pr}\text{Ba}_2\text{Cu}_3\text{O}_y$ and high T_c above 95 K for $\text{Nd}\text{Ba}_2\text{Cu}_3\text{O}_y$ single crystal prepared under the oxy-

gen-reduced atmosphere, which is suspected to minimize the amount of the Ba-site Pr or Nd ions, seem to support the role of Ba-site Pr or Nd in the superconductivity [8,9].

When we try to synthesize a doped superconductor, for example $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_y$, all Ca ions do not enter only into the Y-site. Some of them also enter into the Ba-site leaving BaCuO_2 as a secondary phase [10]. The Y^{3+} -site Ca^{2+} may suppress the superconductivity rapidly by increasing the hole concentration on the CuO_2 plane above the optimum region although the Ba²⁺-site Ca^{2+} hardly change it, that is, the superconducting property is sensitively affected by the distribution state of doping ions between Y- and Ba-site. Therefore, the measurement of distribution state of doping ions among the various sites of a superconductor is very important for the correct understanding of the material. For most cases, however, the analysis of experimental data has been carried out on the assumption that all the doping ions are substituted into the intended site. In this work, we have measured the distribution of Pr ions between Y- and Ba-site of superconductors with nominal compositions of $Y(\text{Ba}_{1-z}\text{Pr}_z)_2\text{Cu}_3\text{O}_y$ ($0 \leq x_n \leq 0.3$) and the

Corresponding author: Fax: 82-42-868-5475

e-mail: dhha@kriss.re.kr

effect of impurity on the superconducting parameters has been also discussed.

II. Experiments

Samples were prepared by mixing and heating Y_2O_3 , $BaCO_3$, Pr_6O_{11} and CuO powders in the nominal composition of $Y(Ba_{1-x_n}Pr_{x_n})_2Cu_3O_y$. Each material was sintered between 945 °C and 995 °C in oxygen atmosphere with increasing the sintering temperature as Pr content increases. Resistivity was measured by the conventional four probe method for each sample with a typical size of $1 \times 2 \times 10$ mm³. XRD data were collected using $CuK\alpha$ line at 0.04° step for 5 s in the range of 2θ between 20° and 120°. Crystallographic structure and the mass ratio of YBCO phase to secondary phase for each sample were analyzed by the Rietveld method [11]. Average valence state of Cu and oxygen content were measured by the iodometric titration method [12]. Total hole concentration (P_t), hole concentration on the CuO_2 layer (P_{pl}) and that on the Cu-O layer (P_{ch}) were calculated from the average valence state of Cu and the oxygen content using the Tokura's rule [13].

III. Results and Discussion

Fig.1 shows XRD patterns of $Y(Ba_{1-x_n}Pr_{x_n})_2Cu_3O_y$ samples. As Pr content increases, (020) and (200) peaks of YBCO phase between 46° and 48° merge into a single peak which indicates the lattice symmetry of the sample changes from the orthorhombic to the tetragonal structure around $x_n = 0.2$. c-axis parameter decreases monotonically due to the dominant effect of the substitution of large Ba^{2+} ions by small Pr^{3+} ions. Contrary to the starting material of $Y_{1-x}Pr_xBa_2Cu_3O_y$ for which $BaCuO_2$ is precipitated as a secondary phase [14], Y_2BaCuO_5 secondary phase is formed due to the unintended partial displacement of Y-site by Pr ion as described by the Eq. (1). Peaks of Y_2BaCuO_5 increase with increasing Pr content, but there is no trace of impurity phase for the sample of $x_n = 0.0$. Here, A and B are the mole numbers of YBCO and Y_2BaCuO_5 phase respectively. α and β are

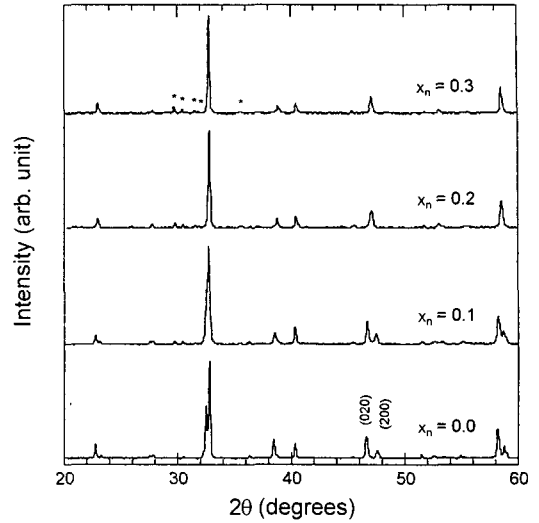
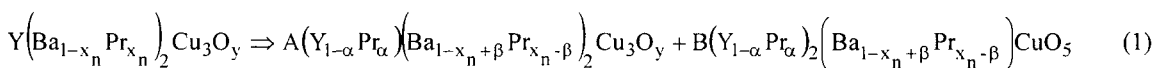


Fig. 1 X-ray powder diffraction patterns of the $Y(Ba_{1-x_n}Pr_{x_n})_2Cu_3O_y$ samples. x_n is the nominal composition. (*) marks denote peaks from the Y_2BaCuO_5 secondary phase.

the correction parameters for the actual Pr concentration on the Y- and Ba-site. In the Eq. (1), we assumed that the Pr occupancies on the Y- and Ba-site of YBCO phase is the same as those of Y_2BaCuO_5 phase. Y ion is supposed not to enter into the Ba-site since the ionic radius of Y^{3+} ion is fairly small compared with that of Ba^{2+} ion [15]. Actually, we could observe no trace of Y_2BaCuO_5 phase in the XRD pattern of the sample of $x_n = 0.0$.

The mass fraction of YBCO and Y_2BaCuO_5 phase contained in each sample was measured by the Rietveld analysis of the XRD data. Rietveld analysis was carried out with a RIETAN program for two phases material [16]. XRD peaks of YBCO phase are well indexed on the basis of the orthorhombic structure with Pmmm symmetry for $x_n < 0.2$ or on the basis of the tetragonal structure with $P4/mmm$ symmetry for $x_n \geq 0.2$. Those of Y_2BaCuO_5 are well refined on the basis of the orthorhombic structure with Pnma symmetry. Mass ratio of YBCO to Y_2BaCuO_5 phase contained in the sample is shown in Fig. 2. The portion of Y_2BaCuO_5 impurity phase increases with increasing Pr content.



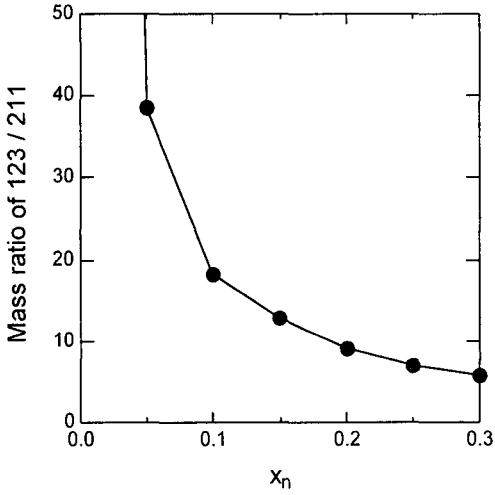


Fig. 2 Mass ratio of YBCO and Y_2BaCuO_5 phase contained in the the $Y(Ba_{1-x_n}Pr_{x_n})_2Cu_3O_y$ samples. x_n is the nominal composition.

Fig. 3 is the temperature dependence of the resistivity for $Y(Ba_{1-x_n}Pr_{x_n})_2Cu_3O_y$ samples. The samples have single step superconducting transition indicating that Pr ions are substituted uniformly into the sample. As Pr content increases, resistivity at the normal state is monotonically increased and the superconductivity is disappeared at $x_n = 0.35$. It is considered that the superconductivity is deteriorated more and more with increasing Pr content mainly due to the reducing of the hole concentration on the CuO_2 plane as discussed later. However, Fig. 1 and Fig. 3 show that the superconductivity is maintained in the tetragonal structure up to about $x_n = 0.6$.

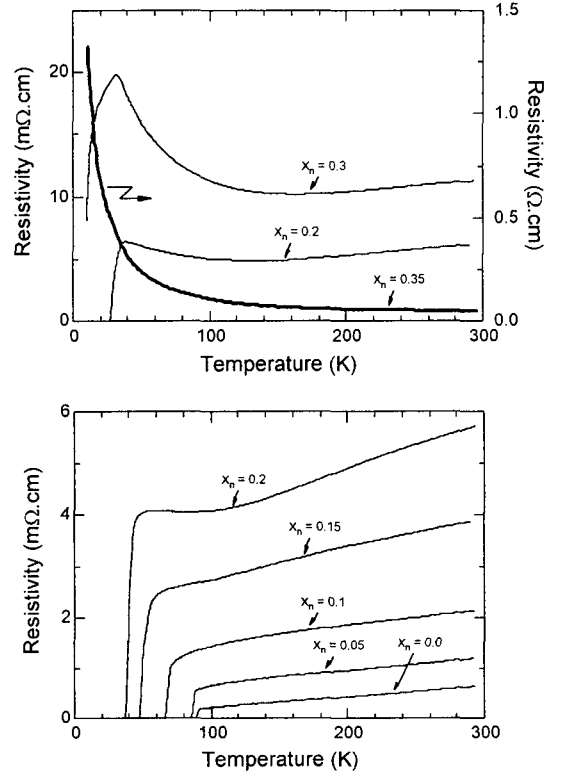


Fig. 3 Temperature dependence of the electrical resistivity of the $Y(Ba_{1-x_n}Pr_{x_n})_2Cu_3O_y$ samples. x_n is the nominal composition

We summarize lattice parameters and superconducting transition temperature (T_c) of each sample and the parameters of eq. (1) in Table I. T_c is determined by the resistivity measurement. The parameters of eq. (1) are calculated from the data of Fig. 2 by assuming that the number of each ion on both sides of

Table I. Lattice parameters and superconducting transition temperature of $Y(Ba_{1-x_n}Pr_{x_n})_2Cu_3O_y$ samples and the parameters of eq. (1). x_n is the nominal composition. Actual Pr concentration at the Y- and Ba-site is given by α and $x = x_n - \beta$. Parameters of eq (1) are determined by the Rietveld analysis of the XRD data. $T_{c(zero)}$ of $x_n = 0.3$ sample was determined by the extrapolation.

x_n	a (Å)	b (Å)	c (Å)	$T_{c(zero)}$ (K)	A	B	α	β
0.0	3.8193	3.8847	11.6834	89.5	~1.0	~0.0	~0.0	~0.0
0.05	3.8220	3.8854	11.6701	85.5	0.992	0.024	0.038	0.020
0.1	3.8262	3.8820	11.6530	65.5	0.986	0.042	0.066	0.036
0.15	3.8392	3.8731	11.6340	47.0	0.979	0.064	0.096	0.054
0.2	3.8549	3.8547	11.6019	36.5	0.968	0.097	0.139	0.083
0.25	3.8567	3.8567	11.5819	25.5	0.961	0.117	0.163	0.100
0.3	3.8569	3.8569	11.5516	~7	0.952	0.145	0.195	0.125

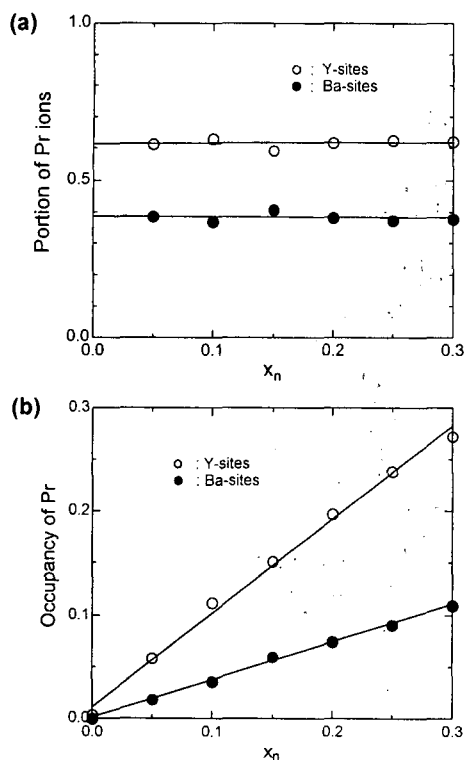


Fig. 4 (a) The portion of Pr ions entered into the Y- and Ba-site of $Y(Ba_{1-x_n}Pr_{x_n})_2Cu_3O_y$. (b) Occupation of Pr ion on the Y- and Ba-site of $Y(Ba_{1-x_n}Pr_{x_n})_2Cu_3O_y$. x_n is the nominal composition.

eq. (1) is the same. Table I shows that the amount of Y_2BaCuO_5 phase is fairly much although it displays itself only as tiny peaks in the XRD patterns. For example, the molar ratio of YBCO to Y_2BaCuO_5 phase is about 4.1 : 1 for $x_n = 0.3$.

Fig. 4(a) shows that some of Pr ions enter into the Y- and Ba-site of YBCO and Y_2BaCuO_5 phase. Unexpectedly, majority of Pr ions (about 60 %) enter into the unintended Y-site regardless of Pr content. As Pr content increases, the occupancy of Pr ion on the Y- and Ba-site of YBCO and Y_2BaCuO_5 phase increases linearly as shown in Fig. 4(b). Up to the present, however, the analysis of experimental data has been carried out on the assumption that all the doping ions are substituted only into the intended sites. Fig. 3(a) shows that a large amount of doping ions may enter into the unintended sites under certain circumstance which can result in the unavoidable error in the characterization of oxide superconductors.

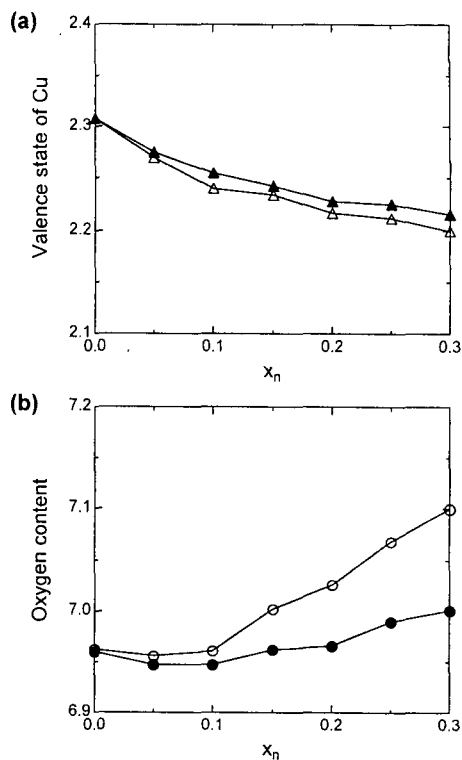


Fig. 5 (a) Average valence state of Cu and (b) oxygen content of $Y(Ba_{1-x_n}Pr_{x_n})_2Cu_3O_y$ before (open marks) and after (closed marks) the impurity correction. x_n is the nominal composition.

In Fig. 5, we show the average valence state of Cu and the oxygen content of $Y(Ba_{1-x_n}Pr_{x_n})_2Cu_3O_y$ samples measured by the iodometric titration method before and after the correction of the impurity effect. Pr ion is assumed to have Pr^{3+} state on the Ba-site since ionic radius of Pr^{4+} (0.96 Å) [15] is too small to occupy the Ba-site. Every experimental method reports different results on the valence state of Pr ion on the Y-site, however, Pr ion is supposed here to have an average valence state of +3.5 on the Y-site as Matsuda et al. [16] reported. As Pr content increases, valence state of Cu reduces but oxygen content increases in order to maintain the sample neutral charge. After the correction of the impurity effect, valence state of Cu increases slightly but oxygen content reduces considerably as compared with those before the correction.

Fig. 6 shows the hole concentration on the CuO_2 plane (P_{pl}) and Cu-O chain (P_{ch}) calculated using the

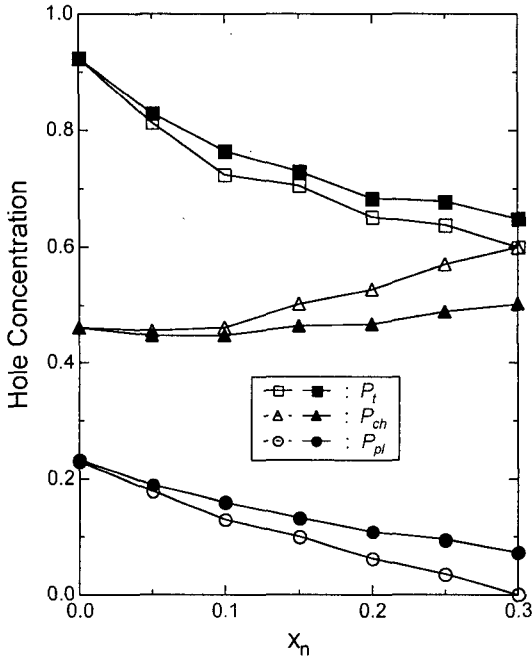


Fig. 6 Total hole concentration per unit cell (squares), hole concentration on the Cu-O layer (triangles) and that on the CuO_2 layer (circles) of $Y(\text{Ba}_{1-x_n}\text{Pr}_{x_n})_2\text{Cu}_3\text{O}_y$ before (open marks) and after (closed marks) the impurity correction. x_n is the nominal composition.

data of Fig. 4 by the Tokura's rule. As Ca concentration increases, P_{ch} increases but P_{pl} reduces, indicating that the holes transfer from the CuO_2 plane to the Cu-O chain. Pr ions substituted into the Y-site supply 0.5 holes per Pr ion while those on the Ba-site reduce 1 hole per Pr ion. Therefore, the total hole concentration per unit cell, $P_t = P_{ch} + 2 P_{pl}$ decreases monotonically due to the dominant effect of Pr ion on the Ba-site. Compared with the impurity corrected P_t , the uncorrected P_t decreases more rapidly since all Pr ions are supposed to enter into the Ba-site in this case.

Before the impurity correction, P_{pl} decreases below 0.06 for $x_n \geq 0.25$ which is known as the lower limit for the superconductivity in the electronic phase diagram. If the impurity effect is not corrected, $x_n = 0.25$ and 0.3 samples with $P_{pl} < 0.06$ will also have superconductivity which obviously contradict to the electronic phase diagram of high T_c superconductors. After the impurity correction, however, P_{pl} has a value above 0.06 for the samples of $x_n \geq 0.3$ as

shown in Fig. 5. The resistivity shows metallic behavior at low Pr content. As P_{pl} reduces, however, the resistivity at normal state increases monotonically and shows up-turn around T_c for $P_{pl} < 0.12$. Fig. 4 and Fig. 5 show that the effect of impurity correction in the characterization of YBCO superconductors can be quite large although it is contained in the sample as little as can be barely observed in the XRD pattern.

IV. Conclusion

We have measured the fraction of Pr ions entered into the Y- and Ba-site of superconductors with nominal compositions of $Y(\text{Ba}_{1-z}\text{Pr}_z)_2\text{Cu}_3\text{O}_y$ ($0 \leq x_n \leq 0.3$) by analyzing the x-ray diffraction data. About 60 % of Pr ions enter into the Y-site while the others enter into the Ba-site irrespective of Pr content. The unintended substitution into the Y-site results in the formation of Y_2BaCuO_5 secondary phase. Various superconducting parameters like the hole concentration and the oxygen content etc. are considerably changed after the impurity correction. Our results show that the effect of impurity phase should not be neglected in the characterization of superconductors although it is contained in the sample so little that can be barely observed as tiny peaks in the XRD patterns.

References

- [1] H. B. Radousky, *J. Mater. Res.*, **7**, 1917-1955 (1992).
- [2] K. Kodama, S. Shamoto, H. Harashina, M. Sato, M. Nishi and K. Kakurai, *Physica C* **263**, 333-335 (1996).
- [3] A. Matsuda, K. Kinoshita, T. Ishii, H. Shibata, T. Watanabe and T. Yamada, *Phys. Rev. B* **38**, 2910-2913 (1988).
- [4] J. Fink, N. Nucker, H. Romberg, M. Alexander, M. B. Maple, J. J. Neumeier and J. W. Allen, *Phys. Rev. B* **42**, 4823-4826 (1990).
- [5] M. Merz, N. Nucker, E. Pellegrin, P. Schweiss, S. Schuppler, M. Kielwein, M. Knupfer, M. S. Golden, J. Fink, C. T. Chen, V. Chakarian, Y. U. Idzerda and A. Erb, *Phys. Rev. B* **55**, 9160-9172 (1997).
- [6] H. A. Blackstead and J. D. Dow, *Phys. Rev. B* **51**, 11830-11837 (1995).
- [7] H. A. Blackstead, J. D. Dow, D. B. Chrisey, J. S. Horwitz, M. A. Blank, P. J. McGinn, A. E. Kunzinger and D. B. Pulling, *Phys. Rev. B* **54**, 6122-6125 (1996).
- [8] Z. Zou, K. Oka, T. Ito, Y. Nishihara, *Jpn. J. Appl.*

- Phys. **36**, L18-L20 (1997).
- [9] M. Nakamura, H. Kutami and Y. Shiohara, *Physica C*, **260**, 297-304 (1996).
- [10] D. H. Ha et al, to be published in *Physica C*.
- [11] R. A. Young, "Introduction to the Rietveld Method" in *The Rietveld Method*, eds. R. A. Young, Oxford: Oxford University, 1-38 (1993).
- [12] A. I. Nazzal, V. Y. Lee, E. M. Engler, R. D. Jacowitz, Y. Tokura and J. B. Torrance, *Physica C* **153-155**, 1367-1368 (1988).
- [13] Y. Tokura, J. B. Torrance, T. C. Huang and A. I. Nazzal, *Phys. Rev. B* **38**, 7156-7159 (1988).
- [14] K. Kinoshita, A. Matsuda, H. Shibata, T. Ishii, T. Watanabe and T. Yamada, *Jpn. J. Appl. Phys.*, **27**, L1642-L1645 (1988).
- [15] R. D. Shanon, *Acta. Crystallogr. A* **32**, 751-767 (1974).
- [16] F. Izumi, "Rietveld analysis programs RIETAN and PREMOS and special applications" in *The Rietveld Method*, eds. R. A. Young, Oxford: Oxford University, 236-253 (1993).