Effect of Pr and Ca Substitution on the 
\((La_{1-x-u}Pr_xCa_u)(Ba_{1.5}Sr_{0.5})Cu_3O_y\) Superconductors

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In the fully oxygenated single phase \((La_{1-x-u}Pr_xCa_u)(Ba_{1.5}Sr_{0.5})Cu_3O_y\) \((0 \leq x \leq 1.00, 0 \leq u \leq 0.20)\) system, if \(u = 0\), the z-coordinate of the Ba site, \(z(Ba)\), and \(d_{Ba-bp}\) (distance between the Ba site and the basal plane) are lowered by increasing the amount of Pr in the \((La_{1-x}Pr_x)(Ba_{1.5}Sr_{0.5})Cu_3O_y\) series. On the contrary, if \(u \neq 0\), \(z(Ba)\) and \(d_{Ba-bp}\) are raised by increasing the amount of Ca ion in the \((La_{1-x-u}Pr_xCa_u)(Ba_{1.5}Sr_{0.5})Cu_3O_y\) \((0 \leq x \leq 0.30, 0 \leq u \leq 0.20)\) series. Linear relationships are found between \(z(Ba)\), \(d_{Ba-bp}\) and the oxygen stoichiometry \((y)\). \(T_c\) and \(p_{sh}\) (the hole concentration in CuO$_2$ layers) increase with increasing the angle \(\angle Cu(2)-Ba-Cu(2)\). Relative positions of the Cu(2) and Ba sites are important in determining the \(T_c\) of these 123 compounds.

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1. INTRODUCTION

Existence of the superconductivity around 90 K in the most of the RBa$_2$Cu$_3$O$_y$ (abbreviated as R123, with R = rare earth) compounds are found $^{1-3}$. $T_c$ does not depend on the ionic radius and the magnetic properties of the R ion. On the contrary, partial substitution of the R by the Pr ion, $T_c$ depends on the amount of Pr and the radius of the R ion $^{4-7}$. Ion-size effect is found in the \((R_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}\) series. For a larger lanthanide, the decreasing rate of the $T_c$ is enhanced with the same amount of substitution. For example, in the \((R_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}\) system, for \(x = 0.3\), if \(R = \text{Nd}\), $T_c$ is 7.5 K; and if \(R = \text{Yb}\), $T_c$ is 69.5 K $^4$. Similar results happen in the partial substitution of Sr for Ba ion. For example, in the \(R(Ba_{2-x}Sr_x)Cu_3O_{7-\delta}\) system, for \(x = 0.5\), if \(R = \text{La}\), $T_c = 52$ K; and if \(R = \text{Ho}\), $T_c = 87$ K $^8$.
Many investigations show that lowering the $T_c$ in the partial substitution of Pr for R is related to the valence of the Pr ion, which is greater than 3. It suppresses the superconductivity by a reduced number of carriers in the CuO$_2$ planes 9–11 and effectively leaving the holes localized on the Pr ion. Another mechanism explaining the results is the so-called pair breaking, which is due to spin dependent exchange scattering of mobile holes in the CuO$_2$ valence band by magnetic Pr ions 5,12–15.

The substitution of Ca in the (R$_{1-x}$Pr$_x$Ca$_u$)Ba$_2$Cu$_3$O$_{7-\delta}$ system causes a hole doping and results in increasing $T_c$ 10,15,16. Similar results happen in the (La$_{1-x}$Pr$_x$Ca$_u$)(Ba$_{1.5}$Sr$_{0.5}$)Cu$_3$O$_y$ system 17. In the (Y$_{1-x}$Pr$_x$Ca$_u$)Ba$_2$Cu$_3$O$_{7-\delta}$ series, Neumeier et al. suggest that the valence of Ca ion is 2+, which may counteract the effect caused by the Pr ion if it is in a valence of 4+ or a mixed valence state 10. Adding an appropriate amount of Ca to (Y$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{7-\delta}$, holes are created to the unit cell and prevent the magnetic pair breaking. In our previous reports, 20 % of the Pr ions is assumed in the tetravalent state in the (La$_{1-x}$Pr$_x$)(Ba$_{1.5}$Sr$_{0.5}$)Cu$_3$O$_{7-\delta}$ series 17. Introducing Ca into the La site, hole concentration in the CuO$_2$ planes ($p_{sh}$) do increase with the amount of Ca ion increased 17.

In order to find the structural factors governing the $T_c$ of these Pr containing 123 compounds, Rietveld refinement is employed for the analysis of the (La$_{1-x}$Pr$_x$Ca$_u$)(Ba$_{1.5}$Sr$_{0.5}$)Cu$_3$O$_y$ (0 ≤ x ≤ 1.00, 0 ≤ u ≤ 0.20) system.

2. EXPERIMENTAL

X-ray powder diffraction patterns were used for the Rietveld refinement. The computer software, X-window version of the fat-Rietan-94, is revised by Isumi. Models for the structural refinement was based on the crystal structure of a tetragonal YBa$_2$Cu$_3$O$_y$ compound 18. Labeling of the oxygen atoms defined as that of Capponi et al. 19 was as follows: O(1) site was the apical oxygen between Cu(1) and Cu(2) sites, O(2) site on the superconducting CuO$_2$ planes, O(3) site on the basal plane. Occupation numbers in the O(1) and O(2) sites were assumed as 1. Chemical bond length and the distance between atomic sites were calculated from the coordinates of the atomic positions in the unit cell.

3. RESULTS and DISCUSSION

Several series of compounds with the compositions of (La$_{1-x}$Pr$_x$)(Ba$_{1.5}$Sr$_{0.45}$)Cu$_3$O$_y$ (0 ≤ x ≤ 1.00), (La$_{1-u}$Ca$_u$)(Ba$_{1.5}$Sr$_{0.45}$)Cu$_3$O$_y$ (0 ≤ x ≤ 0.20)