Abstract

A structural study of the incorporation of Pr-ion into the Y-site was realized in polycrystalline samples of (Y_{1-x}Pr_x)Ba_2Cu_3O_7 through of Rietveld analysis of X-ray diffraction patterns, bond valence method and electronic density diagrams. The crystalline structure stabilized into orthorhombic phase (Pmmm) for x=0, but the unit cell increases its symmetry by doping the Y-site and stabilizing into a tetragonal phase (P4/mmm) for x=0.5. Moreover, the structural results obtained were correlated with the magnetization measurements, where the T_c decreased from 90K (x=0.0) to 49K (x=0.3). The oxygen content in the compounds was checked by means of μ-Raman spectroscopy, observing the frequency position of O(4)-A_g phonon mode.

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1. Introduction

An elegant probe of the nature of cuprate superconductors is the substitution of Y atom by others members of Lanthanides, (Y_{1-x}Ln_x)Ba_2Cu_3O_7 [1]. Among these atoms, only Ce and Pr are not superconducting at concentration x=1, with x_{critical}~0.50 [2]. The (Y_{1-x}Pr_x)Ba_2Cu_3O_7 oxide is a fascinating
system because it sheds lights on the mechanism of superconductivity in cuprate oxide superconductors. Moreover, the nature of the non-superconducting cuprates has not been fully investigated, although it has been suspected that the absence of superconductivity may have some relationship to the presence of the rare-earth ion in the 4+ state.

The electronic properties in high-Tc superconducting compounds are indeed very important because they define the superconducting properties of the materials. The electronic bands states in the electronic structure are very sensitive to short-range order in the atomic positions [3]. Furthermore, the crystallochemical aspects of electronic structure of oxide superconductors are due to the individual properties of constituent ions and also the effect of the atomic substitutions on the electronic properties. We have investigated the (Y1-xPrx)Ba2Cu3O7 system in some detail to understand the relation between the oxygen content, crystal structure and magnetic properties, on basis of the results of Rietveld analysis, bond valence method and electronic density diagrams, correlating the results with magnetization measurements and oxygen content.

2. Experimental

Polycrystalline samples of (Y1-xPrx)Ba2Cu3O7, with x=0.0, 0.10, 0.30, 0.50 were prepared by standard solid state reaction technique using stoichiometric amounts of high purity powders precursors, such as: Y2O3, Pr6O11, BaCO3 and CuO from Alfa Aesar. The resultant powders were reground and pelletized into disc-shape. We applied thermal treatments for three times consisting of the following steps: calcinated to 1203K for 24h, synthesized to 1208K for 24h, and then annealed to 773K for 20h in oxidizing atmosphere.

X–ray powder diffraction data were collected at room temperature with universal powder diffractometer, HGZ (Cu Kα radiation) in Bragg-Brentano geometry. The diffraction range was between 10º and 80º and step of 0.02º. The standard analyzing program called Fullprof was used to perform the Rietveld refinements, bond valence sums and electronic density diagrams. The μ-Raman spectra were carried out by using a YAG laser (λ=532nm) and RH800 Horiba Jovin-Yvon Raman spectrometer with CCD detector cooling by air in back-scattering configuration. The laser power was kept low as possible (0.5mW) to avoid deoxygenation of the sample. The magnetization measurements, M(T), was obtained using a magnetic property measurement system (MPMS) with SQUID sensor from Quantum Design in field cooling process with a external field of 5 Oe, for range of temperatures between 5 and 100 K.

3. Results

The x-ray diffraction patterns of [Y1-x,Prx]Ba2Cu3O7 showed a very good crystallinity. The analysis by Rietveld refinement revealed that the crystalline structure stabilized into an orthorhombic phase (Pmmm) for x=0, but the unit cell increases slightly its symmetry until it is stabilized in a tetragonal phase (P4/mmm) for x=0.5. Figure 1 illustrated a selected refined pattern for [Y1-x,Prx]Ba2Cu3O7. The refined structural parameters are shown in table 1, the experimental and theoretical profiles fit very well, the R’s factors and goodness of fitting, S, was used as numerical criteria of fitting [4]. The change of the unit cell symmetry observed could be attributed to some oxygen atoms (anions) are released out of the structure by doping [5] or as expressed by others authors [6] that exists some kind of disorder in the basal plane due this fact the oxygen atom O(1) and O(5) are slightly moved from its sites (0.5,0,0) and (0,0.5,0), respectively. On the other hand, it is possible that the occurrence of either the tetragonal or the orthorhombic structure in samples of similar oxygen stoichiometry can be understood in terms of the relative populations of the O(1) and O(5) sites. Unequal populations of the O(1) and O(5) sites result in
disordered orthorhombic structures; a tetragonal structure results when the O(1) and O(5) populations are equal. In our samples the oxygen content is close to 7, as we will show by Raman measurements.

![Graph](image)

**Fig. 1.** Selected refined XRD pattern for [Y$_{0.7}$Pr$_{0.3}$]Ba$_2$Cu$_3$O$_7$

As we can seen from the Rietveld refinements results in table 1, the c-axis lattice constant increases slightly as the Pr content increases, it changes from 11.6618Å ($x=0$) to 11.6495Å ($x=0.5$). One interpretation of this fact is that the praseodymium doping decrease the interlayer antiferromagnetic coupling of Cu ions, so a strong hybridization between the Pr 4f and the CuO$_2$ valence band would not only suppress the conduction in the CuO$_2$ superconducting planes but would also suppress the interlayer antiferromagnetic coupling. We understood that exist a competing mechanisms in the strong chemical pressure in the Pr-site and magnetic coupling between Pr and CuO$_2$ superconducting planes through the atomic distances among CuO$_2$-Pr-CuO$_2$.

In the early studies of the structure of YBa$_2$Cu$_3$O$_7$, many authors obtained the number of oxygen to be close to 7 [9]. This fact is clearly related to the valency of the cations in the structure. According to the principle of valence equilibrium, we must expect a mixed valency for copper (Cu$^{II,III}$) atoms. The mixed valence at copper site in any given superconductor may be viewed as involving just two oxidation states. It is essential for metallic properties and for superconductivity that the two oxidation states be present on one crystallographic site. We have applied the bond valence sums [7,8] to estimate the oxidation state of the cations in all our samples by using the structural data from table 1. It can be seen in table 2 that the Cu(2) bond valence sums (BVS) is higher in $x=0.0$ but lower in $x=0.5$, suggesting that the hole concentration on CuO$_2$ superconducting planes decreases. So the superconductivity is completely suppressed at $Y_{0.5}Pr_{0.5}Ba_2Cu_3O_7$. Also some deviations exist in calculating the bond valence sums of Pr and Y, since we can only obtain the average bond length of Pr-O bond and Y-O bond. The Pr-O bond is longer than Y-O bond, so the calculated BVS of Y is a little smaller than the real value while that of Pr is a little larger it means that the increasing of Pr-ion content affect the charge carriers in the Cu(2)O$_2$ planes and the charge in the charge reservoirs by decreasing the BVS values at Cu(2) and Ba sites, respectively. Therefore, the effect of the superconductivity suppression by Pr becomes stronger in $[Y_{0.5}Pr_{0.5}]Ba_2Cu_3O_7$.

We have obtained information about the charge distribution around the atoms from the knowledge of their electronic density diagrams. Figure 2 shows the contour plots of the charge density of the valence electrons for $[Y_{1-x}Pr_x]Ba_2Cu_3O_7$ system in the two planes, i.e., [001]∥[010] and [001]∥[020]. The high density at Pr-site and the lack of contours around it indicates that this site is almost completely ionized. It also shows that this ion is not completely decoupled from the planes CuO$_2$ above and below. The
presence of the Pr-ion perturbates in short range order the atomic positions of O(2) and O(3). Therefore, there is not a magnetic isolation of the Y-site by the magnetic ion and it interferes with the superconducting properties through the magnetization measurements. Moreover, the contours surrounding the Cu(I) and O ions are not characteristic of ordinary ionic compound, but partly covalent.

**Tabla 1. Crystallographic parameters.**

| Pr Content | x=0.0 | x=0.10 | x=0.30 | x=0.50 |
|------------|-------|--------|--------|--------|
| Unit Cell Symmetry | Pmnnm | Pmnnm | Pmnnm | P4/mnm |
| a= | 3.8255 | 3.8201 | 3.8419 | 3.8848 |
| b= | 3.8871 | 3.8846 | 3.8963 | 3.8848 |
| c= | 11.6618 | 11.6561 | 11.6773 | 11.6495 |
| Volume (Å³) | 173.412 | 172.971 | 174.799 | 175.81 |
| Pr refined content | 0.0 | 0.06 | 0.36 | 0.46 |
| Atomic Positions | | | | |
| (Y,Pr) (0.5, 0.5,0.5) | | | | |
| Ba (0.5, 0.5,z) | 0.1873 | 0.1877 | 0.1889 | 0.1868 |
| Cu(1) (0, 0, 0) | 0.3716 | 0.3658 | 0.3682 | 0.3654 |
| Cu(2) (0, 0, z) | 0.3932 | 0.3819 | 0.3605 | 0.3671 |
| O(1) (0.5, 0, 0) | 0.3878 | 0.3647 | 0.3659 | -- |
| O(2) (0.5, 0, z) | 0.1650 | 0.1667 | 0.1614 | 0.1589 |
| O(3) (0, 0.5, z) | -- | -- | -- | -- |
| R values (%) | | | | |
| Rp= | 18.4 | 13.9 | 31.0 | 14.1 |
| Rwp= | 25.2 | 18.6 | 37.1 | 18.1 |
| Rexp= | 12.4 | 10.2 | 25.0 | 10.9 |
| S= | 4.11 | 3.31 | 2.20 | 2.77 |
| Bond Lengths (Å) | | | | |
| (Y,Pr)-O(2) | 2.308 | 2.381 | 2.539 | 2.484 |
| (Y,Pr)-O(3) | 2.322 | 2.477 | 2.478 | -- |
| Average (Y,Pr)-O(2,3) | 2.315 | 2.429 | 2.509 | -- |
| Angles (degree) | | | | |
| Cu(2)-O(2)-Cu(2) | 62.61° | 62.60° | 56.05° | 58.64° |
| Cu(2)-O(3)-Cu(2) | 60.65° | 57.89° | 57.07° | -- |

**Tabla 2. The calculated BVS of each cation.**

| Cations | x=0.0 | x=0.10 | x=0.30 | x=0.50 |
|---------|-------|--------|--------|--------|
| Y | 2.027 | 0.732 | 1.068 | 0.569 |
| Pr | -- | 1.929 | 1.473 | 0.785 |
| Ba | 4.160 | 0.953 | 1.256 | 1.065 |
| Cu(1) | 1.943 | 1.887 | 1.211 | 1.464 |
| Cu(2) | 1.113 | 1.072 | 1.068 | 0.561 |

We have correlated the structural data with magnetic properties. Figure 3 illustrates the DC magnetization measurements where is seen clearly a sharp drop at the diamagnetic onset temperature for all the powders except for x=0.5, where the superconductivity is suppressed. The Tc onset of the samples varies with the magnetic Pr content. Its decreases from 90K (x=0.0) to 49K (x=0.3). Moreover, a saturation of the diamagnetic signal is observed only in the superconducting samples at low temperatures pointed out the bulk nature of the compounds.
On the other hand, magnetic susceptibilities studies [10] suggest that Pr is present in mixed valency state, the proportion depending on the oxygen stoichiometry. The suppression of $T_c$ in $[Y_{1-x},Pr_x]Ba_2Cu_3O_7$ remains an open question. One approach is based on the assumption that extra electrons coming from Pr$^{4+}$ ions fill holes in the CuO$_2$ planes, and therefore reduce the positive charge carrier concentration and suppress $T_c$. On the other hand, experimental and theoretical evidences suggest the pair-breaking effect in the CuO$_2$ conduction band, it means that Pr causes a strong spin-exchange scattering of the mobile holes and hence suppresses the superconductivity.

![Figure 2](image-url) Two dimensional electronic density diagrams at two planes [001] and [010] for a) $x=0.0$, b) $x=0.30$ and c) $x=0.50$.

![Figure 3](image-url) DC magnetization versus temperature.

![Figure 4](image-url) Selected Raman spectra for $x=0.0$, 0.10 and 0.30 at room temperature.
It was possible to check the oxygen content by means of μ-Raman spectroscopy observing the Raman shift of the apical oxygen O(4) like as in the case of the canonical YBa$_2$Cu$_3$O$_7$ [11]. The frequency of the O(4)-A$_g$ phonon mode is intimate linked to O(4) oxygen atom in the Barium plane. In our work, all the samples were oxygen annealed in an identical way and it is close to 7, therefore the oxygen content was not disturbed by Pr substitution, so the decreasing of Tc cannot be attributed to an oxygen deficiency. Figure 4 shows the Raman spectra for all the samples where we can observe clearly how the frequency of O(4)-A$_g$ phonon mode not change from 500cm$^{-1}$ pointed out that the oxygen content not change from O$_{6.99±0.05}$.

Summary

The description of the Tc suppression by praseodymium in the [Y$_{1-x}$Pr$_x$]Ba$_2$Cu$_3$O$_7$ system suggest two balanced or competing mechanisms for localization: a magnetic pair breaking, due to the strong hybridization between the Pr 4f-orbital and the CuO$_2$ conduction band, and hole localization, based on the assumption that the Pr ions remain in a mixed valence state significantly above 3+ decreasing the hole concentration.

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