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A comparative study of Pr substitution at Y and Ba sites in YBa2Cu3O7-δ

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ABSTRACT

Aimed at identifying the factors which suppress the superconductivity in cuprate perovskites I have investigated the effect of substituting Pr ions at the Y and Ba sites in $YBa_2Cu_3O_{7-\delta}$ system using structural, transport, iodometric, and photoemission studies. The rate of Tc depression in the case when Pr substitutes the Ba site is much higher than the case when it substitutes the Y. This is explained as being due to a combined effect of the factors such as depletion of itinerant holes due to depletion of the oxygen content, the Pr 4f–O 2p hybridization, shortening of *c*-axis causing Cooper pair-breaking, and the loss of orthorhombicity.

1. Introduction

The mystery of evolution of superconductivity in cuprates remains illusive past more than two decades of its discovery [1–4]. Identification of the factors which suppress superconductivity in them must be explored in order to unravel the mechanism of superconductivity [4,5]. The Pr substitution in YBCO-123 system continues to hold the interest of researchers in this regard [5–9]. Most of the studies have been carried out substituting Pr at Y site. Many of these have, however, reported some Pr ions occupying the Ba site even though the entire Pr substitution was intended for the Y [6–8]. The Pr ions at the Ba site are ascribed to play significant role in quenching of superconductivity [5–7]. The tendency of Pr^{3+} ions (ionic radii 1.013 Å) to occupy the Ba^{2+} site (1.34 Å) is ascribed to the closer values of the ionic radii of the two compared to that of the Y^{3+} (0.893 Å). Thus, Pr^{3+} has a substantial solubility (~15%) at the Ba site [10]. In this work, I have intentionally substituted the Pr at Ba site to compare the outcome with the case when the Pr is substituted at Y, with regard to quenching of superconductivity. Besides a careful characterization, the powerful X-ray photoemission spectroscopy (XPS) [4,5] was employed to explore the electronic structure.

2. Experimental procedures

Polycrystalline $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ and $Y(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ for x = 0.02, 0.05, 0.10 were prepared by solid state reaction. Appropriate quantities of high purity (≥99.99%) oxides were mixed and heated thrice at 975 º C for 24 h, 24 h and 16 h, respectively, with intermediate grindings. The resulting powders were reground and pressed into pellets. The pellets were sintered at 990 ºC for 12 h and followed by oxygen annealing at 450 ºC for 24 h. The O_2 pressure and annealing duration were varied to try pumping in more oxygen in the Pr-substituted samples. The X-ray diffraction (XRD) patterns were recorded on Philips Diffractometer using Fe Kα radiation. The dc-resistivity was measured using a four-point probe method in the temperature range 10–300 K using a closed cycle He cryostat (APD Cryogenics, USA). The oxygen contents were determined by iodometric titration (±0.02) [11]. The XPS spectra were recorded using VG3000 spectrometer. The C *1s* peak at 284.6 eV was used to calibrate the spectra.

3. Results and discussion

The XRD patterns for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ and $Y(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ for x = 0, 0.5 and 0.1 (Fig. 1) depicts that the samples are single phase. Interestingly, the double-peaked features clearly visible for the [020] and [200] peaks pairs (at 2θ ~60°) and also for the [123] and [213] peaks pairs (at 2θ ~75°), start merging as the Pr content is increased in $\underline{Y}(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ until for the x = 0.10 the pattern becomes tetragonal and the peaks completely merge. On the contrary, there is no visible change when the Pr substitutes the Y. Table 1 shows how the lattice parameter *c* decreases rapidly with Pr content while *a* increases and *b* decreases; the two finally become nearly equal for x = 0.10, indicating that the sample completely turns tetragonal. On the contrary, when Pr substitutes the Y, there is no notable change in *a* and *b* values while the *c* increases slightly similar to Ref. [12]. Table 1 shows the Tc, the O_2 content, and the orthorhombicity $\{100|(b-a)/(b+a)|\}$ in the two series. The resistivity (Fig. 2, Table 1) shows that Tc decrease slowly when the Pr substitutes the Y while it decreases very rapidly when it substitutes the Ba. The observed shrink in *c*-axis, when Pr is substituted at Ba site, must be placed in context of pioneer work by Blackstead et al. [3]. They predicated that *c*-axis would remarkably shrink when Pr_{Ba} defects (i.e. Pr^{+3} on Ba^{+2} sites) are created in the samples. This would weigh against superconductivity as these

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☆ This work is dedicated to my beloved father G.K. Singhal who sadly passed away during this work.

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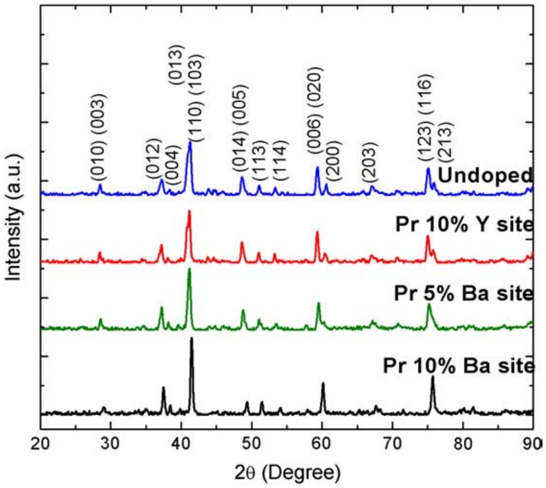

Fig. 1. The XRD patterns of the pure and the Pr substituted (at Ba and Y site) YBCO samples.

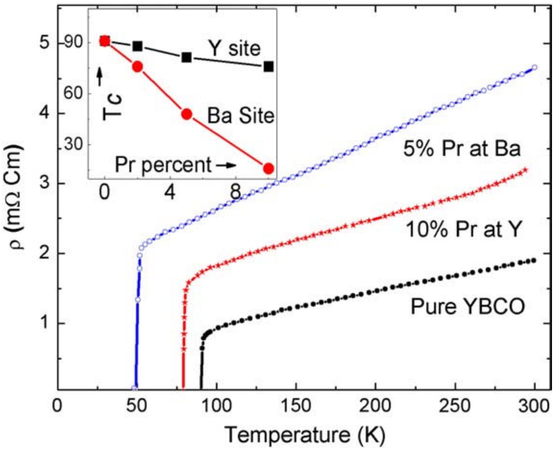

Fig. 2. The resistivity *vs* temperature for the pure and the Pr substituted YBCO samples. Inset compares the rate of Tc suppression of the samples (Pr substituted at Y and Ba sites).

defects would cause Cooper pair-breaking. Clearly the shortening of *c*-axes and the consequent pair-breaking defects (Pr_{Ba}) cause destruction to the superconductivity. Our findings agree with this prediction.

The distance between Ba (in the Ba–O_2 plane) and the nearest O atoms in the Cu–O_2 plane is 2.97 Å in our pristine sample but it reduces to 2.92 Å for the sample 10% Pr-substituted at Ba (from software ATOM 2.5) [13]. This would lead to a greater Pr 4f–O 2p hybridization and the consequent localization of the itinerant holes. However, the distance 2.92 Å is much larger compared to the corresponding distance 2.41 Å in the case of 10% Pr substitution at Y [14]. This implies that the degree of Pr 4f-O 2p hybridization in samples (Pr at Ba) ought to be substantially smaller than when Pr is substituted at the Y. But, the suppression of Tc is much higher when the Pr is doped at Ba! Consequently, the hybridization alone cannot account for the high rate of Tc depression in the case when Pr substitutes the Ba.

Turning attention to the oxygen content determined from iodometry (Table 1) it is not difficult to surmise that its depletion with increase in Pr content in the sample (Pr at Ba) may significantly contribute to the high rate of Tc depression. The depletion of O content is substantiated by the O *1s* XPS spectra. The spectra for all the samples were asymmetric in shape (Inset, Fig. 3a). The main peak, at ~530.5 eV, is due to the bulk O content [15–17]. There are reports [18–20], which indicate that the high energy shoulders arise mainly due to surface contamination ascribed to the chemisorbed oxygen of the hydroxyl groups OH, or other radicals such as CO, or CO_2–CO_3, or the absorbed H_2O or O_2. Therefore, I scraped the samples *in-situ* until the signal coming from C *1s* peak got minimized. I separated out the bulk peak by fitting three Gaussians to the spectra and the bulk O peaks are shown in Fig. 3a. It is clearly visible that the O content is much lower in the case when the Pr (10%) substitutes the Ba than when it substitutes the Y. The much higher depletion in O content when Pr substitutes Ba, seems to substantially contribute to the high rate of Tc depression. Could then the high rate of Tc depression be entirely due to the depletion of oxygen! No, that cannot be so because the O content of even the sample with 10% Pr at the Ba site is 6.74 (Table 1) and principally the sample must superconduct with Tc ~60 K [21,22], on the contrary, it depicts a Tc as low as ~10K.

Though it is not clear why the O content in samples (Pr at Ba) decreases with Pr concentration, one may speculate that it may be due to the contraction in the unit cell. All our efforts to pump in more O_2 were to no avail. A plausible explanation for this may be as follows: it is known that the O coordination number generally scales with ion size. In replacing a large Ba ion (with large coordination number) with a smaller Pr ion, stability considerations might promote a smaller coordination number around Pr. Thus, with added Pr, the O atoms would be removed from the chain sites that are in proximity to substituted Pr atoms.

In light of the observed oxygen depletion, I measured the XPS spectra of the cations also (Y, Ba, Cu, Pr). The Pr 3d XPS spectra show important changes (Fig. 3b) while the spectra of other cations showed no notable change upon doping. For the samples (10% Pr at Ba) the Pr $3d_{5/2}$ core level peak shifts to lower side than that of a reference compound Pr_2O_3, with trivalent Pr. On the contrary, there is hardly any such shift in the sample (Pr at Y). This clearly shows that the Pr ions in the sample (Pr at Y site) retains a trivalent state while in the sample (Pr at Ba site), it is less than 3+. This is consistent with the O depletion, from the charge neutrality considerations.

Table 1
The Tc values, the oxygen content, the lattice parameters and the orthorhombicity (O.R.) as a function of Pr percent for the Pr-substituted (at Y and Ba sites) YBCO samples.

Pr %	Tc (K)	O_2 content	*a* (Å)	*b* (Å)	*c* (Å)	V (Å^3)	O.R.
			±0.001	±0.001	±0.001		
			Pr substituted at Ba site				
0	90.2	6.91	3.816	3.887	11.668	173.07	1.84
2	76.4	6.86	3.822	3.879	11.653	172.76	1.48
5	48.3	6.83	3.825	3.876	11.651	172.73	1.34
10	10	6.74	3.844	3.849	11.644	172.31	0.13
			Pr substituted at Y site				
2	88	6.90	3.815	3.889	11.667	173.08	1.64
5	85	6.85	3.816	3.889	11.673	173.22	1.63
10	76	6.83	3.817	3.887	11.678	173.27	1.65

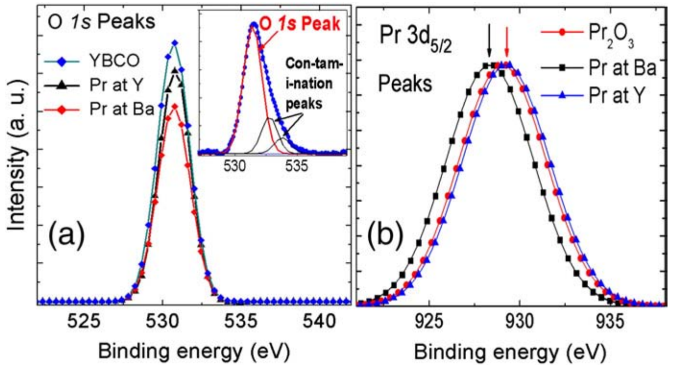

Fig. 3. (a). The O*1s* Gaussian (bulk oxygen) peaks for the pure YBCO and the samples 10% Pr substituted at the Ba and the Y sites each. Inset shows the O *1s* XPS spectra, along with Gaussian fits for YBCO (b). The Pr 3d 5/2 XPS spectra for pure YBCO and the 10% Pr substituted at the Ba and Y sites.

4. Conclusion

I studied $YBa_2Cu_3O_{7-\delta}$ with Pr substituting both the Y and the Ba sites. The rate of Tc depression, in the case when Pr substitutes the Ba, is much higher than the case when it is substituted at the Y. This is explained as being due to a composite effect of the depletion of itinerant holes due to depletion of the oxygen content, the Pr 4f–O 2p hybridization, shortening of *c*-axis causing Cooper pair-breaking, and the loss of orthorhombicity. Further studies are required to pinpoint which of these factors is more prevalent.

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