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Abstract

We present a systematic structural, transport, iodometric, susceptibility and x-ray photoemission study of the $Y(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ system for $x = 0.00, 0.025, 0.05, 0.075$ and 0.10 with Pr^{3+} (smaller in ionic radii but higher in valence than Ba^{2+}) substituted at the Ba site. It is successfully shown that a higher valence cation can be substituted for a lower valence one. The rate of the T_c depression in these is observed to be much higher than that in the case when Pr^{3+} is substituted at the Y^{3+} site. This is explained as being due to a composite effect of the depletion of itinerant holes due to the progressive depletion of the oxygen content in the samples, the Pr 4f–O 2p hybridization and change in the in-plane coherence length (ξ_{ab}) resulting from change in the in-plane atomic distances, using Ginzburg–Landau theory.

1. Introduction

It is well known that different rare-earth ions (except Pr, Ce and Tb) when substituted in place of Y ions in $YBa_2Cu_3O_{7-\delta}$ (YBCO) yield superconductivity with nearly the same $T_c \sim 90$ K [1]. Ce and Tb substitution, on the other hand, yield the stable perovskites $BaCeO_3$ and $BaTbO_3$ rather than the $YBa_2Cu_3O_{7-y}$ structure [2–5]. However, Pr forms a single-phase non-superconducting PrBCO-123 compound. Because of the unique behaviour, Pr substitution studies have been a focus of special interest for determining how Pr quenches the superconductivity. In the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system as the Pr concentration is increased the T_c monotonically decreases, with superconductivity vanishing at a concentration of

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$x \approx 0.55$ [6–9]. The normal-state electrical behaviour also undergoes a transition from metallic (for $x < 0.55$) to a semiconducting one at roughly the same concentration (for $x > 0.55$). Although several groups had reported observing superconductivity in the pristine PrBaCuO system [10–14], it is still not concluded whether Pr-123 is a superconductor or not [15]. Another debate that had raged on Pr substitution was on the mechanism of quenching of superconductivity, pair breaking or hole quenching or Pr 4f–O 2p hybridization [16–19]. Finally, a consensus did emerge in favour of the Pr 4f–O 2p hybridization. Despite all these studies Pr substitution continues to hold the interest of researchers [20–30]. Of late, there has been a revival of interest in the effect of internal chemical and external hydrostatic pressure on the superconducting properties of the YBCO system. Ferreira *et al* [31], for instance, have recently studied the effects of hydrostatic pressure (up to 1.11 GPa) on the fluctuation conductivity in the system. Khosrobadi *et al* [32] have, on the other hand, examined its structural and electronic properties under mechanical as well as internal chemical pressure (substituting the smaller Sr^{2+} ion in place of Ba^{2+}).

Most studies on the (YPr)BCO-123 system have been carried out substituting Pr^{3+} at the Y^{3+} site. A number of these have, however, reported some Pr ions occupying the Ba site even though the entire Pr substitution was intended for the Y site [13, 14, 30, 33]. The Pr ions at the Ba site have, in these, been ascribed as playing a significant role in quenching of superconductivity in the system [13, 14]. The tendency of Pr^{3+} (ionic radii 1.013 Å) to occupy Ba^{2+} site (1.34 Å) has been ascribed to the closer values of the ionic radii of the two compared to that of Y^{3+} (0.893 Å). Thus, Pr^{3+} has a substantial solubility at the Ba site. Of the largest rare-earth ions Pr is the only one to have small enough size mismatch to achieve appreciable solubility at the Ba site [34, 35]. Harada *et al* [36] emphasize that the solubility limit of Pr at the Ba site in the YBCO(123) system has been reported to be 15% [36]. This is what led us to the idea of intentionally substituting Pr^{3+} at the Ba^{2+} site and studying the outcome with regard to the quenching of superconductivity and the Pr valence. There were other reasons too that encouraged us to go in for this study. For instance, Pr when substituted in Y-123 and Y-124 shows different T_c suppression rates: slower in the latter [37]. In intermediate valence 4f chalcogenide systems like SmS, SmSe, SmTe and others, the substitution of ions smaller than Sm^{2+} drives the Sm^{2+} to a higher valence state Sm^{3+} as a result of the internal chemical or the lattice pressure [31, 32, 38–41] so generated. In high T_c systems, on the other hand, it is generally the higher valence ion that is replaced by a lower valence ion to dope holes. It was, therefore, thought interesting to try substituting a higher valence ion for a lower valence one in the YBCO system.

In this paper we discuss the behaviour of YBCO-123 system as Pr^{3+} is progressively substituted for Ba^{2+}. The samples were characterized with XRD, resistivity, susceptibility and wet titration measurements for estimating the amount of oxygen in the samples. The powerful XPS technique was employed for determining changes in the electronic structure and for monitoring of the itinerant hole concentration.

2. Experimental details

Polycrystalline samples of $Y(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ were prepared for $x = 0.00, 0.025, 0.05, 0.075$ and 0.10 by the usual solid state reaction technique using a microprocessor controlled furnace (Linn, Germany). Appropriate molar quantities of high purity starting oxides Y_2O_3 (Wako Pure Chemical Industries Ltd, 99.99%), BaO (Fluka Chemicals, 99.99%), CuO (Aldrich 99.9999%) and Pr_2O_3 (Aldrich, 99.9%) were mixed and heated thrice at 975 °C for 24, 24 and 16 h respectively with several intermediate grindings to ensure perfect homogeneity to help complete the solid state reaction. The resulting powders were reground and pressed into

pellets. The pellets were sintered at 990 °C for 12 h and this was followed by oxygen annealing at 450 °C for 24 h. In all the cases slow cooling was adopted. Annealing times and the oxygen pressure were varied to try pumping in more oxygen in the Pr-substituted samples.

X-ray diffraction (XRD) patterns were recorded at room temperature (290 K) using a Philips-make powder diffractometer model PW 1840 with Fe Kα (1.937 A) radiation with a Mn filter to check the phase purity of the samples and calculating their lattice parameters.

Four-probe dc resistivity measurements were carried out using an APD closed cycle refrigerator for the temperature range 300–19 K. The magnetic susceptibility was measured using a SQUID from 100 K down to 4 K at CBPF, Rio de Janeiro and Instituto de Física, Campinas-CP, Brazil. The oxygen content of the samples was determined by the iodometric titration technique to within ± 0.02 accuracy [42].

The core level photoemission studies were carried out using an x-ray photoelectron spectrometer at IUC, Indore, India. To identify the photoelectron peaks and Auger peaks, full scan spectra were recorded using both Al Kα (1486.6 eV) and Mg Kα (1253.6 eV). The final spectra were recorded using the Mg Kα radiation at 50 eV pass energy of the spectrometer. The measured resolution was about 0.85 eV. The samples were mounted in the form of compressed hard pellets and were scraped uniformly with diamond files before carrying out the measurements. Final spectra were taken only when the feature coming from carbon contamination of the surface (C 1s peak) merged in the spectrum background. The vacuum in the chamber was $\sim 4.4 \times 10^{-10}$ Torr. We kept scraping the samples *in situ* to get uncontaminated surface throughout the measurements. No shift was observed due to charging of the samples. The Fermi level (E_f) was aligned by recording the valence band (VB) spectrum of *in situ* cleaned gold foil. In order to check for any deviation in E_f, VB spectra of gold were recorded immediately after taking the photoemission spectrum of each sample under present study.

3. Results

The paramount points of our study that distinguish it from other earlier ones are: (i) substituting Pr for Ba, an ion that is smaller in size but having a higher valence, and (ii) the resulting higher rate of T_c suppression.

3.1. XRD, resistivity and the susceptibility data

For clarity in the presentation of our findings first we present the results of XRD, resistivity and susceptibility studies performed on these samples. Figure 1 showing the XRD patterns of all the Y(Ba$_{1-x}$Pr$_x$)$_2$Cu$_3$O$_{7-\delta}$ ($x = 0.00, 0.025, 0.05, 0.075$ and 0.10) samples recorded at the room temperature depicts that all the samples were single phase with no detectable impurity phase [36, 43, 44]. The peaks [200], [020]; [023], [203]: [013], [103] and [123], [213] show that the $x = 0, 0.025, 0.05, 0.075$ samples are orthorhombic. The double-peaked features that are clearly visible for the [020] and [200] peaks pairs (occurring at around $2\theta = 60°$) and also the [123] and [213] peaks pairs (occurring at around $2\theta = 75°$) start getting merged as the Pr content is increased until for the sample $x = 0.10$ the pattern becomes tetragonal and we get the peaks completely merged into one single peak; see figure 1. Table 1 shows how lattice parameter c, as expected, decreases with increase in Pr content while a increases and b decreases; the two finally become equal for $x = 0.10$, indicative of the sample completely turning tetragonal. Table 1 also shows a decrease in the orthorhombicity $\{200|(b-a)/(b+a)|\}$, the T_c, the oxygen content and the volume of the unit cell as the Pr content increases in the samples. In the case where Pr^{3+} (ionic radii 1.013 Å) goes to the Y^{3+} (0.893 Å) the c is reported
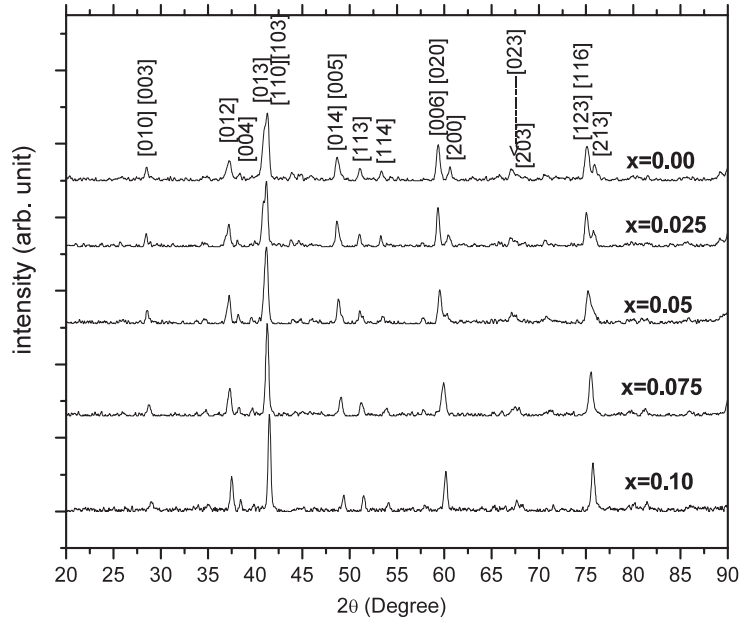
Figure 1. XRD data for $Y(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ for $x = 0.00, 0.025, 0.05, 0.075$ and 0.10 samples. There is no sign of any impurity phase. The double-peaked structures (e.g. [020] and [200] and also the [123] and [213]) get merged into single peaks for the $x = 0.10$ sample, indicating its transition from the orthorhombic to the tetragonal phase.

Table 1. Values of the various parameters T_c, ΔT, oxygen content, orthorhombicity (OR), lattice parameters (a, b, c) and the unit cell volume (V) and Ginzburg number (Gi) for the $Y(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ samples.

x	T_c (K) ±0.05	ΔT (K) ±0.05	$O_{(7-\delta)}$ ±0.02	OR	a (Å) ±0.001	b (Å) ±0.001	c (Å) ±0.001.00	V (Å^3) 89.89	Gi
1.20	6.91	1.843	3.816	3.887	11.668	173.069	0.094		
0.025	78.80	6.85	6.86	1.480	3.822	3.879	11.653	172.762	0.087
0.05	48.32	8.04	6.83	1.342	3.825	3.876	11.651	172.734	0.072
0.075	22.85	20.17	6.78	0.935	3.832	3.868	11.645	172.604	—
0.10	—	—	6.74	0.129	3.844	3.849	11.644	172.309	—

to rather increase [9, 30]. The resistivity data shown in figure 2, including the susceptibility data in the inset, further emphasize that the samples are single phase and the T_c is decreasing with the Pr content. In the case where Pr is substituted at the Y site the superconductivity is sustained up to 55% [9, 30] but in our case just 10% Pr is sufficient to quench the superconductivity. Thus the T_c suppression rate for our samples is much higher.

Following Ferreira *et al* [31], we have calculated fluctuation conductivity $(\Delta\sigma)$ from our resistivity data using the equation

$$\Delta\sigma = \left(\frac{1}{\rho} - \frac{1}{\rho_r}\right), \tag{1}$$

where ρ_r is the regular resistivity obtained by the extrapolating the linear behaviour observed at high temperatures [31]. Figure 3 shows the inverse logarithmic derivative of the conductivity
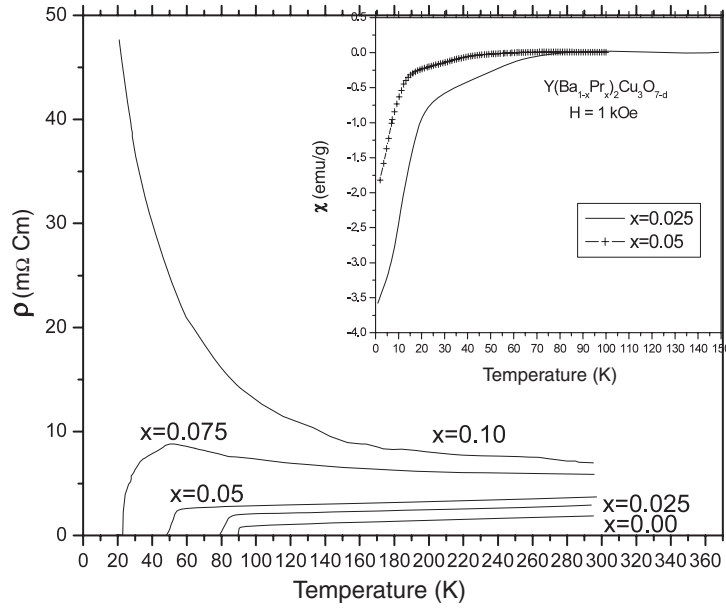
Figure 2. Resistivity and $\chi_{a.c.}$ data. The sharp superconducting transition and absence of any fine structure indicate the single-phase nature of the $Y(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ samples.
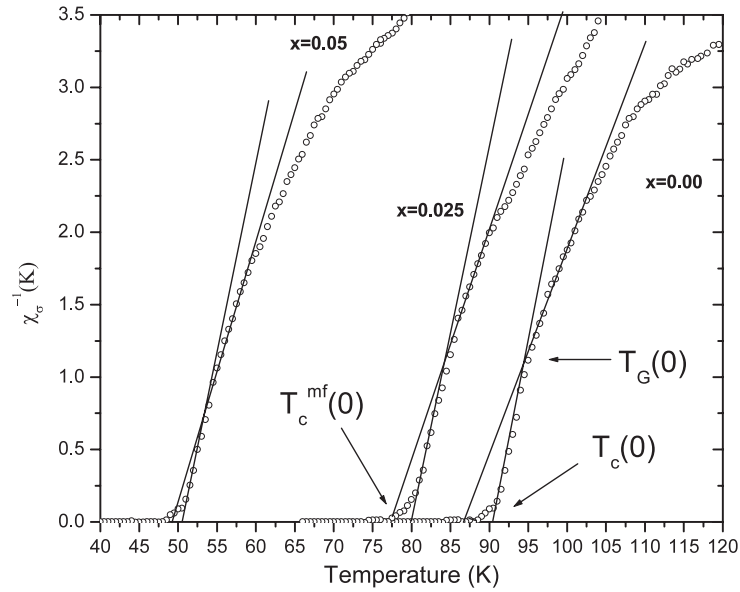

Figure 3. Inverse logarithmic derivative of the conductivity χ_σ^{-1} as a function of the temperature near the superconducting transition for the $Y(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ samples. The temperature T_G identifies the Ginzburg temperature.

denoted by χ_σ^{-1} as a function of temperature near the superconducting transition [31]:

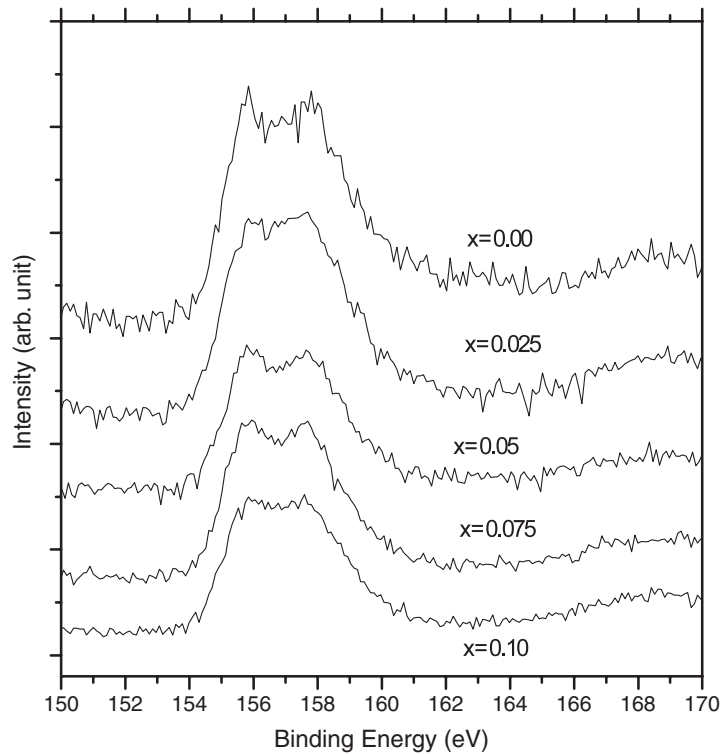$$\chi_\sigma^{-1} = -\frac{d}{dT}(\ln(\Delta\sigma)), \tag{2}$$

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Figure 4. The Y 3d XPS spectra for the $Y(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ samples. There is no noticeable change in the position of the peaks on Pr substitution, implying that no Pr is migrating to the Y site; otherwise it must have brought about definite changes in the position and/or the shape of these Y 3d peaks.

where $\Delta\sigma$ is fluctuation conductivity near T_c. In figure 3, we denote as T_G the crossover temperature delimiting the Gaussian and critical intervals and assign this temperature to the intersection between the straight line fitted to these regimes in the χ_σ^{-1} plots. From T_G and T_c^{mf} for each case we have calculated the Ginzburg number (only for $x = 0.00, 0.025$ and 0.05), given by $Gi = (T_G - T_c^{mf})/T_c^{mf}$. The Gi number decreases with increase in the Pr content as shown in table 1. We will return to the significance of this behaviour later, in section 4 of this paper.

3.2. XPS data

Prior to measuring the XPS spectra of these samples the C 1s peak was minimized as far as possible (almost merged into the background) by scraping all the sample surfaces to get a clean surface. First of all look at the Y 3d XPS spectra (figure 4). The spectra show the Y $3d_{5/2}$ and Y $3d_{3/2}$ peaks located at ~156 eV and ~158 eV respectively. It must be noted that these Y 3d XPS spectra do not show any noticeable changes [30, 33] on Pr substitution, implying that no Pr is migrating to the Y site; otherwise it must have brought about definite changes in the position and/or the shape of these Y 3d peaks. Figure 5 shows the treated Ba $3d_{3/2}$ core level along with the fits (Gaussian + Lorentzian). Figure 6, similarly, depicts the Pr $3d_{5/2}$ spectra, extracted from the Cu $2p_{3/2}$–Pr $3d_{5/2}$ composite by making fits (Gaussian + Lorentzian). With increase in the Pr concentration the Ba $3d_{3/2}$ and Pr $3d_{3/2}$ spectra both show a small progressive
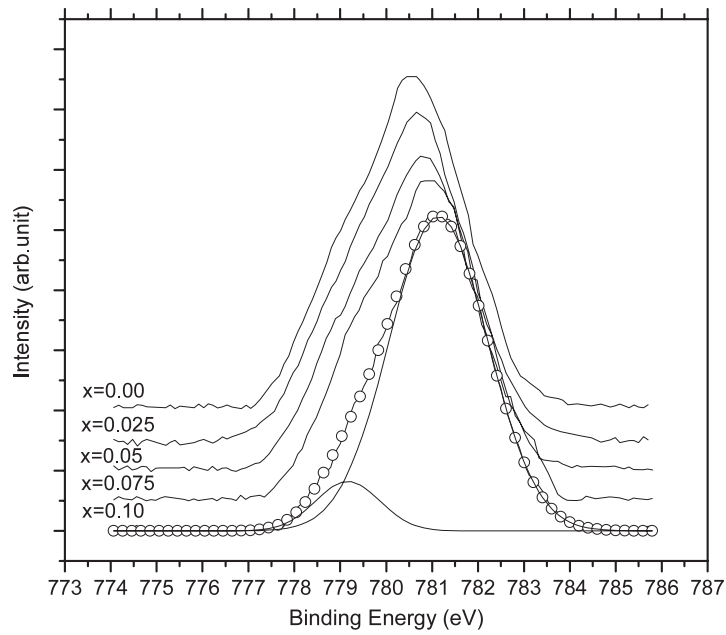
Figure 5. The Ba $3d_{5/2}$ XPS spectra of the $Y(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ samples. The Ba $3d_{5/2}$ peak shifts to higher energy side and decreases in intensity with increase in the Pr content. The $x = 0.10$ spectrum has been shown with (Gaussian + Lorentzian) fits.
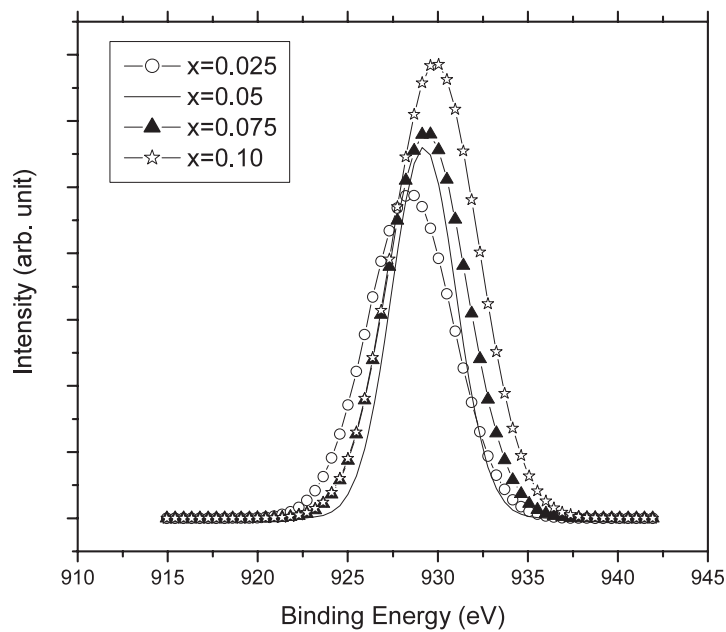

Figure 6. The Pr $3d_{5/2}$ XPS spectra for the $Y(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ samples. Again, the Pr $3d_{5/2}$ peak shifts to higher energy but its intensity tends to increase with the Pr concentration.

shift in the binding energy to the higher energy side, which may be interpreted as an increase in the valence of the Ba and Pr cations. The Ba–Pr–O plane appears to behave as if Ba and

Table 2. The energy position and intensity (area under the peak) of the Ba $3d_{5/2}$, Pr $3d_{5/2}$ and O 1s peaks for the $Y(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ samples. The Ba $3d_{5/2}$, Pr $3d_{5/2}$ peaks both shift to higher energy but the former loses intensity while the latter gains. The O 1s pre-peak intensity tends to decrease with an increase in Pr concentration.

	Ba $3d_{5/2}$		Pr $3d_{5/2}$		O 1s	
x	Energy (eV)	Area (au)	Energy (eV)	Area (au)	Energy (eV)	Area (au)
0.00	780.61	1090.3	—	—	529.02	3802.4
0.025	780.67	1067.1	928.47	21.185	529.03	3530.9
0.05	780.79	1030.8	929.22	22.215	529.01	3317.3
0.075	781.02	1011.3	929.37	32.588	529.01	3214.1
0.10	781.14	967.6	929.85	41.317	529.03	2990.1

Pr cations show a common average valence that may lie between 2+ and 3+ and this valence progressively increases as the Pr^{3+} content increases. This is also borne out by the fact that our observed value of binding energy for Pr $3d_{5/2}$ (928.47 and 929.85 eV for 2.5% and 10% samples respectively) is still substantially smaller than the reported value of 933.2 eV for it for Pr_2O_3. Furthermore, the intensities (area under the spectra) of the Ba $3d_{5/2}$ and Pr $3d_{5/2}$ spectra show an opposite behaviour with the Pr doping. While the Pr $3d_{5/2}$ intensity (area under the peak), as expected, increases with the Pr content, the Ba $3d_{5/2}$ intensity shows a corresponding decrease (table 2). Liu *et al* [45] say that the lower binding energy peak is due to the electronically different nature at the cleavage plane. It is well known how quickly O tends to leak from the surface of the 123 system in ultrahigh vacuum ambience at room temperature [46]. We are therefore confident that the higher intensity and higher binding energy peak indicate a genuine Ba $3d_{5/2}$ peak.

4. Discussion

Apart from being experimentally simpler the advantage of the chemical pressure studies is that one can arrive at an optimum way to reach higher (or lower) T_c by suitable substitution of a cation by another of lower (or higher) ionic radii. For example, Fernandes *et al* [47] have, on complete substitution by the larger Gd^{3+} ion (0.938 Å) for Y^{3+} (0.88 Å), observed a reduction of 2 K in the T_c. Lu and Chen [48] have, on substituting the smaller Sr^{2+} (1.12 Å) ion for the Ba^{2+} (1.34 Å) in $Y_2(Ba_{1-x}Sr_x)_4Cu_7O_{14+\delta}$ up to a limit of 15%, observed an increase in T_c by 7.5 K/(Sr formula unit). Licci *et al* [49] have, however, observed a contrary result for YBCO-123; on complete substitution of the smaller Sr^{2+} ion for the Ba^{2+}, the T_c is reduced by 20 K. In our case since the Pr^{3+} ion is smaller than the Ba^{2+} ion, following the results of Fernandes *et al* [47] the T_c should have increased, but it shows a significant decrease even within the solubility limit of 15%. Blackstead and Dow [13, 14] observed some of the Pr ions occupying the Ba site even though the Pr substitution was intended exclusively for the Y site. They claimed that Pr at the Ba site caused pair breaking [16] in Cu–O chains leading to the depression of the T_c. Later studies [17–19] have, however, clearly established that it is the Pr 4f–O 2p hybridization and the consequent localization of the hole carriers in the Cu–O_2 planes that is the main mechanism causing depression of the T_c in the case of Pr substitution at the Y site.

Ferreira *et al* [31] from the study of the thermal fluctuation contribution to the conductivity (σ), by focusing on the asymptotic regimes very close to the pairing transition, have estimated the Ginzburg number [50]. The Ginzburg number (Gi) was observed to increase on applying hydrostatic pressure to a YBCO single crystal. Furthermore, the coherence length ξ_c (along the c-axis) was found not to change but the ξ_{ab} (in the ab-plane) was found to decrease. Following

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the Ginzburg–Landau (GL) theory, they therefore, calculated *Gi* using the relation

$$Gi = \alpha \left[\frac{k_B}{\Delta c \xi_c(0) \xi_{ab}^2(0)} \right]^2. \tag{3}$$

Gi was found to increase and this they ascribed to decrease in the in-plane coherence length. They have thus concluded that the superconducting properties of the optimally doped YBCO depend much more on the variation of the atomic distances within the atomic layers than that along the *c*-axis.

We have similarly estimated the *Gi* in our case which, as can be seen from table 1, decreases with Pr substitution; the *Gi* decreases from 0.096 for the pristine sample to 0.072 for the $x = 0.05$ sample. In the study of Ferreira *et al* [31] the application of hydrostatic pressure, in addition to other effects, is bound to lead to a decrease in *c*, akin to what we observe in our samples. Despite this, Ferreira *et al* [30], from their analysis of the 3D-G fluctuation conductivity amplitude, report not observing any change in the out-of-plane coherence length (ξ_c) with pressure and rather attribute the change in *Gi* to the change in the in-plane coherence length (ξ_{ab}). Following Ferreira *et al* [31] we would also like to conclude that the decrease in the values of *Gi* observed by us is due to changes in the values of *a* and *b* and hence the increase in the in-plane coherence length (ξ_{ab}). As can be seen from table 1, the value of *a* increases while that of *b* decreases with increase in Pr concentration in our samples, and the average value $(a + b)_{av}$ decreases (not shown). From the GL theory we can therefore similarly conclude that the increase in ξ_{ab} would lead to depression of the T_c. Moreover, the large change in the value of *Gi* and hence ξ_{ab} in our samples would imply a higher rate of T_c depression.

The distance between Ba (in the Ba–O_2 plane) and the nearest O in the Cu–O_2 plane is 2.97 Å in our pristine sample but it reduces to 2.95 Å for the 10% Pr-substituted one (calculated from the software ATOM 2.5) [51]. This would naturally lead to perhaps a greater Pr 4f–O 2p hybridization and the consequent localization of the itinerant holes. For this reason, the decrease in value of *c* would, unlike in the case of Ferreira *et al* [31], also lead to a reduction in T_c in the present case due to the presence of the Pr ion. However, the Pr–O_2 distance 2.95 Å is seen to be much smaller compared to the corresponding distance 2.41 Å in the case of 10% Pr substitution at the Y site, calculated by Peng *et al* [9]. This implies that the degree of Pr 4f–O 2p hybridization in our samples ought to be substantially smaller than when Pr is substituted at the Y site. Consequently, this hybridization alone cannot account for the observed high rate of T_c depression. Turning our attention to the oxygen content (table 1) it is not difficult to surmise that its depletion with increase in Pr concentration would substantially contribute to the high rate of T_c depression. This is clearly revealed by the O 1s XPS spectra [52, 53] (figure 7) wherein the so-called pre-peak at ∼529 eV is continuously decreasing in intensity as the Pr concentration increases.

Could then the high rate of T_c depression be entirely due to the depletion of oxygen! No, that cannot be so because the oxygen content of even the semiconducting sample with 10% Pr substitution is 6.74 as estimated from the iodometric method (table 1), and this must superconduct with ∼60 K T_c [54–58]. The high rate of T_c depression has thus to be a composite effect of depletion of the oxygen content, localization of holes through Pr 4f–O 2p hybridization, and increase in ξ_{ab} resulting from changes in the in-plane lattice constant values.

Although it is not fully clear why the oxygen content in our Pr-doped samples goes on decreasing with increase in Pr concentration, one may speculate that it may be due to the contraction in the unit cell volume (table 1). All our efforts to pump in more oxygen in these doped samples were to no avail. A plausible explanation for this may be as follows: it is well known that the oxygen coordination number generally scales with ion size. In replacing a large Ba ion (with its large coordination number) with a smaller Pr ion, stability considerations might
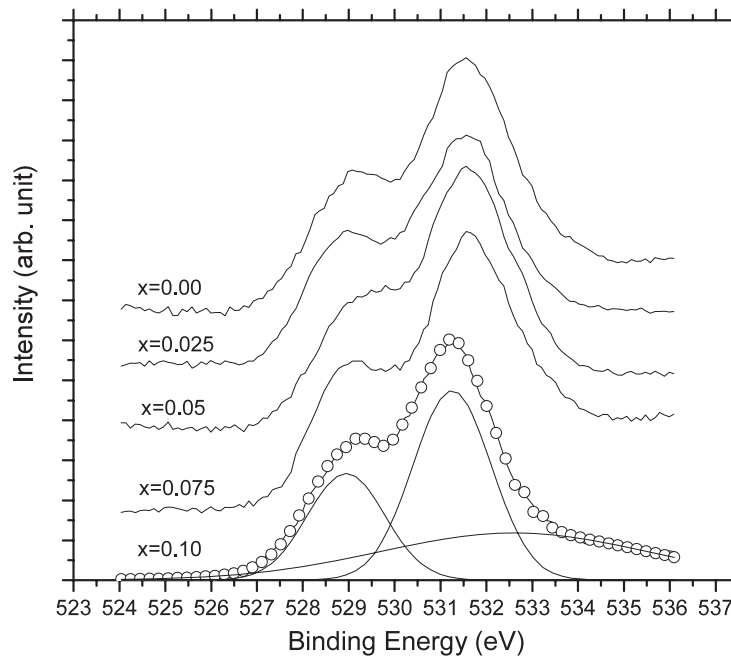
Figure 7. The O 1s XPS spectra for the $Y(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ samples. The intensity of the pre-peak (area below the first fit to the spectrum) at $\sim$529 eV shows a gradual decrease with the increase in Pr concentration indicating depletion of the itinerant holes. The last spectrum shows the (Gaussian + Lorentzian) fits also.

promote a smaller coordination number around Pr. Thus, with added Pr, oxygen atoms would be removed from the chain sites that are in proximity to substituted Pr atoms. Also, the phase transition from orthorhombic to tetragonal and the rearrangement of oxygen atoms in the Cu–O chain (O(1) and O(5)) are known to take place [55].

5. Conclusion

In conclusion, we have shown that it is possible to substitute a higher valence cation for a lower one and synthesize good quality single-phase YBCO(123) samples with up to 10% of Pr^{3+} replacing the Ba^{2+} in the system. The samples show a rapidly decreasing T_c with increase in Pr concentration and phase transition from orthorhombic to tetragonal. The XPS results clearly show that no observable amount of Pr goes to the Y site. It also shows that the Pr valence in these samples is considerably less than 3+. Furthermore, the high rate of T_c depression is explained as being due to a composite effect of the depletion of itinerant holes due to the progressive depletion of the oxygen content in the samples, the Pr 4f–O 2p hybridization and change in the in-plane coherence length (ξ_{ab}) resulting from change in the in-plane atomic distances, using GL theory.

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