Hole states in Eu_{0.9-x}Pr_{x}Ca_{0.1}BaSrCu_{3}O_{7-δ} studied by X-ray absorption spectroscopy

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The hole states located on different oxygen sites have been investigated in Eu_{0.9-x}Pr_{x}Ca_{0.1}BaSrCu_{3}O_{7-δ} with increasing Pr\textsuperscript{3+} substitution by high-resolution oxygen K-edge and copper L-edge X-ray absorption spectra. The results reveal that the hole states are depleted systematically by the substitution and in turn lead to a reduction in Tc. However, the rate at which the depletion occurs is lower in Eu_{0.9-x}Pr_{x}Ca_{0.1}BaSrCu_{3}O_{7-δ} compared to that in Y_{1−x}Pr_{x}Ba_{2}Cu_{3}O_{6−δ} and Dy_{1−x}Pr_{x}Ba_{2}Cu_{3}O_{6−δ}. This is due to the partial substitution of Ba\textsuperscript{2+} by Sr\textsuperscript{2+} ions and R (rare earth element) by Ca\textsuperscript{2+} ions in the present case. The depletion of hole states gives evidence in support of the hole-depletion models based on Pr 4f-O 2p hybridization. The possible reasons for the anomalous behavior of Pr\textsuperscript{3+} ions in RBa_{2}Cu_{3}O_{7−δ} are also discussed.

Introduction

The materials R Ba_{2}Cu_{3}O_{7−δ} (R123) where R = rare earth element, are known to show a superconducting transition temperature (Tc) above 90 K except where R = Ce, Pr or Tb.\textsuperscript{12} Though isomorphic structure is not formed where R = Ce or Tb unlike the other rare earth based R123 compounds,\textsuperscript{2} ideal orthorhombic structure similar to that of other superconducting R123 compounds is formed but no superconductivity is exhibited by PrBa_{2}Cu_{3}O_{7−δ} (Pr123).\textsuperscript{3,4} This anomalous behavior of PrBa_{2}Cu_{3}O_{7−δ} is not fully understood although much has been published about the aspects related to non-superconducting nature of this compound.\textsuperscript{4,5} Recently, there have been some reports suggesting superconductivity in Pr123 but these have met with considerable skepticism owing to the lack of reproducibility of data and the existence of an anomalously long c axis reported for the structure of Pr123.\textsuperscript{6,10–15}

Several models have been proposed during the past few years to explain the anomalous behavior of PrBa_{2}Cu_{3}O_{7−δ}. The most widely discussed deal with the hole filling\textsuperscript{16–18} or pair breaking mediated by the hybridization of praseodymium 4f and oxygen 2p states of the CuO\textsubscript{2} planes.\textsuperscript{19} The hole filling model assumes that Pr has a valence of more than +3 whereby the extra electrons from Pr neutralize the mobile holes which in turn brings the compound to a near insulating regime. However, this model has not met with great success since a valence exceeding +3 for Pr is not supported by many experimental findings.\textsuperscript{20–24} On the other hand, pair breaking appeared to be a more promising model as it can explain the suppression of superconductivity in R_{1−x}Pr_{x}Ba_{2}Cu_{3}O_{7−δ} through the hybridization of praseodymium 4f and oxygen 2p states of the CuO\textsubscript{2} planes leading to the localization of the holes, although pair breaking by itself cannot account for the insulating behavior of PrBa_{2}Cu_{3}O_{7−δ}.\textsuperscript{25} Recently, two models have been proposed by Fehrenbacher and Rice (FR)\textsuperscript{23} and Liechtenstein and Mazin (LM),\textsuperscript{26} both of which involve the transfer of holes from the pd\textsubscript{z} state to the pd\textsubscript{z} state. In the FR model the 4f\textsubscript{LM} orbital of Pr\textsuperscript{3+} ion is hybridized with pd\textsubscript{z} orbitals of neighboring planar oxygen ions. The pd\textsubscript{z} holes are treated as planar (p\textsubscript{z}) in the FR model, whereas they have comparable amounts of p\textsubscript{x,y} and p\textsubscript{z} character in the LM model. These models are well supported by a polarization dependent X-ray absorption study on detwinned Y_{1−x}Pr_{x}Ba_{2}Cu_{3}O_{6−δ} single crystals.\textsuperscript{7} Although both FR and LM models can explain the insulating behavior of PrBa_{2}Cu_{3}O_{7−δ}, they do not account for a high value of nearly 17 K for the antiferromagnetic ordering of praseodymium moments (Neel temperature T\textsubscript{N} for this compound).\textsuperscript{8,9}

Earlier experimental reports have demonstrated that the hole states play a vital role in superconductivity in the p-type cuprate superconductors. Therefore, knowledge of the electronic structure near the Fermi level of these compounds is important to understand the mechanism of superconductivity. The X-ray absorption spectra are determined by electronic transitions from a selected atomic core level to the unoccupied electronic states near the Fermi level. X-Ray absorption near edge structure (XANES) is therefore a direct probe of the character and local density of the hole states responsible for the high temperature superconductivity. It has been generally accepted that the hole states in p-type cuprate superconductors are located on oxygen sites. Moreover, there are several non-equivalent oxygen sites in these materials. Therefore it becomes necessary to understand the distribution of hole states among different oxygen sites and their role in superconductivity as well.

The recent works on bulk and thin films of PrBa_{2−δ}Sr_{δ−x}Cu_{3}O_{7−δ} show that strontium doping at the barium site increases the distance between Pr\textsuperscript{3+} and O\textsuperscript{2−} ions in the CuO\textsubscript{2} plane and consequently leads to a dramatic decrease of resistivity in doped samples.\textsuperscript{8} Very recently, Liu et al.\textsuperscript{27} also suggested in support of the above observations that chemical substitution of Sr for Ba in YBa_{2−δ}Sr_{δ}Cu_{3}O_{7−δ} gives rise to higher hole concentrations, leading to an overdoped state. As a result, a decrease in Tc was found from 92 K when x = 0.0 to 84 K when x = 0.8, which was the maximum solubility of Sr without modifying the phase. Similarly, the holes induced by the Ca\textsuperscript{2+} ions in Pr_{0.5}Ca_{0.5}Ba_{2}Cu_{3}O_{7−δ} thin films lead to the recovery of the high temperature superconductivity for the Pr123 phase.\textsuperscript{44} Recently, this was also well brought out by Merz et al.\textsuperscript{45} based on their polarization dependent X-ray absorption spectral studies on Y_{1−x}Ca_{x}Ba_{2}Cu_{3}O_{6−δ} single crystals. They found that the maximum hole counts correspond to the composition...
All these reports clearly indicate that the substitution of Ba\(^{2+}\) partially by Sr\(^{2+}\) ions and R by Ca\(^{2+}\) ions induces and creates the holes, in contrast to the substitution of Pr\(^{3+}\) ions at the R site which always depletes the hole content. Moreover, it has been reported that Eu\(_{1−x}\)Pr\(_{x}\)BaSrCu\(_{2}\)O\(_{7−δ}\) becomes an insulator when x < 0.5. However, Eu\(_{1−x}\)Pr\(_{x}\)BaSrCu\(_{2}\)O\(_{7−δ}\) and Eu\(_{1−x}\)Pr\(_{x}\)BaSrCu\(_{2}\)O\(_{7−δ}\) do show superconductivity unlike Eu\(_{1−x}\)Pr\(_{x}\)BaCuO\(_{2}\), even when x = 0.5 (Table 1). X-ray absorption studies on Y\(_{1−x}\)Pr\(_{x}\)BaCuO\(_{3}\) and Dy\(_{1−x}\)Pr\(_{x}\)BaCuO\(_{3}\) indicate that the depression of T\(_{c}\) is due to the depletion of the hole states by Pr\(^{3+}\) substitution and the rate at which the depletion occurs is comparable for both systems.\(^{25}\) However, there has been no report of X-ray absorption spectroscopy on R123 by substituting Ba\(^{2+}\) partially by Sr\(^{2+}\) ions and R by Ca\(^{2+}\) and Pr\(^{3+}\) ions. Therefore, we have chosen a series of compounds corresponding to the composition Eu\(_{1−x}\)Pr\(_{x}\)Ca\(_{2}\)BaSrCu\(_{2}\)O\(_{7−δ}\), where x = 0.1–0.5, for the present study. Preliminary data for the present and the related systems, viz. Eu\(_{1−x}\)Pr\(_{x}\)BaSrCuO\(_{3}\), and Eu\(_{1−x}\)Pr\(_{x}\)BaSrCu\(_{2}\)O\(_{7−δ}\) where x = 0.0–0.5, have been reported elsewhere.\(^{27,28}\)

The corresponding T\(_{c}\) values are reproduced in Table 1. It has been shown in the present study that the hole states are depleted systematically which in turn leads to reduction in T\(_{c}\) by the substitution of Pr\(^{3+}\) ions in Eu\(_{1−x}\)Pr\(_{x}\)Ca\(_{2}\)BaSrCu\(_{2}\)O\(_{7−δ}\). However, the rate at which the depletion occurs is lower when compared to those of the Y\(_{1−x}\)Pr\(_{x}\)BaCuO\(_{3}\), and Dy\(_{1−x}\)Pr\(_{x}\)BaCuO\(_{3}\) systems.

### Results and discussion

The oxygen contents of Eu\(_{0.9}\)Pr\(_{0.1}\)Ca\(_{2}\)BaSrCu\(_{2}\)O\(_{7−δ}\) where x = 0.1, 0.2, 0.3, 0.4, or 0.5 were determined by iodometric titrations and the oxygen contents (7 − δ) have been given in Table 1. These values remain unaltered at ±0.97 ± 0.02 with increasing praseodymium substitution, indicating that Pr is in trivalent state and is substituting at the europium site. The ionic size of Ca\(^{2+}\) is closer to that of Eu\(^{3+}\) ion, rather than that of Ba\(^{2+}\).\(^{29}\) But its valence would favor its going to the Ba Sr site. However, an earlier study on Eu\(_{1−x}\)Ca\(_{x}\)SrBaCu\(_{2}\)O\(_{7−δ}\) by Waje et al.\(^{31}\) found that the lattice parameter ‘a’ increased with increasing calcium concentration ‘x’ indicating that Ca substitutes at the europium site.

The oxygen K-edge X-ray absorption spectra of Eu\(_{0.9}\)Pr\(_{0.1}\)Ca\(_{2}\)BaSrCu\(_{2}\)O\(_{7−δ}\) where x = 0.1, 0.2, 0.3, 0.4 or 0.5 obtained by the X-ray fluorescence yield technique are shown in Fig. 1. All these spectra were normalized to their respective absorption cross-sections of the actual oxygen contents given in Table 1. The salient features of these spectra are as follows. There are two prepeaks at 528.3 and 529.4 eV with a shoulder at 527.5 eV, and a broad peak at 537 eV. The low-energy transitions with energy below 532 eV are ascribed to transitions from the oxygen 1s core electrons to holes with predominant 2p character on the oxygen sites. The transitions with energy above 532 eV are attributed to the transitions to oxygen 2p states, which are hybridized with barium-4d, strontium-3d, praseodymium-4d, and 5f states.\(^{24}\)

The system Eu\(_{0.9−x}\)Pr\(_{x}\)Ca\(_{2}\)BaSrCu\(_{2}\)O\(_{7−δ}\) is isomorphic with YBa\(_2\)Cu\(_3\)O\(_{7−δ}\) (orthorhombic structure with space group \(Pnma\)) at lower Pr\(^{3+}\) concentrations. However, with increasing Pr\(^{3+}\) concentration, i.e., when x = 0.3 and above, the phase changes from orthorhombic structure to tetragonal structure.\(^{25,26}\) The tetragonal structure is again isomorphic with YBa\(_2\)Cu\(_3\)O\(_{6−δ}\).\(^{22}\) We therefore adopted the same scheme of assignments for the present oxygen 1s absorption spectra as the samples belong to both orthorhombic as well as tetragonal phases. A study on R(Ba\(_1−x\)R\(_x\))Cu\(_{2}\)O\(_{2}\) \((R = Nd or Pr)\) by soft X-ray absorption spectroscopy also supports the present assignments.\(^{33}\) The orthorhombic crystal structure of Eu\(_{0.9}\)Pr\(_{0.1}\)Ca\(_{2}\)BaSrCu\(_{2}\)O\(_{7−δ}\) has four non-equivalent oxygen sites, viz. O(2) and O(3) within the Cu(2)O layers, O(4) in the BaO and SrO planes, and O(1) in the Cu(1)O chains along the b axis.
The observed multiple transitions at energy below 532 eV are related to the chemical shifts of oxygen 1s binding energies for different oxygen sites. The differences in the chemical shifts of oxygen 1s core levels can be obtained by using local density approximation (LDA) band-structure calculations. Based on LDA calculations for YBa$_2$Cu$_3$O$_{7-\delta}$ by Krakauer et al., the oxygen 1s energy levels of the sites O(2) and O(3) in the Cu(2)O$_2$ planes were very close to each other and found to be 0.29 eV higher than that of the O(1) site in the Cu(1)O chains which in turn was 0.4 eV higher than the energy level of the O(4) site in the BaO planes. Based on these LDA calculations and earlier reports on isomorphic systems, viz. YBa$_2$-Cu$_3$O$_{7-\delta}$-PrBa$_2$Cu$_3$O$_{7-\delta}$ and DyBa$_2$Cu$_3$O$_{7-\delta}$, the following assignment scheme for the oxygen 1s absorption spectra of Eu$_{0.9}$-Pr$_{0.1}$BaSrCuO$_{7-\delta}$ is made. The shoulder at 527.5 eV is assigned to the transition from the oxygen 1s core level to the superposition of oxygen 2p hole states originating from the apical oxygen sites, viz., O(4) sites in the BaO and SrO planes, and oxygen sites in Cu(1)O planes, viz., O(1). The high energy prepeak at 528.3 eV is due to the transition into oxygen 2p holes on O(2) and O(3) sites situated in the Cu(2)O$_2$ planes. The peak at 529.4 eV is ascribed to the transition into the conduction band, in other words the upper Hubbard band (UHB) which is predominantly formed by copper 3d states with some admixture of oxygen 2p states. As a consequence of the strong on-site correlation effects on the copper sites in cuprate superconductors, the upper Hubbard band is always assumed to be present. The spectral weight of the component corresponding to the transition to the hole states on O(2) and O(3) sites situated in Cu(2)O$_2$ planes decreases, while the component corresponding to the transition to the upper Hubbard band increases, with increasing Pr$^{3+}$ substitution for Eu$^{3+}$ in Eu$_{0.9-x}$-Pr$_x$Cu$_3$BaSrCuO$_{7-\delta}$. These observations clearly demonstrate that the chemical substitution of Pr$^{3+}$ for Eu$^{3+}$ in Eu$_{0.9-x}$-Pr$_x$Cu$_3$BaSrCuO$_{7-\delta}$ reduces the hole states in Cu(2)O$_2$ planes.

To estimate the hole states on different oxygen sites and to understand the variation of hole states for different praseodymium substitution, the oxygen K-edge X-ray absorption spectra as shown in Fig. 1 were resolved into different Gaussian components by the following procedure. By fixing the band positions obtained by plotting the second derivative form, the bandwidths were evaluated over a series. It was found that the bandwidths obtained from the fits were almost constant for a particular band over a series. These bandwidths were averaged over a series for a particular band. Then the resultant bandwidths were fixed for the final fit and the band positions allowed to vary. The goodness of fit was judged by the $\chi^2$ value. The relative intensities of each Gaussian component were obtained by integrating the area under the band. The errors in the relative intensities of each Gaussian component were obtained as standard errors (the square root of the mean square error) for the best fits. As an illustrative example, the pre-edge structure of oxygen 1s X-ray absorption spectrum of Eu$_{0.9}$Pr$_{0.1}$BaSrCuO$_{7-\delta}$ on oxygen sites originating from the (a) CuO$_2$ ribbons, (b) CuO$_2$ planes and (c) the upper Hubbard band (UHB) as a function of Pr$^{3+}$ substitution. The solid lines are guides to the eyes.
Cu are normalized to that corresponding to the transition due to L\textsubscript{3} Cu(2p\textsubscript{3/2}), viz. O(1), is constant with increasing praseodymium substitution (Fig. 3). On the other hand, the spectral weight at 528.3 eV corresponding to oxygen 2p hole states on the O(2) and O(3) sites situated in the Cu(2)O\textsubscript{2} planes decreases systematically, while the spectral weight of the upper Hubbard band at 529.4 eV is found to increase at the cost of hole states on the O(2) and O(3) sites in the Cu(2)O\textsubscript{2} planes with increasing praseodymium substitution (Fig. 3).

The praseodymium M\textsubscript{x}-edge and copper L\textsubscript{3}-edge X-ray absorption spectra of Eu\textsubscript{0.9}Pr\textsubscript{x}Ca\textsubscript{0.1}BaSrCu\textsubscript{1-x}O\textsubscript{y}, where x = 0.1, 0.2, 0.3, 0.4 or 0.5 obtained by the X-ray absorption spectroscopy (XAS) method are shown in Fig. 2. The bands centered at 931 and 951 eV are called copper L\textsubscript{3} and L\textsubscript{2} white lines, and are assigned to the transitions from the ground states of Cu\textsuperscript{2+}, Cu(2p\textsubscript{3/2,1/2})3d\textsuperscript{10}O\textsuperscript{2-} into the excited states, Cu(2p\textsubscript{3/2,1/2})3d\textsuperscript{9}O\textsuperscript{2-}, respectively, where (2p\textsubscript{3/2,1/2})\textsuperscript{1} denotes a hole containing 2p\textsubscript{3/2} or 2p\textsubscript{1/2} states.\textsuperscript{44,45} The shoulders situated to high energy of each main band are assigned to the transitions from the excited states, Cu(2p\textsubscript{3/2,1/2})3d\textsuperscript{9}L\textsuperscript{1,2}, respectively, where L\textsuperscript{1,2} denotes a ligand hole on the oxygen 2p orbital. These high-energy shoulders are therefore identified as the holes in the CuO\textsubscript{2} layers and CuO\textsubscript{3} ribbons.\textsuperscript{44,45} The shoulders to low energy of both copper L-edges are due to praseodymium M\textsubscript{x} and M\textsubscript{4} white lines respectively and are assigned to the transitions from 3d\textsubscript{6} ground states to 4f states of Pr\textsuperscript{3+}. Attempts were made to resolve the copper L\textsubscript{3}-edge and praseodymium M\textsubscript{x}-edge X-ray absorption spectra and as a representative example the results of the spectral correlation to the composition Eu\textsubscript{0.9}Pr\textsubscript{x}Ca\textsubscript{0.1}BaSrCu\textsubscript{1-x}O\textsubscript{y}, including the resolved Gaussian components and their assignments are shown in Fig. 2(b). The resultant spectral weights for Gaussian components corresponding to the transitions, viz. the hole contents in the CuO\textsubscript{2} layers and CuO\textsubscript{3} ribbons, and praseodymium M\textsubscript{x} white line, are plotted as a function of praseodymium substitution in Fig. 5. All these spectral weights are normalized to that corresponding to the transition due to Cu\textsuperscript{2+} at 931 eV. The spectral weight corresponding to the total hole decreases while that corresponding to the praseodymium M\textsubscript{x} white line increases with increasing praseodymium concentration. The increase in the spectral weight corresponding to the M\textsubscript{x} white line confirms that Eu\textsuperscript{3+} ions in the Eu\textsubscript{0.9}Pr\textsubscript{x}Ca\textsubscript{0.1}BaSrCu\textsubscript{1-x}O\textsubscript{y} system are partially substituted by Pr\textsuperscript{3+} ions. The decrease in hole content with increasing Pr\textsuperscript{3+} is also evidenced by the oxygen K-edge X-ray absorption spectra as discussed earlier.

The present experimental results based on oxygen K-edge and copper L-edge X-ray absorption spectra for Eu\textsubscript{0.9}Pr\textsubscript{x}Ca\textsubscript{0.1}BaSrCu\textsubscript{1-x}O\textsubscript{y} clearly demonstrate that the hole states responsible for superconductivity get depleted progressively by the praseodymium substitution.\textsuperscript{46} These should in principle reduce the T\textsubscript{c}, which is indeed found to be the case. Thus these results give evidence in support of the hole-depletion models based on Pr 4f-O 2p, hybridization.\textsuperscript{25,26} By comparing the depletion of hole states upon praseodymium substitution in Eu\textsubscript{0.9}Pr\textsubscript{x}Ca\textsubscript{0.1}BaSrCu\textsubscript{1-x}O\textsubscript{y} with those in Y\textsubscript{1-x}Pr\textsubscript{x}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{y} and Dy\textsubscript{1-x}Pr\textsubscript{x}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{y}, it is found that the rate at which the depletion of hole states occurs in the present case is lower than in Y\textsubscript{1-x}Pr\textsubscript{x}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{y} and Dy\textsubscript{1-x}Pr\textsubscript{x}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{y}.\textsuperscript{23} This is due to the partial substitution of Ba\textsuperscript{2+} by Sr\textsuperscript{2+} and Eu by Cu\textsuperscript{2+} ions which keeps inducing and creating the holes which in turn leads to a decrease in the rate of hole depletion in the present case.

It is well known that the phenomenological Judd–Ofelt model can account for the observed intensities for 4f-4f transitions of all the rare earth ions except Pr\textsuperscript{3+}.\textsuperscript{44–46} In the case of Pr\textsuperscript{3+} ions, the 5d level is relatively low lying which results in a strong mixing with the 4f orbital. This is reflected by the abnormal intensity reported for the transition H\textsubscript{4} \rightarrow \textsuperscript{5}P\textsubscript{J} in the absorption spectra measured in the uv-visible region for Pr\textsuperscript{3+} ion in different host materials.\textsuperscript{44–46} The models proposed by FR and LM consider that the 4f\textsuperscript{6}e\textsuperscript{8} orbital of Pr\textsuperscript{3+} is strongly localized and hybridized with p\textsubscript{o} orbitals of neighboring planar oxide ions.\textsuperscript{46} These models do not consider 4f-5d mixing for Pr\textsuperscript{3+} ion. The abnormal intensity reported for the transition H\textsubscript{4} \rightarrow \textsuperscript{5}P\textsubscript{J} and the non-applicability of Judd–Ofelt theory for the Pr\textsuperscript{3+} ions suggest that the 4f orbital is strongly perturbed by the 5d orbital. One should take this effect into account when the 4f orbital of Pr\textsuperscript{3+} ion is considered for hybridization. This may be one of the reasons that both FR and LM models could not account for a high value of nearly 17 K for the antiferromagnetic ordering of praseodymium moments (Neel temperature, T\textsubscript{N}) for PrBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7}.\textsuperscript{6,9}

**Conclusion**

High resolution oxygen K-edge and copper L\textsubscript{3}-edge X-ray
absorption spectra for Eu$_{0.9-x}$Pr$_x$Ca$_2$BaSrCu$_{2+2x}$O$_{8+x}$ as a function of Pr substitution have been obtained by using a bulk sensitive X-ray fluorescence yield technique. The spectral weight of the pre-edge structure in the oxygen K-edge and copper L-edge X-ray absorption spectra for Eu$_{0.9-x}$Pr$_x$Ca$_2$BaSrCu$_{2+2x}$O$_{8+x}$ clearly demonstrate that the hole states are depleted by the praseodymium substitution, which explains the reduction in the $T_c$ of Eu$_{0.9-x}$Pr$_x$Ca$_2$BaSrCu$_{2+2x}$O$_{8+x}$. This is due to the partial substitution of Ba$^{2+}$ ions by Eu and Cu$^{+}$ ions, which induces and creates the holes. Our results give evidence in support of the hole-depletion models based on Pr 4f- O 2p hybridization. Further, the anomalous behavior of Pr$^{4+}$ can be well explained if one takes into account the 4f-5d mixing in which the 5d level is low lying and which strongly mixes with the 4f orbital of Pr$^{4+}$ ions unlike those of other rare earth metal ions.

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