Superconductivity and valence state of Tb in Lu1−x Tb x Ba2Cu3O7−δ (0≤x≤0.7)

K. I. Gnanasekar, P. Selvam, H. V. Keer, R. Pinto, S. C. Purandare, A. S. Tamhane, L. C. Gupta, and R. Vijayaraghavan

Superconductivity and valence state of Tb in $Lu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ $(0 \leqslant x \leqslant 0.7)$

K. I. Gnanasekar, P. Selvam, and H. V. Keer
Department of Chemistry, Indian Institute of Technology, Bombay-400 0076, India

R. Pinto, S. C. Purandare, A. S. Tamhane, L. C. Gupta, and R. Vijayaraghavan
Tata Institute of Fundamental Research, Colaba, Bomaby-400 005, India

Although both lutetium and terbium do not form superconducting $REBa_2Cu_3O_{7-\delta}$, we report here the formation of superconducting phase in thin films. Films are highly c-axis oriented with high current densities (3.0×10^6 A cm^{-2} at 77 K) observed in $Lu_{0.5}Tb_{0.5}Ba_2Cu_3O_{7-\delta}$. X-ray photoelectron spectroscopic analysis of Tb in the above film indicates that Tb is in a trivalent state. Further, as the redox potential of Tb ($Tb^{4+} + e^- \rightarrow Tb^{3+} : E^0 = 3.1$ V) is close to that of Pr ($Pr^{4+} + e^- \rightarrow Pr^{3+} : E^0 = 3.2$ V), we suggest that Pr also would be in a trivalent state and the mechanism by which the latter depresses T_c must be of trivalent origin.

Praseodymium and terbium are the two rare earths (REs) that exhibit mixed valence characteristics in simple oxides.[1,2] When substituted partially in RE-1:2:3 phase, praseodymium alone depressed the T_c while terbium does not.[3] Various mechanisms which include hole filling,[4] hybridization of extended Pr ($4f$) orbitals with Cu—O band,[5] magnetic pair breaking,[6] and localization[7] have been proposed to account for the behavior of praseodymium and most of them are centered around its valence state which is under controversy. While magnetic[8] and chemical studies[4] account for a higher valence, x-ray photoemission studies,[9] and x-ray appearance near-edge structures[10] have shown that praseodymium is in trivalent state. On the contrary, neutron diffraction[11] and some x-ray absorption studies[12] have revealed that praseodymium is in mixed valence state. As there is considerable controversy over the valence state of praseodymium even among different spectroscopic measurements, in order to probe the oxidation state of praseodymium, the authors found it worthwhile to study the valence state of terbium in $Lu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ as the latter has the redox potential close to that of praseodymium, $Tb^{4+} + e^- \rightarrow Tb^{3+} : E^0 \approx 3.1$ V and that of praseodymium is 3.2 V.[13] However, even the partial substitution of terbium in bulk RE-1:2:3 phase resulted in mixed phase compound due to the formation of $BaTbO_3$. This impurity phase segregates out and hence the valence state of terbium could not be studied. On the other hand, *in situ* laser deposition has been used as a synthesis tool to grow single phase materials not possible with standard solid state methods and hence offers unique possibilities in terms of exploring the structure property relationship in complicated systems.[3] It appears that the modified growth conditions such as reduced growth temperature, plasma formation, and the involvement of ions, atomic species, and substrates allow the synthesis of certain compounds in thin film form.

Bulk samples with the nominal composition of $Lu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ with $0 < x < 0.65$ were prepared by mixing stoichiometric amounts of 99.99% purity Lu_2O_3, $BaCO_3$, Tb_4O_7, and CuO. The details of preparation of samples have been reported elsewhere.[14] The samples were pelletized and were used as targets for the growth of thin films on $\langle 100 \rangle$ $LaAlO_3$, $\langle 100 \rangle$ MgO, and $\langle 100 \rangle$ $SrTiO_3$ substrates by pulsed laser deposition technique that has been described elsewhere.[15] Films were characterized by x-ray diffraction (XRD) technique and the composition was analyzed by energy dispersive x-ray analysis. X-ray photoelectron spectroscopic (XPS) measurements were performed with VG scientific ESCALAB Mark-II spectrometer which has been calibrated with In ($3d_{5/2}$) core level having binding energy of 443 eV and C(1s) core level energy at 284.5 eV. The binding energies reported here were corrected from reference carbon. Mg-K$_\alpha$ radiation of 1253.6 eV was used and the resolution of the beam was about 0.8 eV. The pressure of the sample chamber was lower than 10^{-8} Torr.

Although bulk materials of the composition $LuBa_2Cu_3O_{7-\delta}$ (Ref. 16) and $TbBa_2Cu_3O_{7-\delta}$ (Ref. 17) are multiphasic, $Lu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ forms in thin films. XRD pattern of bulk sample of pure Lu-1:2:3 compound is multiphasic and does not superconduct [Fig. 1(a)]. However, thin films of $Lu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ are highly c-axis oriented and without any impurity phase for x up to 0.6 [Fig. 1(b)]. All
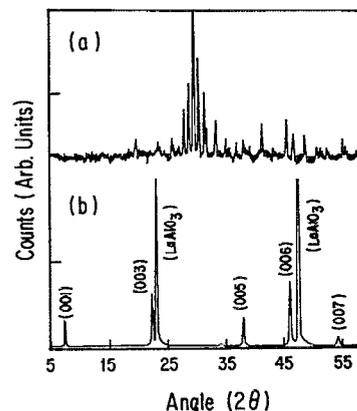

FIG. 1. XRD of nominal composition of (a) bulk $LuBa_2Cu_3O_{7-\delta}$ material. (b) Thin film of $Lu_{0.5}Tb_{0.5}Ba_2Cu_3O_{7-\delta}$.
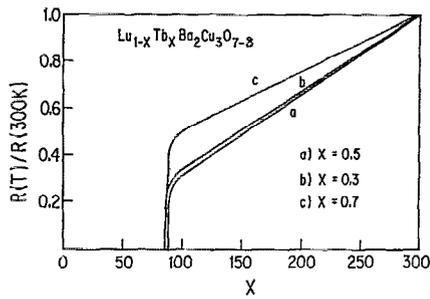
FIG. 2. Normalized resistance $[R(T)/R(300)$ K] as a function of temperature of $Lu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ thin films.

FIG. 4. SEM micrograph of $Lu_{0.5}Tb_{0.5}Ba_2Cu_3O_{7-\delta}$ thin film.

these films are highly metallic and superconducting with T_c of about 88 K, typical of well-formed 1:2:3 phase with $\Delta(T) \simeq 1.5$ K (Fig. 2). J_c for the films was measured using patterned 10-μm-wide bridges and using 1 μV/mm criterion. The value of J_c thus measured for $Lu_{0.5}Tb_{0.5}Ba_2Cu_3O_{7-\delta}$ was 3.0×10^6 A cm^{-2} at 77 K and 3.0×10^7 A cm^{-2} at 10 K which compares favorably with that of standard Y-1:2:3 films. Shown in Fig. 3 is the J_c versus temperature plot of $Lu_{0.5}Tb_{0.5}Ba_2Cu_3O_{7-\delta}$. Such a graph can be fitted well by Ambegaokar and Baratoff's equation for S-I-S junctions.[18] Unlike other RE-1:2:3 films, the morphology of terbium-doped films is different and show well-connected grains as evident from the scanning electron microscopy (SEM) micrograph, consistent with high transport behavior (Fig. 4).

On the basis of these comparisons, it is quite reasonable to derive that terbium ion is trivalent just as other rare earth ions are in these compounds. However, Fincher et al. have suggested a tetravalent state for terbium in $Y_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ system.[3] Therefore, to check whether the mechanism of depression of superconductivity (in the case of praseodymium) is of mixed valence origin, we have studied the core level XPS of terbium $(4d)$ level in these compounds. Although similar photoemission studies for praseodymium in Pr-1:2:3 as well as in $RE_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ conclude a trivalent state, the Pr $(3d_{5/2})$ spectrum directly overlies the Cu $(2p_{3/2})$ level so that data analysis is difficult and approximate.[9] However in the case of terbium, the binding energy of Tb $4d$ level ($\simeq 149$ eV) is without any interference from any other constituents and hence the interpretation is straightforward. The XPS
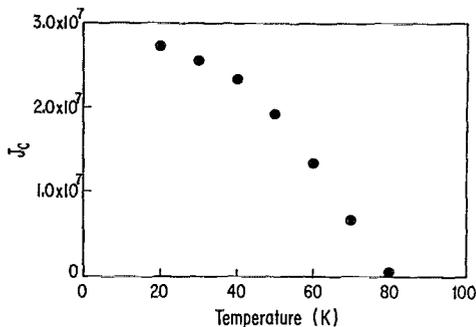
spectrum of Tb $(4d)$ level for $Lu_{0.5}Tb_{0.5}Ba_2Cu_3O_{7-\delta}$ deposited on $\langle100\rangle$ LaAlO$_3$ substrate is shown in Fig. 5. Spectra looks similar to those reported in the literature and show a clear peak with the binding energy at 149.25 eV.[19] For comparison we have recorded XPS of terbium in Tb$_4$O$_7$ (in which about 50% of terbium is trivalent and the remaining is in the tetravalent state).[2] We have chosen BaTbO$_3$ as a reference compound for tetravalent terbium instead of TbO$_2$ as the latter is difficult to synthesis.[20]

In the case of BaTbO$_3$, the XPS spectrum shows a clear slit in the peak. Deconvolution of these spectrum showed that the first peak was at 149.25 eV and we assign this peak for trivalent terbium (Fig. 5). The second peak was at 151.25 eV and we assign this for tetravalent terbium. Although mixed metal oxides of the form ABO$_3$ with perovskite structure are known to incorporate various kinds of tetravalent metal ions at the B site of the crystal, we could observe evidence for the existence of trivalent terbium in BaTbO$_3$ compound. The higher intensity of the peak at 151.25 eV qualitatively accounts for the large fraction of tetravalent ter-

FIG. 3. J_c as a function of temperature of $Lu_{0.5}Tb_{0.5}Ba_2Cu_3O_{7-\delta}$.

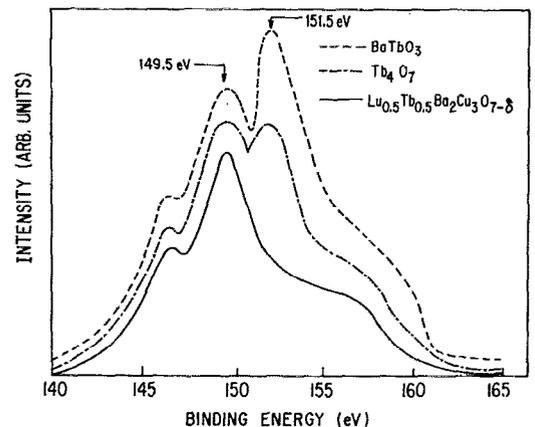FIG. 5. XPS spectra of Tb $(4d)$ level in BaTbO$_3$, Tb$_4$O$_7$, and in $Lu_{0.5}Tb_{0.5}Ba_2Cu_3O_{7-\delta}$ (thin film).

bium ions in these compounds. This observation is further supported by Kemmler *et al.* who found that $BaTbO_3$ also contains trivalent terbium ions from the results of the optical and magnetic investigations.[21] A possible reason for the observation of trivalent terbium ions might also be due to the loss of oxygen at the surface.

On the other hand, Tb_4O_7 shows a broad peak for Tb (4d) level with a splitting (Fig. 5). Deconvolution of the spectrum shows that the first peak centers at 149.5 eV and is characteristic of trivalent terbium ions. The second peak at 151.25 eV is that of tetravalent terbium ions. Comparing the intensities of the peaks, it is clear that the fractions of trivalent and tetravalent terbium ions are the same which is expected for this compound. Had the multiplet pattern been due to different possible spin states associated with the same oxidation state, the relative intensities of the observed peaks for $BaTbO_3$ and Tb_4O_7 should be constant and must be in the ratio 7:9. For Tb_4O_7 the first peak, occurring at 149.5 eV is slightly more intense than the second one at 151.25 eV whereas in the case $BaTbO_3$ the intensity of the latter is significantly larger than the former. These changes in the intensities indicate that the two peaks belong to two different oxidation states of terbium in these compounds.

The XPS spectrum of terbium in $Lu_{0.5}Tb_{0.5}Ba_2Cu_3O_{7-\delta}$ shows only one peak having binding energy of 149.5 eV when compared with the spectrum of terbium in Tb_4O_7 or $BaTbO_3$. Therefore, we conclude that terbium is trivalent in these compounds (Fig. 5). From XPS studies, as terbium substitutes in trivalent state, we infer that praseodymium also would more likely be in the trivalent state as both terbium and praseodymium occupy the same lattice site with a similar environment and have the close redox potential although they exist in mixed valences in the starting materials viz Tb_4O_7, Pr_6O_{11}. These studies indicate that the mechanism by which praseodymium depresses T_c is of trivalent origin. Therefore hybridization of extended 4f orbitals of praseodymium with the conduction band is likely to be favorable which would either lead to the localization of holes or mediate the pair-breaking effect.

The superconducting orthorhombic phase is stabilized in the form of thin films of $Lu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ where both lutetium and terbium do not form respective superconducting RE-123 phase in the bulk. XPS analysis of Tb (4d) level in these films indicate that terbium is trivalent in these compounds. Although both terbium and praseodymium generally exhibit mixed valence characteristics in oxides (between +3 and +4), in superconducting RE-123 oxide, they are stabilized in the trivalent state.

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