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Stabilization of a superconducting $\text{TbSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$ compound and the valence state of terbium

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A single-phase Sr-based Tb-123 phase has been synthesized by chemical stabilization. $\text{TbSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$ exhibits superconductivity at $T_{c,\text{zero}}=22$ K. X-ray diffraction results suggest a relatively small orthorhombicity and neutron diffraction studies indicate an excess oxygen content (≥ 7.2) in the sample. Tb is present as a trivalent ion in the superconducting phase as derived from x-ray photoelectron spectroscopy. © 1995 American Institute of Physics.

It has been well established that a $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Ln-123) phase exists for Ln=Y or lanthanides except Ce and Tb. The superconducting transition temperature T_c has no significant effect on the quaternary element (88–92 K, Ref. 1) except for Pr which does not superconduct while the Ce and Tb analog do not exist owing to the formation of stable ternary oxides,² viz. BaCeO_3 and BaTbO_3 , respectively. However, the partial substitution of Pr for Y in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ results in the suppression of T_c while Tb does not alter the T_c .³ On the other hand, no superconducting single phase has yet been synthesized in the analogous system $\text{LnSr}_2\text{Cu}_3\text{O}_{7-\delta}$ under normal pressure.⁴ Interestingly, such metastable Sr-based 1-2-3 phases have successfully been synthesized by chemical substitution at the Cu site.⁵⁻⁷ In this letter, we focus our attention on the single-phase synthesis and characterization of $\text{TbSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$.

Although the most stable oxidation state of lanthanide elements is trivalent, elements such as Ce, Pr, and Tb exhibit ambivalent (trivalent and tetravalent) states.⁸ Since the redox potential of Tb ($\text{Tb}^{4+} + e^- \rightarrow \text{Tb}^{3+}$; $E^0=3.1$ V) is close to Pr ($\text{Pr}^{4+} + e^- \rightarrow \text{Pr}^{3+}$; $E^0=3.2$ V), it is worthwhile to study the valence state of Tb in superconducting $\text{TbSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$. The results could possibly be extended to the Pr system, since there is considerable controversy over the valence state of Pr. For example, magnetic⁹ and chemical¹⁰ studies account for the tetravalent state, while x-ray photoelectron spectroscopy (XPS)¹¹ and x-ray absorption near-edge spectroscopy (XANES)¹² investigations suggest the trivalent state. On the contrary, neutron diffraction¹³ and x-ray absorption studies¹⁴ have revealed a mixed valence state. Although the spectroscopic studies of pure and substituted Pr-123 indicate a trivalent state, it is however difficult to assess the true value of Pr from the XPS core levels, i.e., the Pr ($3d_{5/2}$) level overlaps directly with the Cu ($2p_{3/2}$) level and hence, the dilemma. On the other hand, the interpretation of Tb core level spectra is straightforward and it is free from interferences. Hence, we report here the XPS results of the Tb ($4d_{5/2}$) level in $\text{TbSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$.

Polycrystalline samples with the nominal composition of $\text{TbSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$ were prepared by a conventional solid-state route with stoichiometric amounts of 99.99% purity Tb_4O_7 , SrCO_3 , CuO , and ReO_3 . The experimental details can be seen elsewhere.⁷ The phase purity of the samples was checked by a JEOL JDX 8030 x-ray diffractometer (XRD), fitted with a secondary beam graphite monochromator using Cu $K\alpha$ radiation. The composition of the sample was analyzed by energy dispersive x-ray (EDX) analysis. The electrical resistivity of the samples were measured by a standard four-probe technique. ac-susceptibility measurements were carried out on a pellet using an ac susceptometer (Sumitomo superconducting property measurement system) in a field of 0.1 Oe and 313 Hz. XPS measurements were performed in a VG Scientific ESCALAB Mark-II spectrometer with a base pressure of about 10^{-9} mbar. The binding energies reported here were corrected from reference carbon (1s) core level energy at 284.5 eV. The excitation source was Mg $K\alpha$ radiation (1253.6 eV) and the surfaces were cleaned prior to analysis by scraping.

Figure 1 depicts the XRD patterns of $\text{TbSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$ and for comparison the Y analog is also included. All the peaks could be indexed on the basis of orthorhombic symmetry (1-2-3 type) and the unit cell parameters were derived using a least-squares fit method. The lattice constants are $a=3.822$ Å; $b=3.826$ Å, and $c=11.507$ Å, which suggests that the observed orthorhombicity $e=(b-a)/(b+a)$ is relatively small compared to the $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system.¹⁵ The impurity lines indicated by an asterisk (*) in the XRD of $\text{TbSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$ do not pertain to any known Re/Tb containing phases. From the resistivity plots of $\text{TbSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$ (Fig. 2), it can be seen that the compound exhibits moderate metallic behavior and superconducts at about ($T_{c,\text{zero}}$) 22 K. The inset of Fig. 2 shows the $\chi'-T$ variation ($T_c \approx 23$ K) for $\text{TbSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$ which is in close agreement with that obtained from the $\rho-T$ plot. Saturation of the signal at low temperature (in the $\chi'-T$ plot) shows the bulk nature of superconductivity in this sample. Neutron diffraction results show that oxygen content in these compounds is ≥ 7.2 ,¹⁶

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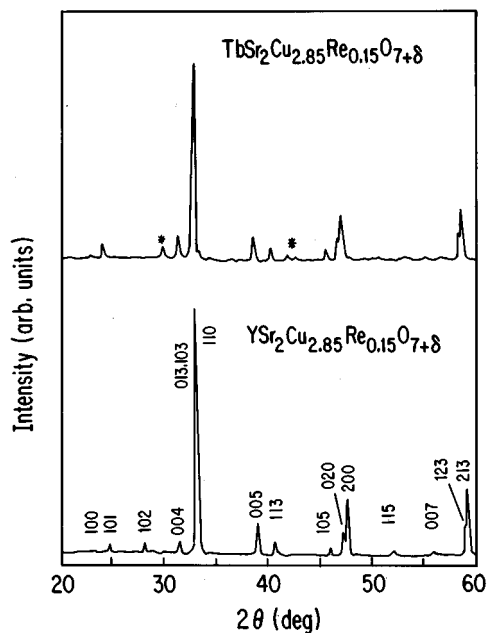


FIG. 1. XRD traces of $\text{TbSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$ and $\text{YSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$. Unidentified impurity phase is marked by asterisk (*).

indicating that the Re atom could be in a higher valence (6+) state. This is well supported by the analysis of the Re ($4f_{7/2}$) core level spectrum which suggests that Re is in a hexavalent (~ 45.1 eV) state.¹⁷ From these results, it can be derived that terbium ions exist in a trivalent state like the other Ln ions in $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Existence of Tb in a +3 valence state has been reported in partially substituted $\text{Y}_{1-x}\text{Tb}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Lu}_{1-x}\text{Tb}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ by Fincher and Blanchet³ and Gnanasekar *et al.*,¹⁸ respectively.

The XPS spectra of the Tb ($4d_{5/2}$) core level of $\text{TbSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$ and Tb_4O_7 are shown in Fig. 3. A single peak at 149.5 eV corresponds to Tb in the trivalent state in $\text{TbSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$. For comparison we have carried out the analysis for Tb_4O_7 , which is also the starting material. The latter shows the presence of two peaks of equal intensity indicative of both trivalent and tetravalent states

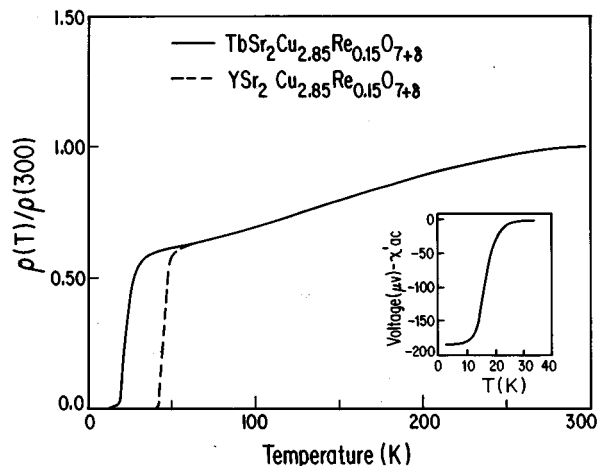


FIG. 2. Normalized resistivity plot of $\text{TbSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$ and $\text{YSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$. The inset shows the χ'_{ac} of $\text{TbSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$.

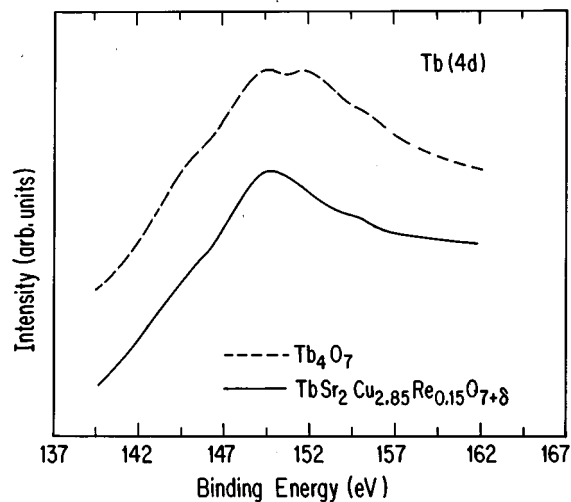


FIG. 3. XPS core level $[\text{Tb}(4d_{5/2})]$ spectra of $\text{TbSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$ and Tb_4O_7 .

with binding energies, respectively, at 149.5 and 151.2 eV.¹⁸⁻²⁰ This suggests that Tb is of trivalent origin in the superconducting Tb-123 phase. Since both Tb and Pr have nearly the same redox potential (3.1 and 3.2 V) and both occupy the same coordination site (eightfold coordination) in the Ln-123 structure, one can presume that the Pr ion could be in the trivalent state both in Pr-123 and Pr-substituted Ln-123 systems. Hence, T_c suppression in $\text{Ln}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ and the antiferromagnetic insulating nature of Pr-123 could be attributed to the hybridization of a $\text{Pr}(4f)$ orbital with the conduction band of Cu ($3d_{x^2-y^2}$)— $\text{O}(2p)$ which leads to either pair breaking or a hole localization effect²⁰ with a possible +3 valence state of Pr.

In summary, a superconducting $\text{TbSr}_2\text{Cu}_{2.85}\text{Re}_{0.15}\text{O}_{7+\delta}$ is stabilized in the bulk form by partial substitution of Cu by Re. The XPS analysis of the $\text{Tb}(4d_{5/2})$ core level indicates that terbium is in the trivalent state like the other lanthanides. On this basis, it may be deduced that Pr also in the +3 valence state and the suppression of superconductivity in Pr-substituted Ln-123 systems and the antiferromagnetic insulating nature of Pr-123 may not be due to the much discussed tetravalent state of the Pr ion.

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- ¹M. B. Maple, Y. Dalichaouch, J. M. Ferreira, P. R. Hake, B. W. Lee, J. J. Neumeier, M. S. Torikachvili, K. N. Yang, H. Zhou, R. P. Guertin, and M. V. Kuric, *Physica B* **148**, 155 (1987), and references cited therein.
- ²L. Soderholm, K. Zhang, D. G. Hints, M. A. Beno, J. D. Jorgenson, C. U. Segre, and I. K. Schuller, *Nature* **328**, 604 (1987).
- ³C. R. Fincher, Jr. and G. B. Blanchet, *Phys. Rev. Lett.* **67**, 2902 (1991).
- ⁴B. Okai, *Jpn. J. Appl. Phys.* **29**, L2180 (1990).
- ⁵T. Den and T. Kobayashi, *Physica C* **196**, 141 (1992).
- ⁶Q. Xiong, Y. Q. Wans, J. W. Chu, Y. Y. Sun, K. Matsuishi, H. H. Feng, P. H. Hor, and C. W. Chu, *Physica C* **198**, 70 (1992).
- ⁷M. Murugesan, M. S. R. Rao, L. C. Gupta, R. Pinto, M. Sharon, and R. Vijayaraghavan (unpublished).
- ⁸J. D. Lee, *Concise Inorganic Chemistry*, 4th ed. (Chapman and Hall, 1993).
- ⁹W. H. Li, J. W. Lynn, S. Skanthakumar, T. W. Clinton, A. Kebede, C. S. Jee, J. E. Crow, and T. Mihalasin, *Phys. Rev. B* **40**, 5300 (1989).

- ¹⁰J. J. Neumeier, T. Bjornholm, M. B. Maple, and I. K. Schuller, *Phys. Rev. Lett.* **63**, 2516 (1989).
- ¹¹U. Neukirch, C. J. Simons, P. Sladeczek, C. Laubschat, O. Strebel, G. Kaindl, and D. D. Arma, *Europhys. Lett.* **5**, 567 (1988).
- ¹²L. Soderholm and G. L. Goodman, *J. Solid State Chem.* **81**, 121 (1989).
- ¹³J. J. Neumeier, T. Bjornholm, M. B. Maple, J. J. Rhyne, and G. A. Gotaas, *Physica C* **166**, 191 (1990).
- ¹⁴F. W. Lytle, G. Von der Laan, R. B. Gregor, E. M. Larsen, C. E. Violet, and J. Wong, *Phys. Rev. B* **41**, 8955 (1990).
- ¹⁵G. V. Subba Rao and U. V. Varadaraju, in *Chemistry of High Temperature Superconductors*, edited by C. N. R. Rao (World Scientific, Singapore, 1991).
- ¹⁶A. Sequiera, H. Rajagopal, M. Murugesan, M. S. R. Rao, L. C. Gupta, R. Pinto, M. Sharon, and R. Vijayaraghavan (unpublished).
- ¹⁷W. T. Tysoe, F. Zaera, and G. A. Simorjai, *Surf. Sci.* **200**, 1 (1988); Our XPS results (unpublished).
- ¹⁸K. I. Gnanasekar, P. Selvam, H. V. Keer, R. Pinto, S. C. Purandare, A. S. Tamhane, L. C. Gupta, and R. Vijayaraghavan, *Appl. Phys. Lett.* **65**, 1296 (1994).
- ¹⁹B. D. Padalia, W. C. Lang, P. R. Moris, L. N. Watson, and D. J. Fabian, *Proc. R. Soc. London* **354**, 269 (1977).
- ²⁰M. B. Maple, B. W. Lee, J. J. Neumeier, G. Nieva, L. M. Paulius, and C. L. Seaman, *J. Alloys Compd.* **181**, 135 (1992).