JOURNAL OF SOLID STATE CHEMISTRY **96**, 468–469 (1992)

In Defense of the Bromine Method for the Determination of Hole Concentration in Superconducting Thallium Cuprates*

J. GOPALAKRISHNAN, R. VIJAYARAGHAVAN, R. NAGARAJAN,
AND C. SHIVAKUMARA

*Solid State and Structural Chemistry Unit, Indian Institute of Science,
Bangalore 560 012, India*

Communicated by J. M. Honig, November 18, 1991

There are two sources for a hole concentration in thallium cuprates, one arising from the chemistry and the other from the overlap of Tl (6*s*) with the conduction band of CuO_2 sheets. Our method based on the oxidation of bromide ions directly determines the holes arising from the chemistry of the material.

There are two different sources for holes in thallium cuprates. One is the chemistry of the material, which includes chemical composition, defects, etc., and the other is the overlap of Tl (6*s*) with the conduction band of CuO_2 sheets at the Fermi level (*1*, *2*). We designate the former uncompensated holes (type I) and the latter compensated holes (type II), because in type II, an equivalent number of electrons would be present in the Tl (6*s*) band. This distinction between the two types of holes is made here to better explain our stand on the origin of holes in thallium cuprates and their determination by the bromine method. In a given thallium cuprate, the holes present may be of type I or type II, or both. Band structure calculations (*3*) have shown that in general the holes are type I in single-thallium-layer cuprates, while they are of type II in double-thallium-layer cuprates. The presence of both types of holes in some thallium cuprates cannot be ruled out and band structure calculations do not take the defects into account. Moreover, it appears that type II holes may exist in certain single-thallium-layer cuprates also (*2*).

Wet-chemical procedures for the characterization/determination of holes in thallium cuprates have been reported by Goodenough and co-workers (*4*, *5*) and by us (*6*). The procedure reported in (*4*, *5*) determines the total oxidation present in the material, above the formal valences of Tl^+, Cu^+, and O^{2-}. From the data, Goodenough and co-workers compute what would be a formal oxidation state for copper *assuming* that all the thallium is in the 3^+ state. A copper oxidation state less than 2^+ is taken to indicate the existence of Tl (6*s*)–CuO_2 band overlap (type II holes). In cases where all Tl is in the Tl^{3+} state, as in $TlBaLaCuO_5$ and $TlBa_{1.4}La_{0.6}CuO_5$ (see Ref. (*7*), Table I), the value in excess of 2^+ is taken as the hole concentration in the CuO_2 sheets. The problem is that we have no way of finding out independently by experiment whether

---

[*] Contribution No. 820 from the Solid State and Structural Chemistry Unit.

0022-4596/92 $3.00

there is a Tl (6*s*)–CuO_2 band overlap in a material or not. Only by *assuming* that all the thallium is present as 3^+ could they obtain a hole concentration in single-thallium-layer cuprates (*7*).

On the other hand, the procedure reported by us (*6*) determines *directly* a hole concentration without making an assumption about thallium valency. This hole concentration is the actual hole concentration in cases where there is no Tl (6*s*)–CuO_2 band overlap as in the $TlBa_2Ca_{1-x}Y_xCu_2O_7$ system, where we have shown (*6*) that the hole concentration correlates with T_c in a manner analogous to other superconducting cuprates. In cases where the holes are both of type I and type II, our method determines only the type I holes. This appears to be the case with nominal $Tl_2Ba_2CaCu_2O_8$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$ superconductors. The procedure of Goodenough *et al.* (*4, 5*) misses the type I holes in these systems. In cases where the holes are exclusively of type II, our method dramatically shows no hole concentration (because there are no type I holes), even though the samples are superconducting. $Tl_2Ba_2CuO_6$ closely approximates to this behavior where the holes appear to be exclusively type II.

It may be relevant here to comment about the nature of defects that would be involved in accommodating thallium deficiency in double-thallium-layer cuprates. The defects are most likely not simple point defects. Electron microscopy work (*8, 9*) has shown that one of the common *extended defects* in these materials involves intergrowth of single-thallium-layer defects with double-thallium-layer regions. Thus, a defective material such as $Tl_{1.79}Ba_2CaCu_2O_{7.59}$ would approximately consist of 79% of $Tl_2Ba_2CaCu_2O_8$ and 21% of $TlBa_2CaCu_2O_7$, forming random intergrowths (assuming, of course, no other defects are present). The consequences of such an intergrowth defect toward creation of holes are indeed intriguing. One possibility is that the holes are type I in single-thallium-layer regions and type II in double-thallium-layer regions.

In conclusion, the origin of holes in thallium cuprates is indeed complex and there is no satisfactory method, wet-chemical or physical, as yet which resolves the different possibilities. We believe that the wet-chemical method reported by us (*6*) definitely provides additional insight into this complex problem.

Acknowledgment

This work is supported by the Department of Science and Technology, Government of India.

References

1. D. E. Cox, C. C. Torardi, M. A. Subramanian, J. Gopalakrishnan, and A. W. Sleight, *Phys. Rev. B* **38,** 6624 (1988).
2. M.-H. Whangbo and C. C. Torardi, *Acc. Chem. Res.* **24,** 127 (1991).
3. D. Jung, M.-H. Whangbo, N. Herron, and C. C. Torardi, *Physica C* **160,** 381 (1989).
4. M. Paranthaman, A. Manthiram, and J. B. Goodenough, *J. Solid State Chem.* **87,** 479 (1990).
5. A. Manthiram, M. Paranthaman, and J. B. Goodenough, *Physica C.* **171,** 135 (1990).
6. J. Gopalakrishnan, R. Vijayaraghavan, R. Nagarajan, and C. Shivakumara, *J. Solid State Chem.* **93,** 272 (1991).
7. A. Manthiram, M. Paranthaman, and J. B. Goodenough, *J. Solid State Chem.* **96,** 463–466 (1992).
8. B. Raveau, C. Michel, M. Hervieu, D.Groult, and J. Provost, *J. Solid State Chem.* **85,** 181 (1990).
9. S. S. P. Parkin, V. Y. Lee, A. I. Nazzal, R. Savoy, T. C. Huang, G. Gorman, and R. Beyers, *Phys. Rev. B* **38,** 6531 (1988).