JOURNAL OF SOLID STATE CHEMISTRY 109, 410–412 (1994)

LETTER TO THE EDITOR

Superconductivity and Hole Source in $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$

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Communicated by J. M. Honig, September 13, 1993

Mercury cuprates $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$ ($x = 0.0$–0.7) were synthesized, and their structure and superconductivity were characterized. Single phases of $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$ can be obtained for $x = 0.0$–0.7; they crystallize in a tetragonal structure, and their *a*- and *c*-parameters decrease smoothly with increasing *x*. The superconducting transition temperature of $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$ decreases with increasing *x*, and superconductivity vanishes for $x \geq 0.5$. These observations and tight-binding electronic band structure calculations suggest that the hole source of $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$ is not the Hg 6*s* band but the interstitial oxygen atoms in the HgO_δ sheet. © 1994 Academic Press, Inc.

The superconductivity of the *p*-type cuprate superconductors requires the presence of holes in their CuO_2 layers (1–5). Holes may be generated by oxygen excess, cation vacancy, or substitution of cations with different valences (e.g., Sr^{2+} for La^{3+}), all of which are based on nonstoichiometry of the chemical compositions. Another mechanism of hole creation is lowering the bottom of the rock-salt layer 6*s* band below the Fermi level of the CuO_2 layer $x^2 - y^2$ band, as found for the $22(n-1)n$ phases of thallium cuprates containing double rock-salt Tl–O layers (5–8). In the $12(n-1)n$ phases of thallium cuprates containing single rock-salt Tl–O layers, however, the Tl 6*s* bands lie above the Fermi level so that holes are not generated by the band-overlap mechanism (6). The $22(n-1)n$ and the $12(n-1)n$ thallium cuprates behave differently, because the Tl 6*s* bands of the single rock-salt Tl–O layers lie higher in energy than those of the double rock-salt Tl–O layers, while the CuO_2 layer $x^2 - y^2$ bands of the two phases are nearly of the same energy (6). The $x^2 - y^2$ bands of the CuO_2 layers are antibonding between the copper and oxygen atoms in the in-plane Cu–O bonds (5, 9, 10), so that shortening of the in-plane Cu–O bonds raises the $x^2 - y^2$ bands (11). Thus, when the in-plane Cu–O bonds of the $12(n-1)n$ phases are strongly shortened, the $x^2 - y^2$ bands are raised high enough to make the Fermi level rise above the bottom of the Tl 6*s* bands, thereby creating holes in the CuO_2 layers. For example, the copper atoms of $Tl(SrR)CuO_5$ (R = La, Nd) (12, 13) are in the oxidation state of +2, thereby implying that there are no holes in the CuO_2 layers. However, $Tl(SrR)CuO_5$ (R = La, Nd) is a superconductor because the very short in-plane Cu–O bonds significantly raise the $x^2 - y^2$ bands (11). The isostructural analogue $Tl(BaR)CuO_5$ (R = La, Nd) (7, 8, 14) is not a superconductor, probably because the in-plane Cu–O bonds are not short enough (11). Since Ba^{2+} is larger than Sr^{2+}, the *a*-parameter and, hence, the in-plane Cu–O bond length of $Tl(Sr_{1-x}Ba_xR)CuO_5$ ($x = 0.0$–1.0) increase gradually with increasing *x*. Therefore, the $x^2 - y^2$ bands are gradually lowered in energy as *x* increases, and $Tl(Sr_{1-x}Ba_xR)CuO_5$ eventually loses superconductivity for $x > 0.3$ (15).

Interest in high-temperature cuprate superconductors has been rekindled by the recent discoveries of superconductivity at 94 K in the single-copper-layer mercury cuprate $HgBa_2CuO_{4+\delta}$ (16), and at 133 K in the two- and three-copper-layer analogues (17). The neutron powder diffraction study of $HgBa_2CuO_{4+\delta}$ (18) shows that the apical oxygen atoms of CuO_6 octahedra form linear O–Hg–O units; the oxygen in excess of the O_4 stoichiometry resides in the interstitial positions on the Hg sheet (i.e., at the center of every Hg_4 square), and $\delta = 0.063$. The hole density of the copper atoms in $HgBa_2CuO_{4+\delta}$ is about 0.12 (i.e., 2δ), a typical value close to which most cuprate superconductors exhibit their maximum superconducting transition temperatures T_c. To examine whether or not the 6*s* band of the $HgO_{2+\delta}$ layer dips below the Fermi level of the CuO_2 layer $x^2 - y^2$ band, we carried out

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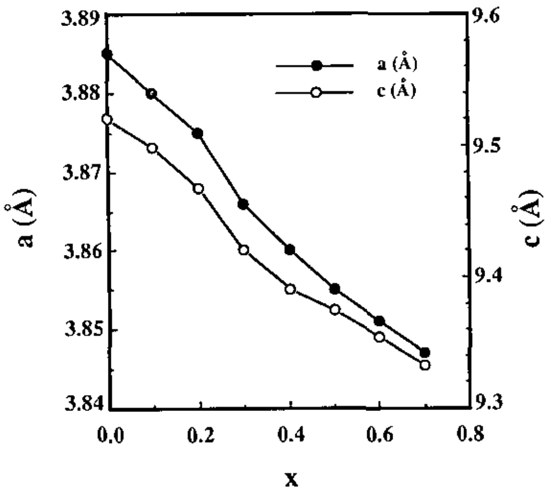

FIG. 1. Variation of the lattice *a*- and *c*-parameters of $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$ as a function of *x*.

extended Hückel tight-binding (EHTB) electronic band structure calculations (6, 9) for the stoichiometric composition $HgBa_2CuO_4$. These calculations reveal that, for any reasonable valence ionization potential of the Hg 6*s* orbital, the bottom of the HgO_2 layer 6*s* band lies well above the Fermi level of the CuO_2 layer $x^2 - y^2$ band. Thus, the band-overlap mechanism of hole creation is not relevant for $HgBa_2CuO_{4+\delta}$. To further probe the role of the interstitial oxygen in $HgBa_2CuO_{4+\delta}$ as a hole source, it is important to investigate its isostructural analogue $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$. As the extent of the Sr substitution increases, the hole concentration in $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$ should be affected by electronic and steric factors. Since Sr^{2+} is smaller than Ba^{2+}, the *a*-parameter and the in-plane Cu–O bond should decrease with increasing *x*, which raises the CuO_2 layer $x^2 - y^2$ band. If the band raising is large enough beyond a certain value of *x*, one may expect hole creation by the band-overlap mechanism. On the other hand, the *a*-parameter decrease should reduce the size of the interstitial sites and hence make their occupation by oxygen energetically unfavorable, thereby reducing the hole density. To determine which of these two factors operate, we synthesized the $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$ phases and characterized their structures and superconducting properties as a function of *x*, as described in the following.

$Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$ samples were prepared by high-pressure and high-temperature reactions in sealed gold tubes. Appropriate quantities of high purity reactants (HgO, BaO_2/BaO, SrO, and CuO) were intimately mixed together in an agate mortar. The total oxygen content in the initial mixture was maintained close to 4.5 per Cu (i.e., $\delta = 0.5$). The mixtures in the form of pellets were loaded into gold tubes ($\frac{3}{8}$″ in diameter and 3″ in length) and sealed. All manipulations, such as weighing, grinding, pelletizing, and loading the tubes, were carried out in a nitrogen-filled dry box. The tubes were heated at 750°C for 6 hr under an external pressure of 1 kbar. The black products were removed, ground inside the dry box, and annealed in dry oxygen at 350°C for 4 hr. Powder X-ray diffraction data were refined by least squares. The test for superconductivity was made by the ac mutual inductance technique. Electrical resistivity measurements were made by the standard four-probe technique.

Single phase samples of $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$ could be obtained up to $x = 0.7$, and the X-ray powder diffraction patterns could be indexed on a primitive tetragonal lattice (space group *P4/mmm*) as for the parent $HgBa_2CuO_{4+\delta}$ (16). Impurity lines start to appear at $x = 0.7$, and their intensity increases with a further increase in *x*. The lattice *a*- and *c*-parameters of the oxygen-annealed samples were plotted as a function of *x* in Fig. 1, which shows that these parameters decrease smoothly with increasing *x*. This is easily explained, since Sr^{2+} is much smaller in size than Ba^{2+}. Table 1 shows the change in the superconducting transition temperature (T_c) as a function of *x* for samples before and after annealing in oxygen. Samples of $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$ as synthesized show a T_c of 95 K, and their T_c does not change after further annealing in oxygen. With increasing *x*, the T_c of $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$ slowly decreases until $x = 0.3$, beyond which the T_c drops sharply. For $x \geq 0.5$ the samples are not superconducting down to 4.2 K, and their resistance increases with decreasing temperature, thereby indicating semiconducting behavior. A similar situation is found for $Y(Ba_{2-x}Sr_x)Cu_3O_7$ (19), but the T_c drop is more drastic in $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$.

So far, our attempts to prepare "$HgSr_2CuO_{4+\delta}$" (i.e., $x = 2$) by various synthetic routes were not successful. However, the corresponding Tl compound, $TlSr_2CuO_5$, is stabilized under normal conditions. This phase is slightly oxygen deficient, is metallic, and has the 1201-type structure with orthorhombic distortion (20, 21). The instability

TABLE 1
Superconducting Transition Temperatures T_c of $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$ Phases[a]

x	Before O_2 annealing	After O_2 annealing[b]
0.0	95	94
0.1	79	87
0.2	66	70
0.3	57	59
0.4	39	42
0.5	21	25
0.6	Semiconducting	Semiconducting
0.7	Semiconducting	Semiconducting

[a] T_c values were measured from the ac mutual inductance data with the precision of ±1 K.

[b] Annealed under identical conditions for all samples: 350°C for 4 hr and then cooled in oxygen.

of "$HgSr_2CuO_{4+\delta}$" is probably related to the large ionic radius of Hg^{2+} (1.02 Å in octahedral coordination, while the corresponding value of Tl^{3+} is 0.88 Å) (22), which will cause a large lattice mismatch between the CuO_2 and the HgO_δ layer portions of the crystal structure.

To summarize, our work shows that the Sr-substituted isostructural analogues of $HgBa_2CuO_{4+\delta}$, i.e., $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$, can be synthesized up to $x = 0.7$. The T_c of $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$ decreases gradually with increasing x, and superconductivity vanishes for $x \gtrsim 0.5$. These results and our EHTB band electronic structure calculations for $HgBa_2CuO_4$ strongly suggest that the hole source of $Hg(Ba_{2-x}Sr_x)CuO_{4+\delta}$ is not the Hg 6*s* band but the interstitial oxygen atoms in the HgO_δ sheet. As x increases, the *a*- and *c*-parameters decrease and the interstitial sites become smaller in size; therefore, it is energetically more difficult for the oxygen to occupy these interstitial sites, thereby reducing the hole density.

ACKNOWLEDGMENTS

Work at North Carolina State University was in part supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Grant DE-FG05-86ER45259. We thank T. G. Calvarese and D. M. Groski of DuPont Company for their technical assistance.

REFERENCES

1. A. W. Sleight, M. A. Subramanian, and C. C. Torardi, *Mater. Res. Bull.* **XIV,** 45 (1989).
2. C. N. R. Rao and B. Raveau, *Acc. Chem. Res.* **22,** 106 (1989).
3. R. J. Cava, *Science* **247,** 656 (1990).
4. M.-H. Whangbo and C. C. Torardi, *Science* **249,** 1143 (1990).
5. M.-H. Whangbo and C. C. Torardi, *Acc. Chem. Res.* **24,** 127 (1991).
6. D. Jung, M.-H. Whangbo, N. Herron, and C. C. Torardi, *Physica C* **160,** 381 (1989).
7. J. B. Goodenough and A. Manthiram, *J. Solid State Chem.* **88,** 115 (1990).
8. A. K. Ganguli and M. A. Subramanian, *J. Solid State Chem.* **90,** 382 (1991).
9. M.-H. Whangbo, M. Evain, M. A. Beno, and J. M. Williams, *Inorg. Chem.* **26,** 1829 (1987).
10. M.-H. Whangbo, D. B. Kang, and C. C. Torardi, *Physica C* **158,** 371 (1989).
11. M.-H. Whangbo and M. A. Subramanian, *J. Solid State Chem.* **91,** 403 (1991).
12. M. A. Subramanian, *Mater. Res. Bull.* **25,** 191 (1990).
13. A. K. Ganguly, V. Manivannan, A. K. Sood, and C. N. R. Rao, *Appl. Phys. Lett.* **55,** 2664 (1989).
14. T. Manako, Y. Shimakawa, Y. Kubo, T. Satoh, and H. Igarashi, *Physica C* **158,** 143 (1989).
15. M. A. Subramanian and M.-H. Whangbo, *J. Solid State Chem.* **96,** 461 (1992).
16. S. N. Putilin, E. V. Antipov, O. Chmaissem, and M. Marezio, *Nature* **362,** 226 (1993).
17. A. Schiling, M. Cantoni, J. D. Guo, and H. R. Ott, *Nature* **363,** 56 (1993).
18. O. Chmaissem, Q. Huang, S. N. Putlin, M. Marezio, and A. Santoro, *Physica C* **212,** 259 (1993).
19. B. W. Veal, W. K. Kwok, A. Umezawa, G. W. Crabtree, J. D. Jorgensen, J. W. Downey, L. J. Nowicki, A. W. Mitchell, A. P. Paulikas, and C. H. Sowers, *Appl. Phys. Lett.* **51,** 279 (1987).
20. A. K. Ganguli and M. A. Subramanian, *J. Solid State Chem.* **93,** 250 (1991).
21. T. Wada, T. Kaneko, and H. Yamauchi, *ISTEC J.* **3,** 21 (1990).
22. R. D. Shannon, *Acta Crystallogr. Sect. A* **32,** 751 (1976).