JOURNAL OF SOLID STATE CHEMISTRY 90, 382–385 (1991)

$Tl_2Ba_{2-x}Sr_xCuO_6$: A System Exhibiting a Compositionally Controlled Superconductor–Metal Transition

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Communicated by J. M. Honig, November 27, 1990

Strontium-substituted thallium cuprates of the type $Tl_2Ba_{2-x}Sr_xCuO_6$ have been synthesized for various values of x. Single phases were obtained for $x \leq 1.2$. The compounds crystallize in the tetragonal structure with space group *I4/mmm* as the parent $Tl_2Ba_2CuO_6$ oxide. Both a and c lattice parameter decrease with increase in x. T_c decreases gradually from 92 to 77 K ($x = 0.8$). Beyond $x = 1.0$ superconductivity is lost. The $x = 1.2$ comparison is metallic down to 4.2 K. © 1991 Academic Press, Inc.

Introduction

Among all the high temperature superconductors discovered in the past 3 years, one of the common features is the existence of Cu–O sheets in all the superconductors. The nature (structural and electronic) of the Cu–O sheets appears to hold the key to understanding the mechanism of superconductivity in these materials. Thus it has been of major interest to both experimentalists and theoreticians to compare the nature of Cu–O layers in superconducting and nonsuperconducting oxides having related structures. One of the ways of doing this has been to study the effect of substituting various elements on the Cu or adjacent sites (Y or Ba in $YBa_2Cu_3O_7$; La in $La_{2-x}Sr_xCuO_4$, etc.) (*1*). It is now known that such substitutions (magnetic or nonmagnetic) at the Cu sites have a strong detrimental effect on the superconducting transition temperature. Substitution at adjacent sites has a less dramatic influence on T_c.

We have been interested in similar substitution studies in the thallium-based superconductors which can be formulated as $Tl_mBa_2Ca_{n-1}Cu_nO_{2n+2+m}$, where $m = 1,2$ (Tl–O layers) and $n = 1$ to 4 (Cu–O layers). $Tl_2Ba_2Ca_2Cu_3O_{10}$ ($m = 2$; $n = 3$) has two Tl–O layers and three Cu–O layers and has the highest T_c (125 K) among all oxide superconductors. $Tl_2Ba_2CuO_6$ ($m = 2$; $n = 1$) under appropriate conditions of synthesis has a T_c of ~90 K (*2*). This superconductor is unique in the sense that it has the highest T_c for any superconductor with a single Cu–O layer. As a part of our ongoing substitution studies in the thallium-based superconductors, we have studied the effect of Sr substitution in $Tl_2Ba_2CuO_6$. In this report we discuss the synthesis, structure, and superconducting properties of $Tl_2Ba_{2-x}Sr_xCuO_6$.

Experimental

Oxides of the type $Tl_2Ba_{2-x}Sr_xCuO_6$ were prepared by heating stoichiometric amounts of Tl_2O_3, BaO_2, SrO_2, and CuO in a sealed

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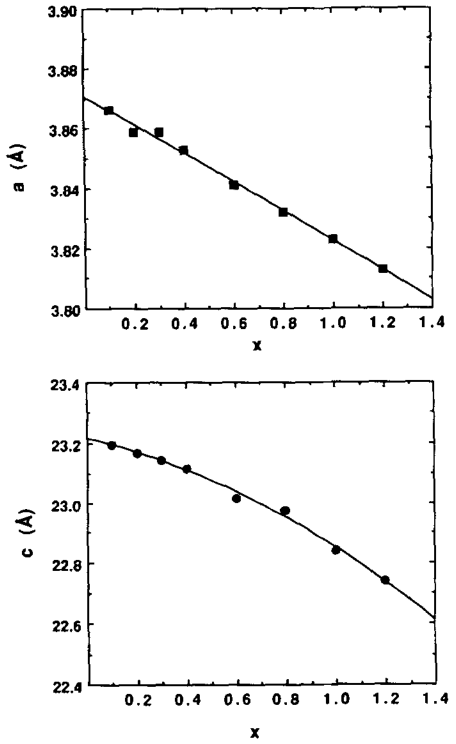

FIG. 1. Variation of *a* and *c* lattice parameters as a function of *x* for $Tl_2Ba_{2-x}Sr_xCuO_6$.

gold tube at 875°C for 6 hr. The samples were cooled to room temperature in the furnace. Powder diffraction patterns were obtained using a Scintag PAD IV X-ray diffractometer. The unit cell parameters were refined using a least-square procedure. The Meissner effect was measured by the ac induction technique. Resistivity was measured by the standard four-probe method.

Results and Discussion

Single phases could be obtained for $x \leq 1.2$ and could be indexed on a body-centered tetragonal lattice (Space group *I4/mmm*) as the parent $Tl_2Ba_2CuO_6$ oxide. Beyond $x = 1.2$, lines due to impurities started appearing and increased in intensity with further increases in Sr concentration. In Figs. 1a and 1b, we show the variation of unit cell parameters with *x*. Both *a* and *c* parameters decrease smoothly as a function of *x*. This is easily explained from ionic size considerations since Sr is much smaller in size than Ba. Figure 2 shows the change in the superconducting transition temperature (T_c) as a function of *x*. Down to $x = 0.8$ there is a gradual change in T_c after which T_c drops sharply and goes to zero at $x = 1.2$. The $x = 1.2$ composition is metallic down to 4.2 K (Fig. 3). Similar behavior can be found in the $Tl_2Ba_{2-x}Sr_xCaCu_2O_8$ system, where T_c decreases from 105 K ($x = 0$) to 44 K ($x = 2.0$) (*3*).

Recently, Jung *et al.* (*4*) carried out tight-binding calculations on the single ($m = 1$) and double ($m = 2$) Tl–O layers of $Tl_mBa_2Ca_{n-1}Cu_nO_{2n+m+2}$, taking into consideration the effect of local distortions. Their calculations revealed that in the case of double Tl–O layer compounds, the Tl 6*s* bands overlap at the Fermi level with the Cu $3d_{x^2-y^2}$ bands, whereas the Tl 6s bands are located well above the Fermi level in the case of single Tl–O layer compounds. In other words, creation of holes in the copper oxygen sheets is achieved by an internal redox mechanism in the double Tl–O layer

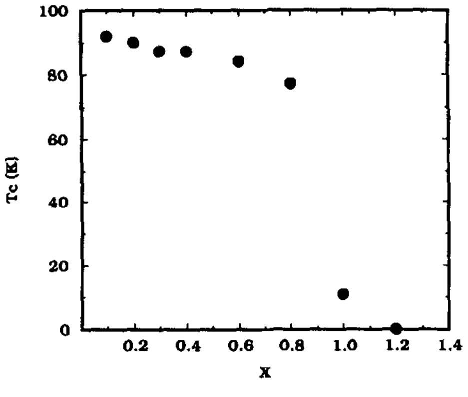

FIG. 2. Variation of superconducting transition temperature (T_c onset) as a function of *x* for $Tl_2Ba_{2-x}Sr_xCuO_6$.

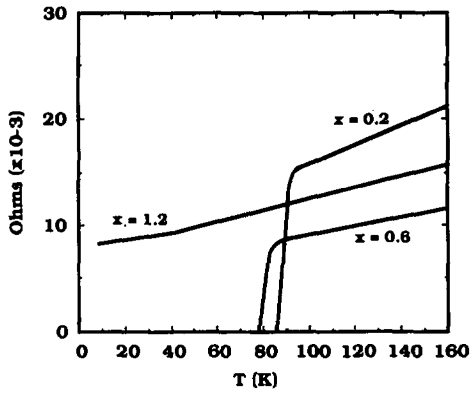

FIG. 3. Electrical resistivity data of representative compounds in the system $Tl_2Ba_{2-x}Sr_xCuO_6$. $x = 1.2$ sample is metallic.

cuprates. Neutron diffraction studies (*5*, *6*) as well as recent wet chemical analysis (*7*) on superconducting $Tl_2Ba_2CuO_6$ samples have shown no significant extra oxygen (in fact the wet chemical analysis showed oxygen content to be less than 6) or cation vacancies. Substitution of less electropositive Sr for more electropositive Ba in Tl_2Ba_2 CuO_6 should bring down the Tl 6*s* level and should increase the overlap of Tl 6*s* with Cu $3d_{x^2-y^2}$ and hence increase the hole concentration. If this is true, the Cu–O distance should decrease as x increases. Since the Cu–O distance is roughly one half of the *a* lattice parameter (this is true for thallium cuprates as the Cu–O sheets are flat), the *a* lattice parameter should decrease as x is increased. In the case of $Tl_2Ba_{2-x}Sr_xCuO_6$, the observed rapid decrease of the *a* lattice parameter (Fig. 1a) is mainly caused by size effects and any decrease due to an increase in covalency of the Cu–O bond should be too small to notice. The decrease of T_c with increase in x is probably associated with the overdoping of the Cu–O sheets; when $x = 1.2$, the phase becomes a normal metal. Thus, this transition is very similar to the one observed in $La_{2-x}Sr_xCuO_4$ where the superconductor–metal transition is brought about by an overdoping of holes through the substitution of Sr^{2+} for La^{3+} ($x > 0.3$) (*8*).

Earlier, Veal *et al.* (*9*) examined the system $YBa_{2-x}Sr_xCu_3O_7$ and discussed the possible ways in which Sr substitution might lower T_c. In their view the depression of T_c is indirectly caused by a change in the structure around the Sr ion and additional oxygen vacancies at the O1 sites (chain) in the Sr-doped samples. It is also argued that the electronic structure is not affected significantly by the substitution of Ba by Sr. The effects of Sr substitution of the lattice parameter and the superconducting properties are similar in both $YBa_{2-x}Sr_xCu_3O_7$ and $Tl_2Ba_{2-x}Sr_xCuO_6$. However, in the case of $YBa_{2-x}Sr_xCu_3O_7$, the decrease in T_c may be directly related to the oxygen vacancies, whereas the changes in Cu–O band width (resulting in an increase in the overlap of Tl 6*s* at the Fermi level) due to Sr substitution may play an important role in the observed decrease of T_c in $Tl_2Ba_{2-x}Sr_xCuO_6$. Neutron diffraction and muon spin rotation studies of $TlBa_{2-x}Sr_xCu_2O_6$ are in progress to further characterize these phases in terms of oxygen stoichiometry and carrier concentration, respectively.

Acknowledgments

We thank R. B. Flippen for magnetic measurements and C. M. Foris for X-ray data.

References

1. R. BEYERS AND T. M. SHAW *in* "Solid State Physics" (H. Ehrenreich and D. Turnbull, Eds.), Vol. 42, p. 135, Academic Press (1989).
2. C. C. TORARDI, M. A. SUBRAMANIAN, J. C. CALABRESE, J. GOPALAKRISHNAN, E. M. MCCARRON, K. J. MORRISSEY, T. R. ASKEW, R. B. FLIPPEN, U. CHOWDHRY, AND A. W. SLEIGHT, *Phys. Rev. B* **38**, 225 (1988).
3. E. A. HAYRI AND M. GREENBLATT, *Physica C* **156**, 775 (1988).
4. D. JUNG, M.-H. WHANGBO, N, HERRON, AND C. C. TORARDI, *Physica C* **160**, 381 (1989).
5. J. B. PARISE, C. C. TORARDI, M. A. SUBRAMANIAN, J. GOPALAKRISHNAN, A. W. SLEIGHT, AND E. PRINCE, *Physica C* **159**, 239 (1989).

6. Y. SHIMAKAWA, Y. KUBO, T. MANAKO, AND H. IGARASHI, *Phys. Rev. B* **40,** 11,400 (1989).
7. M. PARANTHAMAN, A. MANTHIRAM, AND J. B. GOODENOUGH, *J. Solid State Chem.* **87,** 479 (1990).
8. J. B. TORRANCE, Y. TOKURA, A. I. NAZZAL, A. BEZINGE, T. C. HUANG, AND S. S. P. PARKIN, *Phys. Rev. Lett.* **61,** 1127 (1988).
9. 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)