PHYSICAL REVIEW B VOLUME 38, NUMBER 16 1 DECEMBER 1988

Emergence of superconductivity in a Bi-Sr-Cu-O system

Gang Xiao, M. Z. Cieplak, and C. L. Chien
Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218

(Received 26 August 1988)

Solid solutions of $(Bi_{2-x}Sr_x)_2CuO_6$ $(0.8 \le x \le 1.5)$ have been synthesized. A metal-insulator transition is observed as the Sr composition is reduced to 0.9. The emergence of superconductivity depends critically on the minimum Sr content. Only when $x \ge 0.95$, does the superconductivity occur. The behavior is different from that observed in the $La_{2-x}Sr_xCuO_4$ system where doping La_2CuO_4 by Sr brings the system into a metallic and superconducting phase, with gradually increasing T_c.

$Bi_2Sr_2Ca_{n-1}Cu_nO_y$ (Refs. 1–3) and $Tl_2Ba_2Ca_{n-1}Cu_nO_y$ (Refs 4–7) $(n=1,2,3)$ are two newly discovered high-T_c systems in the cuprate superconductor family, achieving record high transition temperatures (T_c). The value of T_c was found to increase with the number (n) of the Cu-O_2 planes present in the unit cells of the perovskite structures, in agreement with the long-standing speculation. Although they exhibit some special features, these new high-T_c oxides share many similar characteristics seen in the La-(Ba,Sr)-Cu-O, and Y-Ba-Cu-O oxides discovered earlier. Among the common features are the existence of the Cu-O_2 planes, the anisotropic electronic properties, and the positive charge carriers.

One of the most crucial questions in all cuprate superconductors is the formation of the active carriers. In $(La\text{-}Sr)_2CuO_4$ and $YBa_2Cu_3O_7$, the carriers are holes, which are formed through different means in the two cases. The parent compound of La_2CuO_4 and the oxygen deficient $YBa_2Cu_3O_y$ are antiferromagnetic insulators. The holes in $La_{2-x}Sr_xCuO_4$ are introduced by doping the Sr^{2+} ions into the La^{3+} sites of the insulating La_2CuO_4. In $YBa_2Cu_3O_y$, the hole concentration is dictated by the oxygen content. By varying the Sr or oxygen content, both systems undergo an insulator-metal transition. Simultaneously, superconductivity emerges with increasing T_c as a consequence of the increasing hole concentration. The ability of monitoring carrier concentration has facilitated tremendously the understanding of these oxide superconductors. Unfortunately, an insulator counterpart in either Bi-Sr-Ca-Cu-O or Tl-Ba-Ca-Cu-O systems has not been found yet. Nor could one control the oxygen content, since quenching from high temperature does not have adverse effect on T_c.[8]

In this work, we have investigated the metal-insulator transition and the emergence of superconductivity in the $Bi_2Sr_2CuO_6$ phase (the 2:2:0:1 phase) without Ca. Although it has the lowest T_c of the series, the structure of the 2:2:0:1 phase is unique, containing isolated single Cu-O_2 planes similar to the $(La\text{-}Sr)_2CuO_4$ system. We have found Bi and Sr to be mutually soluble in a certain composition range. Metallic behavior and the appearance of superconductivity depend sensitively on the relative composition of Bi and Sr.

Samples are synthesized by using a solid-state reaction method. Appropriate portions of Bi_2O_3, $SrCO_3$, and CuO powders were well mixed and pressed into pellets. The first annealing was carried out in oxygen at 800 °C for 12 h. After grinding and pressing, the samples were again annealed at 850 °C for 12 h. It has been found that an excess of Cu is beneficial in forming the desired phase. X-ray diffraction measurements were performed using a Philips APD 3720 x-ray diffractometer with Cu $K\alpha$ radiation.

The superconducting and normal-state properties of the samples were measured on a superconducting quantum interference device (SQUID) magnetometer and a four-probe resistivity electrometer. For the resistivity measurements, four fine Cu wires were attached to the rectangularly shaped samples $(2\times1\times15\ mm^3)$ with silver paint.

Michel *et al.*[1] first observed superconductivity in the Bi-Sr-Cu-O system with T_c near 7 K. The single-phase material was identified to be $BiSrCuO_{3.5+\delta}$ with an orthorhombic subcell of lattice parameters $a=5.32$ Å, $b=26.6$ Å, and $c=48.8$ Å. More recent results[3,9] have indicated that the single-phase composition is $Bi_2Sr_2CuO_6$.

Because the ionic size of Bi^{3+} (1.20 Å) and Sr^{2+} (1.18 Å) are almost identical, given the two different charge states, we have suspected that the hole concentration and hence superconductivity may be dictated by the relative composition of Bi and Sr in the solid solution of $(Bi_{2-x}Sr_x)_2CuO_6$. A series of samples with $0.85 \le x \le 1.5$ were made in the same batch and under identical conditions. X-ray diffraction patterns of two samples with $x=0.85$ and 1.50 are shown in Fig. 1. The samples are essentially single phase with small traces of CuO as indicated by *. The patterns can be indexed with a pseudotetragonal structure with lattice parameters $a=5.37$ Å and $c=24.42$ Å, consistent with the values determined by other groups.[3,9] It is noted that *all* of the samples have the same pseudotetragonal structure with almost identical lattice parameters (i.e., identical peak positions). However, the intensities of the diffraction peaks differ systematically with the relative composition of Bi and Sr. This indicates that the relative compositions of Bi and Sr can be varied in the Bi-Sr sublattice, and Bi^{3+} and Sr^{2+} can mutually substitute each other in the range of interest.

In Fig. 2, we present the temperature dependence of the normalized resistivity. The sample with $x=0.85$ exhibits semiconducting behavior, and the sample with $x=0.90$ is metallic as seen from the positive temperature coefficient of resistivity, but there is a resistivity upturn at very low

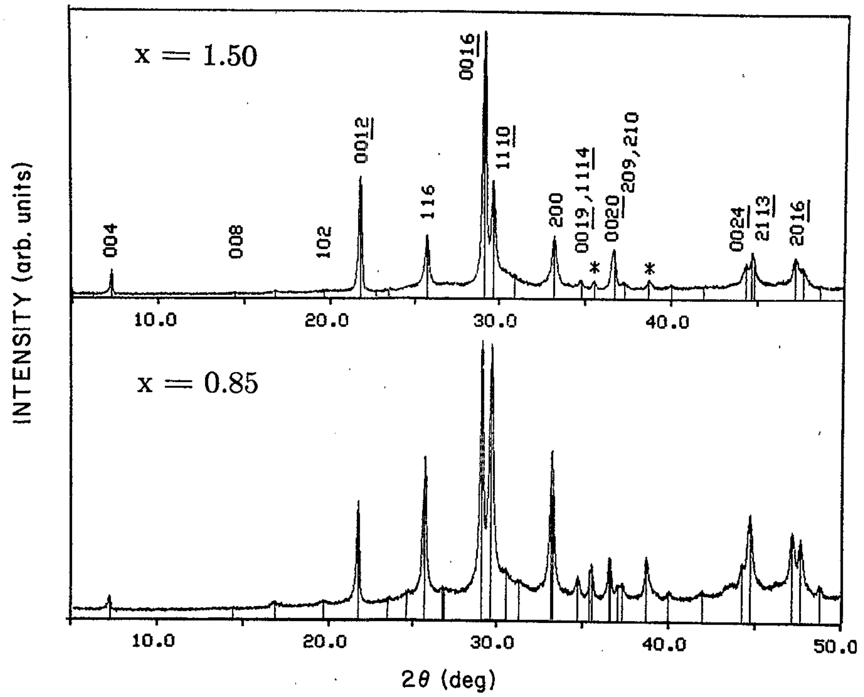

FIG. 1. $\theta-2\theta$ x-ray diffraction patterns of a Sr-poor sample ($x=0.85$) and a Sr-rich sample ($x=1.5$). Notice that the positions of the diffraction peaks match each other, but the intensities differ significantly.

temperatures. No superconducting transitions were observed in either samples down to 4 K. Magnetization measurement down to 1.5 K did not reveal any superconducting transition either. However, by increasing the Sr content to above 0.95, the superconducting phase appears with a midpoint T_c of 7 K. The resistivity exhibits linear temperature dependence, as observed in other cuprate-oxide superconductors. It should be noted that the linearity of resistivity extends from $T=300$ K to very low temperature (~ 10 K).

The superconducting phase was also confirmed by magnetization measurement. A typical magnetization curve of the superconducting $x=0.95$ sample is shown in Fig. 3 exhibiting a T_c of 7 K. The inset in Fig. 3 shows the tem-

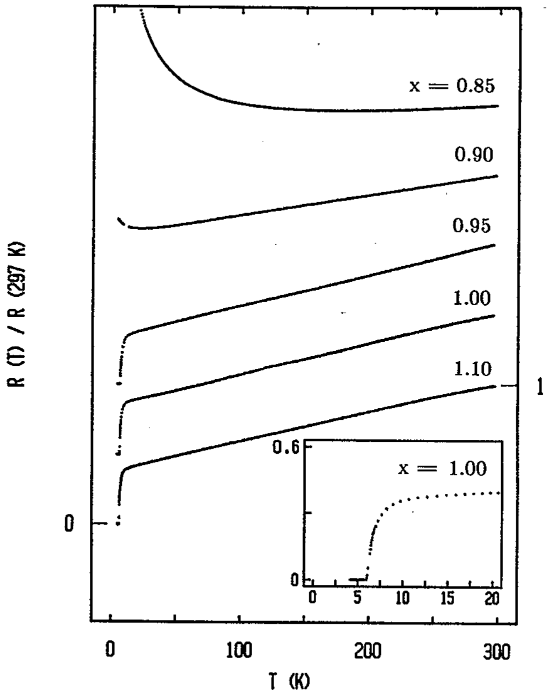

FIG. 2. Temperature dependence of the normalized resistivity of the $(Bi_{2-x}Sr_x)_2CuO_6$ samples with $x=0.85$, 0.90, $\overline{0.95}$, 1.00, and 1.10.

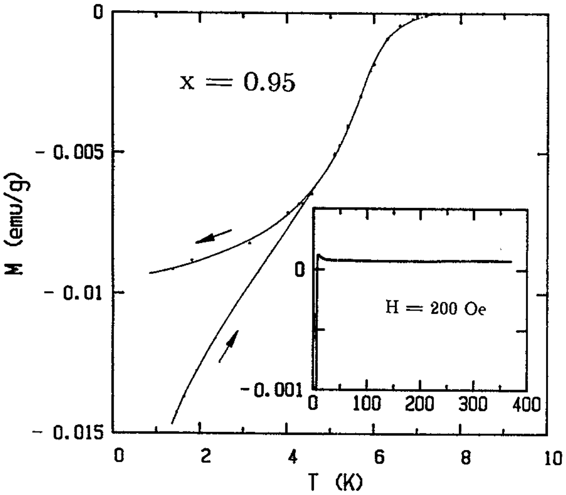

FIG. 3. Temperature dependence of magnetization under an external magnetic field of 10 Oe for a sample with $x=0.95$. The temperature increasing curve is the zero-field-cooled data, and the temperature decreasing curve is the field-cooled data. The inset shows the temperature dependence of magnetization in the normal state. The measuring magnetic field was 100 Oe.

perature dependence of the normal-state susceptibility measured under an external field of 200 Oe. The susceptibility is essentially temperature independent, indicating the absence of Cu moment in the system. The slight increase of the susceptibility prior to the superconducting transition is probably due to a small amount of magnetic impurities in the sample.

The normal-state resistivity at 297 K and the midpoint T_c of the samples are shown in Fig. 4 as functions of the Sr content. The resistivity shows a minimum in $Bi_{2.1}Sr_{1.9}CuO_6$ with a value of 2.2 mΩ cm, typical of oxide superconductors. Most interestingly, the appearance of superconductivity depends sensitively on the relative compositions of Bi and Sr. The boundary between the superconducting and nonsuperconducting phase is very sharp and less than 5 at.% wide. The resistivity minimum also coincides with the boundary.

The data shown in Figs. 2 and 4 suggest that there is a metal-insulator transition around $x = 0.95$. Such a behavior can be most likely explained by the changing carrier concentration. By partially replacing the Sr^{+2} ions by Bi^{3+}, one effectively reduces the hole carrier density. This is similar to the $La_{2-x}Sr_xCuO_4$ system[10] where a metal-insulator transition is observed as the Sr content is reduced to below 0.05. However, unlike the $La_{2-x}Sr_xCuO_4$ system where T_c increases linearly with Sr content up to a maximum T_c of 38 K, the appearance of superconductivity in $(Bi_{2-x}Sr_x)_2CuO_6$ is more dramatic. There is an abrupt emergence of superconductivity. Furthermore, once superconductivity is achieved, higher Sr content does not further enhance the value of T_c. The fact that superconductivity is destroyed by a small amount of excess Bi ions indicates that $Bi_2Sr_2CuO_6$ requires a minimum carrier density to sustain superconductivity.

Overall the emergence of superconductivity in $Bi_2Sr_2CuO_6$ is rather different from that seen in the $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_y$. This is most likely due to the different band structures in these systems. In the latter two compounds, the Cu-O bands dominate the Fermi level.[11–14] However, in $Bi_2Sr_2CaCu_2O_8$ ($T_c = 80$ K), several band-structure calculations[15–18] reveal that there are electron pockets near the Brillouin-zone edge due to the Bi-O planes. The role of the conducting Bi-O planes has been speculated to enhance the coupling between the $Cu\text{-}O_2$ planes. In $Bi_2Sr_2CuO_6$ without Ca, the electron pockets due to the Bi-O planes are reduced significantly.[18] This accounts for the much lower T_c. It is likely that a small excess of Bi^{3+} causes the electron pockets to be filled up completely, thus destroying superconductivity in an abrupt fashion.

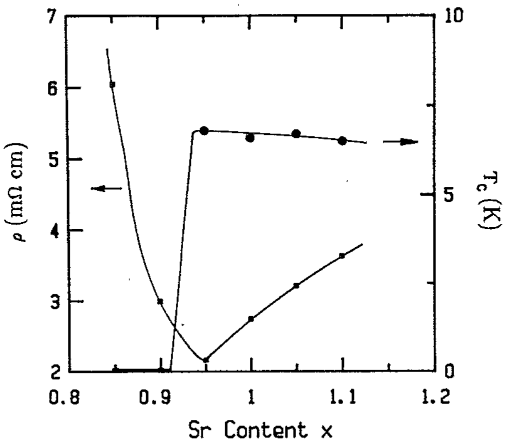

FIG. 4. Resistivity at $T = 297$ K and superconducting transition temperature T_c vs the Sr content x for the $(Bi_{2-x}Sr_x)_2CuO_6$ system.

The apparent solubility of Bi and Sr in the 2:2:0:1 phase may have important consequences in the high-T_c 2:2:1:2 ($n = 2$) and 2:2:2:3 ($n = 3$) phases as well. Experimentally, it is difficult to isolate the two phases. Most samples exhibit varying proportions of the two superconducting phases. This is mainly caused by the epitaxial growth of the two pseudotetragonal structures with identical a axis. The results of this work suggest that this unfortunate complication may also in part lie in the mutual solubility of the Bi and Sr ions which hinders the orderly arrangement of the substructures containing Bi and Sr.

In summary, a metal-insulator transition and the emergence of superconductivity in solid solution $(Bi_{2-x}Sr_x)_2CuO_6$ have been observed. Bi^{3+} and Sr^{2+} can be mutually substituted near the composition of $Bi_2Sr_2CuO_6$ due to the almost identical ionic sizes of the elements. Superconductivity appears abruptly as the Sr content increases above 0.95. It is speculated that such a behavior is caused by the special band features of the Bi-O planes.

This work was supported by National Science Foundation Grant No. MEM-87-18498 and DMR-86-07150.

---

[1] C. Michel, M. Hervieu, M. M. Borel, A. Grandin, F. Deslandes, J. Provost, and B. Raveau, Z. Phys. B **68**, 421 (1987).

[2] H. Maeda, Y. Tanaka, M. Fukutomi, and A. Asano, Jpn. J. Appl. Phys. **27**, L209 (1988).

[3] J. M. Tarascon, W. R. McKinnon, P. Barboux, D. M. Hwang, B. G. Bagley, L. H. Greene, G. Hull, Y. LePage, N. Stoffel, and Giroud, Phys. Rev. B **38**, 8885 (1988).

[4] Z. Z. Sheng, A. M. Hermann, A. El Ali, C. Almasan, J. Estrada, T. Datta, and R. J. Matson, Phys. Rev. Lett. **60**, 937 (1988).

[5] Z. Z. Sheng and A. M. Hermann, Nature (London) **332**, 138 (1988).

[6] M. A. Subramanian, J. C. Calabrese, C. C. Torardi, J. Gopalakrishnan, T. R. Askew, R. B. Flippen, K. J. Morrissey, U. Chowdhry, and A. W. Sleight, Nature (London) **332**, 420 (1988).

[7] R. M. Hazen, L. W. Finger, R. J. Angel, C. T. Prewitt, N. L. Ross, C. G. Hadidiacos, P. J. Heaney, D. R. Veblen, Z. Z. Sheng, A. El Ali, and A. M. Hermann, Phys. Rev. Lett. **60**, 1657 (1988).

[8] T. M. Shaw, S. A. Shivashankar, S. J. LaPlaca, J. J. Cuomo, T. R. McGuire, R. A. Roy, K. H. Kelleher, and D. S. Yee, Phys. Rev. B **37**, 9856 (1988).

[9] J. B. Torrance, Y. Tokura, S. J. LaPlaca, T. C. Huang, R. J. Savoy, and A. I. Nazzal, Solid State Commun. **66**, 703 (1988).

[10] D. G. Hinks, B. Dabrowski, K. Zhang, C. U. Segre, J. D. Jor-

gensen, L. Soderholm, and M. A. Beno, in *High-Temperature Superconductors,* edited by M. B. Brodsky, R. C. Dynes, K. Kitazawa, and H. L. Tuller (Materials Research Society, Pittsburgh, 1988), Vol. AA99, p. 9.

[11] L., F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).

[12] J. Yu and A. J. Freeman, Phys. Rev. Lett. **58**, 1035 (1987).

[13] L. F. Mattheiss and D. R. Hamann, Solid State Commun. **63**, 395 (1987).

[14] J. Yu, S. Massidda, A. J. Freeman, and D. D. Koeling, Phys. Lett. A **122**, 203 (1987).

[15] M. S. Hybertsen and L. F. Mattheiss, Phys. Rev. Lett. **60**, 1661 (1988).

[16] H. Krakauer and W. E. Pickett, Phys. Rev. Lett. **60**, 1665 (1988).

[17] S. Massidda, J. Yu, and A. J. Freeman, Physica C **152**, 251 (1988).

[18] P. A. Sterne and C. S. Wang (unpublished).