Superconductivity up to 114 K in the Bi-Al-Ca-Sr-Cu-O Compound System without Rare-Earth Elements

C. W. Chu, J. Bechtold, L. Gao, P. H. Hor, Z. J. Huang, R. L. Meng, Y. Y. Sun, Y. Q. Wang, and Y. Y. Xue

Department of Physics, Texas Center for Superconductivity and Space Vacuum Epitaxy Center,
University of Houston, Houston, Texas 77004

(Received 26 January 1988)

Stable superconductivity up to 114 K has been reproducibly detected in Bi-Al-Ca-Sr-Cu-O multiphase systems without any rare-earth elements. Pressure has only a slight positive effect on T_c. These observations provide an extra material base for the study of the mechanism of high-temperature superconductivity and also the prospect of reduced material cost for future applications of superconductivity.

PACS numbers: 74.10.+v, 74.70.Ya

An avalanche of research activities has resulted from the recent discoveries of the 30- and 90-K superconductivity, respectively, in the 2-1-4 single-layer ternaries[1] $(La_{1-x}M_x)_2CuO_{4-y}$ (M = Ba, Sr, and Ca; $0 \le x < 0.2$; $y < 0.1$) and the triple-layer 1-2-3 quaternaries[2] $ABa_2Cu_3O_{7-\delta}$ (A = rare-earth element; $\delta < 0.45$). Great progress has been made on the understanding of their physical and chemical properties in both the normal and superconducting states. At the same time, many theoretical models[3] have also been advanced to account for the observations. In spite of the extensive efforts, the fundamental question concerning the mechanism responsible for superconductivity at such high temperatures, especially in the 90-K range and above, remains unsettled. One approach toward an answer to this question is to search for new material systems with high superconducting transition temperatures T_c and thus to broaden the material base for contrast and comparison. A new high-T_c system without the use of rare-earth elements will reduce the material cost and will make even more practical applications of superconductivity. In this Letter, we report the observation by electrical and magnetic measurement of stable and reproducible superconductivity in compound systems with nominal compositions represented by $BiAl_{1-y}CaSrCuO_{7-\delta}$, $Bi_2Al_{1-y}(Ca_{1-x}Sr_x)Cu_2O_{7-\delta}$, and $Bi_2Al_{1-y}(Ca_{1-x}Sr_x)_2Cu_2O_{8-\delta}$, where $0 \le y \le 0.3$ and $0.4 \le x \le 0.95$. The samples investigated survived repeated thermal cycling for two weeks without any sign of degradation. A brief news report of the observation of superconductivity in a Bi-Sr-Ca-Cu-O system between 75 and 105 K appeared in the Nippon Keizai Shinbun [Japan Economic News] on 22 January 1988. No details were given concerning composition, processing, or structure in the report.

From our previous studies on the 60- and 90-K superconductors, at both ambient and high pressures, it is rather clear[4] that atomic size and the valence state play a crucial role in the formation of these high-T_c oxide superconductors, and both will dictate the final crystal structures. In addition, no effort to date has succeeded in the replacement of Cu atoms without the degradation or complete destruction of superconductivity. Therefore, we have focused our studies on trivalent-element oxide compounds consisting of Cu. At the same time, we vary the valence state of Cu and adjust the average atomic size so that the elements will crystallize to a certain superconducting form. Recently, Michel *et al.* did demonstrate[5] that $Bi_2Sr_2Cu_2O_{7-\delta}$ becomes superconducting at 22 K. This was the first time that one obtained superconductivity above 20 K in oxides without the use of any rare-earth element.

The samples investigated were synthesized by the standard solid-state reaction technique in the following steps: calcination of pellets of a thoroughly ground mixture of appropriate amounts of Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO in air at 750–890 °C in a platinum or alumina crucible, rehomogenization of the calcinated pellets following their crushing and regrinding, sintering of the pellets of

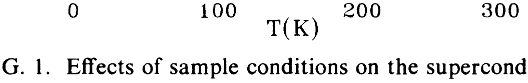

FIG. 1. Effects of sample conditions on the superconducting properties of BCSCO and BACSCO compounds: sample *a*, BCSCO-1 (heat treated at 860 °C); *b*, BCSCO-1 (885 °C); *c*, BCSCO-1 (901 °C); *d*, BACSCO-1 (875 °C, prolonged annealing); *e*, BCSCO-2 (860 °C); *f*, BACSCO-1 (885 °C, slow quenching); and *g*, BCSCO-1 (885 °C, prolonged annealing, slow quenching).

TABLE I. Heat-treatment conditions for samples in Fig. 1.

Sample	Temperature (°C)	Time (min)	Quenching	
a, BCSCO-1	860	60	Air cool	(≃10 min)
b, BCSCO-1	885	60	Air cool	(≃10 min)
c, BCSCO-1	910	60	Air cool	(≃10 min)
d, BACSCO-1	875	300	Slow cool in furnace	(≃120 min)
e, BCSCO-2	860	60	Air cool	(≃10 min)
f, BACSCO-1	885	30	Slow cool in furnace	(≃120 min)
g, BCSCO-1	885	90	Slow cool in furnace	(≃120 min)

the rehomogenized material at the same temperature range, and finally air quenching of the sintered pellets to room temperature. The pellets were then cut into bar samples of dimension $\simeq 3\times0.9\times0.9$ mm^3 for measurements. Pt electrical leads were attached to the samples by In contacts or Au paste. A standard four-probe technique was used to determine at 17 Hz the resistance R. The magnetization M of the samples at ambient pressure was measured after cooling in a field of 30 Oe with a PAR model M155 vibrating-sample magnetometer. The high-pressure environment was provided by a Be-Cu clamp, with silicone oil as the pressure medium contained in a Teflon high-pressure cell. The pressure was determined at low temperature by a superconducting Pb manometer situated next to the sample. The magnetic field effect on the superconducting transition was determined in a superconducting magnet up to 6 T. The temperature was measured by a Chromel-Alumel thermocouple, a Au+0.07% Fe-Chromel thermocouple, a carbon glass thermometer, or a diode thermometer, depending on the type of measurements. All thermometers used have been calibrated against each other and against the published calibration tables of Au+0.07% Fe-Chromel and Chromel-Alumel thermocouples.

Differential thermogravimetric analyses showed that reactions of the ingredients occurred between ≃760 and ≃840 °C and the final compound melted at ≃890 °C for the $BiCaSrCuO_{7-\delta}$ (BCSCO-1) and $BiCaSrCu_3O_{7-\delta}$ (BCSCO-2) compound. These temperatures set the window for synthesis temperatures. They varied somewhat with the compositions in $BiAl_{1-y}CaSrCuO_{7-\delta}$ (BACSCO-1), $Bi_1Al_{1-y}(Ca_{1-x}Sr_x)Cu_2O_{7-\delta}$ (BACSCO-2), $Bi_2Al_{1-y}(Ca_{1-x}Sr_x)_2Cu_2O_{8-\delta}$ (BACSCO-3), and $BiAl_{1-y}(Ca_{1-x}Sr_x)_2Cu_3O_{7-\delta}$ (BACSCO-4). The results also indicated that heating the final compound up to its melting point did not produce a loss of oxygen as in the case of the 1-2-3 compounds, suggesting possibly better stability of the new compounds.

Our prepared compounds apparently can have up to three transitions, depending on the synthesis conditions. Preliminary x-ray powder diffraction results displayed complex patterns which could not be fitted by either the 2-1-4 or 1-2-3 structure. However, lines similar to those of $Bi_2SrCu_2O_{6-\delta}$ (2-1-2) appeared to be present in most of the samples, which are clearly multiphase. It should be pointed out that our $Bi_2SrCu_2O_{7-\delta}$ superconducts at ≃5 K and $Bi_2Sr_2Cu_2O_{7-\delta}$ (2-2-2) does not. All samples with nominal compositions given above were found to exhibit similar superconducting properties, although the sizes of the Meissner-effect signals were different. Unfortunately, the size varied in an unsystematic way be-

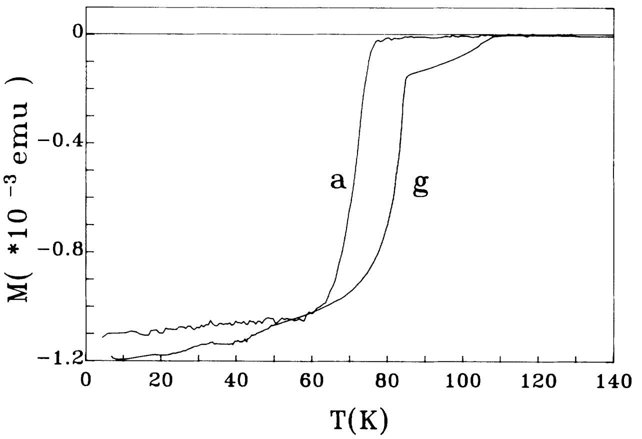

FIG. 2. dc magnetization of samples *a* and *g* of BCSCO-1. A small diamagnetic signal also persists up to ≃110 K.

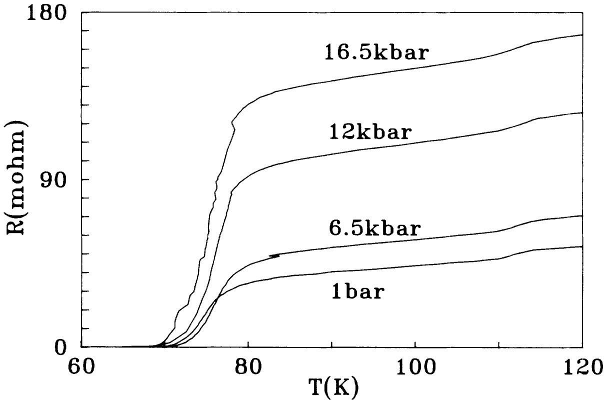

FIG. 3. Pressure effect on R of BCSCO-1, sample g.

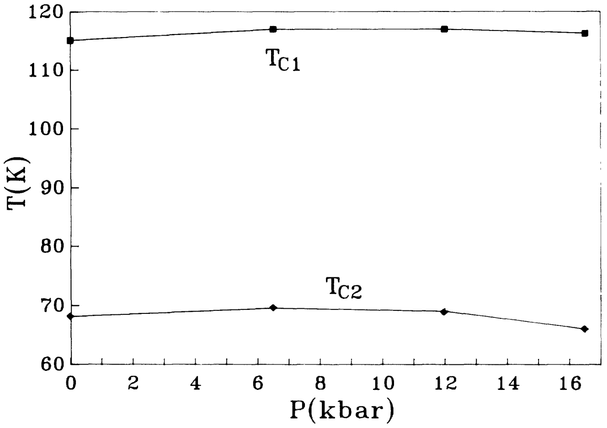

FIG. 4. Pressure effect on T_c's of the two transitions.

cause of the accompanying change in the synthesis conditions. Therefore, only results on some samples are shown. The synthesis temperature and sintering time were found to affect the superconducting properties of various samples sensitively, as displayed in Fig. 1 (also see Table I). The highest transition occurs at $\simeq 114$ K and the lowest one at $\simeq 81$ K. Magnetization results during field cooling at 30 Oe are given in Fig. 2 for two BCSCO-1 samples. About 30% Meissner effect was observed below $\simeq 80$ K and a small but clear Meissner-effect signal was detected up to $\simeq 110$ K. Magnetic field suppresses all transitions. It broadens the transition, suggesting the percolative nature of the samples. With use of the 50% R drop, the estimated upper critical field at 0 K, $H_{c2}(0)$, and the coherence length at 0 K, $\xi(0)$, are $\simeq 113$ T and $\simeq 30$ Å, respectively, for the 80-K transition. The poor quality of the data prevents us from estimating the $H_{c2}(0)$ for the higher-T_c transitions in these compounds. The pressure effect on $R(T)$ for BCSCO-1, sample *g*, is shown in Fig. 3. R increases rapidly with pressure in contrast to that for the 2-1-4 and 1-2-3 compounds.[6] The pressure dependence of T_c for the two transitions is given in Fig. 4. Both T_c's increase initially at a rate of $\simeq 0.3$ K/kbar and then decrease with pressure beyond 12 kbar. The similarity between the pressure effect on T_c with different values is in strong contrast to that[7] for the 90- and 60-K $EuBa_2Cu_3O_{7-\delta}$. The implication of this observation is currently under investigation.

It should be pointed out that a small Meissner effect (<0.1%) has also been detected in BCSCO-1, sample *a*, shown in Fig. 1 above 130 K, the limit of our vibrating-sample magnetometer, and the sample displayed a R drop starting from 180 K. An oxygen-rich sample was found to show a significantly large paramagnetic signal at low temperature instead of superconductivity.

In conclusion, superconductivity up to 114 K has been observed in a Bi-Al-Ca-Sr-Cu-O multiphase compound system, with only a minor role for Al. Presently, the exact stoichiometry and the crystal structure of the superconducting component, which appears to be different from the 2-1-4, 1-2-3, 2-2-2, or 2-1-2 structure described earlier, are being determined. The observations (1) will provide an extra material system for contrast in unraveling the superconducting mechanism in the unusually high-T_c oxides, (2) will reduce the material cost for future full-scale applications of superconductivity, and (3) may lead to even higher and stable T_c in the near future.

Technical assistance from C. Kinalidis, J. C. Chu, T. Lambert, R. Purumandla, and D. Ho is greatly appreciated. Research at the University of Houston is supported by the Low Temperature Physics Program National Science Foundation Grant No. DMR 8616539, NASA Grant No. NAGW-977, the Texas Center for Superconductivity at the University of Houston, and the T. L. Temple Foundation.

---

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987); P. H. Hor, L. Gao, R. L. Meng, Z. J. Huang, Y. Q. Wang, K. Forster, J. Vassiliou, C. W. Chu, M. K. Wu, J. R. Asbhurn, and C. J. Torng, Phys. Rev. Lett. **58**, 911 (1987).

[3] For a review, see *Novel Superconductivity,* edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987), pp. 295–577.

[4] See, for example, P. H. Hor, R. L. Meng, Y. Q. Wang, L. Gao, Z. J. Huang, J. Bechtold, K. Forster, and C. W. Chu, Phys. Rev. Lett. **58**, 1891 (1987); C. W. Chu, in the Proceedings of The International Union of Pure and Applied Physics Symposium, Washington, DC, 1987 (to be published).

[5] C. Michel, M. Herviert, M. M. Borel, A. Grandin, F. Des Landeo, J. Provost, and B. Raveau, to be published.

[6] C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, Phys. Rev. Lett. **58**, 405 (1987); C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, and Z. J. Huang, Science **235**, 567 (1987).

[7] C. W. Chu, Z. J. Huang, R. L. Meng, L. Gao, and P. H. Hor, to be published.