RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 10 1 APRIL 1987

Superconducting phase transitions in the La-M-Cu-O layered perovskite system, M=La, Ba, Sr, and Pb

D. U. Gubser, R. A. Hein,* S. H. Lawrence, M. S. Osofsky, D. J. Schrodt, L. E. Toth,† and S. A. Wolf
Naval Research Laboratory, Washington, D.C. 20375-5000

(Received 5 February 1987)

We report results of our studies of the La-M-Cu-O system, M=La, Ba, Sr, and Pb. T_c and the magnetic moment are correlated with annealing schedules and x-ray structural analyses. The occurrence of superconductivity is associated with the formation of Cu^{3+} ions producing an expansion of the c parameter of the unit cell. We have found magnetic and resistive anomalies near 65 K in some La-Ba-Cu-O samples. These samples show a slight depression of the superconducting transition temperature.

Observation of superconductivity in the La-Ba-Cu-O system[1] at temperatures over 30 K has sparked worldwide enthusiasm and research on this new class of high-temperature superconductors. High-temperature superconductivity ($T_c > 10$ K) had been reported in only two other oxide systems, the Li-Ti-O system possessing a cubic spinel structure,[2] and the Ba-Pb-Bi-O system possessing the perovskite structure,[3] with maximum transition temperatures of 13.7 and 13 K, respectively. The new La-Ba-Cu-O oxide system, with T_c's reported above 40 K,[4-7] possesses a layered perovskite K_2NiF_4-type crystal structure and is metallic at room temperature. The earliest data on the La-Cu-O layered perovskite system date to the early 1960's.[8,9] In 1973, Goodenough, Demazeau, Pouchard, and Hagenmuller reported on an oxygen defect phase in the La-Sr-Cu-O system where the Cu ion assumes a +3 valency.[10] In 1979 Shaplygin, Kakhan, and Lazarev[11] reported metallic conductivities in the compounds $La_{2-x}M_xCuO_4$ with M=Ca, Sr, Ba, and Pb. The initial report of superconductivity in the M=Ba compound has been confirmed by several groups[4-7] and superconductivity has subsequently been observed in the M=Sr (Refs. 12 and 13) and M=Ca (Ref. 13) compounds. Both zero resistance and partial flux expulsion (Meissner effect) have been observed in these samples giving evidence that the compounds are bulk superconductors.

The La-M-Cu-O compounds are prepared either by coprecipitation from aqueous solutions of La, Cu, and M nitrates or by reacting powdered mixtures of oxides and carbonates of La, Cu, and M. Various reaction temperatures and reaction times have been reported as well as various post-reaction annealing schedules which improve the superconducting properties.

Our materials were prepared from reagent-grade powders of La_2O_3, $BaCO_3$, $SrCO_3$, $CaCO_3$, PbO_2, and CuO. These powders were mixed in appropriate ratios to form the desired compounds and calcined in air at temperatures between 1000 °C and 1100 °C for approximately 12 h. The materials were then reground into powder, pressed into small disks (nominally 1-cm diameter by 2-mm height) and sintered in air at temperatures between 1000 °C to 1100 °C for 12 h. The calcined powders and the sintered pellets were x-rayed following each process to ensure the K_2NiF_4 phase was present. In one case the La-Ba-Cu-O powder was calcined a second time before pressing and sintering. This recalcining did improve the structural quality of the compound, as evidenced by the sharpness of the x-ray lines, but slightly lowered the onset of the superconducting transition and produced magnetic and electrical anomalies near 65 K (discussed later). Calcining and/or sintering in a pure oxygen atmosphere at 1100 °C produced substantial phases other than the K_2NiF_4 phase which were not superconducting.

The La-Ba-Cu-O compounds were prepared in three compositions, $La_{2-x}Ba_xCuO_4$ where x=0.1, 0.2, and 0.3. The resistive transitions were measured on the sintered pellets by attaching four leads with indium solder. The resistivity of the pellets was relatively high ($\simeq 10000$ $\mu\Omega$ cm), which we assume is due to the granular nature of the loosely compacted and sintered pellet rather than the intrinsic resistivity of the material itself. Similarly, the transition is broadened and the critical current ($\simeq 5.0$ A/cm^2) is low because of the granularity. Figure 1 shows the resistive and magnetic transition for the x=0.1 sample which had the sharpest transition and the highest onset

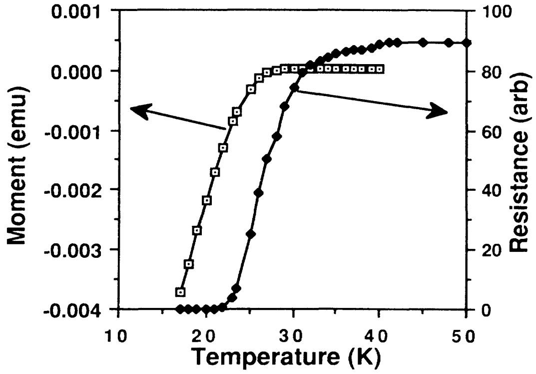

FIG. 1. Resistance and magnetic moment plotted vs temperature of $La_{1.9}Ba_{0.1}CuO_4$. The onset temperature for superconductivity in the resistive transition is 40 K. Magnetic moment was measured cooling in 100 Oe and represents about 10% flux exclusion.

temperature. The onset temperature T_0 was 40 K and the $R = 0$ point was 24 K. The magnetic moment was measured cooling in a 100-G ambient field and was still changing at 10 K (the lowest temperature measured), but at this point it represented about a 10% flux exclusion (subsequent Sr samples showed over 50% exclusion). T_0, determined magnetically, of this sintered material is about 28 K.

An interesting anomaly in the resistive and magnetic transition appears around 65 K in some of our samples. Figure 2 shows the magnetic moment of two $La_{1.9}Ba_{0.1}CuO_4$ samples, one of which had been reacted only once at 1100 °C for 12 h (a), while the other had been reacted a second time also at 1100 °C for 12 h (b). X-ray spectra of these samples are shown in Fig. 3. The twice-reacted sample (similar thermal history as the sintered samples), which shows the anomaly, has slightly sharper x-ray lines indicating a more homogeneous composition, and the c parameter is smaller. It also has a slightly depressed T_0 (28 vs 32 K).

The anomaly at high temperature in the twice-reacted $La_{1.9}Ba_{0.1}CuO_4$ may be associated with an electronically driven distortion of the lattice similar to a charge-density-wave (CDW) transition. Such transitions remove carriers from the conduction process and are usually detrimental to superconductivity.[14] Similarly, the CDW structural distortion is removed by crystalline defects of various types[15] and may explain the absence of an anomaly in the slightly less homogeneous once-reacted samples. The tendency for a structural instability is often correlated with low-frequency phonon modes that are important for high T_c. The anomalies observed in our samples also suggest that such low-frequency modes may be present and may be responsible for the very high T_c in these materials.[16]

Magnetic transitions for $La_{1.8}Sr_{0.2}CuO_4$ and $La_{1.7}Ca_{0.3}CuO_4$ samples are shown in Fig. 4. T_0, determined magnetically, for these samples are 36 and 24 K, respectively. Samples having the composition Ba, $x = 0.1$ and 0.2; Sr, $x = 0.1$ and 0.2; and Ca, $x = 0.3$, showed x-ray spectra characteristic of nearly single phase K_2NiF_4 structure and had higher and sharper transitions than other compositions.

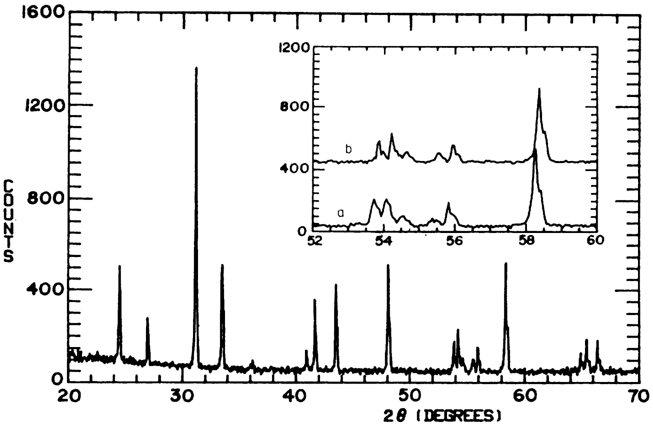

FIG. 3. The x-ray powder diffraction pattern for the twice-calcined sample of $La_{1.9}Ba_{0.1}CuO_4$. The pattern shows a single-phase K_2NiF_4 structure. The inset compares a portion of this pattern [(b) upper trace] with the same region of the x-ray pattern for the (a) singly calcined sample. Note that the singly calcined sample has broader lines at a slightly smaller 2θ (indicating a larger lattice parameter).

Three compositions of $La_{2-x}Pb_xCuO_4$ with $x = 0.1$, 0.2, and 0.3 were also made. These samples were processed in a similar manner as were the Sr, Ba, and Ca samples. The Pb, $x = 0.1$ sample had an x-ray spectrum with nearly single-phase K_2NiF_4 structure. In the lowest resistivity of the three compositions, however, the sample showed no sign of superconductivity and had activated conductivity. Various subsequent annealing procedures were attempted to improve the conductivity of this sample. An inert gas anneal at 750 K for 12 h produced the lowest resistivity of about 30000 Ω cm, but again there was no sign of superconductivity.

Superconductivity in this new class of high T_c compounds appears to be intimately connected with the valence of the Cu^{3+} ion.[12] In La_2CuO_4 the copper is in

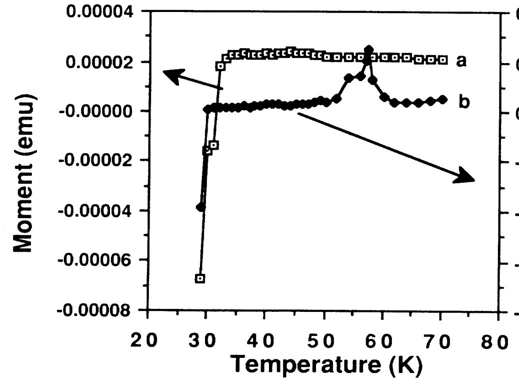

FIG. 2. This figure shows the (a) once-reacted and (b) twice-reacted samples of $La_{1.9}Ba_{0.1}CuO_4$ plotted vs temperature. The anomaly in the twice-reacted sample near 60 K is clearly visible as is the reduction in the onset temperature for superconductivity.

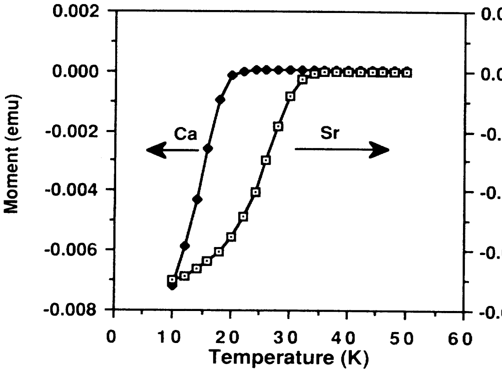

FIG. 4. The magnetic moment of $La_{1.8}Sr_{0.2}CuO_4$ and $La_{1.7}Ca_{0.3}CuO_4$ plotted vs temperature. The magnetic moment for the sample at 10 K represents almost 60% flux expulsion (100-Oe ambient field).

TABLE I. Sample parameters.

Material	*a* (Å)	*c* (Å)	*c/a*	T_0 (K)
$La_{1.8}Ca_{0.2}CuO_4$	3.790	13.159	3.47	22.5
$La_{1.7}Ca_{0.3}CuO_4$	3.782	13.162	3.48	25
$La_{1.9}Ba_{0.1}CuO_4$	3.786	13.238	3.49	30[a]
$La_{1.9}Ba_{0.1}CuO_4$	3.787	13.256	3.50	33[a]
$La_{1.8}Ba_{0.2}CuO_4$	3.801	13.301	3.50	31
$La_{1.9}Sr_{0.1}CuO_4$	3.771	13.233	3.51	36.5
$La_{1.8}Sr_{0.2}CuO_4$	3.777	13.261	3.51	37
$La_{1.7}Sr_{0.3}CuO_4$	3.798	13.111	3.45	<4
$La_{1.9}Pb_{0.1}CuO_4$	3.801	13.191	3.47	. . .
$La_{1.8}Pb_{0.2}CuO_4$	3.772	13.120	3.48	. . .
$La_{1.7}Pb_{0.3}CuO_4$	3.791	13.158	3.47	. . .

[a] T_0 measured by dc susceptibility.

the +2 valence state. The addition of Ba, Sr, Ca, and Pb either forces some of the Cu ions into the +3 valence state, creating a mixed valence compound, or produced oxygen vacancies.[17,18] The preservation of Cu^{3+} by minimizing the oxygen vacancy formation with suitable processing procedures is essential to superconductivity. The extra electrons from Cu provide carriers which make the material highly conductive and superconductive in some cases. The relative amounts of Cu^{3+} ions can be inferred from the x-ray structural analysis. Cu^{3+} produces an expansion of the *c* parameter relative to the *a* parameter if the oxygen content remains constant.[17] Table I lists the *a* and *c* parameters for the compounds shown as well as the T_0 values of the samples. The correlation of superconductivity with the size of the *c/a* ratio is clearly evident.

Reacting or annealing the compounds in oxygen can be either detrimental or beneficial depending on the presence of second-phase higher oxides. If second-phase higher oxides are present, then annealing in oxygen at high temperatures will promote the growth of this phase at the expense of the LaM_xCuO_4 oxide. An associated reduction of the *c* parameter in the K_2NiF_4 structure is observed. In this situation, annealing in a reducing atmosphere rather than an oxidizing one promotes the growth of LaM_xCuO_4 oxide and enhances the superconducting properties. If, on the other hand, one has a single phase K_2NiF_4 structure or a second phase of lower oxides, then a low-temperature oxygen anneal which does not nucleate a higher oxide second phase will promote the formation of more Cu^{3+} by ensuring that more oxygen vacancies are filled. Thus we see that annealing schedules and procedures may vary significantly depending on the exact chemistry of the compound.

In summary, we have prepared $La_{2-x}M_xCuO_4$ superconducting compounds with M_x = Ba, Sr, and Ca. With M = Pb, the compound of the same structure is not superconducting. The reason for this change in behavior is unclear but is most likely associated with the ability of Pb to promote Cu^{3+} ions versus oxygen vacancies. Correlation of the presence of Cu^{3+} ions with the *c/a* ratio has been demonstrated, and a reason for the variety of apparently conflicting annealing procedures has been suggested.

The authors thank C. Vold, J. Wallace, S. Qadri, J. Claassen, T. Francavilla, V. Kresin, J. Krebs, D. Papaconstantopoulos, and W. Pickett for their assistance and valuable discussions. One of us (M.S.O.) was partially supported by the Office of Naval Technology.

---

[*] Permanent address: Catholic University of America, Washington, DC 20064.

[†] Permanent address: National Science Foundation, Washington, DC 20550.

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

[2] D. C. Johnston, H. Prakash, W. H. Zachariasen, and R. Viswanathan, Mater. Res. Bull. **8**, 777 (1973).

[3] A. W. Sleight, J. L. Gillson, and P. E. Bierstedt, Solid State Commun. **17**, 27 (1975).

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

[5] S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. (to be published).

[6] H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka (unpublished).

[7] S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka (unpublished).

[8] M. Foex, A. Mancheron, and L. Line, C. R. Acad. Sci **250**, 3027 (1960).

[9] J. M. Longo and P. M. Raccah, J. Solid State Chem. **6**, 526 (1963).

[10] J. B. Goodenough, G. Demazeau, M. Pouchard, and P. Hagenmuller, J. Solid State Chem. **8**, 325 (1973).

[11] I. S. Shaplygin, B. G. Kakhan, and V. B. Lazarev, Zh. Neorg. Khim. **24**, 1478 (1979) [J. Inorg. Chem. **24**, 820 (1979)].

[12] R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman, Phys. Rev. Lett. **58**, 408 (1987).

[13] K. Kishio, K. Kitazawa, S. Kanbe, I. Yasuda, N. Sugii, H. Takagi, S. Uchida, K. Fueki, and S. Tanaka (unpublished).

[14] G. Bilbro and W. L. McMillan, Phys. Rev. B **14**, 1887 (1976).

[15] W. W. Fuller, O. M. Chaikin, and N. P. Ong, Phys. Rev. B **24**, 1333 (1981).

[16] V. Z. Kresin (unpublished).

[17] N. Nguyen, J. Choisnet, M. Hervieu, and B. Raveau, J. Solid State Chem. **39**, 120 (1981).

[18] C. Michel and B. Raveau, Rev. Chim. Miner. **21**, 407 (1984).