

## Possible High $T_c$ Superconductivity in the Ba–La–Cu–O System

J.G. Bednorz and K.A. Müller

IBM Zürich Research Laboratory, Rüschlikon, Switzerland

Received April 17, 1986

Metallic, oxygen-deficient compounds in the Ba–La–Cu–O system, with the composition  $\text{Ba}_x\text{La}_{5-x}\text{Cu}_5\text{O}_{5(3-y)}$  have been prepared in polycrystalline form. Samples with  $x=1$  and  $0.75$ ,  $y>0$ , annealed below  $900^\circ\text{C}$  under reducing conditions, consist of three phases, one of them a perovskite-like mixed-valent copper compound. Upon cooling, the samples show a linear decrease in resistivity, then an approximately logarithmic increase, interpreted as a beginning of localization. Finally an abrupt decrease by up to three orders of magnitude occurs, reminiscent of the onset of percolative superconductivity. The highest onset temperature is observed in the 30 K range. It is markedly reduced by high current densities. Thus, it results partially from the percolative nature, but possibly also from 2D superconducting fluctuations of double perovskite layers of one of the phases present.

### 1. Introduction

“At the extreme forefront of research in superconductivity is the empirical search for new materials” [1]. Transition-metal alloy compounds of *A*15 ( $\text{Nb}_3\text{Sn}$ ) and *B*1 ( $\text{NbN}$ ) structure have so far shown the highest superconducting transition temperatures. Among many *A*15 compounds, careful optimization of Nb–Ge thin films near the stoichiometric composition of  $\text{Nb}_3\text{Ge}$  by Gavalev et al. and Testardi et al. a decade ago allowed them to reach the highest  $T_c = 23.3$  K reported until now [2, 3]. The heavy Fermion systems with low Fermi energy, newly discovered, are not expected to reach very high  $T_c$ 's [4].

Only a small number of oxides is known to exhibit superconductivity. High-temperature superconductivity in the Li–Ti–O system with onsets as high as 13.7 K was reported by Johnston et al. [5]. Their x-ray analysis revealed the presence of three different crystallographic phases, one of them, with a spinel structure, showing the high  $T_c$  [5]. Other oxides like perovskites exhibit superconductivity despite their small carrier concentrations,  $n$ . In Nb-doped  $\text{SrTiO}_3$ , with  $n = 2 \times 10^{20} \text{ cm}^{-3}$ , the plasma edge is below the highest optical phonon, which is therefore unshielded

[6]. This large electron-phonon coupling allows a  $T_c$  of 0.7 K [7] with Cooper pairing. The occurrence of high electron-phonon coupling in another metallic oxide, also a perovskite, became evident with the discovery of superconductivity in the mixed-valent compound  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  by Sleight et al., also a decade ago [8]. The highest  $T_c$  in homogeneous oxygen-deficient mixed crystals is 13 K with a comparatively low concentration of carries  $n = 2\text{--}4 \times 10^{21} \text{ cm}^{-3}$  [9]. Flat electronic bands and a strong breathing mode with a phonon feature near  $100 \text{ cm}^{-1}$ , whose intensity is proportional to  $T_c$ , exist [10]. This last example indicates that within the BCS mechanism, one may find still higher  $T_c$ 's in perovskite-type or related metallic oxides, if the electron-phonon interactions and the carrier densities at the Fermi level can be enhanced further.

Strong electron-phonon interactions in oxides can occur owing to polaron formation as well as in mixed-valent systems. A superconductivity (metallic) to bipolaronic (insulator) transition phase diagram was proposed theoretically by Chakraverty [11]. A mechanism for polaron formation is the Jahn-Teller effect, as studied by Höck et al. [12]. Isolated  $\text{Fe}^{4+}$ ,  $\text{Ni}^{3+}$  and  $\text{Cu}^{2+}$  in octahedral oxygen environment

show strong Jahn-Teller (J.T.) effects [13]. While  $\text{SrFe(VI)O}_3$  is distorted perovskite insulator,  $\text{LaNi(III)O}_3$  is a J.T. undistorted metal in which the transfer energy  $b_\pi$  of the J.T.  $e_g$  electrons is sufficiently large [14] to quench the J.T. distortion. In analogy to Chakraverty's phase diagram, a J.T.-type polaron formation may therefore be expected at the borderline of the metal-insulator transition in mixed perovskites, a subject on which we have recently carried out a series of investigations [15]. Here, we report on the synthesis and electrical measurements of compounds within the Ba-La-Cu-O system. This system exhibits a number of oxygen-deficient phases with mixed-valent copper constituents [16], i.e., with itinerant electronic states between the non-J.T.  $\text{Cu}^{3+}$  and the J.T.  $\text{Cu}^{2+}$  ions, and thus was expected to have considerable electron-phonon coupling and metallic conductivity.

## II. Experimental

### 1. Sample Preparation and Characterization

Samples were prepared by a coprecipitation method from aqueous solutions [17] of Ba-, La- and Cu-nitrate (SPECPURE JMC) in their appropriate ratios. When added to an aqueous solution of oxalic acid as the precipitant, an intimate mixture of the corresponding oxalates was formed. The decomposition of the precipitate and the solid-state reaction were performed by heating at 900 °C for 5 h. The product was pressed into pellets at 4 kbar, and reheated to 900 °C for sintering.

### 2. X-Ray Analysis

X-ray powder diffractograms (System D 500 SIEMENS) revealed three individual crystallographic phases. Within a range of 10° to 80° (2 $\theta$ ), 17 lines could be identified to correspond to a layer-type perovskite-like phase, related to the  $\text{K}_2\text{NiF}_4$  structure ( $a=3.79$  Å and  $c=13.21$  Å) [16]. The second phase is most probably a cubic one, whose presence depends on the Ba concentration, as the line intensity decreases for smaller  $x(\text{Ba})$ . The amount of the third phase (volume fraction > 30% from the x-ray intensities) seems to be independent of the starting composition, and shows thermal stability up to 1,000 °C. For higher temperatures, this phase disappears progressively, giving rise to the formation of an oxygen-deficient perovskite ( $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14}$ ) as described by Michel and Raveau [16].

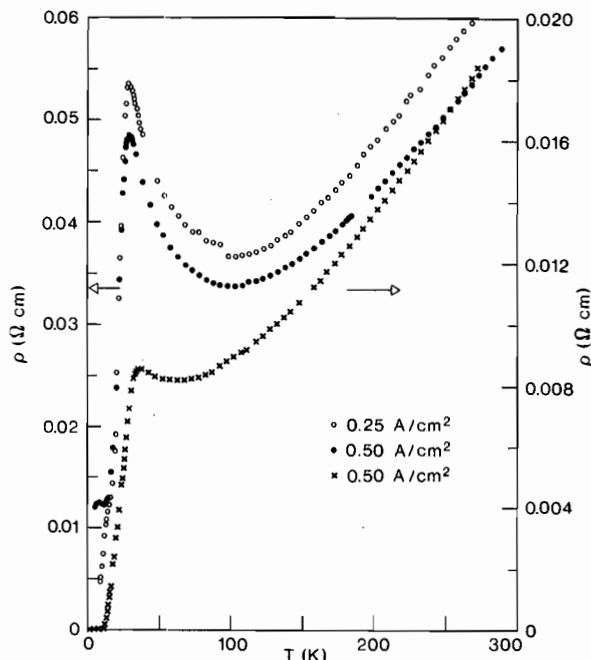


Fig. 1. Temperature dependence of resistivity in  $\text{Ba}_x\text{La}_{5-x}\text{Cu}_5\text{O}_{5(3-y)}$  for samples with  $x(\text{Ba})=1$  (upper curves, left scale) and  $x(\text{Ba})=0.75$  (lower curve, right scale). The first two cases also show the influence of current density

### 3. Conductivity Measurements

The dc conductivity was measured by the four-point method. Rectangular-shaped samples, cut from the sintered pellets, were provided with gold electrodes and contacted by In wires. Our measurements between 300 and 4.2 K were performed in a continuous-flow cryostat (Leybold-Hereaus) incorporated in a computer-controlled (IBM-PC) fully-automatic system for temperature variation, data acquisition and processing.

For samples with  $x(\text{Ba}) \leq 1.0$ , the conductivity measurements, involving typical current densities of 0.5 A/cm<sup>2</sup>, generally exhibit a high-temperature metallic behaviour with an increase in resistivity at low temperatures (Fig. 1). At still lower temperatures, a sharp drop in resistivity (> 90%) occurs, which for higher currents becomes partially suppressed (Fig. 1: upper curves, left scale). This characteristic drop has been studied as a function of annealing conditions, i.e., temperature and  $\text{O}_2$  partial pressure (Fig. 2). For samples annealed in air, the transition from itinerant to localized behaviour, as indicated by the minimum in resistivity in the 80 K range, is not very pronounced. Annealing in a slightly reducing atmosphere, however, leads to an increase in resistivity and a more pronounced localization effect. At the same time, the onset of the resistivity drop is shifted

0.06

0.04

0.02

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

Fig. 2.  
annealed  
0.2 x 1

lowa  
for s:  
of a  
noun  
1,040  
vanis  
mixel  
tron-  
of ele  
curve  
of 0.  
decre  
vide  
13 K  
on an  
also s  
for g

III. I

The  
is qu  
the

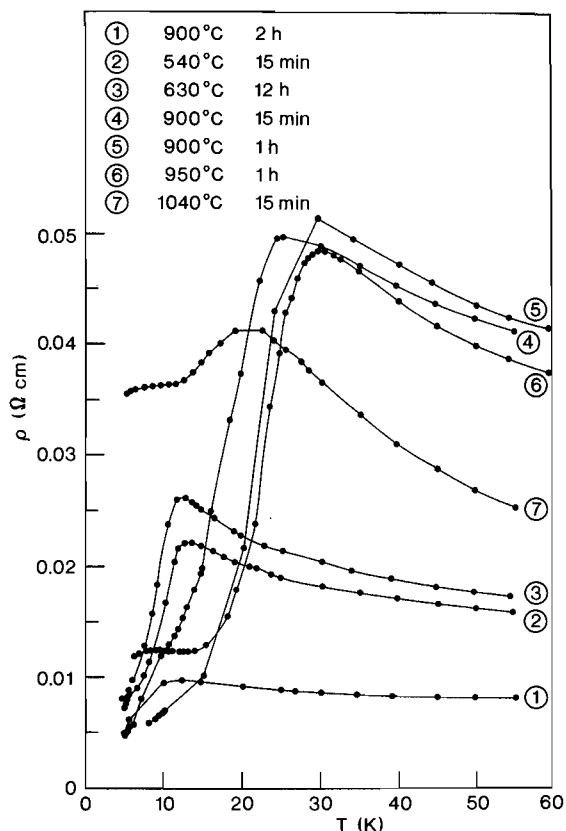


Fig. 2. Low-temperature resistivity of samples with  $x(\text{Ba})=1.0$ , annealed at  $\text{O}_2$  partial pressure of 0.2 bar (curve ①) and  $0.2 \times 10^{-4}$  bar (curves ② to ⑦)

towards the 30 K region. Curves ④ and ⑤, recorded for samples treated at 900 °C, show the occurrence of a shoulder at still lower temperature, more pronounced in curve ④. At annealing temperatures of 1,040 °C, the highly conducting phase has almost vanished. As mentioned in the Introduction, the mixed-valent state of copper is of importance for electron-phonon coupling. Therefore, the concentration of electrons was varied by the Ba/La ratio. A typical curve for a sample with a lower Ba concentration of 0.75 is shown in Fig. 1 (right scale). Its resistivity decreases by at least three orders of magnitude, giving evidence for the bulk being superconducting below 13 K with an onset around 35 K, as shown in Fig. 3, on an expanded temperature scale. The latter figure also shows the influence of the current density, typical for granular compounds.

### III. Discussion

The resistivity behaviour of our samples, Fig. 1, is qualitatively very similar to the one reported in the Li-Ti-O system, and in superconducting

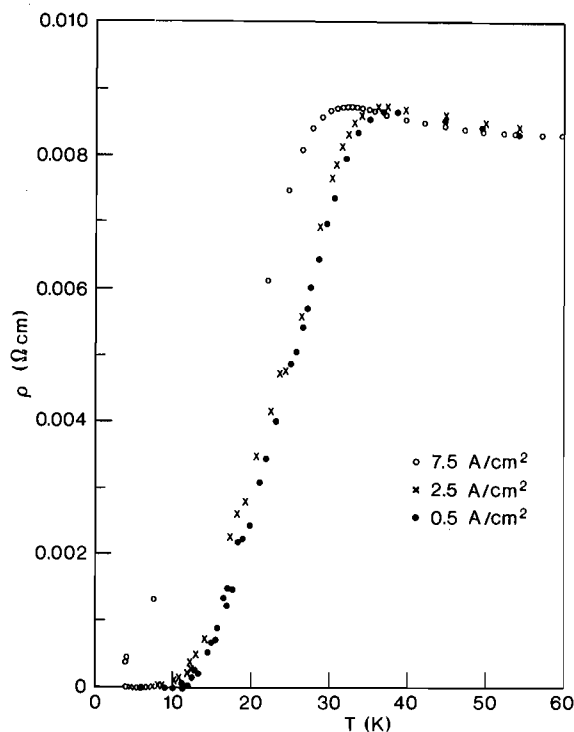


Fig. 3. Low-temperature resistivity of a sample with  $x(\text{Ba})=0.75$ , recorded for different current densities

$\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  polycrystalline thin films [5, 18]. Upon cooling from room temperature, the latter exhibit a nearly linear metallic decrease of  $\rho(T)$ , then a logarithmic type of increase, before undergoing the transition to superconductivity. One could, of course, speculate that in our samples a metal-to-metal structural phase transition occurs in one of the phases. The shift in the drop in  $\rho(T)$  with increasing current density (Fig. 3), however, would be hard to explain with such an assumption, while it supports our interpretation that we observe the onset of superconductivity of percolative nature, as discussed below. In  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ , the onset of superconductivity has been taken at the resistivity peak [18]. This assumption appears to be valid in percolative systems, i.e., in the thin films [18] consisting of polycrystals with grain boundaries, or when different crystalline phases with interpenetrating grains are present, as found in the Li-Ti-O [5] or in our Ba-La-Cu-O system. The onset can also be due to fluctuations in the superconducting wave functions. We assume one of the Ba-La-Cu-O phases exhibits this behaviour. Therefore, under the above premises, the peak in  $\rho(T)$  at 35 K, observed for an  $x(\text{Ba})=0.75$  (Fig. 1), has

to be identified as the start to superconductive cooperative phenomena in the isolated grains. It should be noted that in granular Al, Cooper pairs in coupled grains have been shown to exist already at a point where  $\rho(T)$  upon cooling has decreased by only 20% of its highest value. This has been proven qualitatively [19] and more recently also quantitatively [20] by the negative frequency shift occurring in a microwave cavity. In 100 Å films, a shoulder in the frequency shift owing to 2D fluctuations was observed above the  $T_c$  of the grains. In our Ba-La-Cu-O system, a series of layer-like phases with considerable variety in compositions are known to exist [16, 21], and therefore 2D correlations can be present.

The granularity of our system can be justified from the structural information, and more quantitatively from the normal conductivity behaviour. From the former, we know that more than one phase is present and the question arises how large are the grains. This can be inferred from the logarithmic fingerprint in resistivity. Such logarithmic increases are usually associated with beginning of localization. A most recent example is the Anderson transition in granular Sn films [22]. Common for the granular Sn and our samples is also the resistivity at 300 K, lying in the range of 0.06 to 0.02 Ωcm, which is near the microscopic critical resistivity of  $\rho_c = 10 L_0 \hbar / e^2$  for localization. From the latter formula, an interatomic distance  $L_0$  in the range of 100 Å is computed, thus a size of superconducting grains of this order of magnitude must be present. Upon cooling below  $T_c$ , Josephson junctions between the grains phase-lock progressively [23] and the bulk resistivity gradually drops to zero by three orders of magnitude, for sample 2 (Fig. 1). At larger current densities, the weaker Josephson junctions switch to normal resistivity, resulting in a temperature shift of the drop, as shown in Fig. 3. The plateau in resistivity occurring below the 80% drop (Fig. 1) for the higher current density of 0.5 A/cm<sup>2</sup>, and Fig. 2 curve ⑥) may be ascribed to switching of junctions to the normal state.

The way the samples have been prepared seems to be of crucial importance: Michel et al. [21] obtained a single-phase perovskite by mixing the oxides of La and Cu and BaCO<sub>3</sub> in an appropriate ratio and subsequent annealing at 1,000 °C in air. We also applied this annealing condition to one of our samples, obtained by the decomposition of the corresponding oxalates, and found no superconductivity. Thus, the preparation from the oxalates and annealing below 950 °C are necessary to obtain a non-perovskite-type phase with a limited temperature range of stability exhibiting this new behaviour. The formation of this phase at comparatively low temperatures is favoured by the intimate mixture of the compo-

nents and the high reactivity of the oxalates owing to the evolution of large amounts of H<sub>2</sub>O and CO<sub>2</sub> during decomposition.

#### IV. Conclusion

In the concentration range investigated, compounds of the Ba-La-Cu-O system are metallic at high temperatures, and exhibit a tendency towards localization upon cooling. Samples annealed near 900 °C under reducing conditions show features associated with an onset of granular superconductivity near 30 K. The system consists of three phases, one of them having a metallic perovskite-type layer-like structure. The characterization of the new, apparently superconducting, phase is in progress. An identification of that phase may allow growing of single crystals for studying the Meissner effect, and collecting specific-heat data to prove the presence of high  $T_c$  bulk superconductivity.

The authors would like to thank H.E. Weibel for his help in getting familiar with the conductivity measurement system, E. Courtens and H. Thomas for discussions and a critical reading of the manuscript.

#### References

1. Tinkham, M., Beasley, M.R., Larbalestier, D.C., Clark, A.F., Finnemore, D.K.: Workshop on Problems in Superconductivity, Copper Mountain, Colorado, August 1983, p. 12
2. Beasley, M.R., Geballe, T.H.: Phys. Today **36** (10), 60 (1984)
3. Müller, J.: Rep. Prog. Phys. **43**, 663 (1980)
4. Ott, H.R.: Unconventional Superconductivity. Zürich Phys. Soc. Seminar, Zürich, February 13, 1986
5. Johnston, D.C., Prakash, H., Zachariasen, W.H., Viswanathan, R.: Mat. Res. Bull. **8**, 777 (1973)
6. Baratoff, A., Binnig, G.: Physics **108 B**, 1335 (1981)  
Baratoff, A., Binnig, G., Bednorz, J.G., Gervais, F., Servoin, J.L.: In: Superconductivity in *d*- and *f*-Band Metals, Proceedings IV Conference in 'Superconductivity in *d*- and *f*-Band Metals'. Buckel, W. and Weber, W. (eds), p. 419, Kernforschungszentrum Karlsruhe 1982
7. Binnig, G., Baratoff A., Hönig, H.E., Bednorz, J.G.: Phys. Rev. Lett. **45**, 1352 (1980)
8. Sleight, A.W., Gillson, J.L., Bierstedt, F.E.: Solid State Commun. **17**, 27 (1975)  
Batlogg, B.: Physica **126 B**, 275 (1984)
9. Thanh, T.D., Koma, A., Tanaka, S.: Appl. Phys. **22**, 205 (1980)
10. Mattheis, F., Hamann, D.R.: Phys. Rev. B **26**, 2682 (1982); *ibid.* **28**, 4227 (1983)
11. Chakraverty, B.K.: J. Phys. Lett. **40**, L99 (1979); J. Phys. **42**, 1351 (1981)
12. Höck, K.-H., Nickisch, H., Thomas, H.: Helv. Phys. Acta **56**, 237 (1983)
13. Englmann, R.: In: The Jahn-Teller Effect in Molecules and Crystals. London, New York: Wiley Interscience 1972
14. Goodenough, J.B., Longo, M.: Magnetic and other properties of oxide and related compounds. In: Landolt-Boernstein New

- Series. Vol III/4a: Crystal and solid state physics. Hellwege, K.H., Hellwege, A.M. (eds.), p. 262, Fig. 73. Berlin, Heidelberg, New York: Springer-Verlag 1970
15. Bednorz, J.G., Müller, K.A.: (in preparation)
  16. Michel, C., Raveau, B.: *Chim. Min.* **21**, 407 (1984)
  17. Bednorz, J.G., Müller, K.A., Arend, H., Gränicher, H.: *Mat. Res. Bull.* **18** (2), 181 (1983)
  18. Suzuki, M., Murakami, T., Inamura, T.: *Shinku* **24**, 67 (1981) (in Japanese)  
Enomoto, Y., Suzuki, M., Murakami, T., Inukai, T., Inamura, T.: *Jpn. J. Appl. Phys.* **20**, L661 (1981)
  19. Müller, K.A., Pomerantz, M., Knoedler, C.M., Abraham, D.: *Phys. Rev. Lett.* **45**, 832 (1980)
  20. Stocker, E., Buttat, J.: *Solid State Commun.* **53**, 915 (1985)
  21. Michel, C., Er-Rakho, L., Raveau, B.: *Mat. Res. Bull.* **20**, 667 (1985)
  22. Van Haesendonck, C., Bruynseraede, Y.: *Phys. Rev. B* **33**, 1684 (1986)
  23. Deutscher, G., Entin-Wohlman, O., Fishman, S., Shapira, Y.: *Phys. Rev. B* **21**, 5041 (1980)

J.G. Bednorz  
K.A. Müller  
IBM Zürich Research Laboratory  
Säumerstrasse 4  
CH-8803 Rüschlikon  
Switzerland

#### Note Added in Proof

Chemical analysis of the bulk composition of our samples revealed a deviation from the ideal La/Ba ratios of 4 and 5.66. The actual ratios are 16 and 18, respectively. This is in agreement with an identification of the third phase as CuO.