CHEMISTRY LETTERS, pp. 429-432, 1987.

New High Temperature Superconducting Oxides. $(La_{1-x}Sr_x)_2CuO_{4-\delta}$ and $(La_{1-x}Ca_x)_2CuO_{4-\delta}$

Kohji KISHIO,* Koichi KITAZAWA,* Shinsaku KANBE, Isamu YASUDA, Nobuyuki SUGII, Hidenori TAKAGI,†,†† Shin-ichi UCHIDA,†,†† Kazuo FUEKI,* and Shoji TANAKA†

Department of Industrial Chemistry, University of Tokyo, Bunkyo-ku, Tokyo 113

† Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113

†† Engineering Research Institute, University of Tokyo, Bunkyo-ku, Tokyo 113

Solid solution systems of $(La_{1-x}Sr_x)_2CuO_{4-\delta}$ and $(La_{1-x}Ca_x)_2CuO_{4-\delta}$ with x=0.05, 0.075, and 0.10 were found to exhibit the superconductivity through a.c. magnetic susceptibility and electrical resistivity measurements. The onset critical temperature for $(La_{0.90}Sr_{0.10})_2CuO_{4-\delta}$ was 37 K, the highest among all the superconducting materials ever known, while that for $(La_{0.95}Ca_{0.05})_2CuO_{4-\delta}$ was 18 K.

Until recently, the superconducting material with the highest critical temperature T_c has been Nb_3Ge for which the highest onset T_c so far reported is 23.6 K.[1] Bednorz and Müller[2] reported that the resistivity drop of the Ba-La-Cu-O system set in at temperatures around 35 K, although the finite resistivity state lasted down to 13 K. In the succeeding paper, Bednorz, Takashige and Müller[3] observed a small diamagnetism in the same material below about 30 K. Uchida et al.[4] and Takagi et al.[5] then reported that the maximum diamagnetic susceptibility was obtained for the pure phase of $(La_{1-x}Ba_x)_2CuO_{4-\delta}$ which was as large as 30% of that expected for the perfect diamagnetism. Furthermore, they showed the zero resistivity state in the same phase with x=0.075, lasted up to 22 K with the onset T_c also about 35 K. Therefore, they concluded that this is the phase which is responsible for the high T_c superconductivity.

This letter reports that we found new superconducting oxide systems $(La_{1-x}Sr_x)_2CuO_{4-\delta}$ and $(La_{1-x}Ca_x)_2CuO_{4-\delta}$, of which the former exhibited even higher T_c, 37 K for the onset T_c and 33 K for the appearance of the substantially zero resistivity state.

The powder specimens of $(La_{1-x}Sr_x)_2CuO_{4-\delta}$ and $(La_{1-x}Ca_x)_2CuO_{4-\delta}$ with compositions of x=0.05, 0.075, and 0.10 were prepared by mixing, in ethanol, the prescribed amounts of commercial powders, 99.95% purity $La_2(CO_3)_3$, 99.9% $SrCO_3$, 99.99% CuO (all from Kojundo Kagaku Co.) and Suprapur $CaCO_3$ (Merck). The mixtures were first calcined at 700 °C for 3 h and heat-treated at 1000 °C for 12 h. For the preparation of the resistivity samples, the calcined powders were pulverized, cold-pressed into disk shapes, and then sintered at 1000 °C for 5 h. All the heat treatments were conducted in air. The color of the obtained powders and sintered bulks were all in deep black. The powder X-ray diffraction analysis confirmed the presence of a single phase with K_2NiF_4 crystal structure in the case of x(Sr)=0.05, whereas a trace or a minor secondary phase $LaCuO_3$ was observed to be present for the rest of the specimens. A monotonic compositional dependence of the tetragonal lattice parameters was recognized in each series of the two systems.

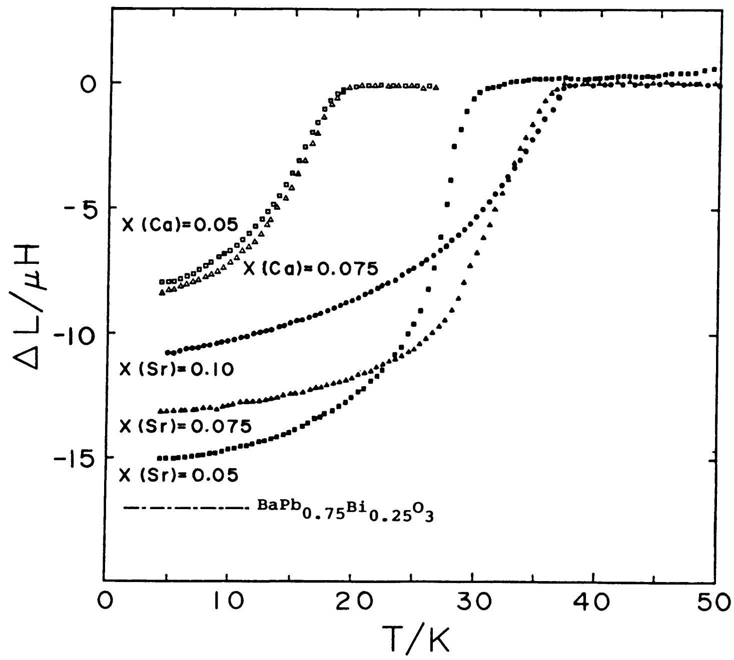

Fig. 1. Shape of the inductance signal in the superconducting transition region for $(La_{1-x}Sr_x)_2CuO_{4-\delta}$ and $(La_{1-x}Ca_x)_2CuO_{4-\delta}$. Net volume of specimens : x(Sr)=0.05 (0.093 cm^3), x(Sr)=0.075 (0.082 cm^3), x(Sr)=0.10 (0.059 cm^3), x(Ca)=0.05 (0.091 cm^3) and x(Ca)=0.075 (0.088 cm^3); $BaPb_{0.75}Bi_{0.25}O_3$ (0.068 cm^3).

The a.c. magnetic susceptibility measurements at 1 kHz with the aid of a commercial L-meter (Kokuyo Electric Co., Ltd., KC-530), were conducted on powder specimens in a cryostat. The inductance of the employed sensing coil (bore diameter, 6 mm) was 310 μH at the room temperature. A typical loading of the specimen powder was about 0.4 g.

The temperature was measured by Au(Fe)-Ag thermocouple. The specimens for the resistivity measurements were cut out of the sintered pelletts and shaped into nearly square rods of about 2x3x10 mm^3. The electrodes for the d.c. four probe method were prepared by evaporating the gold films. The measurements were conducted in a different cryostat, in which the Au(Fe)-Ag thermocouple of the same lot, as was used in the susceptibility measurement, was employed. In one of the resistivity runs, the emf of the thermocouple was simultaneously calibrated against the NBS-calibrated germanium thermometer (Lake Shore Co.).

Figure 1 shows the observed a.c. susceptibility signal expressed as the difference in the inductance of the sensing coil with and without the specimen charged in it. The dotted horizontal line is a rough guide to show the level to which the signal reaches for the case of another superconducting oxide powder of $BaPb_{0.75}Bi_{0.25}O_3$ (T_c=11.7 K) which is known to be a bulk superconductor.[6)] From the figure, it is seen that a specimen with x(Sr)=0.10 shows a sharp increase in the apparent diamagnetic susceptibility at 37 K. The one with x(Sr)=0.05 which was concluded to be a single phase from the X-ray analysis, exhibited the sharpest transition.

No hysteresis was observed in the inductance change with lowering and raising the temperature. Since the particles of the specimens were much finer than those of $BaPb_{0.75}Bi_{0.25}O_3$, the slightly smaller diamagnetic signal for the specimens seems to suggest that the volume fraction of the superconducting region in the present specimens was rather close to unity.

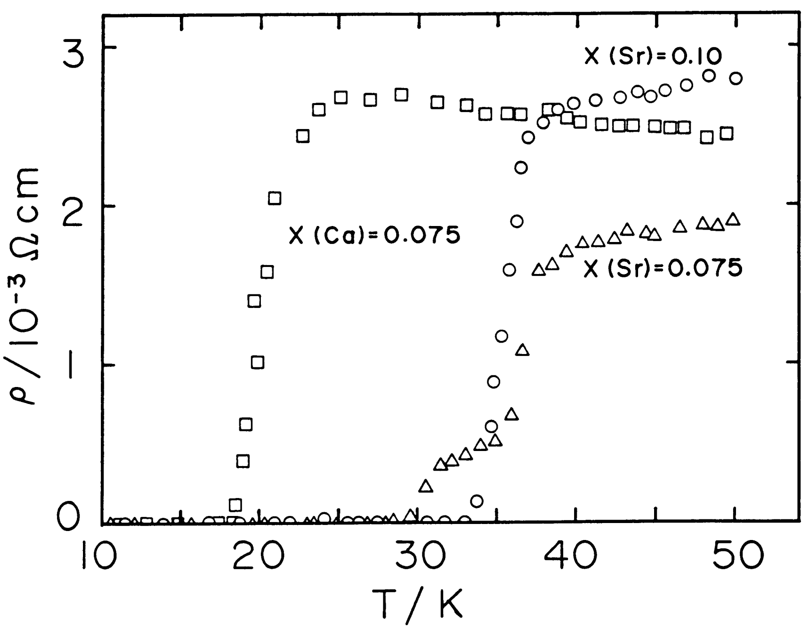

Fig. 2. Resistivity vs. temperature relations of the polycrystalline sintered $(La_{1-x}Sr_x)_2CuO_{4-\delta}$ (x=0.075 and 0.10) and $(La_{1-x}Ca_x)_2CuO_{4-\delta}$ (x=0.075).

Figure 2 represents the observed resistivity for x(Sr)=0.075, 0.100, and x(Ca)=0.075 obtained at gradually raising the temperature. As can be seen in this figure, the specimen with x(Sr)=0.10 exhibits a sharp decrease in resistivity at 37 K which is in agreement with the susceptibility measurement. This is the highest onset T_c among all the superconducting substances ever known. Furthermore, the zero resistivity state survived up to 33 K for the same specimen at the measuring current level of 2.7 mA. This temperature is higher by more than 10 K than that obtained for the recently discovered another high T_c superconducting substance,[2-5] $(La_{1-x}Ba_x)_2CuO_{4-\delta}$, in which 22 K has so far been reported as the highest value.[5] The resistivity curve of x(Ca)=0.075 in Fig.2 again shows the evidence of the presence of the superconductivity.

For all the oxide specimens investigated in this study, the resistivity values at the room temperature are in the range of 5 to 7 x 10^{-3} Ωcm. The resistivity of specimens for x(Sr)=0.075 and x(Sr)=0.10 decreased almost linearly with temperature down to T_c. On the other hand, the temperature dependence of the resistivity for x(Ca)=0.075 was semiconductive below about 80 K.

The deviation of the stoichiometry for the oxygen composition, δ, and its correlation with the parameters for the superconductive behavior of the present oxide systems, $(La_{1-x}[Sr\ or\ Ca]_x)_2CuO_{4-\delta}$, have not been clearly known at present time. These points as well as the characterization of the detailed crystal structures are in progress.

The authors would like to thank Messrs. H. Sato, H. Ishii, H. Yanagisawa, and H. Eisaki of the Department of Applied Physics for performing some of the measurements. The present work has been partially supported by the Grant-in-Aid of Scientific Research, the Special Project Research on New Superconducting Materials, from the Ministry of Education, Science and Culture of Japan.

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(Received December 22, 1986)