High $T_c$ Superconductivity of La–Ba–Cu Oxides

Shin-ichi UCHIDA,¹ Hidenori TAKAGI,⁴ Koichi KITAZAWA⁵
and Shoji TANAKA

Department of Applied Physics, University of Tokyo, Hongo, Tokyo 113
¹Also at Engineering Research Institute, University of Tokyo, Yayoi, Tokyo 113
²Department of Industrial Chemistry, University of Tokyo, Hongo, Tokyo 113
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A broad superconducting transition with an onset near 30 K is observed for La–Ba–Cu oxides in the measurement of magnetic susceptibility. The superconductivity is of bulk nature and reproducible after several heat cycles.

More than a decade has passed since the highest superconducting critical temperature $T_c=23.7$ K was recorded in Nb₃Ge.¹ It is a central subject in today's material science to search for new superconducting materials with higher $T_c$'s because of their expected strong impact on the technology as well as on the science. In recent years the frontier of superconducting materials has continually been extended, giving birth to new classes of materials.²⁻⁴ Heavy fermion superconductors, organic superconductors and compound superconductors having low carrier concentrations are typical examples. However, superconducting $T_c$ has not yet exceeded 15 K in these materials.

Among conducting oxides, two are known to exhibit superconductivity with $T_c$ higher than 10 K. Superconductivity in LiTi₂O₄ with the onset of 13.7 K was reported by Johnston et al. in 1973.⁵ The BaPb₁₋ₓBiₓO₃ system is superconducting for $x<0.35$.⁶ The highest $T_c=13$ K was observed in 1975 by Sleight et al. at $x=0.3$.⁶ In both materials mixed valence or charge disproportionation of Ti and Bi, i.e., (Ti³⁺, Ti⁵⁺) and (Bi³⁺, Bi⁵⁺), is thought to play an essential role bringing about a high-$T_c$ superconducting state.⁷

Another candidate is La–Ba–Cu oxide. This material has been investigated extensively by Michel and his coworkers.⁸ Quite recently Bednorz and Müller⁹ have reported that the Ba–La–Cu–O system with the composition BaₓLa₃₋ₓCu₂O₅₋₃₋y is a potential material as a third high-$T_c$ oxide. Resistivity measurement on polycrystalline samples showed that a sample prepared under a certain condition is superconducting below 13 K. The most interesting fact is that the resistivity starts to decrease at 30 K with lowering temperature. They suggested that this might correspond to an onset of superconductivity in a part of the sample.

In this letter we report the occurrence of high $T_c$ superconductivity in the oxide composed of La, Ba and Cu cations from measurements of magnetic susceptibility. The measurements were made using a SQUID magnetometer (SHE, model 805) on polycrystalline powder specimens at low magnetic fields below 10 Oe to investigate the Meissner effect associated with superconductivity. The temperatures were calibrated using standard superconductors, Pb, Nb and Nb₃Sn. The starting materials were prepared by two methods:

one was a mixing of La₂O₃, BaCO₃ and CuO and the other a coprecipitation from solutions of La-, Ba- and Cu-acetates with oxalic acid in appropriate cation ratios, La:Ba:Cu = (1-x):x:1 in both cases. The starting material with a composition of $x=0.15$ was reacted at 900°C in air. The analysis of X-ray powder diffraction indicated mainly perovskite structure, probably based on (La·Ba)CuO₃, mixed with layer-type perovskite, possibly (La·Ba)₂CuO₄, and a small amount of other unidentified phases.

The sintered powder was then reduced from 30 minutes at 900°C in an Ar–O₂ atmosphere. As compared with the initial powder, the amount of the perovskite phase was considerably reduced relative to the layer-type phase, but the annealed sample is still a mixture of these dominant phases.

Temperature dependences of the susceptibility on typical samples are shown in Figs. 1 and 2. A large diamagnetism was observed in both samples. The diamagnetic response increases with decreasing temperature, still increasing even at 5 K. The magnitude of diamagnetic susceptibility corresponds to about 10% of the perfect diamagnetism ($\chi = -1/4\pi$) for the sample shown in Fig. 1.¹¹ Therefore, about 10% of the total volume of the sample is considered to be in the superconducting state at 5 K. This indicates that the observed superconductivity is probably bulk in nature, although the superconducting state is not formed over the whole

Fig. 1. Magnetic susceptibility of a sample prepared from a mixture of oxides and carbonates as a function of temperature.
specimen.

For the sample shown in Fig. 2, the onset of superconductivity is observed at still higher temperature. Even at 29 K the diamagnetic susceptibility is significantly larger than ordinary diamagnetic contributions, such as a core diamagnetism or a Landau-Peierls diamagnetism. The result is reproducible, exhibiting exactly the same magnetic response after several heat-cycles.

The broad transition observed is probably due to inhomogeneity of the sample, as frequently observed in other oxide superconductors. Thus the result of the magnetic susceptibility indicates that a high-$T_c$ superconducting state is certainly realized in a part of the sample.

Efforts are under way to identify the superconducting phase and to synthesize the material composed of a single phase, as well as to investigate the dependences of $T_c$ on various parameters, Ba composition, oxygen deficiency and annealing conditions.

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References

11) To estimate the susceptibility, we used the mass density of LaCuO$_3$, since the phase exhibiting superconductivity has not yet been identified.