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High-T_c Superconductivity of La–Ba–Cu Oxides. II. —Specification of the Superconducting Phase

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Occurrence of high-T_c superconductivity with T_c near 30 K is observed for the single phase of $(La \cdot Ba)_2CuO_{4-y}$ by both magnetic susceptibility and resistivity measurements. This indicates that high-T_c superconductivity in La–Ba–Cu oxide is realized in the K_2NiF_4-type structure, $(La \cdot Ba)_2CuO_{4-y}$.

In a preceding paper,[1] we observed high-T_c superconductivity with T_c near 30 K in the La–Ba–Cu oxides. This material was suggested by Bednorz and Müller to be a high T_c superconductor as a result of their resistivity measurement.[2] In both cases, the starting material was prepared to have a composition $(La \cdot Ba)CuO_3$ and the products were annealed in low oxygen pressure. The samples were apparently composed of more than two phases; dominantly the perovskite and the layer-perovskite like (K_2NiF_4-type) phase and the annealing of "as-prepared" powders in the cation ratios $(La \cdot Ba)$:Cu=1:1 in a reduced atmosphere results in a remarkable increase in the fraction of the K_2NiF_4-type phase. The superconducting phase, however, has not yet been specified.

In this letter, we present evidence that the K_2NiF_4-type phase, $(La \cdot Ba)_2CuO_{4-y}$, is responsible for the high-T_c superconductivity. We prepared the samples in the cation ratios $(La \cdot Ba)$:Cu=1:1 which were annealed at various oxygen pressures. The volume fraction of the superconducting phase was estimated by measuring the diamagnetic susceptibility. It was found that the increase in the fraction of K_2NiF_4-type phase extimated from X-ray analysis corresponded to the increase in the volume fraction of the superconducting phase. This suggests that the high-T_c superconductivity may be realized in the K_2NiF_4-type phase, probably $(La \cdot Ba)_2CuO_{4-y}$.

In order to confirm the occurrence of the superconductivity in the K_2NiF_4-type phase, we have synthesized a single phase $(La \cdot Ba)_2CuO_{4-y}$. The powdered specimen was prepared by reacting the mixture of La_2O_3, $BaCO_3$ and CuO in cation ratios La:Ba:Cu$=2(1-x):2x:1$ ($x=0$, 0.05, 0.075, 0.10 and 0.15) at 1100°C in air for 24 hours.[3] The X-ray powder diffraction pattern of the prepared sample is shown in Fig. 1, which indicates that almost a single phase with K_2NiF_4-type structure is synthesized. No trace of the perovskite phase nor any other phase is observed.

The results of the magnetic susceptibility measurement on the K_2NiF_4-type single phase with $x=0.075$ is shown in Fig. 2. A rather steep superconducting transition as compared with the previous result is seen at around 29 K. About 30% of the total volume is estimated to be in the superconducting state at 5 K, that is much larger than the previous result. The superconductivity was observed also for the samples with $x=0.05$, 0.10 and 0.15 but not for $x=0$. The effect of the annealing in the reduced atmosphere was examined, and it was found that the annealing results in the disappearance of the superconductivity.

We have also made a resistivity measurement on the

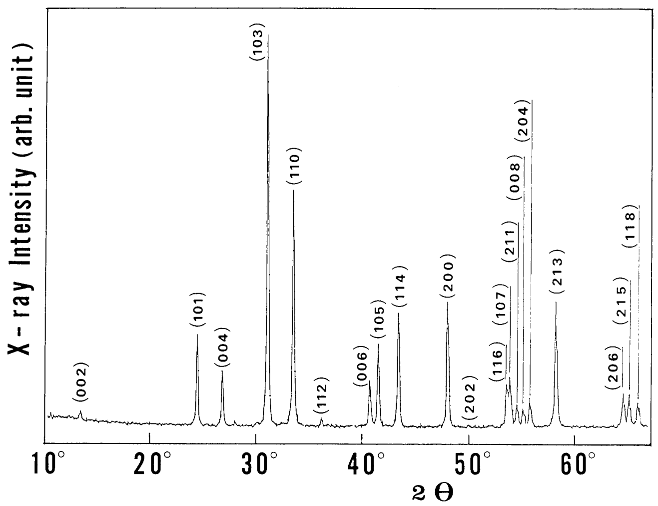

Fig. 1. X-ray powder diffraction pattern of the sample prepared from the mixture of La_2O_3, $BaCO_3$, CuO in cation ratio $(La \cdot Ba)$:Cu=2:1.

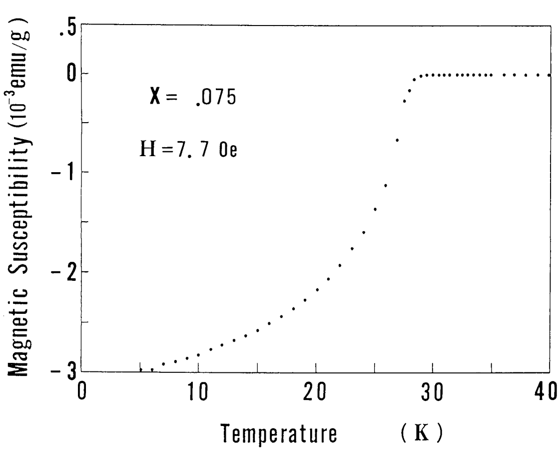

Fig. 2. Temperature dependence of the magnetic susceptibility for the single phase ($x=0.075$) with K_2NiF_4-type structure.

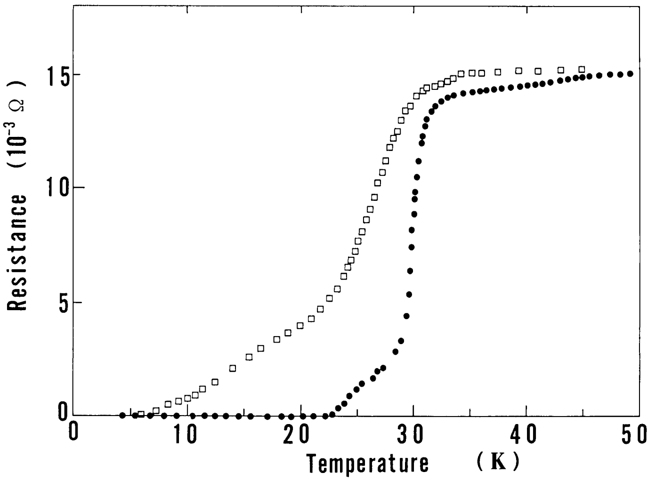

Fig. 3. Temperature dependence of the resistance. Closed circles show the single phase with K_2NiF_4-type structure ($x=0.075$) and open squares show the sample prepared in the manner reported in the preceding paper.[1]

sintered pellet of the powder with $x=0.075$ as shown in Fig. 3. the measurement was made by the usual four-probe method with gold-evaporated electrodes. The resistivity gradually decreases with lowering temperature and then drops abruptly at around 32 K. The resistivity below 22 K is smaller than the limit of our instrumental resolution. Combined with the magnetic susceptibility data, it can be said that the sample is actually superconducting.

We conclude from these results that high-T_c superconductivity is realized in the K_2NiF_4-type phase, $(La \cdot Ba)_2CuO_{4-y}$. In this structure, the substitution of La with Ba will lead to the Cu-mixed-valence state, Cu^{2+}-Cu^{3+}. On the other hand, the reduction of the oxidation degree will bring Cu^{3+} back to Cu^{2+}, destroying the mixed-valence state. Thus, the mixed-valence seems to play an important role in the present high-T_c superconductor as in the case of $LiTi_2O_4$[4] and $BaPb_{1-x}Bi_xO_3$.[5]

The broad transition and the incomplete Meissner effect are probably due to the inhomogeneity in the sample, such as the fluctuation of the La/Ba composition or the oxygen deficiency. Attempts are now in progress to improve the homogeneity as well as to obtain single crystals.

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