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LETTERS TO THE EDITOR

First Synthesis of $Bi_2Sr_2CaCu_2O_y$ with the Highest T_c of 96 K

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By the combination of heat treatment in flowing (99.8% N_2 + 0.2% O_2) gas and in flowing H_2 gas, we have succeeded in synthesizing $Bi_2Sr_2CaCu_2O_y$ having the stoichiometric cation composition with the highest T_c of 96 K among the Bi2212 related compounds prepared so far. The oxygen content y was measured to be 8.72 by the method of coulometric titration. Alternating current magnetic susceptibility measurements for powdered samples revealed that the superconducting transition of this Bi2212 phase is rather sharp and the Meissner volume fraction is comparable with $YBa_2Cu_3O_7$.

Much effort was made unsuccessfully towards preparing the high-T_c $Bi_2Sr_2CaCu_2O_y$ (Bi2212) phase with a stoichiometric cation composition (*1–6*). It was found that substitutions of Pb for Bi (*4*, *7*), or Y for Ca (*4*, *6*, *7*) and/or changing the cation ratio (*8*, *9*) stabilize the high-T_c phase showing superconductivity at 85 ~ 90 K. Their superconducting transition was, however, broad and the superconducting fraction was much smaller than that of the stoichiometric high-T_c compound $YBa_2Cu_3O_7$. To make clear the nature of the superconductivity of the Bi2212 phase, the preparation of a pure Bi2212 phase with a stoichiometric cation composition has been desired. This letter describes the first synthesis of superconducting $Bi_2Sr_2CaCu_2O_y$ (Bi2212) having the stoichiometric cation composition; it has the highest T_c of 96 K among the Bi2212 related compounds prepared so far (*1–10*).

Samples were prepared by solid state reactions of Bi_2O_3, $Sr(NO_3)_2$, $CaCO_3$, and CuO with 99.99% purity. The raw materials with stoichiometric cation composition were mixed thoroughly, pelletized, and heated in air at 600°C for 1 day. Then, the sample thus prepared was again ground and exposed to a heat treatment at 250°C under flowing H_2 gas. After these preliminary reactions, the sample was pelletized, heated at 785°C in flowing (99.8% N_2 + 0.2% O_2) gas for 2 days and cooled rapidly at a rate of about 100°C/min under the same condition of flowing gas. A key point for succeeding in the preparation is the heat treatment under H_2 gas, which produces fine powders and promotes the chemical reactions. The oxygen content y in the chemical formula $Bi_2Sr_2CaCu_2O_y$ was measured to be 8.72 by coulometric titration according to the method of Kurusu *et al.* (*11*). This value seems to be fairly large given the usual valences of the constituent cations. The average valence of Bi was also determined to be +3.16 by the same method. The excess oxygen should cause "hole-doping," although some part of this may be cancelled by an increase of the Bi valency from +3.

In Fig. 1, a typical X-ray diffraction (XRD) pattern is shown; it can be indexed by a pseudotetragonal system (a = 5.410 Å and c = 30.89 Å) with a lattice modulation along the b axis ($\mathbf{k}^* = 0.206\mathbf{b}^*$). No secondary phase, such as $Bi_2Sr_2CuO_y$ and

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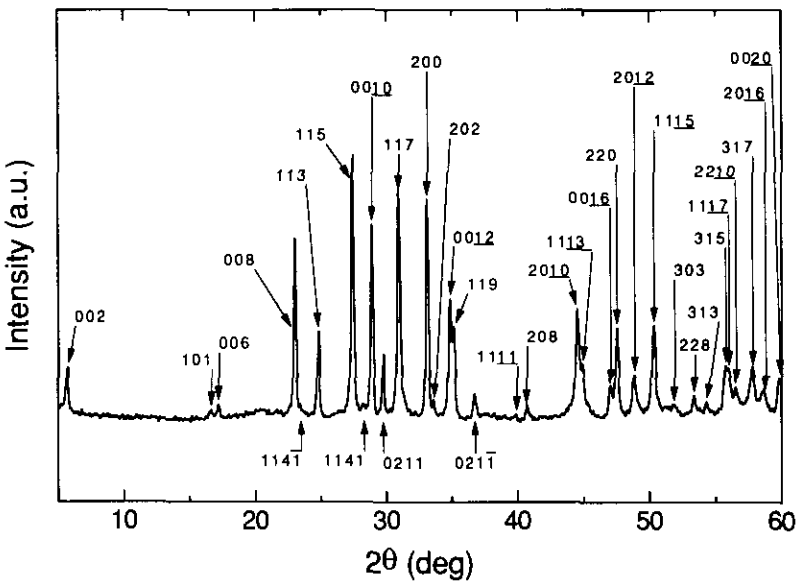

FIG. 1. A typical XRD pattern of $Bi_2Sr_2CaCu_2O_y$ with stoichiometric cation composition using Cu$K\alpha$ radiation. Indices shown above the pattern are based on a pseudotetragonal unit cell with a = 5.410 Å and c = 30.89 Å. As indicated below the pattern, main satellite peaks due to the lattice modulation are indexed with four indices h, k, l and m by $\mathbf{q}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{k}^*$, where $\mathbf{q}^*$ is a diffraction vector and $\mathbf{k}^* = 0.206\mathbf{b}^*$.

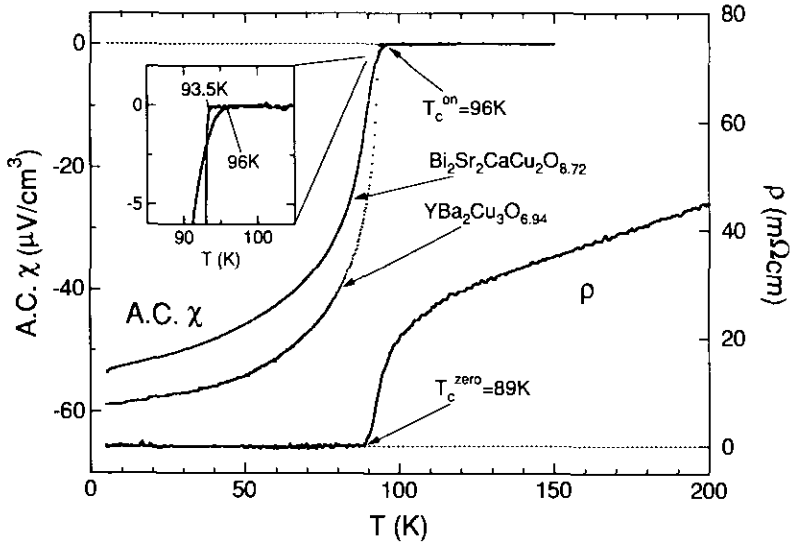

FIG. 2. Temperature dependence of ac χ and electric resistivity ρ of $Bi_2Sr_2CaCu_2O_y$. As a reference, ac χ of $YBa_2Cu_3O_7$ is also indicated. An enlarged graph of ac χ around the superconducting transition is shown as the inset.

Ca_2CuO_3, was detected. The lattice modulation may originate from the existence of excess oxygens in the Bi_2O_2 block as reported by Yamamoto *et al.* (*12*).

Figure 2 shows the temperature dependence of the ac magnetic susceptibility (χ) and electric resistivity (ρ). The ac χ was measured with a conventional Hartshorn bridge under a magnetic field of 10 mOe oscillating at 270 Hz. Powder samples were used in order to exclude the shielding effect due to weak coupling that commonly appears in the case of sintered bulk samples. The ac χ revealed that the superconducting transition is rather sharp, comparable to that of the Bi2212 related compounds reported to date. The onset temperature of the transition, T_c^{on}, is 96 K from the ac χ measurement. On the other hand, T_c^{zero} where the resistivity becomes zero is 89 K as shown in the figure. These values are the highest reported so far for the Bi2212 related compounds. Moreover, the value of the superconducting fraction is high and comparable with that of $YBa_2Cu_3O_7$. Thus, we have succeeded in synthesizing an intrinsic superconductive Bi2212 phase with a stoichiometric cation composition. Preliminary experiment indicates that the oxygen content can be reduced to $y = 8.25$ by heating at 777°C under flowing, high-purity nitrogen gas; the T_c for the reduced Bi2212 does not change much. Investigation of the dependence of chemical and physical properties on oxygen content is now in progress.

References

1. H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, *Jpn. J. Appl. Phys.* **27,** L209 (1988).
2. J. M. Tarascon, Y. Le Page, P. Barboux, B. G. Bagley, L. H. Greene, W. R. McKinnon, G. W. Hull, M. Giroud, and D. M. Hwang, *Phys. Rev. B* **37,** 9382 (1988).
3. H. Nagano, R. Liang, Y. Matsunaga, M. Sugiyama, M. Itoh, and T. Nakamura, *Jpn. J. Appl. Phys.* **28,** L364 (1989).
4. H. W. Zandbergen, W. A. Groen, A. Smit, and G. van Tendeloo, *Physica C* **168,** 426 (1990).
5. G. Triscone, J.-Y. Genoud, T. Graf, A. Junod, and J. Muller, *Physica C* **176,** 247 (1991).
6. H. Mazaki, M. Kakihana, and H. Yasuoka, *Jpn. J. Appl. Phys.* **30,** 38 (1991).
7. A. Maeda, M. Hase, I. Tsukada, K. Noda, S. Takebayashi, and K. Uchinokura, *Phys. Rev. B* **41,** 6418 (1990).
8. Y. Idemoto and K. Fueki, *Physica C* **168,** 167 (1990).
9. F. A. Karbarz, O. D. Lacy, K. C. Goretta, U. Balachandran, S. Donglu, J. G. Chen, X. Ming, and M. C. Hash, *Mater. Res. Bull.* **25,** 251 (1990).
10. T. Ishida, K. Koga, S. Nakamura, Y. Iye, K. Kanoda, S. Okui, T. Takahashi, T. Oashi, and K. Kumagai, *Physica C* **176,** 24 (1991).
11. K. Kurusu, H. Takami, and K. Shintomi, *Analyst* **114,** 1341 (1989).
12. A. Yamamoto, M. Onoda, E. Takayama-Muromachi, F. Izumi, T. Ishigaki, and H. Asano, *Phys. Rev. B* **42,** 4228 (1990).