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A New High-T_c Oxide Superconductor without a Rare Earth Element

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We have discovered a new high-T_c oxide superconductor of the Bi–Sr–Ca–Cu–O system without any rare earth element. The oxide $BiSrCaCu_2O_x$ has T_c of about 105 K, higher than that of $YBa_2Cu_3O_7$ by more than 10 K. In this oxide, the coexistence of Sr and Ca is necessary to obtain high T_c.

KEYWORDS: oxide superconductor, Bi–Sr–Ca–Cu–O system, rare earth, high T_c, new stable superconductor

Soon after the discovery of high-T_c superconductors of the layered perovskites $(LaBa)_2CuO_4$[1)] and $(LaSr)_2CuO_4$[2)] with T_c of about 40 K, $YBa_2Cu_3O_7$[3)] with T_c of 94 K was synthesized. The discovery of these materials stimulated many researchers to investigate new oxide superconductors of still higher T_c and extensive studies have been carried out to search for these oxides. Up to now, however, no new stable supercondutors with T_c higher than that of $YBa_2Cu_3O_7$ have been reported. The values of T_c have not improved by the substitution of other rare earth elements for yttrium.

In order to find high-T_c superconductors, we believe that it is important to investigate other classes of oxides which do not include rare earth elements. This led us to study the superconducting oxide system including the Vb-element group such as Bi and Sb of trivalent elements, and we discovered a new high-T_c superconducting material $BiSrCaCu_2O_y$. This oxide has T_c of about 105 K, being higher than that of $YBa_2Cu_3O_7$ by more than 10 K.

The value of T_c in the Bi–Sr–Cu–O oxide system which does not include Ca is very low being about 8 K.[4,5)] In order to obtain high T_c, the coexistance of Sr and Ca in the Bi oxide system is found to be absolutely necessary.

The Bi–Sr–Ca–Cu–O oxide samples were prepared from powder reagents of Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO. The appropriate amounts of powders were mixed, calcined at 800–870°C for 5 h, thoroughly reground and then cold-pressed into disk-shape pellets (20 mm in diameter and 2 mm in thickness) at a pressure of 2 ton/cm^2. Most of the pellets were sintered at about 870°C in air or in an oxygen atmosphere and then furnace-cooled to room temperature.

The electrical resistivity was measured by the standard four-probe method for a bar-shaped specimen of about $1\times2\times20$ mm^3 cut out from the pellets. Magnetization measurements were carried out with a vibrating sample magnetometer. The temperature was measured by Au7%Fe-Chromel thermocouples. Figure 1 shows the resistivity vs temperatue curves of $BiSrCaCu_2O_x$ oxides thus prepared. Specimen (a) was sintered at a relatively low temperature of 800°C for 8 h while specimen (b) was sintered at a higher temperature of 882°C for 20 min followed by annealing at 872°C for 9 h. In the case of the lower sintering temperatue, the onset temperature (T_c^{on}) of the superconducting transition is about 83 K and the zero resistance state (T_c^{off}) is reached at 75 K (low-T_c phase). On the other hand, in the case of a higher sintering temperature, a high-T_c phase appears, the onset temperature of which is about 120 K and T_c extraporated to zero resistance is as high as 105 K. The value of T_c^{off} is higher than that of $YBa_2Cu_3O_7$ by more than 10 K. Since a little amount of the low-T_c phase still remained in the sample, a complete zero resistance state is achieved at 75 K which corresponds to that of the low-T_c phase. We have not succeeded in synthesizing the oxides with a single phase of the high-T_c material at this moment. From our preliminary experiments, we know that sintering at high temperatures for a short duration of time is effective enough to increase the relative amount of the high-T_c phase. This may indicate that the high-T_c phase is stable at elevated temperatures.

Figure 2 shows the magnetization vs temperature curve for the specimen (b) in Fig. 1 which was sintered at the higher temperatures. A Meissner effect showing a perfect diamagnetic state is observed exactly in the same temperature range as in curve (a) shown in Fig. 1. We conclude, therefore, that the present high-T_c phase is indeed superconducting.

The high-T_c phase appears near the composition ratios of Bi:Sr:Ca = 1:1:1. As the composition deviates from

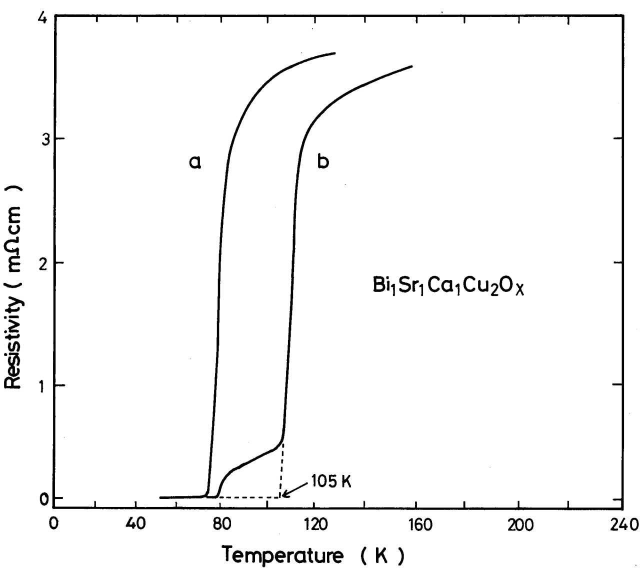

Fig. 1. Temperature dependence of resistivities in $Bi_1Sr_1Ca_1Cu_2O_x$ oxides (a) sintered in air at 800°C for 8 h, then cooled in a furnace and (b) sintered at 882°C for 20 min followed by annealing at 872°C for 9 h.

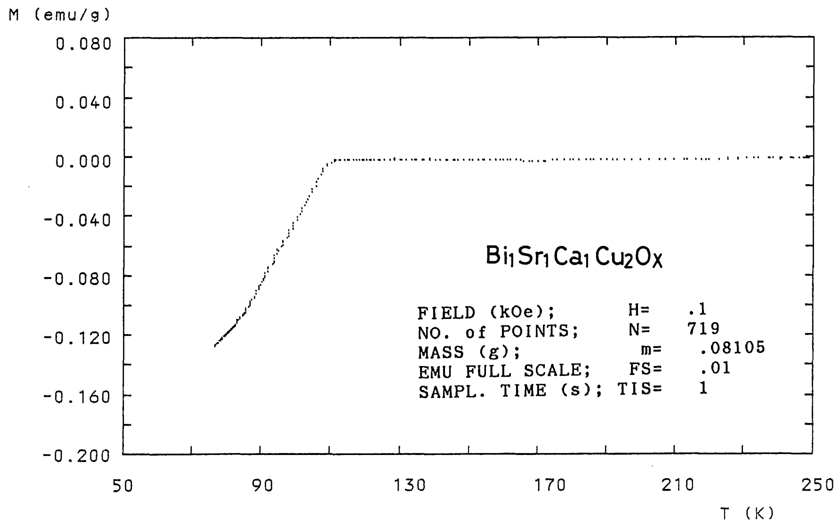

Fig. 2. Magnetization of $Bi_1Sr_1Ca_1Cu_2O_x$ for the sample (b) in Fig. 1 in a field of 100 Oe.

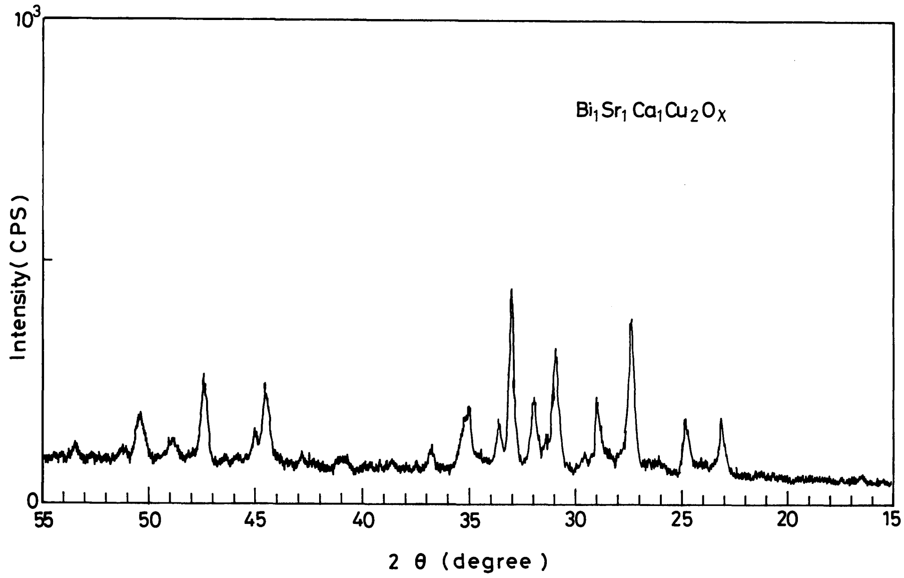

Fig. 3. X-ray (Cu kα) diffraction pattern of the $Bi_1Sr_1Ca_1Cu_2O_x$ oxide superconductor for the sample (b) in Fig. 1.

this ratio, a low-T_c phase tends to appear irrespective of the sintering conditions. In $BiSrCaCu_yO_x$ oxides, the oxide of $y=1$ is not superconducting. According to the results of the X-ray diffraction analyses, the starting material corresponding to the composition of $Bi_1Sr_1Ca_1Cu_2O_x$ seems to form a single phase. While in the nominal composition of oxides with $y>2$, unreacted CuO remained in the sample. A typical X-ray diffraction pattern for the oxide of $y=2$ (sample (b) in Fig. 1) is shown in Fig. 3. Although the structure of this oxide is not identified yet, it appears to be different from those of $(LaSr)_2CuO_4$ and $YBa_2Cu_3O_7$.

This material having high T_c above 105 K may have potential application in various industrial fields in the near future. It should be noted that these oxides are extremely stable in water and moisture and that no change in the superconducting properties has been observed even after the thermal cyclings between 4 K and room temperature or above.

Furthermore, the oxide has two phases with different T_c and their structures seem to be different from those of high-T_c oxide superconductors discovered up to now. We believe that this new oxide will contribute greatly to elucidating the high-T_c superconducting mechanism.

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