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HIGH TEMPERATURE SUPERCONDUCTIVITY IN THE COMPOUND $(BiCaSr)Cu_xO_y$

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An onset of superconductivity at 90 K and a zero resistance at 72 K were observed in the new high T_c compound $BiCaSrCu_xO_y$. No evidence was found for a sharp resistance drop above 100K as reported by Maeda et al. A maximum in the T_c value was measured for a Cu fraction x = 2. Quenching experiments reveal that also in this compound the oxygen content is crucial for a high T_c.

After many years of intense search, superconductors with a transition temperature higher than 30 K in the La-Ba-Cu-O compound [1] and higher than 90K in the single phase $(RE)Ba_2Cu_3O_7$ compound, with RE = Y, Gd, Ho, Dy, Yb, Lu, ... [2,3] have been discovered. Since this explosion of the high T_c superconductors, numerous groups reported extremely unstable phases of the $(RE)Ba_2Cu_3O_7$compounds, displaying signals indicative of superconductivity at much higher temperatures [4,5]. Exotic compounds such as Y-Ba-F-Cu-O [6,7], Ba-K-Bi-O [8] were also investigated in order to search for higher T_c values. In this paper we report on the new superconducting $BiCaSrCu_xO_y$ oxide compound with a maximum onset temperature $T_{co} \simeq 90$ K, and reaching a zero resistance state at $T_{cf} \simeq 70$ K. The sharp drop in resistance at 105 K as reported by Maeda et al [9] could not be reproduced. We discuss the influence of the preparation on T_c, as well as the transport and diagmagnetic properties of this new high T_c compound.

The $BiCaSrCu_xO_y$ compounds with nominal composition were prepared through a solid state reaction of the appropriate amounts of pro analysis Bi_2O_3, CaO or $CaCO_3$, $SrCO_3$ and CuO. We explored a variety of preparation conditions and obtained our best results as follows. The pure powders were rigorously mixed in atomic ratios of Bi/Ca/Sr/Cu = 1/1/1/2 and pressed into pellets (typically 1 cm in diameter and 2mm thick) and heated in flowing oxygen at 880°C for 9 hours. The furnace was allowed to cool down slowly to room temperature over a period of 10 hours yielding black pellets. In comparison to the Y-Ba-Cu-O system, the new materials are considerably more sensitive to the preparative details and we observed a wide range of transition temperatures throughout the course of this work.

The critical temperature was determined by an inductive and a resistive method. The rf susceptibility (frequency : 26.5 MHz) is measured by observing the change in eigenfrequency of a L-C circuit which is driven by a back diode (stability = 3Hz). Using a He flow cryostat, measurements between 300 K and 20 K can be performed. The temperature is measured by a calibrated platinum resistor. A four terminal dc measurement was used to determine the resistance. Bar samples of dimensions 10mm×1mm×2mm were cut from the sintered pellets, and silver paint was used for the electrical contacts. The sample current was of the order of 10mA.

The onset of the superconducting ordering has been obtained from the rf susceptibility measurements. The critical temperature T_c is defined as the onset of an important frequency change in the L-C circuit. Our experiments indicate that the critical temperature of the $BiSrCaCu_xO_y$ compound is largely determined by the sintering conditions (annealing temperature and cooling rate) as well as the Cu content.

Starting from $SrCO_3$, Bi_2O_3, CaO (or $CaCO_3$) and CuO powders, we prepared several $BiSrCaCu_xO_y$ samples with a copper content x varying between 1.5 and 3, while keeping the same sintering conditions. In a first set of experiments, our samples were fired at 800°C for 8 hours and subsequently furnace cooled (10 hours). From Fig. 1 it is clear that, for these preparation conditions, the T_c values obtained from susceptibility measurements are nearly independent of the Cu fraction. A second set of samples were fired at 870°C for 3 hours and subsequently furnace cooled. Most of these samples showed signs of partial melting, an effect which becomes more important when the Cu fraction decreases. The critical temperature clearly reaches a maximum for x=2 (see

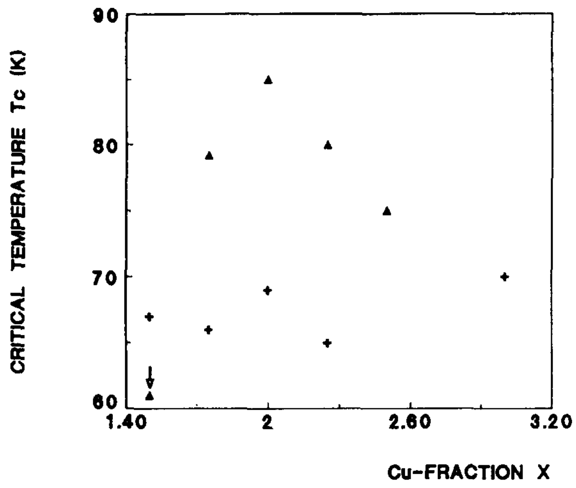

Fig.1 Influence of the Cu-fraction x and the annealing conditions (▲ 880°C ; + 800°) on the critical temperature.

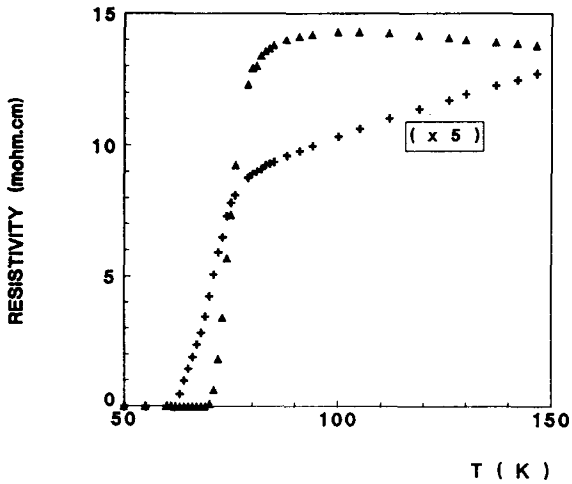

Fig.2 Resistivity versus temperature for $BiCaSrCu_2O_y$ sample 19 (+) and 26 (▲). The resistivity of sample 26 is scaled up by a factor of 5.

Fig. 1). We note that for x=1.5 no sign of superconductivity was observed above 10 K.

It is well known that for $YBa_2Cu_3O_7$ material the tetragonal- orthorhombic phase transformation occuring around 750°C [10], is essential to obtain the high T_c phase. Therefore, we have checked whether fast cooling in oxygen after sintering at 880°C destroys the high T_c superconductivity. For a cooling rate slower than 1°C/s , the superconducting properties remain essentially unchanged. When the cooling rate is increased to 10°C/s, no sign of superconductivity is observed above 40 K. This indicates that also for these compounds the proper amount of oxygen has to be included in the material structure. Preliminary oxygen evolution experiments confirm that the samples absorb oxygen around 500°C.

We have also studied in detail the temperature dependence of the resistivity in the $BiCaSrCu_2O_y$ compounds for different annealing treatments (Fig. 2). Table I contains an overview of the results obtained for four typical samples. The resistivity ρ is measured at T_{co} ; T_{co} corresponds to the temperature where the first sign of superconductivity is observed ; T_{cf} is the temperature where the superconducting transition is complete. The samples showing a metallic resistance behaviour have a resistivity value which is comparable to the values reported for $YBa_2Cu_3O_7$. From our resistivity measurements we may conclude that except for the sample which shows a semiconducting behaviour above T_{co} ($\rho \simeq 14$ mΩcm), no sign of superconductivity is observed at the T_c value reported for the $YBa_2Cu_3O_7$ compound. The high T_{co} value for the semiconducting sample may be explained by the presence of superconducting fluctuations in a granular material structure. On the other hand, we also note that this sample was sintered at a temperature which is very close to the melting temperature of the Bi component. The Bi content which is present in the superconducting phase can therefore be smaller than in the metallic samples.

Table 1: Annealing conditions and critical temperatures

sample	Annealing * conditions	ρ (mΩ cm)	T_{co} (K)	$T_{c(50\%)}$ (K)	T_{cf} (K)
14	800°C (4h) 800°C (8h)	1.7	75	65	59
19	idem 14 cooling (1°C/s)	1.7	84	70	64
25	890°C (20') 880°C (9 h)	4.2	76	65	61
26	890°C (9 h)	14	90	75	71

* All samples furnace cooled except sample 19

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