High $T_c$ Superconductivity in Metallic Oxide Compounds

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Different preparation techniques were elaborated for obtaining La-Ba-Cu-O, La-Sr-Cu-O, Y-Ba-Cu-O, Y-Sr-Cu-O, Y-La-Ba-Cu-O and Y-La-Ba-Sr-Cu-O metallic oxide superconductors. Physical and chemical properties of them were analysed by thermogravimetry, powder X-ray, SEM, electron microprobe and SIMS which hint at a multiple-phase structure of the compounds in question. $T_c$ for one part of samples is higher than 50 K and for the other part falls into liquid nitrogen temperature range above 90 K. Superconductivity was confirmed by magnetic measurements too. A change in Fermi-surface topology due to the increasing additive material content and a supplementary percolation process can be treated as the main effects for high-$T_c$ superconductivity.

The first La-Ba-Cu-O and La-Sr-Cu-O experiments [1,2,3] has motivated further experimental and theoretical studies on high-temperature superconductivity. Among them the aim of our investigations was to find the possible higher-$T_c$ superconductors and to find out the effect of the preparation technique and of the compositon on the superconducting parameters.

In order to avoid the uncertainty concerning the working samples a well-considered preparation technique and a systematic analytical investigation were elaborated.

Because of this, the optimum value of ionic radii, of the substitution of lanthanides with alkaline earths and that of the ratio of lanthanides plus alkaline earths to the copper and the redox processes of Cu were taken into account during the preparation process.

Although the "hot" metallic oxide superconductors provided very valuable results to date, but the preparation techniques are not unambiguous in the meaning of preparative chemistry and the samples are not ever reproducible. This recognition led us to perform systematic chemical and physical investigations in order to find the methods and compositions giving higher than earlier $T_c$ in oxide compounds.

To this date the following types of compounds were prepared and measured:

1. (La$_{1.6}$Ba$_{0.4}$)CuO$_4$-6
2. (La$_{0.8}$Ba$_{0.2}$)CuO$_4$-6
3. (La$_{1.8}$Sr$_{0.2}$)CuO$_4$-6
4. (La$_{0.8}$Sr$_{0.2}$)CuO$_4$-6
5. (Y$_{1.2}$Ba$_{0.8}$)CuO$_4$-6
6. (Y$_{0.6}$Ba$_{0.2}$)CuO$_4$-6
7. (Y$_{0.8}$Ba$_{0.2}$)CuO$_4$-6
8. (Y$_{1.6}$Sr$_{0.4}$)CuO$_4$-6
9. (Y$_{0.4}$La$_{0.4}$Ba$_{0.2}$)CuO$_4$-6
10. (Y$_{0.4}$La$_{0.4}$Sr$_{0.2}$)CuO$_4$-6

Two kinds of La-based and three kinds of Y-based oxide systems can be found to be successful in this respect, namely compounds 1, 2, 5, 6, and 7. The La-Sr samples did not exhibit superconductivity or $T_c$ has usual values, the Y-Sr compound was not superconducting and the multi-component samples 9 and 10 do not have superconductivity until liquid nitrogen temperatures.

The La-Ba-Cu-O samples prepared by the solid state reaction method from starting materials/pure Merck's chemicals/ La$_2$O$_3$, BaCO$_3$, CuO for kind I samples, La$_2$O$_3$, Ba(NO$_3$)$_2$, CuO/NO$_3$$_2$/3H$_2$O for kind II samples. The weighing quantities were chosen so that the ratio of (La+Ba)/Cu was 2/1 in kind I and 1/1 in kind II samples. These mixtures were pulverized and homogenized in an agate mortar. Thermogravimetric analysis of the powders was done in temperature interval of 100$^\circ$C-1500$^\circ$C with the aim to determine the optimum temperature for solid state reaction. On the basis of thermogravimetric data, the heat treatment for both kinds of samples were accomplished at 900$^\circ$C for 14 h in ambient atmosphere in quartz crucibles. The furnace was heated up gradually during 3 h.

A powder x-ray diffraction after pulverizing the reacted mixtures unambiguously demonstrates the microcrystalline structure of the samples and the absence of amorphous phases. The reacted powders were then pressed into pellets of 13 mm diameter and 1 mm thickness on 20 kbar pressure in the circumstances of vacuum. The pellets were sintered again at 900$^\circ$C for 14 h and cooled after this process in the furnace to room temperature.

A similar but not the same method was used for the preparation of Y-based compounds.

By analyzing pictures one can come to the conclusion that lower ratio of (La+Ba)/Cu or (Y+Ba)/Cu is more favourable for the parameters of superconductivity. This is supported by experiments.

The dependence of resistance on temperature was measured by a conventional four-point technique in La-samples, where the electrical leads were attached to the peri-
Fig. 1.

Fig. 2.

phy of the samples. On the other hand, in the case of Y-samples, a six-probe arrangement was used based on evaporated gold contacts.

Results for the dependence of the resistivity R on temperature T are demonstrated in Fig. 1 and 2. The drop of resistance starts at $T(I) = 51.2$ K and $T(II) = 56$ K for La-based oxides and the zero-resistivity state is reached at $T(I) = 49$ K and $T(III) = 53$ K. Using the midpoint method, the critical temperature has a value of $T_c = 50.2$ K or $T(II) = 54.5$ K for kind (I) or for kind (II) respectively. The Y-based samples have similar slope for the resistivity-temperature curves and $T^O = 90.5$ K, $T^I = 80.8$ K, $T^C = 94.4$ K and $T^C = 88.2$ K. From these values of critical temperature results as $T_c = 85.8$ K and $T_c = 88.6$ K.

Magnetic measurements were performed at temperature of 4.2 K. It can be stated that the external magnetic field penetrates into the samples and that about 10 vol.% or 13 vol.% for the La-samples and at least 18 vol.% or 23 vol.% for the Y-samples are in Meissner's state at this temperature.

A measurement accomplished in 7 days after the preparation of a new kind multiple-phase (Y$_{0.8}$Ba$_{0.2}$)(Cu$_{0.4}$O$_{2.4}$)$_2$ sample showed a high-temperature zero-resistivity state at 105 K with an onset of 173 K. Magnetic investigation demonstrates a partial penetration of the external field which is 79 vol.% at 77 K in 762 Oe.

Repeating measurements in 4 days later a shift of the onset by amount of 3 K was observed, zero-resistivity occurred at 101 K and the shape of the curve R-T also changed a little. These hint at unstable and changing in time phases.

During the third experiment, resistivity of the sample increased continuously with decreasing temperature until 77 K, which means that the superconductivity ceased in 22 days after preparation.

Depending on these investigations, a supposition seems to be admissible, by which the contribution of Ba ions modifies the Fermi-surface of the originally semiconducting La-Cu-O and Y-Cu-O systems so as to become superconducting. Moreover it must be noted, that a percolation process can probably play a role in this transition.

An interesting phenomenon was observed during this study, namely the temporal instability of the phases. Notably some of the samples lost their superconducting character at room temperature in 6-15 days after preparation. An increase in the onset temperature of some Y-based samples by the amount of 2-3 K was also experienced on the effect of cooling down and heating up during the experiments.

The change in Fermi-surface topology due to the additive material of Ba can be taken as the main reason of the occing high-$T_c$ superconductivity, which is supplemented by a percolation process.

In these multiple-phase structures probably only one of the phases is responsible for superconductivity.

REFERENCES