

PREPARATION AND CHARACTERIZATION OF Ca AND Sr DOPED $Y_{1-x} M_x Ba_2 Cu_3 O_{7-d}$ MATERIALS

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ABSTRACT

A series of samples which have the general formula $Y_{1-x} M_x Ba_2 Cu_3 O_{7-d}$ where $M = Ca$ or Sr , $x = 0.0, 0.1, 0.2, 0.3$ and 0.4 and $d = \text{oxygen deficiency}$ has been prepared. Investigations of the samples to study the difference between Ca and Sr substitutions have been carried out by means of D.C. resistivity, A.C. susceptibility, X-ray diffraction and Infra Red measurements. Results shows that the Ca doped samples have lower resistivity in general and they are superconductors at liquid nitrogen temperature but Sr doped samples were not superconductors down to $L.N_2$ temperature.

INTRODUCTION

Following the discovery of Benors and Muller (1) of superconducting materials with $T_c = 30$ K several attempts have been carried out (2-5) to find other superconducting materials and to increase the critical temperature T_c value. The authors have participated in this race (6-13) by doping the superconducting compounds $Y_1 Ba_2 Cu_3 O_{7-d}$ and $Tl_2 Ba_2 Ca_2 Cu_3 O_{10-d}$ with differnt elemnts to study the transport properties and increase the T_c value.

The effects of doping the YBCO system with Ca and Sr on the T_c value and the effect of annealing on the samples stability have been studied. Ion sizes might be the dominant factor controlling the doping ion site selection, e.g. Ca^{2+} is closer in size to Y^{+3} than to Ba^{+2} , i.e. Ca ions are more likley to replace Y sites than Ba or Cu sites.

SAMPLES PREPARATION

All samples were prepared by solid state reaction method. Starting materials were $Y_2 O_3$, $Ca CO_3$, $Ba CO_3$, CuO and $Sr CO_3$. Powders were mixed according to the appropriate ratios of the general formula $Y_{1-x} M_x Ba_2 Cu_3 O_{7-d}$ with $M = Ca, Sr$ and $x = 0.1, 0.2, 0.3$ and 0.4 . After grinding, the powder was first heated to $940^\circ C$ in air for at least 12 hours. Then the furnace was cooled down to room temperature and the powder was reground and made into pellets under 5 tons pressure (300 kg/cm^2). All pellets were then sintered in a following atmosphere of oxygen at $940^\circ C$ for another 12 hours or longer, (where

longer is the better). The rate of temperature increase and decrease was $150^\circ C/\text{hour}$.

Two samples of the general formula $Y_1 Ba_{2-x} M_x Cu_3 O_{7-d}$ where $M = Ca, Sr$ with $x = 0.5$ were prepared with the same heat treatment described above, but they did not exhibit superconductivity when tested by the floating magnet at $L.N_2$ temperature.

All Ca and Sr doped samples with $x=0.0$ $x=0.1$, $x=, 0.2$, $x=0.3$ and $x=0.4$ have undergone a second heat treatment. Those samples were reground and made into pellets, then they were sintered and annealed in a flowing atmosphere of oxygen under the same conditions described above.

RESULTS AND DISCUSSION

A. X-Ray Diffraction

The samples have been examined by X-ray diffraction, and when compared with other results (15,16) they show peaks corresponding to extra phases particularly the Sr doped samples have non superconducting phases. Figure (1-a), Figure (1-b) show X-ray diffraction patterns for Ca and Sr doped samples with $x=0.3$. Peaks around $2\theta = 24$ degree appear in the profile indicating the existance of a possible extra phase in both samples. However the intensity of the peak is weaker in Ca-doped sample than in Sr-doped sample which is consistent with the results obtained by resistance measurement by the simple two-point contact method.

B- Resistance Measurements

Resistance of all samples were checked by simple measurement. The Sr-doped samples gave higher resistance than the Ca-doped samples of the same concentration, this is much evident in the cases where doping exceeds 0.3.

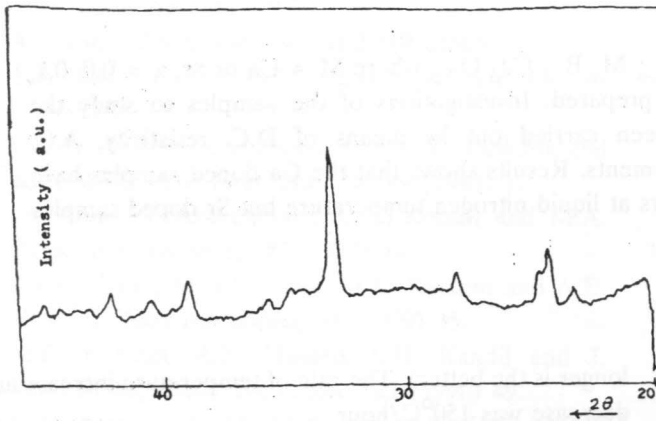


Figure 1-a. X-ray diffraction for calcium doped sample with $x=0.3$.

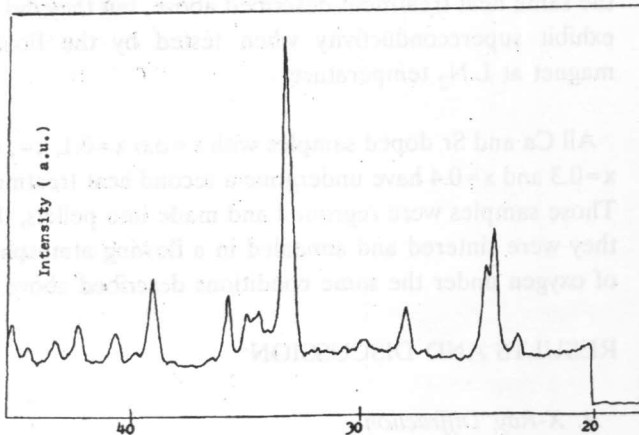


Figure 1-b. X-ray diffraction for strontium doped sample with $x=0.3$.

Temperature dependence of resistance for all samples was carried out in the range from room temperature down to 65 K after the first and second heat treatments. Sr-doped samples did not show superconductivity, but Ca-doped samples were superconductors around liquid nitrogen temperature (78 K) and the undoped sample ($x=0$) was also superconductor but with higher critical temperature value.

Figure (2-a) and Figure (2-b) show the temperature

dependence of the D.C. resistance for the Ca-doped sample with $x=0.1$ after the second heat treatment. The sample clearly shows metallic behaviour with sharp transition around 84 K then the resistance slowly decreases and goes to zero at about 75 K. The transition tail could be due to low T_c phase which may be confirmed by the I.R. Measurements.

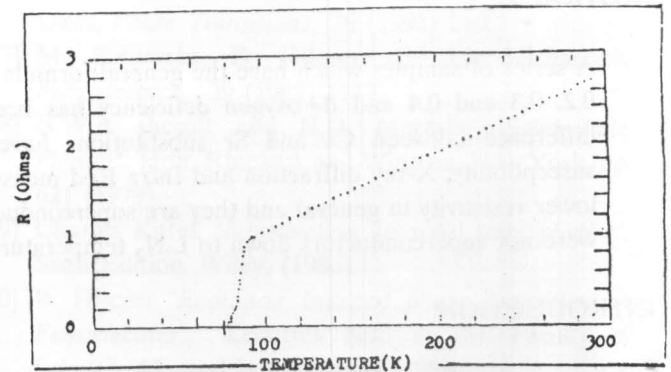


Figure 2-a. D.C. resistance versus temperature for sample $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-d}$.

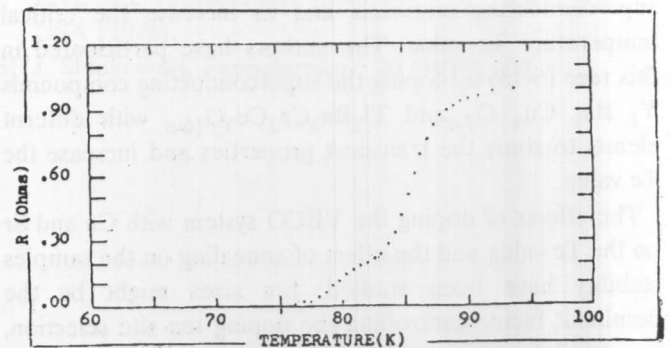


Figure 2-b. D.C. resistance versus temperature for sample $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-d}$.

The Ca-doped sample with $x=0.2$ which is superconductor was reground pressed, sintered and annealed as described above, surprising enough this sample, after the third heat treatment has lost its superconducting behaviour but showed non-superconductivity behaviour down to L.N₂₂ temperature. This sample was expected to show better superconducting behaviour but this semiconductivity is probably due to oxygen deficiency during the third heat treatment. The above results indicate that the extra sintering and annealing in O₂ atmosphere in this experiment seems unfavorable for forming superconducting phases, the other Ca-doped samples with higher Ca concentrations

($x=0.3, x=0.4$) showed a sharp fall of resistance at LN₂ temperature but did not reach zero resistance which indicates superconductivity in addition to non-superconducting phases (according to the percolation theory as confirmed by the X-ray diffraction pattern for Ca-doped sample with $x=0.3$).

C. A.c. Susceptibility Measurements

Meissner effect was checked by measuring the A.C. susceptibility against temperature for the undoped sample $Y_1 Ba_2 Cu_3 O_{7-d}$ at different magnetic fields (0.025, 0.075 and 0.25 Oe) at frequency 131 Hz. In Figure (3-a) the real part of the susceptibility shows that the T_c decreases with increasing magnetic field, and the transition width increases also with the magnetic field which indicates a weak link between the grains. The broad transition is probably due to the inhomogeneity.

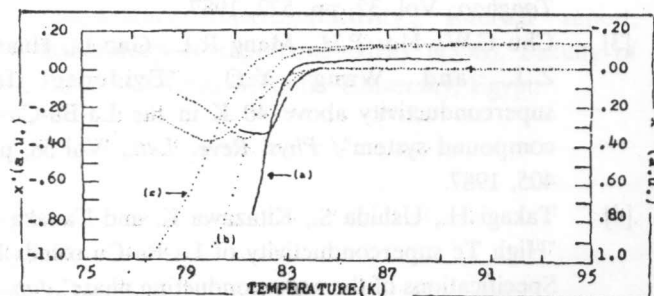


Figure 3-a. A.C. susceptibility at different magnetic fields for sample $Y_1 Ba_2 Cu_3 O_{7-d}$ at a- 0.025 b- 0.075 c- 0.25 Oe.

Figure (3-b) illustrates the decrease of T_c with increasing magnetic field for this undoped sample.

The A.C. susceptibility was also measured for the Ca-doped samples which confirms the superconducting behaviour. The real part of the susceptibility for the Ca-doped sample with $x=0.3$ is shown against temperature in

Figure (3-c) and again the T_c is lower than the undoped sample, also with indication of inhomogeneity.

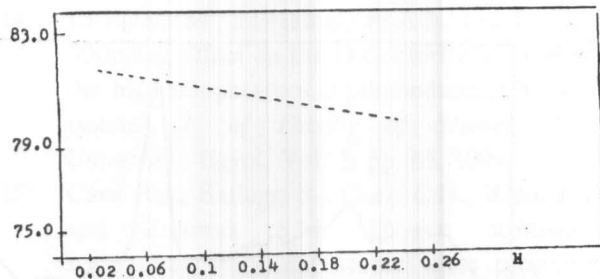


Figure 3-b. The critical temperature versus magnetic field for the Ca-doped sample with $x=0.3$.

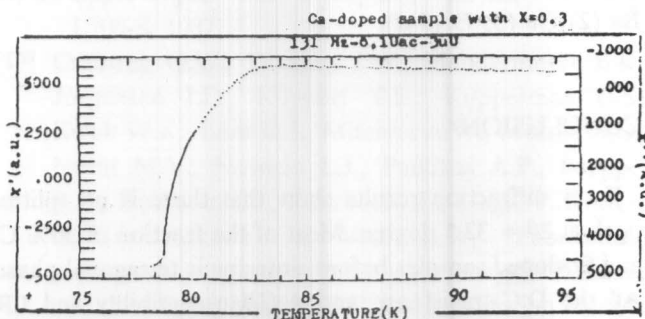


Figure 3-c. A.C. magnetic susceptibility for sample $Y_{0.7} Ca_{0.3} Ba_2 Cu_3 O_{7-d}$.

D. Infra Red Spectroscopy.

Sample for transmission infra red spectroscopy were prepared with about 1% by wt. of the Ca-doped samples and about 99% by wt. of KBr. Samples were transparent enough. First the KBr background spectrum was scanned and then it is subtracted from the mixture of sample with KBr to get the spectrum of the sample. Figure (4) shows the spectrum for the sample with the formula $Y_{0.9} Ca_{0.1} Ba_2 Cu_3 O_{7-d}$ with a peak at a wavenumber $\gamma = 600 \text{ cm}^{-1}$ belongs to unreacted phase $Y_1 Ba_2 Cu_3 O_{7-d}$. However this peak is not much resolved due to the depression of orthorhombic phase. There is another peak at $\gamma = 800 \text{ cm}^{-1}$ due to a second phase in the sample. The estimated oxygen content was found by this method to be near 6.8 which agrees with obtained by iodometric method.

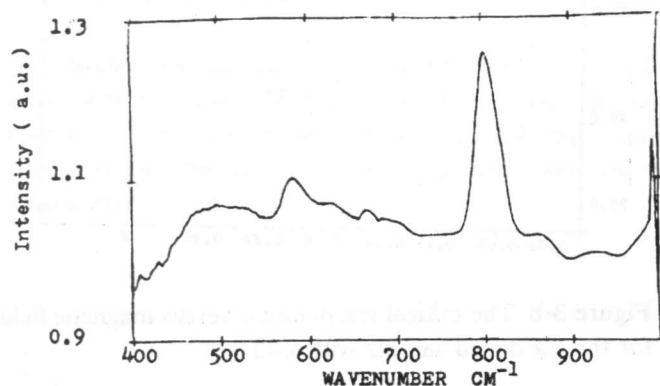


Figure 4. Infra-red transmission for sample Y (.9) Ca (.1) Ba (2) Cu (3) O (7-d).

CONCLUSION

X-ray diffraction results show that there is no splitted peak at $2\theta = 32.5$ degree. Most of the fraction of 30% Ca and Sr-doped samples before sintering is tetragonal phase. All the D.C. resistance and A.C. susceptibility and I.R. measurements confirmed the presence of extra, superconducting phase but with different critical temperature in the Ca-doped samples.

Doping with Ca does not destroy the superconductivity of the YBCO system but decreases the T_c , the depression of T_c is probably due to the local distortion of the lattice in the neighbourhood of the Ca site and the introduction of additional oxygen vacancies [17]. On the other hand doping with Sr destroys the superconductivity probably due to the replacement of Ba sites by the smaller Sr ions which greatly reduces oxygen stoichiometry with a loss of the superconducting phase in the system. This has been shown in the Sr and Ca-doped samples with $x=0.5$ where the Ba sites were replaced by Ca or Sr ions, since oxygen vacancies plays a key role in the appearance or disappearance of superconductivity in the YBCO system, related to the oxidation of Cu^{+2} to Cu^{+3} which increases the superconductivity [14], because Cu^{+3} is directly related to superconductivity.

Although extra heat treatment usually improves the superconducting behavior, in this work the third heat treatment has led to a loss of superconductivity due to insufficient oxygen flow.

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