Influence of Zn impurities on the superconducting Y-Ba-Cu-O compound

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The influence of the Zn impurity has been studied in the superconducting compound $YBa_2Cu_3O_{7-\delta}$ by using two different methods of preparation: substitution of Cu by Zn or addition of Zn at the starting materials. In both cases scanning electron microscopy and electron probe microanalysis studies of the superconducting phase show a substitution of copper by zinc in a partial amount only. The effect of Zn on the superconducting properties of $YBa_2Cu_3O_{7-\delta}$ is found to be quite different from the influence of magnetic impurities.

INTRODUCTION

The effect of impurities on the electrical, mechanical, and thermal properties of the high-T_c materials is of great importance for understanding the superconducting state and for the development of these new compounds. It was shown early that in the $YBa_2Cu_3O_{7-\delta}$ phase (in the following: 1:2:3 phase), a replacement of Y by rare-earth elements has only a minor influence on the critical temperature T_c. On the other hand, it was shown that atoms which are able to replace the Cu atoms on the Cu-O chains [Cu(1) site] or the Cu-O planes [Cu(2) site] have a clear influence on T_c.[1-8] In particular, the Zn impurity, which is not magnetic, unexpectedly altered the superconducting properties without altering the orthorhombic symmetry of the crystal structure. Some contradictory results are observed in the literature concerning the behavior of the doped 1:2:3 phase at high Zn concentrations. According to some authors[8] the critical temperature stabilizes around 50 K whereas, for some others, T_c drops to 0 K.[7]

Most authors prepared the phases containing impurities by substitution of Cu by the impurity atom M at the starting materials and assumed that the end product has the same stoichiometry: $YBa_2(Cu_{1-x}M_x)_3O_{7-\delta}$. In a previous work[4] we called attention to the presence of other phases which could result from the introduction of impurities. If secondary phases are present it is very likely that the substitution of Cu by the impurity atom is not complete. For studying the physical properties of impurity-doped samples it is therefore necessary to look for the real composition of the 1:2:3 phase and the presence of other phases. These other phases may have an indirect influence to the superconducting properties (proximity effect, percolation limit, etc.).

For the investigation of the Zn-doped samples we have processed as follows: We prepared samples by substitution, according to $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ and by addition according to 1 mol $YBa_2Cu_3O_{7-\delta}$ $+3x$ mol ZnO. For the characterization we performed a quantitative analysis of the different components in the different phases present in the sample by scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). On four samples a neutron-diffraction investigation was carried out to obtain information of the occupancy of the O and Cu sites. The oxygen content was determined by iodometry. The influence of Zn doping on the transition temperature to the superconducting phase is reported and discussed in comparison with Fe-doped samples.

EXPERIMENT

Both types of samples described above have been prepared by solid-state reaction in similar conditions. The raw materials (Y_2O_3, $BaCO_3$, CuO, and ZnO) were carefully mixed in a mortar; the samples were calcined at 950 °C for 24 h, then reground, pressed into pellets and sintered at 950 °C. After 72 h at this temperature a slow cool down (2 °C/min) to room temperature was accomplished. All baking procedures were done under flowing oxygen.

The structure of the resulting phase was determined by x-ray diffraction. Phase composition was analyzed by SEM and EPMA with a JEOL JMS-350 equipment. The neutron diffraction investigation was done at the Institut Max von Laue-Paul Langevin (ILL) in Grenoble. The critical temperature of the superconducting phase was measured by a four-contact resistivity measurement.

RESULTS

In Table I we have given the experimental data for both types of samples. Type A has been prepared by addition of Zn, type B by substitution. The results can be summarized as follows: (1) The x-ray investigation shows that the 1:2:3 phase remains orthorhombic for all Zn concentrations. This is in agreement with other published data.[2,6,7] For large impurity contents one could also detect other phases. (2) By SEM and EPMA analysis, we characterized the major phases in the samples. Figure 1 gives an example of the EPMA analysis on a 1:2:3 crystal

TABLE I. Experimental results for the Y-Ba-Cu-O samples prepared by addition of Zn (type *A*) and by substitution of Cu by Zn (type *B*).

Sample No.		1	2	3	4	5	6	7	8	9
Type of sample		*A*	*A*	*A*	*A*	*B*	*B*	*B*	*B*	*B*
Zn/Cu+Zn (at.%)[a]		2.6	5.0	14.0	21.2	1.0	4.2	11.1	15.0	20.0
Zn/Cu+Zn (at.%)[b]		2.7	3.75	4.7	5.0	1.0	2.8	5.5	6.3	7.2
Critical temperature T_c (K)		66	63	61	62	80	60	60	12	4
Transition width (K)		20	12	18	12	16	12	20	12	8
Neutron diffraction analysis										
Lattice parameters (Å)	*a*		3.824			3.824	3.828			3.831
	b		3.893			3.890	3.893			3.898
	c		11.688			11.688	11.688			11.683
Occupancy of sites (%)	Cu(1)		97			100	100			100
	Cu(2)		97			100	98			96
	O(4)		95			96	97			88
Oxygen content measured by iodometry						6.87	6.80		6.79	6.79

[a]Based on initial composition.
[b]Based on EPMA measurements in superconducting phase.

of sample *B*9. For several crystalline grains the spatial variation in the Zn content was less than 5% of the measured value (the instrumental error of the EPMA equipment). The results clearly show that the Zn atoms are replacing the copper. In Fig. 2 we have plotted the Zn concentration in the superconducting phase as a function of the nominal concentration of the starting material. For both series of samples there is only a small region with full substitution of Cu by Zn. For the samples with the addition of Zn we find a saturation at about $x=0.05$. In these compounds the other phases detected by EPMA and x-ray diffraction are mainly CuO and ZnO. With this information about the occurrence of the other phases and with the given initial composition we can calculate the final composition of the prepared samples. For instance, for sample *A*4 we find (in wt. %): 91% $YBa_2(Cu_{0.95}Zn_{0.05})_3O_{7-\delta}$, 1.7% CuO and 7.3% ZnO. For the *B* samples (substitution) we find a saturation at $x=0.08$. In this series the superconducting phase seems to be in equilibrium with Y_2BaCuO_5, $BaCu(Zn)O_2$, and ZnO. This gives us the following composition for sample *B*9 (wt. %): 55% 1:2:3 phase, 16% 2:1:1 phase, 21% $BaCuO_2$, and 8% ZnO. All these phases contain Zn. It is believed that the ZnO phase which is often associated with $BaCuO_2$ is provided by a recrystallization process during the cooling of a melted phase of composition $BaCuZn_3O_5$. This last phase can be seen in sample *B*9. (3) The neutron diffraction data (see Table I) on our samples confirm the recent results of Xiao *et al.*[7] that Zn mainly goes to the Cu(2) site (planes). Furthermore, we see a slight decrease of the O(4) occupancy at high doping levels. A slight decrease of the oxygen content is also found in the iodometric analysis (Table I). But both methods (neutron

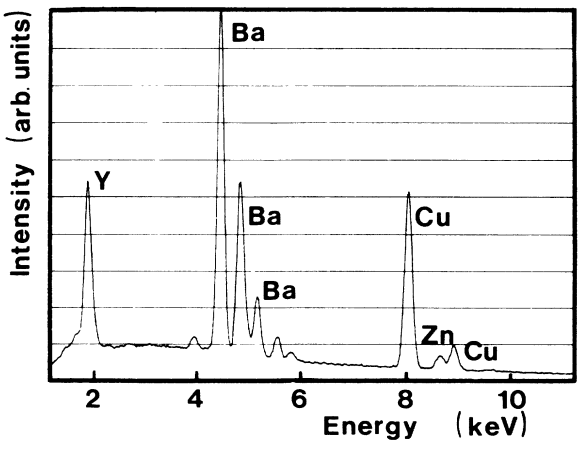

FIG. 1. EPMA microanalysis of the 1:2:3 phase in sample *B*9.

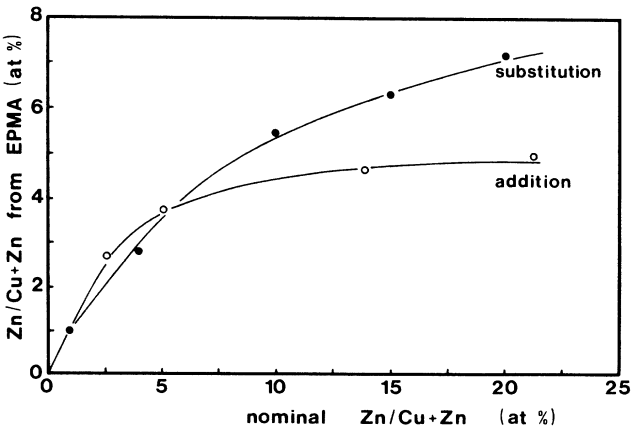

FIG. 2. Zn concentration in the superconducting 1:2:3 phase measured by EPMA as a function of the nominal Zn concentration of the starting materials for the two methods of sample preparation (substitution and addition).

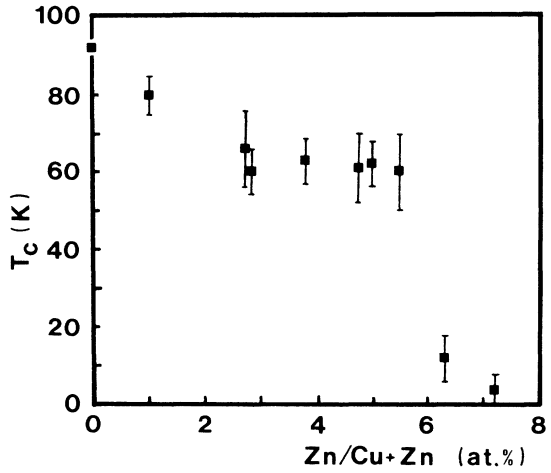

FIG. 3. Critical temperature T_c of the 1:2:3 phase as a function of the Zn concentration measured by EPMA.

diffraction, iodometry) may have a high systematic error due to the presence of other phases. (4) The superconducting transition temperatures are indicated in Table I also. In Fig. 3 the critical temperature has been plotted as a function of the Zn content in the superconducting phase. There is a strong decrease of T_c at low x values, but for $0.02 < x < 0.06$ we find a plateau at about $T_c = 60$ K. For x values higher than 0.06 (samples $B8$ and $B9$), T_c goes to zero.

DISCUSSION

The partial Zn substitution for Cu and the different values of saturation observed in both series show that the environment of the 1:2:3 phase plays an important role. At equilibrium, the chemical potential of Zn is the same in every phase of a specific sample. Because of the appearance of different phases for the two preparation methods, the internal chemical potential of Zn is not the same for the two sample series. Therefore the real Zn content in the 1:2:3 phase cannot be the same in series A and B with the same nominal Zn content.

Since Zn has no magnetic moment, it should have no influence on the critical temperature upon doping in a BCS-type superconductor.[9] On the other hand, Abrikosov and Gorkov[10] have shown that magnetic impurities give rise to a linear depression of T_c at low concentrations. Experimental investigations in conventional superconductors have confirmed the Anderson theorem,[9] but it is valid only in very simple systems. More complex compounds show an influence of T_c on impurities for different reasons (change of electron-phonon interaction, influence of the valence of the impurity atom, ...). The linear depression of T_c by magnetic impurities was found in all compounds where there is an overlap of the wave functions of Cooper pairs and magnetic ions.

Our results on Zn-doped $YBa_2Cu_3O_{7-\delta}$ show a strong depression of T_c by increasing impurity content. The form of the T_c versus Zn concentration curve resembles very much the results of Cava *et al.*,[11] who measured T_c as a function of the oxygen content. But an explanation of the results of $T_c(x)$ by oxygen deficiency cannot be confirmed by our measurements of the oxygen content. We find a slight decrease of the oxygen content, but the value is not large enough compared to the results of Cava *et al.* A further difficulty would be the fact that Zn replaces Cu atoms in the Cu-O planes, whereas the oxygen deficiency responsible for the decrease of T_c is caused by missing O atoms in the Cu-O chains.

We think that the most important and new result of our investigation is the plateau of $T_c(x)$ found for $0.02 < x < 0.06$ in $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$. This means that an increase of Zn has no influence on T_c over a wide range. A behavior like that is also found in the Ga-doped samples,[6] where two plateaus at about 80 and 70 K are seen. On the other hand, a plateau of the $T_c(x)$ curve is never found in $YBa_2Cu_3O_{7-\delta}$ compounds doped with magnetic $3d$ ions.[1-8] A possible explanation of these facts is that pair breaking according to the Abrikosov-Gorkov theory plays an important role in the 1:2:3 phase with magnetic impurities.

For the sharp decrease of T_c for $0 < x < 0.02$ we can give no explanation at present. The suppression of the superconducting behavior for $x > 0.06$ may be due to the presence of a large amount of other phases which bring the system to the percolation limit.

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