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Abstract. The effect of CuO substitution by MS (M = Ni, Fe or Zn) in YBa$_2$Cu$_3$O$_{7-\delta}$ (Y-123) samples is studied by DC resistivity, AC susceptibility and x-ray emission spectroscopy and diffractometry. All samples show sharp x-ray diffraction patterns with no impurity phase lines for M = Ni, Fe or Zn-doped samples. The cell of Ni-, Zn- or Fe-substituted Y-123 samples remains orthorhombic for all concentrations studied. X-ray emission spectroscopy results show that sulphur atoms enter the lattice of Y-123 compounds and form oxyanion groups. The diamagnetic transitions are sharp for all the small concentrations and become broad for MS doping above 10%. The transition temperature T_c decreases with increasing MS concentration when compared with the undoped sample.

1. Introduction

The genesis of high-T_c superconductivity lies itself in substitutional studies [1, 2]. On-site substitutional studies are equally important for both experimentalists and the theoreticians. Of the on-site substitutions the copper site is important, as the superconductivity is supposed to reside in the copper oxide stacks only. For on-site copper substitutions the 3d metallic elements possess a favourable condition due to their closer ionic sizes and outer shell configurations to that of copper. Of the 3d metals (Ni, Fe, Zn, Co, etc), while the Ni and Zn substitute mainly at the Cu(2) site in the YBa$_2$Cu$_3$O$_{7-\delta}$ (Y-123) structure, the Fe and Co ions prefer the Cu(1) site [1–3]. For designing the various 3d metal substitutions in HTSC compounds, one often prefers the 3d metal oxides for the synthesis route [1–3]. We think that, instead of using 3d metal oxides, it will be of prime importance to substitute the 3d sulphides at the Cu–O stacks. In this way the double chemical substitution of Cu or 3d metal together with O or S can take place in the structure. Earlier we succeeded in putting FeS and NiS partially into the Cu(1)–O chains in the Y-123 structure [4–7]. While it is difficult to sulphonate the HTSC samples in a normal SO$_2$ atmosphere, it is possible to get this anion chemically implanted in Cu(1)–O(1) chains with simultaneous 3d metal substitution at the Cu site. Our aim in this paper is to study the effect of MS, i.e. the 3d

metal sulphide substitution in HTSC superconducting materials. The substituted materials are characterized by x-ray diffraction, DC resistivity, AC susceptibility and x-ray emission spectroscopy (XES) techniques.

2. Experimental details

Samples of the Y-123 series doped with M sulphides (MS) were synthesized through the solid state reaction route. Instead of normal M oxides (MO), the MS (i.e. NiS, FeS and ZnS) were used for the synthesis. After mixing properly, these samples were calcined at a temperature of 920 °C for 24 h. This exercise of mixing, pelletizing and firing for 24 h was repeated at least four times to ensure the phase purity of the pristine as well as the substituted materials. In the final step of synthesis all the samples were annealed in a flowing oxygen atmosphere at 940 °C for 24 h and then subsequently were cooled slowly to room temperature over a span of 12 h.

The samples were characterized for phase purity and lattice parameter variation using a x-ray diffractometer equipped with Cu Kα radiation. Four-probe resistivity measurements were performed on a fully computer-controlled automatized home-made system with help of a closed-cycle refrigerator, down to 15 K. AC susceptibility measurements were made on a commercial (Quantum Design) SQUID magnetometer at a low field to ensure the superconducting transition temperature T_c of all the samples. XES was studied by means of S Kα radiation; the details have been given elsewhere [5, 6].

3. Results

Figure 1 depicts the splitting of the [123] and [213] crystallographic planes at room temperature, to demonstrate the non-observability of the orthorhombic–tetragonal (O–T) transition in the currently studied samples. While for the pure ($x = 0.0$) and the maximum ($x = 0.10$) doped ZnS sample the splitting of the two planes is clearly seen, for the FeS doped ($x = 0.15$) samples the two planes more or less merge into one. For the tetragonal transition the intensity positions of the two planes, i.e. [123] and [213] are reversed [8], which is clearly not the situation for the maximum ($x = 0.15$) doped FeS sample in the present study. Detailed variation in the lattice parameters a, b and c have been given elsewhere [4–7].

Figure 2 shows the presence of S in the material through the typical energy-dispersive x-ray spectrum for a $x = 0.03$ sample of the YBa$_2$[(CuO)$_{1-x}$FeS$_x$]$_3$O$_{4-\delta}$ series. It is worth mentioning that the doping concentrations of both Fe and S are small ($x = 0.03$) in the material but still their presence can be seen unambiguously. This result is important in terms of deciding the likely amount of S emitted in the form of the SO$_2$ gas from the material. The presence of S anions in the MS-doped Y-123 systems gets further credence from our XES observations. In figure 3 we show the S Kβ_1 XES for the Y-123:(NiS)$_{0.03}$ sample. It is clear from figure 3 that not only does the S remain in the bulk material but also its energy position is consistent with the formation of SO$_4^{-2}$ anion groups.

Four-probe DC resistivity measurements revealed that the critical transition temperature T_c (i.e. R = 0) decreases with all these substitutions in comparison with the pristine undoped sample. It has been reported earlier that, on substitution of ZnO, NiO and Fe$_2$O$_3$ at Cu–O sites, T_c also decreases [1–3]. The relative decrease in T_c due to 3d metal oxide doping in Y-123 is more pronounced than observed for substitution of the same 3d metal sulphides in the present study. As far as the comparative effect of these 3d sulphides is concerned on
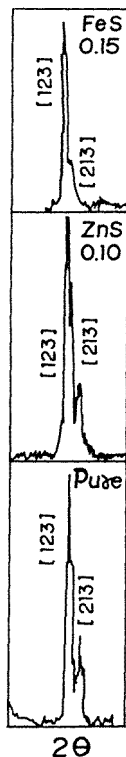
Figure 1. Orthorhombic splittings of [123] and [213] crystallographic planes shown one over the other for pure, ZnS-doped ($x = 0.10$) and FeS-doped ($x = 0.15$) samples of the YBa$_2$[CuO$_{1-x}$MS$_x$]$_3$O$_{4-\delta}$ system.

the superconductivity of Y-123, ZnS has a more deleterious effect on T_c than NiS and FeS do. Secondly, FeS is more effective than NiS [4–7]. A similar order has been observed in the case of 3d metal oxide doping in the Y-123 system with an overall less prominent effect on superconductivity [1–3, 9–11].

AC susceptibility results on these samples corroborated more or less the T_c measurements made resistively on all these samples [5–7]. On increasing the doping concentration the transition width (T_c onset $- T_c$ offset) increases. Here the T_c onset is the onset of the diamagnetic signal and the T_c offset is the near saturation point of the diamagnetic signal. For a comparison of the MO doping with MS doping, in figure 4, the T_c-values of the former are compared with those of the latter, as a function of the dopant concentration. It is clearly evident from figure 4 that the effect of MS is less than MO on the superconducting transition temperature T_c of the Y-123 system.

4. Discussion

The results shown in figures 1–4 can be summarized as follows.

(1) The superconducting transition temperature T_c of the pristine undoped sample decreases on doping with NiS, ZnS and FeS; the order of the deleterious effect on T_c is Zn > Fe > Ni.
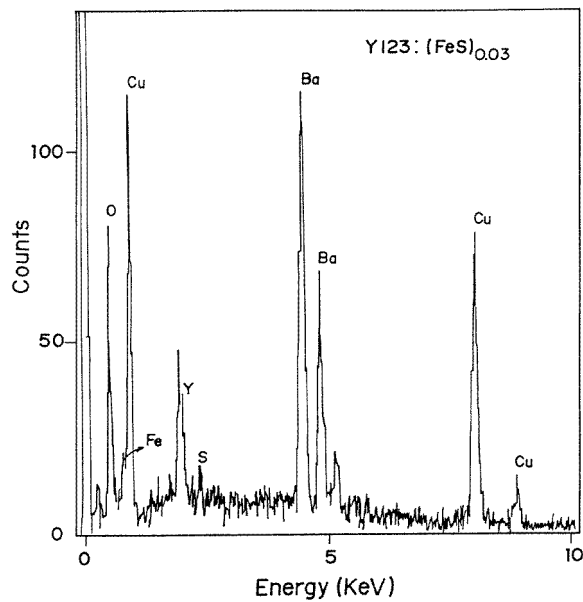
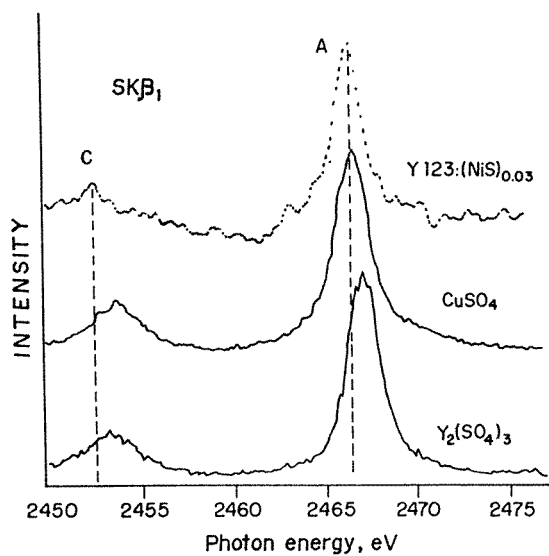**Figure 2.** Energy-dispersive x-ray spectrum of a $YBa_2[(CuO)_{0.97}FeS_{0.03}]_3O_{4-\delta}$ sample.

Figure 3. S $K\beta_1$ XES of $YBa_2[(CuO)_{0.97}NiS_{0.03}]_3O_{4-\delta}$ sample and its comparison with the reference compounds $CuSO_4$ and $Y_2(SO_4)_3$.

(2) In comparison with the 3d metal oxide doping in Y-123, doping with the respective sulphides has a much less deleterious effect on the T_c of the pristine sample.

(3) Both NiS and ZnS substitute for CuO isostructurally in the system at least up to the 10 at.% and 20 at.% doping levels, respectively. Unlike in Fe_2O_3-doped Y-123, the FeS-doped compound does not show any O–T transition.
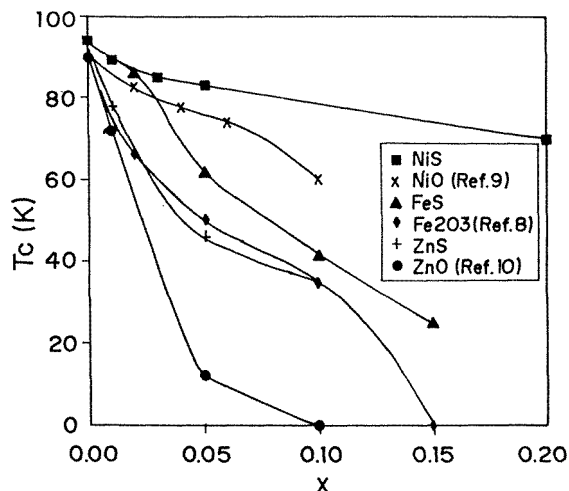
Figure 4. T_c (K) versus M concentration x behaviour for the YBa$_2$ (CuO$_{1-x}$MS,O$_x$)$_3$O$_{4-\delta}$ system.

(4) XES results on NiS- and FeS-doped samples, imply from the sulphur spectrum a possible presence of S at Cu(1) sites in doped materials in the form of SO$_4^{-2}$ oxyanion groups.

On comparison of MS-doped Y-123 compounds, ZnS appears to be more deleterious to T_c than are FeS and NiS. It is worth mentioning here that, while the divalent Zn and Ni substitute mainly at the Cu(2) site, the trivalent Fe substitutes mainly at the Cu(1) site in the Y-123 structure. Also as superconductivity is supposed to reside in the Cu(2)–O(2) planes, hence any modification introduced to these planes decreases superconductivity more rapidly. Perhaps that is the reason why ZnS affects T_c more than FeS does, but this idea is limited owing to the less deleterious effect of NiS in comparison with FeS. The reason behind this discrepancy is that, while the Cu(1) or Fe(III) substitutions decrease the number of mobile carriers (decrease in holes), the Cu(2) or Ni(II) substitution leaves the same nearly unaltered. A decrease in the number of mobile carriers decreases the T_c of the Y-123 system [9]. Hence this way it seems possible that, while Ni substitutes at Cu–O planes (responsible for superconductivity), it is less deleterious to T_c than Fe is. Now, concerning ZnS, divalent Zn substitutes at Cu(2) and localizes the p-type (holes) carriers strongly there in the Cu(2)–O(2) planes, creating apparently a magnetic moment on the Cu(2) site [10, 11]. This strong localization of the carriers in the planes affects T_c anomalously because of this substitution, which is not the situation when the same site is substituted by Ni. As far as the magnetic moments of these 3d ions are concerned, it appears that they do not effect superconductivity. The reason is as follows: in the case of FeS doping, F(III) ions are far away from the Cu(2)–O(2) planes where the superconductivity resides; hence its moment is not effective at all [9]. For the moment on Ni(II) which substitutes at the Cu(2) site, it appears that the moment created on Cu(2) itself (as for Cu/Zn substitution) affects T_c greatly instead of the distributed local moment on the average Cu(2)/Ni(II)–O planes. The moment created by Cu(2) or Zn(II) partial doping on all Cu(2) ions also localizes the hole carriers in Cu(2)–O(2) planes, which in turn decrease T_c much more rapidly.

Now let us discuss the less prominent effect on T_c of MS than the respective MO doping.

As we discussed earlier in [4, 5], for low dopant concentrations the Cu(1) sites in Cu(1)–O(1) chains are substituted by S anions, and the local charge balance of the compound alters. This alternation in the charge balance may favour an increase in the mobility of carriers, resulting in improved superconducting properties. We are now trying to put sulphur anions directly in the Y-123 unit cell at Cu–O chain sites without simultaneous 3d doping. For this job we are undertaking studies on the $YBa_2(CuO_{1-x}CuS_x)_3O_{7-\delta}$ system. The outcome of these results will soon be published elsewhere.

About the XRD results the lattice parameters of the NiS- and ZnS-substituted samples are not far from the reported data on their respective oxide-doped samples. For the FeS-doped samples no O–T transition is observed, while in the case of Fe_2O_3-doped samples the O–T transition has been reported. In the Fe_2O_3 substitution the O–T transition occurs owing to the filling of vacant O(5) sites in Cu–O chains, because of Cu(1) or Fe(III) substitution and an increase in the oxygen content of the system [1, 3, 8, 9]. In the present case while the likely substitution is Cu(1) or Fe(II,III), the filling of O(5) sites is probably balanced by the substitution of S anions at Cu(1) sites [4, 5].

5. Conclusions

Our present study of MS (M = Fe, Ni and Zn)-doped Y-123 showed undoubtedly the presence of SO_4^- ions in substituted Y-123 material. It also shows that 3d metal sulphide doping is less effective in decreasing the T_c of Y-123 than the corresponding MO.

Acknowledgments

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