Effect of Doping by Low Concentration of Iron on Magnetic and Structural Properties of Bi2212

N Boussouf, M-F Mosbah, F Bouaïcha, F Benmaamar and A Amira

1 Laboratoire des Couches Minces et Interfaces. Université Mentouri, Campus de Chaabet-Erssas, 25017 Constantine, Algeria.
2 Laboratoire des Essais Non Destructifs. Université de Jijel, B.P. 98, 18000 Jijel, Algeria.
E-mail: faycalmos@yahoo.fr

Abstract. Superconducting Bi$_2$Sr$_2$Ca$_{2-x}$Fe$_x$Cu$_2$O$_{8+y}$ ceramics samples (0 ≤ x ≤ 0.075) have been prepared in air by solid state reaction method. The structural, magnetic and superconducting properties of the samples have been analyzed by means of X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and AC susceptibility measurements. The increasing of Fe content shows an important decrease of the content of the Bi2212 phase while the Bi2201 parasitic phase content increases and the c lattice parameter is slightly reduced. The rate at which Tc is depressed by substitution by Fe is much lower than the one obtained by transport measurements made by other authors on single and whiskers crystals. The substitution by Fe increases also the broadening of the superconducting transition indicating an effect on the homogeneity of the samples.

1. Introduction
As in the other superconducting cuprates, in Bi$_2$Sr$_2$CaCu$_2$O$_{8+y}$ (Bi2212) the CuO$_2$ planes are believed to carry the superconducting electrons. Numerous studies have been made on substitution in these planes for a better understanding of the superconducting properties. As with other transition metals, substitution or doping by Fe was made in order to improve the critical current density and the pinning of vortices [1-4]. The effect was not only on the critical current density but also on the critical temperature of transition Tc which is generally lowered [5]. The disorder induced by the substitution is associated with more fundamental phenomena related with the origin of high Tc superconductivity as the meaning of carrier concentration in the CuO$_2$ planes and the opening of a pseudo gap in the normal state [6-8]. Observation of order-disorder transitions of the vortex lattice investigated by magnetic measurements in crystals of Fe doped Bi2212 confirm that Fe lies in the CuO$_2$ planes [9]. Substitution by Fe in whiskers of Bi2212 broadens the resistive transition and suggests an inhomogeneous distribution of the Fe atoms [5]. In this work we present a study on the effect of low concentration of Fe on structural and magnetic properties probed by AC susceptibility measurements.

2. Experiments

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High grade purity powders of Bi2O3, SrCO3, CaCO3, CuO and Fe2O3 were weighed with molar ratios of Bi: Sr: Ca: Cu: Fe = 2: 2: 1: 2-x: x (x = 0, 0.0125, 0.025, 0.05, 0.075). The powders were mixed and ground in an agate mortar for 1h to obtain a homogeneous mixture, then fired at 816°C for 16h. The obtained powders were then ground, pressed in pellet shape (13mm diameter and 1mm thickness) under pressure of 5ton/cm2 and finally sintered at 845°C for 25 hours in air. X-ray diffraction (XRD) analysis was made with a Siemens D8-Advance powder diffractometer using CuKα radiation. Diffraction spectra peaks were identified using ICDD data base. The cell parameters were calculated from XRD patterns using CELREF V3 software. The microstructure was examined with a Philips XL 30 scanning electron microscope (SEM). The AC susceptibility of the samples was measured on a commercial Quantum Design SQUID magnetometer.

3. Results and Discussions
The CuKα X-ray diffraction patterns of the samples of Bi2212 (Bi2Sr2CaCu2-xFexO8+δ) are shown in figure 1. The obtained peaks reveal the presence of the Bi2212 phase accompanied by small amount of the Bi2201 phase increasing slowly with the Fe doping level. Traces of CuO, SrCO3, CaCO3 impurities and an unknown phase having a peak at 2θ=37.3° are also detected. These impurity phases suggest that some Fe ions were not substituted into Cu-sites.

![Figure 1. XRD patterns of the Bi-2212 samples undoped (x = 0) and doped with Fe (x = 0.0125; 0.025; 0.05; 0.075).]
The peaks of the undoped Bi2212 sample (x =0) show dominancy of (00l) plans indicating a preferential orientation parallel to ab plans. Introducing Fe, this orientation is conserved until x = 0.05 and disappear for x = 0.075 where most of the peaks diminish drastically beside a strong peak obtained at 33.26° in the (009) plane. This peak is the strongest one for all the samples. We note also that the Bi2212 peaks shift to the higher angle side when x Fe doping concentration increases suggesting that c-axis lattice constant decreases and some dopant ions occupy the lattice sites. However, the partial substitution of Fe3+ at the Cu site increases the oxygen content of the unit cell of Bi2212 because of the higher valence state of Fe3+ compared to the Cu2+ one. The increase of the oxygen content gives a broadening of the X-ray diffraction peak (00l) indicating disorder in the atomic positions and in the structure. In Bi2212, the random Coulomb potential caused by excess oxygen atoms in the BiO planes is supposed to pins the doped holes and may create patch-shaped inhomogeneities [10]. The substitution by Fe at low concentration is supposed to change this scenario.

The c-axis contraction shown in figure 2 may be ascribed to two effects: the smaller ion size of the doping atom (rCu = 0.072 nm for Cu, rFe = 0.064 nm for Fe) and the larger valence of transition metal Fe3+. This latter gives rise to a stronger ionic bonding o the excess oxygen in the BiO planes, causing a tighter binding and hence reducing the c-axis lattice constant. There is a consistent variation in the intensity and the position of the peaks indicating the change in phase composition and the lattice parameters of the samples. The relative contraction of the c-axis parameter is very little (less than 0.2%) and is obtained for values of x lower or equal to 0.05. At higher value (x = 0.075) there is a little increase of the c-axis parameter. This may be a consequence of the staying of some Fe ions out of Cu sites. The same sample (x = 0.075) shows also enhanced presence of the Bi2201 parasitic phase indicating a perturbation on the obtaining of the Bi2212 phase. Fe is very efficient in substituting in Bi2212 whiskers [5] and the situation may be the same in polycrystalline samples. This may give some saturation process as Fe may accommodate in microdomains of Bi2201 phase when the concentration is higher [11].

The SEM micrographs of Bi2212 samples are shown in figure 3 where x indicates the concentration of Fe. It is clear from the figure that the superconducting grains are connected with each other, but with an unfilled space between them. The layered structure which characterizes the growth of Bi2212 grains is clearly revealed by these micrographs. Whiskers are also present and more numerous in the doped sample. Secondary phase having dark contrast and with square or round edges is found distributed in the main matrix of the two samples. The average grain size lies between 3 and 5 µm.

Figure 2. c-axis lattice constant dependence of the Bi2212 samples versus x Fe doping concentration.
The sample with $x = 0.0125$ shows the maximum enhancement of the size of the grain, some grains reaching $10 \mu m$, accompanied by a porosity more pronounced. This indicates an increased and more disordered growth of the grains due to the low concentration of Fe introduced. For $x$ varying from 0.025 to 0.075 the size of the grains begins by a very low value, lower than the undoped sample one, then increases with $x$.

The AC susceptibility measurements made at a temperature varying from 5 to 120 K are reported in figure 4. Figure 4a shows the real ($\chi'$) and the imaginary ($\chi''$) parts of the A.C susceptibility. Figure 4b shows the real ($\chi'$) part of the A.C susceptibility normalized to its value at $T = 5$ K. The real part $\chi'$ of these measurements shows that the substitution of Cu by Fe causes a broadening of the transition and a reduction of superconducting volume fraction. Similar broadening has been observed in resistivity measurements made on Bi2212 whiskers doped by Fe [5]. In resistivity the broadening of the transition may be explained by a poor intergranular connectivity and inhomogeneities in the sample. In susceptibility measurements the broadening of the transition is caused by the inhomogeneities and also

**Figure 3.** SEM micrographs of Bi2212 samples (x indicating the concentration of Fe).

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by the granular quality of the sample. Grains of Bi2212 samples have usually a shape of sheets more or less thick as illustrated by the micrographs of figure 3. These grains present a distribution of demagnetizing factor as their orientation to the applied field is not constant. This fact explains the broadening of the transition of the undoped sample. On the other hand, the introduction of magnetic ions as Fe destroys locally the superconductivity and may result in smaller superconductive grains with reduced diamagnetic signal. The \( \chi(T) \) curve shows two distinct steps, the second one associated with the presence of low Tc phase (the Bi2201 phase). As it was observed in XRD analysis, the

\[ \chi''(T) \]

shows two distinct steps, the second one associated with the presence of low Tc phase (the Bi2201 phase). As it was observed in XRD analysis, the fraction of this parasitic phase increases with the x content of Fe. This is evident in figure 4b where the corresponding kink is near the temperature of the superconducting transition of the Bi2201 phase (about 10 K) for x varying between 0.025 and 0.075. For x = 0.0125 the kink is at much higher temperature.

The effect of substitution by Fe on the superconductive volume fraction has been also observed in YBaSrCu3Oy samples but for much higher concentration of Fe with measurements of DC magnetization at 10 Oe [12]. For this sample, the introduction of Fe enhances the superconductive volume fraction. In our samples, the superconductive volume fraction is lowered by Fe.

The imaginary parts \( \chi'' \) of the susceptibility measurements show that there is only one peak related to intergranular screening current. For x = 0.0125, the peak maxima increases and its position shifts towards a lower temperature. For the other values of x, the peak maxima is not observed but there is a little increase of \( \chi'' \) at lower temperatures. As it is shown in figure 4a, this peak corresponds to the kink indicating the transition of the B2201 phase. Its area reflects the disorder induced by the parasitic phase.

The critical transition temperature Tc decreases monotonically from 80K to 63K with x Fe concentration as it is displayed in figure 5 where the straight line represents a less square fit to the experimental points. This decrease of Tc with doping may be explained by the fact that iron affects the CuO2 planes of the samples. Similar dependence of Tc has been observed in resistivity measurements on Fe doped Bi2212 whiskers [5]. The depression of Tc versus x deduced from these measurements (≈ - 780 K) is much higher than the one we deduce from our measurements: ≈ - 533 K. Beside the difference in the quality of the samples (polycrystalline one compared to whiskers), the main reason

**Figure 4.** AC susceptibility measurements of the Bi2212 samples:

a) Real (\( \chi' \)) and imaginary (\( \chi'' \)) parts of the AC susceptibility versus temperature;

b) Normalized real part (\( \chi'/\chi'(5K) \)) of the AC susceptibility versus temperature
may be the fact that in the resistivity measurements Tc has been taken in the middle of the transition and in our AC susceptibility measurements the beginning of the transition is chosen.

![Graph](image)

**Figure 5.** Tc versus x dependence of Bi2212 samples.

### 4. Conclusion

Doping Bi2212 superconducting ceramic samples by low concentration of Fe has an effect on the quality of the obtained samples and on their superconducting properties. Fe reduces the superconductive volume fraction and broadens the transition. The depression of Tc measured versus x content of Fe is lower than the one deduced from resistivity in whiskers. Part of the difference seems to be due to the method of measuring Tc.

### Acknowledgements.

We are grateful to Drs P. Molinié and A. Leblanc-Soreau for magnetic measurements. This work was supported by CNEPRU D2501/56/06 Algerian government project.

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