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Iron Doping Effect on Composition and Microstructure of $Bi_{2.05}Sr_{1.9}Ca_{1.05}(Cu_{1-x}Fe_x)_2O_{8+\delta}$ $(0 \le x \le 0.15)$ Superconductors

C. De Boeck, D. Ciurchea and P. H. Duvigneaud*

Université Libre de Bruxelles, Laboratoire de Chimie Industrielle et Analytique, CP165, 50, avenue F.D. Roosevelt, B1050 Brussels, Belgium

Abstract

Samples with $Bi_{2.05}Sr_{1.9}Ca_{1.05}(Cu_{1-x}Fe_x)_2O_{8+\delta}$ $(0 \le x \le 0.15)$ *compositions were synthesized by a liquid-mix process able to give single phase compounds. The superconducting phase was carefully investigated by SEM and EDX. Substitution of* x *Fe atoms in the* $Bi_2Sr_2CaCu_2O_{8+\delta}$ *grains corresponds to the removal of 1·7*x *Cu atoms and to the addition of 0·75*x *Bi atoms whereas the sum Sr + Ca remains quite constant. In a first step, this evolution may be explained by the following basic model:* $Fe_2O_3 \rightarrow 2Fe_{cu}^{\bullet} + V_{cu}'' + 3\ CuO$ *which assumes the creation of vacancies in the copper sites of the* $Bi_2Sr_2CaCu_2O_{8+\delta}$ *lattice. However, the apparent increase of Bi content suggests the formation of microdomains of* $Bi_2Sr_2CuO_6$ *phase intergrown in the* $Bi_{2.05}Sr_{1.9}Ca_{1.05}(Cu_{1-x}Fe_x)_2O_{8+\delta}$ *grains, as inferred from X-ray diffraction and SEM which reveals the concomitant* $(SrCa)_{14}Cu_{24}O_{41}$ *secondary phase. The EDX results are more consistent with a* $Bi_2Sr_2CuO_6$*–*$Bi_2Sr_2CaCu_2O_{8+\delta}$ *intergrowth model in which Fe is accommodated in the* $Bi_2Sr_2CuO_6$ *microdomains than with the model of substitution in a* $Bi_2Sr_2CaCu_2O_{8+\delta}$ *single phase. © 1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

It is well known that iron and other 3d elements which have nearly the same ionic radii as copper can replace copper in the superconducting cuprates.

In the case of Fe-doped $YBa_2Cu_3O_{7-\delta}$, it is now admitted that for low Fe content ($x = Fe/(Fe + Cu) < 0.03$), the Fe atoms mainly substitute on the Cu(I) sites of the CuO chains leading only to a slight decrease of T_c ($\sim 2\,K\,x^{-1}$). For higher iron content, T_c decreases more rapidly, due to a partial substitution of Fe on the Cu(II) sites of the CuO_2 planes until the superconductivity vanishes beyond $x = 0.11$.[1,2]

In contrast, nonmagnetic zinc is more effective in suppressing T_c, since zinc mainly substitutes in the CuO_2 planes.[3]

In $Bi_2Sr_2CaCu_2O_{8+\delta}$, (Bi-2212) in which only CuO_2 planes but no CuO chains exist, the incorporation of magnetic iron and cobalt supresses T_c nearly linearly with a slope in the range 5–8 $K\,x^{-1}$. For divalent nickel and zinc, a similar decrease of T_c occurs but it is limited by the poor solubility of those two elements in $Bi_2Sr_2CaCu_2O_{8+\delta}$ ($x < 0.025$).[4,5]

The above results lead to the conclusion that local disorder rather than magnetism is the dominant factor for the suppression of superconductivity in the cuprate superconductors. However, the nature of disorder is not yet clearly understood, namely in the case of Fe-doped $Bi_2Sr_2CaCu_2O_{8+\delta}$.

Usually, large amounts of iron are detected in the Bi cuprates. Indeed, the $Bi_2Sr_3Fe_2O_{9+y}$ compound is isostructural to $Bi_2Sr_2CaCu_2O_{8+\delta}$, with an orthorhombic structure.[6] However, several authors have observed that Bi-2212 samples with $x > 0.08$ are no longer single phase.[7–9] Secondary phases such as $(Sr,Ca)_{14}Cu_{24}O_{41}$ and $Bi_2Sr_2CuO_6$ have been reported.[7,10] Nevertheless, samples with nominal $0.1 < x < 0.2$ still exhibit T_c values in the range 20—40 K.[4,5] In most studies, the real chemical composition of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ superconducting phase was not determined.

Our previous works based on SEM and EDX analysis evidenced substantial changes in the content

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*To whom correspondence should be addressed. Fax: + 32-2650-2952; e-mail: phduvig@ulb.ac.be of all elements in the cuprate phase when copper was replaced by iron.[11,12] At this time, these results were difficult to interpret owing to the presence of uncontrolled secondary phases in our samples, whose nature and stability was still unknown. The progresses made in the knowledge of phase diagrams together with the development of chemical routes of synthesis allowed us to prepare single-phase $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples.[13,14] In the present work, Fe-doped samples prepared by an original process were systematically analyzed by SEM, EDX and XRD in order to clarify our previous interpretation.

2 Experimental

Compositions enriched in bismuth are known to yield $Bi_2Sr_2CaCu_2O_{8+\delta}$ single phase compounds.[15–17] According to our previous results, samples with a nominal composition $Bi_{2{\cdot}05}Sr_{1{\cdot}9}Ca_{1{\cdot}5}(Cu_{1\text{-}x}Fe_x)_2O_{8+\delta}$ were prepared by an original liquid mix technique.[13,14,18] High-purity Bi_2O_3, $SrCO_3$, $CaCO_3$, CuO and Fe were dissolved in a nitric acid solution in order to obtain the 2·05–1·9–1·05–2 composition. An EDTA–ammonia aqueous solution was added to produce metal–EDTA complexes with a concentration of $0{\cdot}025\,\text{mol}\,\text{l}^{-1}$ at pH >6.

The obtained solution was spray dried using a Buchi 190 Mini Spray Dryer. The dried powder was converted into a black foam precursor in a microwave oven. The precursor was then ground and calcined at 800°C in flowing air for 24 h. The resulting powder was ball-milled for 15 h, uniaxially pressed into pellets under a pressure of 400 MPa and sintered in flowing O_2 at 845°C.

The microstructure and phase compositions were analysed in the superconducting grains by SEM and EDX (JEOL JSM-35C); the measured concentrations were normalized taking into account that in the $Bi_2Sr_2CaCu_2O_{8+\delta}$ formula, the sum of the cations is always 7. The crystalline compounds were characterized by powder X-ray diffraction (Siemens D5000, CuK_α, radiation).

3 Results

SEM and EDX analysis show that the matrix consists of needle-like grains of the superconducting cuprate phase. A secondary phase, i.e. $(Sr,Ca)_{14}Cu_{24}O_{41}$, is detected in the Fe-doped samples (Fig. 1). Its amount increases with the iron content. No other phases are detected by SEM.

EDX analysis of iron shows that this element is not detected in the secondary phase. The iron atoms remain concentrated in the cuprate phase. Indeed, the x values determined by EDX are in good agreement with the nominal compositions in the range $0 < x < 0{\cdot}15$.

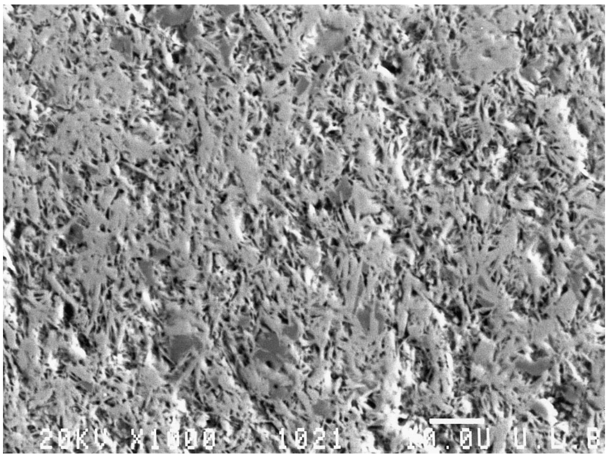

Fig. 1. SEM image of a $Bi_{2{\cdot}05}Sr_{1{\cdot}9}Ca_{1{\cdot}05}(Cu_{1\text{-}x}Fe_x)_2O_{8+\delta}$ sample with $x = 0{\cdot}1$, showing the dark $(Sr,\ Ca)_{14}Cu_{24}O_{41}$ phase.

The results of the EDX analysis performed in the grains of the superconducting phase are depicted in Fig. 2(a)–(d). In those figures the stoichiometric coefficients of the main elements are plotted as a function of the effective iron content in the grains (mole Fe/mole Bi-2212).

Figure 2(a) shows that the substitution of x iron atoms in the Cu-sites corresponds to a decrease of $1{\cdot}7x$ atoms of copper and to an increase of $0{\cdot}75x$ atoms of bismuth. This means that the sum $Cu + Fe$ is continuously decreasing with the increase of x.

Figure 2(b)–(d) shows important fluctuations in the strontium and calcium contents. However, these fluctuations compensate one another to give a nearly constant sum $(Sr + Ca) = 3$.

By X-ray diffraction, only the $Bi_2Sr_2CaCu_2O_{8+\delta}$ phase is detected for the lowest doped samples ($x < 0{\cdot}05$) while for higher Fe content, the $Bi_2Sr_2CuO_6$ phase appears and becomes predominant on the $Bi_2Sr_2CaCu_2O_{8+\delta}$ compound from x–0·1 (Fig. 3).

4 Discussion

If Fe^{3+} is assumed to only replace Cu^{2+} in the CuO_2 planes of the single-phase $Bi_2Sr_2CaCu_2O_{8+\delta}$ compound, the removal of 1·7 atoms of Cu for each Fe atom introduced may be expressed by:

$$Fe_2O_3 \rightarrow 2Fe^{\bullet}_{Cu} + V''_{Cu} + 3CuO \qquad (1)$$

This model states that the charge of Fe^{3+} is balanced by the creation of copper vacancies. Equation (1) does not take into account the

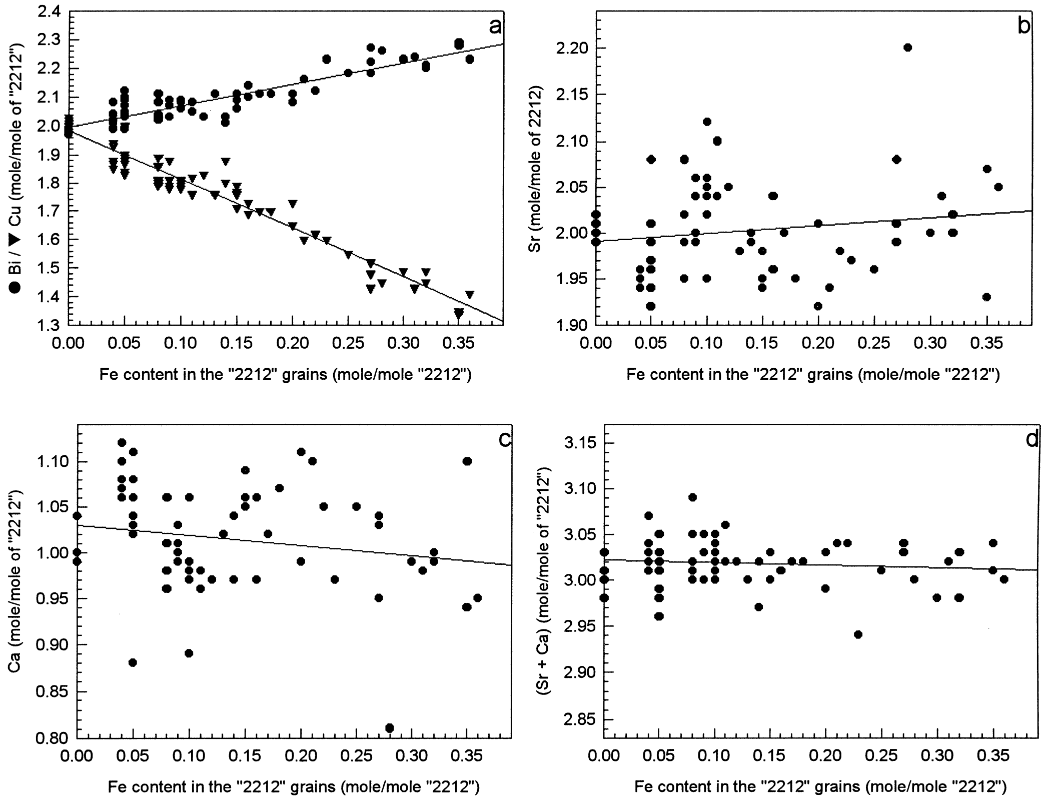

Fig. 2. EDX analysis performed on cations and reported in terms of iron content present in the superconducting phase.

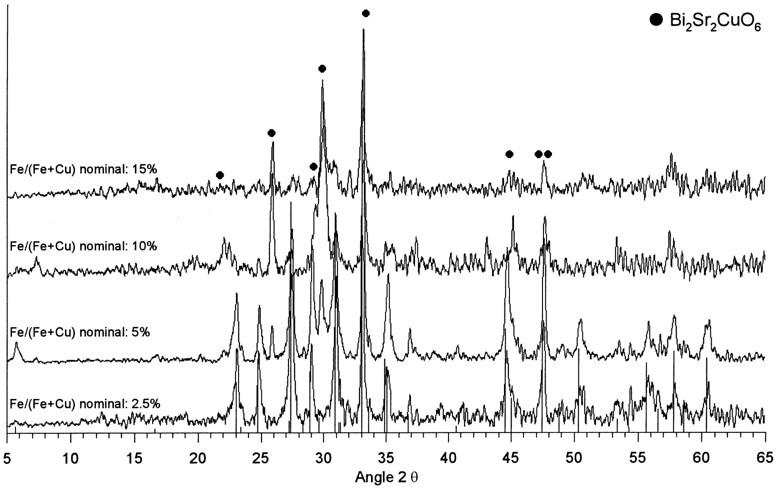

Fig. 3. X-ray diffraction of $Bi_{2\cdot 05}Sr_{1\cdot 9}Ca_{1\cdot 05}(Cu_{1-x}Fe_x)_2O_{8+\delta}(0\leq x\leq 0\cdot 15)$.

apparent excess Bi introduced in the structure. As the sum (Ca + Sr) remains constant with a stoichiometric coefficient close to 3, the excess Bi cannot substitute neither for Sr in the SrO planes, nor for Ca in the Ca planes of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ unit cell.

In previous works,[11,12] we speculated that Bi^{5+}, whose ionic radius (0·76 Å) is close to that of Cu^{2+} (0·73 Å), could completely fill the Cu vacancies since the ratio $Bi_{excess}/V_{cu}'' \approx 1$.

The excess oxygen necessary to compensate the charge excess due to Bi^{5+} could be accommodated on the central Ca layer which is known to accommodate extra-oxygen associated with Fe^{3+}.

From that time, the presence of Bi on the CuO_2 planes has never been confirmed in the Bi-cuprates. Thus, the substitution of Bi up to 10% on the Cu sites seems unlikely in the $Bi_2Sr_2CaCu_2O_{8+\delta}$ structure.

XRD has evidenced the formation of $Bi_2Sr_2CuO_6$ phase at the expense of $Bi_2Sr_2CaCu_2O_{8+\delta}$ in samples with $x\geq 0\cdot 05$ (Fig. 3). In contrast, this phase is not detected by SEM-EDX, even in highly doped samples ($x\geq 0\cdot 1$). This means that the $Bi_2Sr_2CuO_6$ phase consists of crystallites of small sizes (10–100 nm) which have grown within the $Bi_2Sr_2CaCu_2O_{8+\delta}$ matrix with a basal plane preferred orientation.

The continuous formation of $Bi_2Sr_2CuO_6$ crystallites with increasing x provides an alternative explanation of the results presented in Fig. 2(a)–(d). Indeed, the EDX analyses are based on the assumption that the needle-like superconducting phase is only composed of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ compound in which the sum of all cations is considered to be 7. If we assume now that the $Bi_2Sr_2CaCu_2O_{8+\delta}$ and $Bi_2Sr_2CuO_6$ phases are intergrown, the sum of all cations becomes lower than 7. Further, if we assume that the stoichiometric coefficient of Bi remains constant with x and close to 2, the sum (Sr + Ca) becomes decreasing like the sum (Cu + Fe) with respect to Bi, so that the stoichiometry of the matrix tends towards that of $Bi_2Sr_2CuO_6$.

This alternative model, close to that of M. Boekholt *et al.*[7] or Co-doped $Bi_2Sr_2CaCu_2O_{8+\delta}$ gives a more coherent interpretation of the strong decrease of the Cu content with increasing x in the superconducting phase [Fig. 2(a)]. The copper vacancies evidenced in eqn (1) are rather stacking faults than point defects. Therefore, the suppression of CuO_2 and adjacent Ca planes of $Bi_2Sr_2CaCu_2O_{8+\delta}$ giving rise to $Bi_2Sr_2CuO_6$ microdomains and to $Sr_{14-y}Ca_yCu_{24}O_{41}$ seems energetically favourable to accommodate Fe atoms on CuO_2 planes. Indeed, the $Bi_2Sr_2CuO_6$ structure is known to host large amounts of Bi and Fe, i.e. x and $y \leq 0{\cdot}5$ in $Bi_{2+x}Sr_{2-x}Cu_{1-y}Fe_yO_z$[19] together with large amounts of Ca.[20] Moreover, in the compound $Sr_{14-y}Ca_yCu_{24}O_{41}$, the y value is often between 5 and 7.[17,21] This may explain that the sum (Sr + Ca) remains nearly constant in Fig. 2(c).

Thus, the $Bi_2Sr_2CaCu_2O_{8+\delta}$–$Bi_2Sr_2CuO_6$ intergrowth model states that the Fe atoms rather substitute on the CuO_2 planes of a $Bi_2Sr_2CuO_6$ structure than on those of $Bi_2Sr_2CaCu_2O_{8+\delta}$ owing to strong distorsions generated in the latter. According to this model, the existence of a pure solid solution of Fe in the $Bi_2Sr_2CaCu_2O_{8+\delta}$ phase seems strongly limited; the solubility of Fe in single-phase $Bi_2Sr_2CaCu_2O_{8+\delta}$ should not exceed that of divalent cations, i.e. Ni^{2+} and Zn^{2+} ($x \leq 0{\cdot}025$).[4,5,22,23]

The validity of the intergrowth model is still to be confirmed by other experiences. Although HRTEM studies have evidenced intergrowth relations between $Bi_2Sr_2CuO_6$, $Bi_2Sr_2CaCu_2O_{8+\delta}$ and $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ phases in undoped samples[20] and characterized different structures in Fe-doped $Bi_2Sr_2CuO_6$,[19] the structural defects observed in Fe-doped $Bi_2Sr_2CaCu_2O_{8+\delta}$ have still not been clearly correlated with $Bi_2Sr_2CuO_6$ microdomains.

However, the intergrowth model is not in contradiction with Mössbauer studies which have pointed out different oxygen environments for Fe in $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples.[18]

5 Conclusions

The results of the EDX analyses in the superconducting phase are not consistent with the formation of a solid solution of Fe in a $Bi_2Sr_2CaCu_2O_{8+\delta}$ single-phase up to $x \approx 0{\cdot}08$, as previously reported.[7–9] Rather, the introduction of Fe in the $Bi_2Sr_2CaCu_2O_{8+\delta}$ structure results in stacking faults leading to $Bi_2Sr_2CuO_6$–$Bi_2Sr_2CaCu_2O_{8+\delta}$ intergrowth, until the $Bi_2Sr_2CaCu_2O_{8+\delta}$ phase is completely replaced by the $Bi_2Sr_2CuO_6$ phase. For high substitution levels ($x \geq 0{\cdot}1$) the coexistence of a Fe-rich $Bi_2Sr_2CuO_6$ phase and a Fe-poor $Bi_2Sr_2CaCu_2O_{8+\delta}$ contributes, as far as percolation pathes remain, to keep T_c to high values regarding the apparent impurity level.

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