JOURNAL OF MATERIALS SCIENCE 25 (1990) 2165–2169

The orthorhombic-to-tetragonal phase transition in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$

C. J. KIM, H. G. LEE, I. H. KUK, I. S. CHANG, C. S. RIM, P. S. HAN, D. Y. WON
Korea Advanced Energy Research Institute, P.O. Box 7, Taedok Science Town, Taejon Chungnam 302-353, Korea

The phase transition $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$ ($0 \leqslant x \leqslant 0.05$) prepared through solid-state reaction was studied with X-ray diffraction analysis and optical microscope. It was found that the orthorhombic-to-tetragonal phase change was induced between $x = 0.02$ and $x = 0.03$ by X-ray diffraction. The phase transition was also identified by the disappearance of striations in plate-like grains under polarized light. The microstructures of the specimens with compositions of $x = 0.01$ and $x = 0.02$ showed faint striation images. It is considered that a mixture of the orthorhombic and tetragonal phase exists in these compositions.

1. Introduction

Since the discovery of the high-T_c superconductor [1, 2], intense studies have been developed to understand the mechanism of superconductivity. Systematic substitution of impurity elements for the copper site provides a way to elucidate the nature of the superconductivity. Recently, several reports have been published for the substitution effects with metallic elements [3–10]. When transition elements such as iron, cobalt, and nickel substitute for copper in $YBa_2Cu_3O_{7-y}$, the linear decrease of T_c (superconducting transition temperature) is observed with the increasing dopant concentration. In the case of the iron, cobalt and gallium substitution, the orthorhombic-to-tetragonal phase transition is induced [5, 6, 8, 9]. However, the nickel and zinc substitutions stabilize the orthorhombic phase [7, 10]. In contrast with the tetragonal phase quenched from high temperature, which is not a superconductor, the tetragonal phase that is induced by the iron substitution reveals bulk superconductivity [6]. It was supposed that the phase transition was triggered by the impurity atoms located at the Cu_I site on the one-dimensional Cu–O chains [7, 8]. The elements which result in the phase transition are all favour the six-fold coordination of an octahedral site and have a valence state of +3 [7, 8, 11, 12]. It is still unclear how the oxygen ordering on the Cu_I chains is influenced by the substitution elements. It is well known that $YBa_2Cu_3O_{7-y}$ has two kinds of phases. One is a low-temperature orthorhombic phase, which is believed to be responsible for the high-T_c superconductivity. The other is a high-temperature tetragonal phase. The orthorhombic phase possesses two Cu_2 planes, which are placed between two yttrium and barium layers, and one Cu_I chain per unit cell, which is located between two barium layers. The tetragonal phase, however, has only the Cu_2–O plane. It is worthwhile determining which Cu–O bondings dominate high-T_c superconductivity.

In this paper, the phase transition in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$ has been investigated by means of X-ray diffraction analysis and optical microscope observation.

2. Experimental procedure

Ceramic samples of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$ ($0 \leqslant x \leqslant 0.05$) were prepared by the solid state reaction of Y_2O_3, $BaCO_3$, CuO and Fe_2O_3 powders. The content of iron substituted for copper was varied from 0 to 0.05 by 0.01 mol. Powder mixtures of appropriate composition were well mixed, calcined in air at 910° C for 24 h and cooled to room temperature. The reacted powders were ground and then pressed under 300 kg cm^{-2} into 10 mm diameter pellets with a thickness of 5 mm. Specimens for microstructural observation were prepared under 3000 kg cm^{-2} in order to increase density. The pellets were sintered in air at 925° C for 24 h and annealed at 400° C in air for 20 h. An aluminar plate was used for the heating and annealing of all the samples. Resistance measurements were made in disc-shaped samples using the four-point probe method with silver paint contacts. X-ray diffraction data were obtained by powder diffraction utilizing Cu(Kα) radiation and in the range of 2θ from 20° to 80°. Microstructures with an iron content were investigated under optical polarized light.

3. Results and discussion

Fig. 1 shows the microstructural change of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$ oxides with iron content. The microstructure of $YBa_2Cu_3O_{7-y}$ (Fig. 1a) consists of plate-like grains which contains many striations. The striations due to twin lamellae were developed in one or two orientations in each grain. In iron-doped samples with a composition of $x = 0.01$ and $x = 0.02$, the striation images became faint (Fig. 1c). Cross-striation was observed in two orientations that intersected each other. As the iron content is increased, the striation tends to be more faint and the grain was refined. For the $x = 0.03$ sample, the striation was

0022-2461/90 $03.00 + .12 © *1990 Chapman and Hall Ltd.*

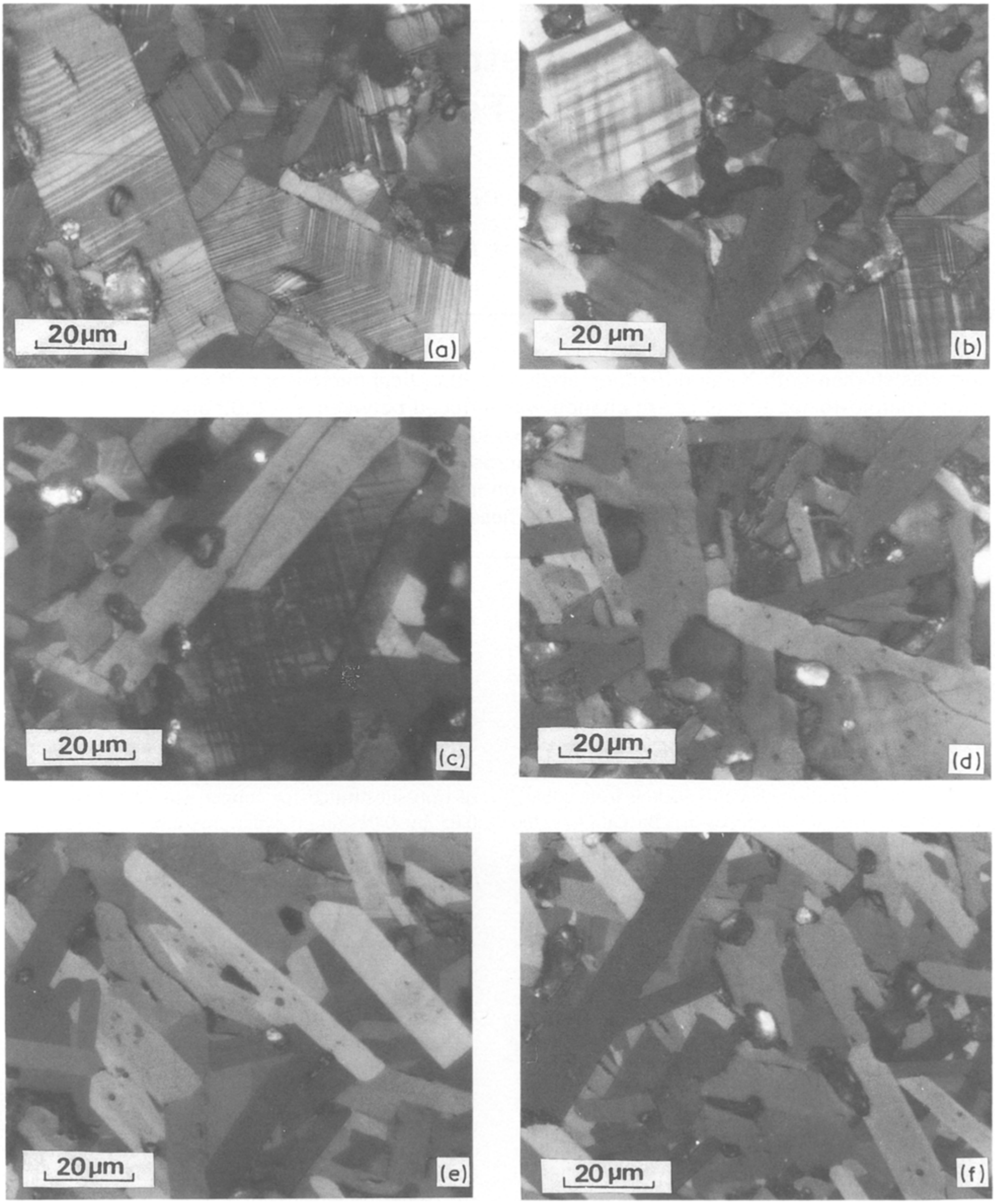

Figure 1 Optical micrographs from $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$ oxides sintered at 920° C for 24 h and annealed at 400° C for 20 h in air. (a) $x = 0$ (b) $x = 0.01$ (c) $x = 0.02$ (d) $x = 0.03$ (e) $x = 0.04$ (f) $x = 0.05$.

partly observed in the whole specimen (the lower side of Fig. 1c). Above $x = 0.03$, no striation was found. The striations in $YBa_2Cu_3O_{7-y}$ is observed due to interference of the twin image under optical polarized light [13]. It is reported that the twin formation in $YBa_2Cu_3O_{7-y}$ is due to orthorhombic distortion resulting from the oxygen ordering on the one-dimensional Cu–O chains [14]. Thus, the disappearance of striations with the iron doping means that the orthorhombic-to-tetragonal phase transition was induced by iron substitution for copper. Fig. 2 shows X-ray diffraction peaks. It can be recognized that all the samples were a single phase of perovskite structure. It was found that an orthorhombic to tetragonal phase transition occurred between $x = 0.02$ and $x = 0.03$. The variation of diffraction patterns with the iron concentration is similar to that of $YBa_2Cu_3O_{7-y}$ due to a transition from a low-temperature orthorhombic phase to a high-temperature tetragonal one. The phase transition is characterized by the change of peaks around $2\theta = 32°$ and 58°. For $YBa_2Cu_3O_{7-y}$, intensity of (110)/(103)

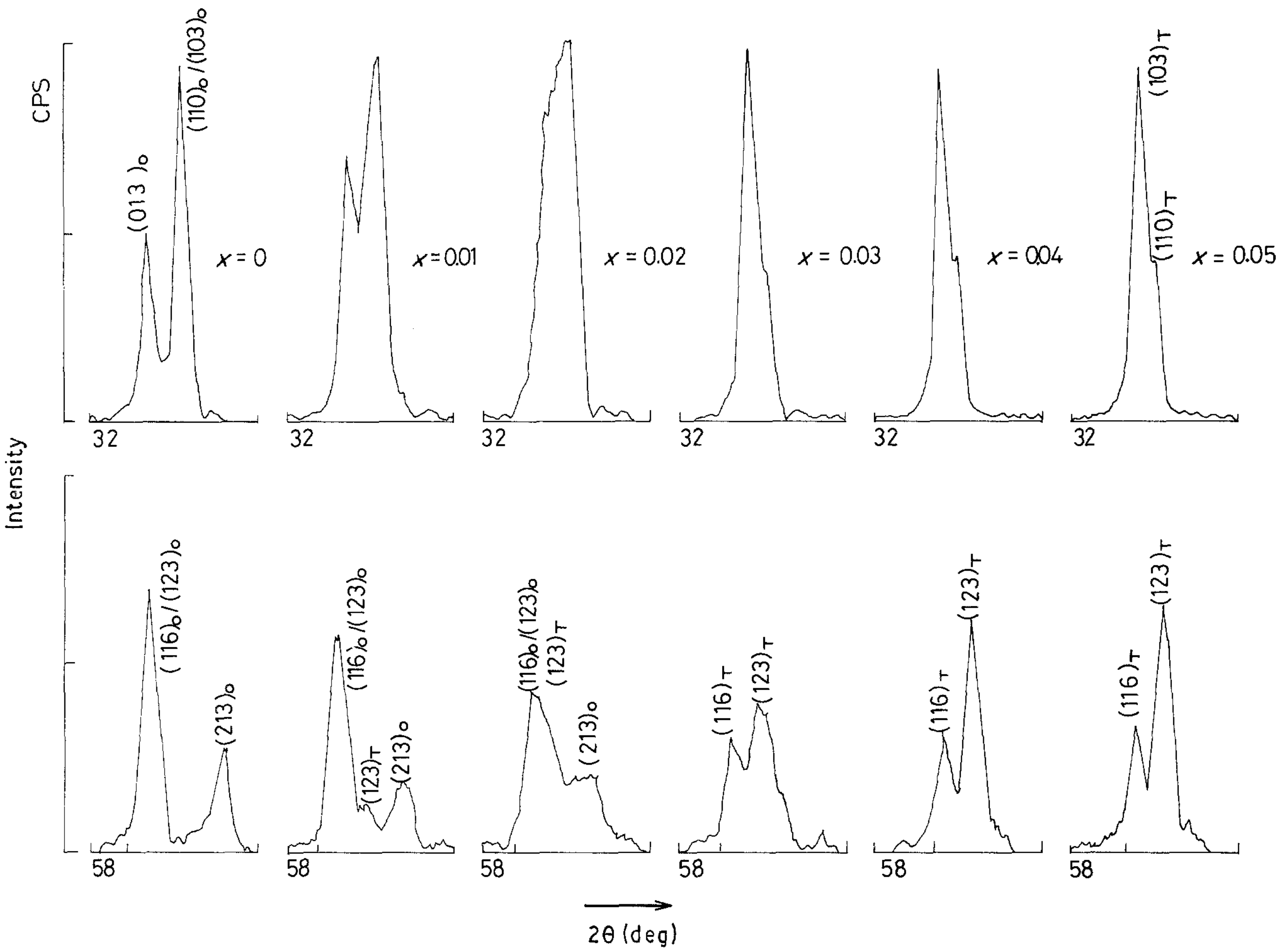

Figure 2 X-ray peaks changes of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$ with iron content x.

peak is higher than that of (013) peak. As the iron content is increased, the intensity ratio between two peaks decreases continuously. At $x = 0.03$, the reversal of peak intensity was observed. The reversal of an intensity ratio between (116)/(123) and (213) peaks placed near $2\theta = 58°$ also occurred at the same concentration. For $x = 0.01$ and $x = 0.02$ samples, however, new peaks were formed at $2\theta = 58.4°$ and 58.27°. The locations of these peaks correspond to those of tetragonal (123) peaks. Samples of $x = 0.04$ and 0.05 show a complete tetragonal phase. The tetragonal (123) peaks were located at $2\theta = 58.32°$ and 58.33°. From the above results, it is considered that the orthorhombic-to-tetragonal phase transition passes through the mixture of the orthorhombic and tetragonal phase.

Fig. 3 shows the lattice parameters for the $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$ systems. Since it is difficult to separate the tetragonal lattice parameters from the mixed-phase patterns, the phases below $x = 0.03$ is expressed with the orthorhombic lattice parameters. The orthorhombic $YBa_2Cu_3O_{7-y}$ has lattice parameters of $a = 0.3822$ nm, $b = 0.3895$ nm and $c = 1.1690$ nm. Parameters a and b were varied with increasing iron content, while the c parameter remained unchanged with the phase transition. The phase transition of $YBa_2Cu_3O_{7-y}$, which occurred by oxygen deficiency and disordering, is accompanied by an increase of c parameter and affects superconducting properties [15]. From the fact that c parameter was unchanged when the phase transition occurred, it is suggested that the phase transition by iron doping is not related to the oxygen deficiency. In comparison with the microstructures of Fig. 1 and the X-ray diffraction data of Fig. 2, it can be recognized that only the phases having the orthorhombic structure reveal the striation by twin lamellae. The twin structure

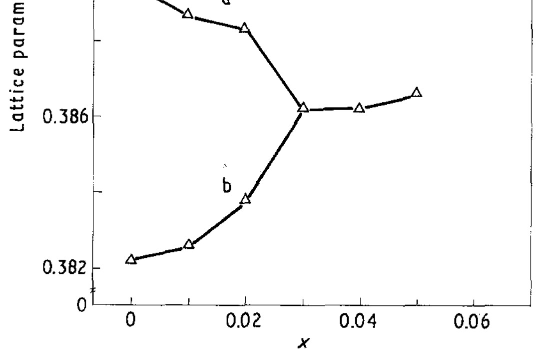

Figure 3 Lattice parameters of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$ as a function of iron content x.

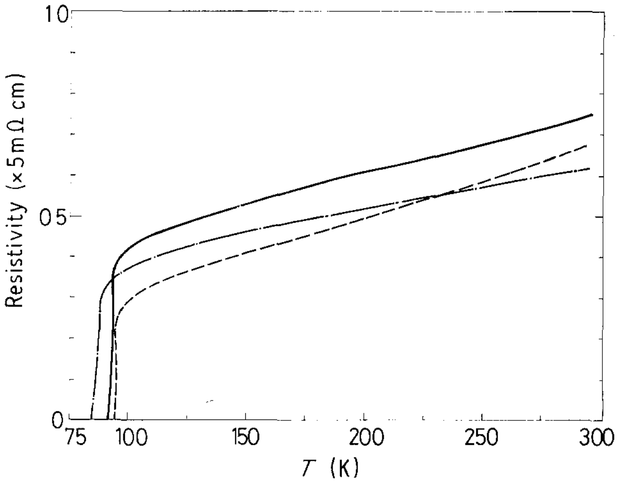

Figure 4 Resistance as a function of temperature for the $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$ (– – – $x = 0$, —— $x = 0.1$, –·–·– $x = 0.02$).

is generated by the oxygen ordering on the one-dimensional Cu–O chains. Therefore, this observation implies that the iron atoms introduced into the copper sites changes of oxygen arrangement on the one-dimensional Cu–O chains.

Fig. 4 shows the relation between the electrical resistivity and temperature. For $x = 0$, zero resistivity is achieved at 93.5 K. The samples for $x = 0.01$ and 0.02 have lower T_c's at 92 K and 84.5 K than that of $YBa_2Cu_3O_{7-y}$. The transition width from the normal to superconducting state was broadened with iron content. It is thought that the reduction of T_c and the broadening effect are related to the volume fraction of the tetragonal phase by iron doping to the orthorhombic one. Maeno *et al.* reported that the tetragonal phase induced by iron doping sustained superconductivity to $x = 0.1$ [6]. In $YBa_2Cu_3O_{7-y}$, T_c is a function of oxygen content. Furthermore, the tetragonal phase having low oxygen content is not a superconductor. Therefore, it is considered that the iron-doped tetragonal phase may have sufficient oxygen content to retain superconductivity.

The factor that determines the crystal structure (orthorhombic or tetragonal) of $YBa_2Cu_3O_{7-y}$ is order–disorder arrangement of oxygen atoms on the one-dimensional Cu–O chains located between two barium layers. The phase transition by iron doping may be discussed at the same point.

The first available factor is a valence state of iron substituted for copper. Generally, iron can be in the +2, +3 and +4 state. In $YBa_2Cu_3O_{7-y}$, the valence of Cu_1 is believed +3 in the orthorhombic phase and +1 in the tetragonal one. Cu_2 is considered to be +2 in both phases [16, 17]. Mössbauer experimentals reported that the iron atoms was introduced into the Cu_1 sites with the +3 state [11, 12]. Since our samples were prepared with the same sintering condition and full annealing in air irrespective of iron content, sufficient oxygen pick-up might be made up. Thus, it is reasonable to assume the valence state of Cu_1 as +3 and Cu_2 as +2. The iron atoms are substituted for the Cu_1 sites having the +3 state and charge difference between two elements is not brought about. It seems that the valence state of iron does not affect on the oxygen arrangement on the one-dimensional Cu–O chains. The other available factor is the anion (oxygen) coordination number around the iron atom. In orthorhombic $YBa_2Cu_3O_{7-y}$, Cu_1 takes a four-fold coordination. Here, two oxygen atoms place on the *b*-axis and two sites on the *a*-axis are vacant. Iron atoms go into the Cu_1 sites and prefer a six-fold coordination of a octahedral site to a four-fold coordination. In order to satisfy these surroundings, oxygen atoms should occupy the vacancy sites on the *a*-axis. The local region where iron atoms were placed has a tetragonal symmetry. The volume fraction of the tetragonal region to the orthorhombic matrix would increase by increasing the iron content.

The gallium, cobalt and iron that are substituted for the Cu_1 site stabilize the tetragonal phase [5, 8, 9] while nickel and zinc stabilize the orthorhombic one [7, 10]. Gallium and cobalt take the +3 state occupying only the Cu_1 site and prefer a octahedral site [7, 8] as does the iron. The valence state of nickel and zinc is +2. It is unclear which copper sites the nickel and zinc atoms were substituted for. If the nickel atoms were substituted for the Cu_1 sites, the oxygen atoms would leave from the *b*-axis to compensate the extra minus charge due to the charge difference between the two elements or the nickel atoms should pick up the oxygen atoms into the vacancy sites on the *a*-axis in order to satisfy its octahedral coordination. As a result, the tetragonal phase would be stabilized. Maeno *et al.* reported that in $YBa_2(Cu_{1-x}Ni_x)_3O_{7-y}$, the orthorhombic phase was stabilized to $x = 0.25$ [7]. Therefore, it is thought that the nickel atoms would be introduced into the Cu_2 sites. The zinc atoms prefer a tetrahedral coordination to an octahedral coordination [18]. When Cu_1 is substituted by the zinc atom, the surroundings would not change significantly, because the coordination numbers of zinc and Cu_1 are the same. Thus, even though the zinc atoms substitute the Cu_1 sites, phase transition would not occur.

We consider the Cu_1 plane where some Cu_1 are substituted by iron atoms. The oxygen bonds around iron crosslinks along the *a* and *b*-axis to satisfy the octahedral coordination of iron. The region that is far from the iron atom may still take the oxygen ordered structure. In our samples, the phase transition is induced between $x = 0.02$ and 0.03. These concentrations correspond to the mixed phase as identified by X-ray diffraction. Thus, the orthorhombic and tetragonal phases would coexist in the concentration. If the oxygen atoms occupy all the vacancy sites on the *b*-axis and some of them on the *a*-axis, the oxygen content $(7-y)$ would be over 7 in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$. It was confirmed, however, that the tetragonal phase induced by iron was not accompanied by a large number of oxygen atoms. The tetragonal phase induced by iron achieved an oxygen content of about 6.8 and in the case of samples doped with $x = 0.033$ of nickel and cobalt, $(7-y) = 6.84$ and 6.85 [6]. Thus, it is suggested that the tetragonal phase induced by iron would have the crystal structure in which an appropriate amount of oxygen vacancies exist on *a* and *b*-axis. Oda *et al.* concluded that the Cu_1 chains have a little contribution on the high-T_c

superconductivity, because the oxygen ordering on the Cu_I chains is broken by the iron atoms substituted for the Cu_I sites [5]. The tetragonal phase induced by iron picks up sufficient oxygen content to retain the superconductivity. Therefore, it is considered that the Cu_I–O chain structure would be retained, not broken.

Acknowledgement

The authors would like to thank Mr Kyung S. Lim and Ki B. Kim for their help with the experiments.

References

1. J. G. BEDNORZ and K. A. MÜLLER, *Z. Phys. B* **64** (1986) 189.
2. C. W. CHU, P. H. HOR, R. L. MENG, G. GAO, Z. J. HAUNG and Y. Q. WANG, *Phys. Rev.* **58** (1987) 405.
3. GANG XIAO, F. H. STREITA, A. GAVRIN, Y. W. DU and C. L. CHIEN, *Phys. Rev. B* **35** (1987) 8782.
4. T. SIEGRIST, L. F. SCHNEEMEYER, J. V. WASZAK, N. P. SINGH, R. L. OPILA, B. BATLOGG, L. W. RUPP and D. W. MURPHY, *ibid.* **36** (1987) 8365.
5. Y. ODA, H. FUJITA, J. TOYODA, T. KANEKO, T. KOHARA, I. NAKADA and K. ASAYAMA, *Jpn J. Appl. Phys.* **26** (1987) L1660.
6. Y. MAENO, M. KATO, Y. AOKI and T. FUJITA, *ibid.* **26** (1987) L1982.
7. E. TAKAYAMA, Y. UCHIDA and K. KATO, *ibid.* **26** (1987) L2087.
8. M. HIRATANI, Y. ITO, K. MIYAUCHI and T. KUDO, *ibid.* **26** (1987) L1997.
9. D. SHINDO, K. HIRAGA, M. HIRABAYASHI, A. TOKIWA, M. KIKUCHI, Y. SYONO, O. NAKATSU, N. KOBAYASHI, Y. MUTO and E. AOYAGI, *ibid.* **26** (1987) L1667.
10. Y. MAENO, T. NOJIMA, Y. AOKI, M. KATO, K. HOSHINO, A. MINAMI and T. FUJITA, *ibid.* **26** (1987) L774.
11. R. GOMÉZ, S. ABURTO, M. L. MARQUINA, M. JIMENEZ, V. MARQUINA and C. QUINTANAR, *Phys. Rev.* **B36** (1987) 7226.
12. X. Z. ZHOU, M. RAUDEPP, Q. A. PANKHURST, A. H. MORRIST, Y. L. LUO and I. MAARTENSE, *ibid.* **B36** (1987) 7230.
13. H. A. HOFF, A. K. SINGH and C. S. PANDE, *Appl. Phys. Lett.* **52** (1988) 669.
14. T. KAJITANI, K. OH-ISHI, M. KIKUCHI, Y. SYONO and M. HIRABAYASHI, *Jpn J. Appl. Phys.* **26** (1987) L1144.
15. M. O. EATOUGH, D. S. GINLEY, B. MOROSIN and E. L. VENTURINI, *Appl. Phys. Lett.* **51** (1987) 367.
16. H. OYANAGI, H. IHARA, T. MATSUBARA, T. MATSUSHITA, M. HIRABAYASHI, M. TOKUMOTO, T. YAO, H. IWASAKI and Y. KIMURA, *Jpn J. Appl. Phys.* **26** (1987) L1233.
17. H. OYANAGI, H. IHARA, T. MATSUBARA, M. TOKUMOTO, T. MATSUSHITA, M. HIRABAYASHI, K. MURATA, N. TERATA, T. YAO, H. IYASAKI and Y. KIMURA, *ibid.* **26** (1987) L1561.
18. A. NAVROTSKY and O. J. KLEPPA, *J. Inorg. Nucl. Chem.* **29** (1967) 2701.

Received 19 July
and accepted 22 November 1988