Structure and superconductivity in Fe$_x$Cu$_{1-x}$Ba$_2$YCu$_2$O$_{7+y}$ superconductors synthesized by high pressure

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Abstract

Comprehensive studies of X-ray diffraction, oxygen content, superconductivity and Mössbauer effect have been made on Fe$_x$Cu$_{1-x}$Ba$_2$YCu$_2$O$_{7+y}$ superconductors (0.00 $\leq x \leq$ 0.70) synthesized by ambient (AM) and high pressure (HP). Results indicate that all the HP-samples have tetragonal structure, smaller lattice parameter $c$ and unit-cell volume than the AM-samples. The studies of oxygen content, and Mössbauer spectroscopy indicate that the HP-samples have higher oxygen content, carrier concentration and average valence of Fe than the AM-samples. Moreover, for the HP-samples more Fe atoms located in CuO$_x$ chains have fivefold-oxygen coordination. These are important reasons for the enhancement of $T_c$ in the HP-samples.

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1. Introduction

To understand the mechanism of high-$T_c$ superconductivity and the correlation among superconductivity, magnetism, composition and structure, the YBa$_2$Cu$_{2−x}$MgO$_{7+y}$ (M=Fe and Co) systems (denoted as Fe$_x$Cu$_{1−x}$Ba$_2$YCu$_2$, O$_{7+y}$) have been extensively studied [1–13]. In Fe$_x$Cu$_{1−x}$Ba$_2$YCu$_2$O$_{7+y}$ system, the value of $T_c$ decreases with increasing Fe content and becomes zero at $x=0.3$ [2,10] and there is a structural transition of orthorhombic-tetragonal phase at $x=0.10\sim 0.15$ [2,3,6,10,11]. Additionally, Fe substitutes for not only Cu (1) in CuO$_x$ chains but also for Cu (2) in CuO$_x$ planes and Fe content in CuO$_x$ planes increases with increasing total Fe content [3,6]. On the other hand, the high-$T_c$ superconductors containing high Fe content is favorable for providing more information for the interplay between superconductivity and magnetism, which is helpful to understand the origin of superconductivity in cuprate superconductors. Thus, the investigations on the cuprate superconductors with high Fe content have attracted more attention.

At early stage of studies on high-$T_c$ superconductors, several groups reported superconductivity in the YSr$_2$Cu$_{3−x}$Fe$_x$O$_{7+y}$ system with $x\geq0.3$ prepared in high-pressure oxygen [12,13] and Ca-doped YSr$_2$Cu$_{3.5}$Fe$_{0.5}$O$_{7+y}$ system [14]. Subsequently, Shi et al. [15] improved superconductivity in YSr$_2$Cu$_{2.7}$Fe$_{0.3}$O$_{7+y}$ by high-pressure oxygen (27 MPa) annealing and enhanced $T_c$ up to 60 K [15]. Recently, the FeSr$_2$YCu$_2$O$_{7+y}$ superconductor was
obtained [16] and the crystal structure and superconductivity were systematically investigated [17].

Very recently, we investigated the influence of preparation condition on the lattice parameters and superconductivity of the Fe$_{x}$Cu$_{y}$Ba$_2$YCu$_2$O$_{7+y}$ system [18] and prepared Fe$_{x}$Cu$_{y}$Ba$_2$(Ba$_{1-x}$Sr$_x$)$_2$YCu$_2$O$_{7+y}$ superconductors with $x = 0.0, 0.5$ and 1.0 [19] using high-pressure technique.

In this paper, comprehensive studies of X-ray diffraction, oxygen content, superconductivity and Mössbauer spectroscopy are made on the Fe$_{x}$Cu$_{1-x}$Ba$_2$YCu$_2$O$_{7+y}$ system prepared by the high-pressure synthesis.

2. Experimental details

Fe$_{x}$Cu$_{1-x}$Ba$_2$YCu$_2$O$_{7+y}$ superconductors (0.00 $\leq x \leq$ 0.80) were prepared in two steps. In the first step, the starting materials, high-purity (99.99%) powders of Y$_2$O$_3$, BaCO$_3$, CuO and Fe$_2$O$_3$ according to the formula of Fe$_{x}$Cu$_{1-x}$Ba$_2$YCu$_2$O$_{7+y}$ ($x = 0.00, 0.06, 0.10, 0.16, 0.32, 0.40, 0.50, 0.60, 0.70, 0.80$) were thoroughly mixed in a mortar. The mixtures were heated in air in the temperature range $880^\circ$C $\leq T \leq 930^\circ$C for at least 70 h with intermediate grindings. Then, the mixtures were reground and pressed into pellets, which were sintered at 930 $^\circ$C for 40 h in air and cooled down to room temperature at a rate of 30 $^\circ$C per hour. The resultant samples were named AM-samples. In the second step, the AM-samples were powdered, mixed with 5 wt% KCLO$_4$ powder and pressed into pellets with diameter of 7 mm and thickness of 5 mm, which were wrapped in gold foil and synthesized at 1000 $^\circ$C under high pressure of 6 GPa for 0.5 h in a belt-type apparatus. The sample chamber of the belt-type apparatus used pyrophyllite as the pressure-transmitting medium and a graphite sleeve as an internal heater. Synthesis temperature was controlled by the input of electrical power inserted on the graphite tube. The resultant products were quenched from high temperature to room temperature by shutting off the electrical power before releasing the pressure. These resultant products were named HP-samples.

Both the AM- and HP-samples were characterized by powder X-ray diffraction (XRD) using MXP18A-HF diffractometer with Cu K$_\alpha$-radiation.

PowderX program [20] was used to refine the lattice parameters. DC magnetic measurements were performed using SQUID magnetometer (quantum design, MPMS type).

3. Results and discussions

3.1. XRD results

XRD patterns of the AM-samples and HP-samples of Fe$_{x}$Cu$_{1-x}$Ba$_2$YCu$_2$O$_{7+y}$ are shown in Figs. 1 and 2, respectively, indicating that all the samples are nearly of single phase except for the AM-sample with $x = 0.80$. The results of Fig. 1 also indicate that solid solubility limit of Fe in Fe$_{x}$Cu$_{1-x}$...
out that there was a little amount of KCL and KCLO₄ due to the addition of KCLO₄ in the HP-samples used as oxidant and the incomplete decomposition during the high-pressure synthesis. To avoid its influence on the results of measurement, the bulk HP-samples were powdered, washed using distilled water and dried below 80°C to determine oxygen content. The purified powder is still superconducting as checked by the magnetization measurements.

The results of iodometric titration indicate that oxygen contents in both the AM- and HP-samples increase with increasing the doping Fe content, as shown in Fig. 4. Also we can find that the HP-samples have more oxygen content than the AM-samples. The oxygen content in the AM-samples is satisfactorily consistent with those reported in references [2,21,24].

3.3. Superconductivity

Fig. 5(a) and (b) shows the M–T curves of AM- and HP-samples, respectively. The dependence of $T_c$ (defined as the onset temperature of the Meissner signal in the $M$–$T$ curves) on Fe content for the HP- and AM-samples is shown in Fig. 6. It can be seen that for the AM-samples $T_c$ decreases quickly with increasing Fe content and becomes zero at $x \geq 0.40$, which is in good agreement with the results of Tarascon et al. [2]. For the HP-samples, however, with increasing Fe content the decrease of $T_c$ is not significant, indicating that the high-pressure synthesis improves superconductivity. The $T_c$, oxygen content and lattice parameters of the AM- and HP-samples are listed in Table 1.

Why can the high-pressure oxygen annealing enhance $T_c$ of $Y$Sr$_2$Cu$_{2.7}$Fe$_{0.3}$O$_{7+y}$ and FeSr$_2$YCu$_2$O$_{7+y}$? There are two explanations given in the following. (1) The improvement of superconductivity in the $Y$Sr$_2$Cu$_{2.7}$Fe$_{0.3}$O$_{7+y}$ superconductor was attributed to the increases of oxygen content and trigonal bipyramidal coordinated Fe at Cu (1) site in CuO$_x$ chains due to the high-pressure oxygen annealing [15]. This explanation is supported by the results of X-ray diffraction, oxygen content and Mössbauer spectroscopy [15]. (2) For the FeSr$_2$YCu$_2$O$_{7+y}$ superconductor prepared by calcining at 900°C in air, subsequent annealing at 800°C in flowing N$_2$ and then oxidizing at 350°C in high-pressure oxygen of 195 atm, superconductivity is caused by both the ordering of Cu and Fe atoms in CuO$_x$ chains and the increase of oxygen content [17,25]. In order to better understand the improvement of superconductivity in the Fe$_{x}$Cu$_{1-x}$Ba$_2$YCu$_2$O$_{7+y}$ superconductors synthesized by the high-pressure synthesis, we performed Mössbauer spectroscopy experiments.

3.4. Mössbauer spectroscopy

The Mössbauer technique is a powerful tool determining the distribution of Fe between Cu (1) and Cu (2) sites in Fe-doped YBCO [3,7,8,13,15]. In order to obtain the

Fig. 3. Lattice parameters $a$, $b$ (1) and $c$ (2) and unit-cell volume (3) of the AM- and HP-samples of Fe$_{x}$Cu$_{1-x}$Ba$_2$YCu$_2$O$_{7+y}$ as a function of Fe content.

Fig. 4. The dependence of oxygen content in the AM- and HP-samples of Fe$_{x}$Cu$_{1-x}$Ba$_2$YCu$_2$O$_{7+y}$ on Fe content.
information for the distribution of Fe between Cu (1) and Cu (2) sites in the AM- and HP-samples, the investigations of Mössbauer spectroscopy were made on two selected samples, (1) AM-sample Fe$_{0.5}$Cu$_{0.5}$Ba$_2$YCu$_2$O$_7.24$ and (2) HP-sample Fe$_{0.5}$Cu$_{0.5}$Ba$_2$YCu$_2$O$_7.41$.

$^{57}$Fe Mössbauer spectra of the selected AM- and HP-samples were recorded by a Wissel System constant acceleration Mössbauer spectrometer with $^{57}$Co (Pd) source at room temperature. The velocity was calibrated using a $\alpha$-Fe foil. The values of isomer shift given here were relative to $\alpha$-Fe at room temperature. A least-square program was used to fit the spectra with Lorenzian line shape.

Fig. 7(1) and (2) shows the results of Mössbauer spectra of AM- and HP-samples, respectively. The spectra can best fit to three doublets (A, B, C). The hyperfine parameters of isomer shift ($\delta$), quadrupole splittings ($\Delta$), Full-width-at-half-maximum or FWHM ($I'$) and site intensity ratio ($I_n/I$) of these three subspectra are summarized in Table 2.
According to the previous Mössbauer spectroscopy studies [3,6,14,15], the doublets A and C are assigned to the Fe located at Cu (1) site and doublet B is related to the Fe located at Cu (2) site. Moreover, the Fe corresponding to A and C sites has tetragonal and five-fold oxygen coordination [3,15], respectively, and the Fe assigned to doublet B has the same pyramidal oxygen configuration as Cu (2) [3,13–15].

By the comparison between the Mössbauer spectrum of the AM-sample and that of its HP-samples, one can find that the intensity of doublet C increases at the expense of doublet A in going from the AM-sample to the HP-sample. This means that the HP-sample has more Fe atoms with fivefold-oxygen coordination in the CuO_x chains than the AM-sample, which is similar to the results of YSr_{2}Cu_{2.7}Fe_{0.3}O_{7-δ} prepared by high-pressure oxygen annealing [15]. From the data listed in Table 2, it can be found that for the AM-sample the sum of integrated intensities of doublets A and C is almost equal to that of doublet C in the spectrum of the HP-sample, indicating that the integrated intensities of Fe located in the CuO_x chains is not nearly changed by the high-pressure synthesis. In Mössbauer spectroscopy, site-integrated intensities are proportional to site-occupancy N if we assume the recoil-free fraction is same. Thus, for the AM-and HP samples, 76% of Fe content occupy Cu (1) sites in the CuO_x chains and 24% of Fe content occupy Cu (2) sites in the CuO_2 planes. The results of Mössbauer spectroscopy indicate that the migration of Fe atoms from CuO_2 planes to CuO_x chains does not take place after the high-pressure synthesis.

From the Mössbauer spectra, it can also be determined that the Fe corresponding to doublets A and B have valence of Fe^{3+} and Fe assigned to doublet C is Fe^{4+} species [15]. This suggests that due to the increase of oxygen and charge balance, the average valence of Fe in the HP-samples is higher than that in the AM-sample. Based on those mentioned above, it can be concluded that the increases of oxygen content and Fe with fivefold-oxygen coordination in CuO_x chains are important reasons for the improvement of superconductivity in HP-samples.

4. Conclusions

In this paper, systematic studies on the Fe_xCu_{1-x}...
Ba$_2$YCu$_2$O$_{7+y}$ superconductors ($x = 0.00–0.70$) prepared by the high-pressure synthesis are presented. XRD analysis indicates that the AM-and HP-samples are nearly of single phase and all the HP-samples have tetragonal structure. Furthermore, the HP-samples have smaller lattice parameter $c$ and unit-cell volume than the AM-samples. The investigations of oxygen content, superconductivity and Mössbauer spectroscopy indicate that the HP-samples have higher oxygen content, average valence of Fe and more Fe with fivefold-oxygen coordination than the AM-samples. The Mössbauer spectroscopy studies confirmed that the high-pressure synthesis does not result in the migration of Fe from the CuO$_2$ planes to the CuO$_x$ chains. The increases of oxygen content and fivefold coordinate Fe in the CuO$_x$ chains due to high-pressure synthesis are important reasons for the improvement of superconductivity in the HP-samples.

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