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A possible explanation of the recovery of superconductivity of quenched $YBa_2Cu_3O_{7-x}$ doped by WO_3

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Abstract. Of two $YBa_2Cu_3O_{7-x}$ samples quenched in air from 900 °C to room temperature, the undoped one is not a superconductor, but the one with 3 wt% WO_3 addition shows a superconducting transition above 88 K. However, it is proven that W does not enter the lattice of $YBa_2Cu_3O_{7-x}$. In this research, experiments have been carried out to reveal the effect of the WO_3 addition on the recovery of superconductivity of the quenched $YBa_2Cu_3O_{7-x}$. The above-mentioned samples were investigated by x-ray powder diffraction, transmission electron microscopy and scanning electron microscopy. Their thermal diffusivities were also measured. Results indicated that W combined with Y, Ba and Cu to form $YBa_2Cu_2WO_{9-\delta}$ small-grain clusters which dispersed in the matrix of $YBa_2Cu_3O_{7-x}$. Differences in both the grain size of $YBa_2Cu_3O_{7-x}$ and the data of thermal diffusivity between the two samples were also observed. This seems to suggest that the reduction of cooling rate be responsible for the recovery of the superconductivity. Our explanation may provide a useful clue for the improvement of the preparation technique of $YBa_2Cu_3O_{7-x}$ superconducting thin films.

1. Introduction

From the viewpoint of practical utilization, large-area $YBa_2Cu_3O_{7-x}$ (YBCO) superconducting thin film has attracted more attention of researchers than in other high-T_c superconducting systems. A lot of progress has been made in this respect. The phase formed in vacuum and at high temperature (above 880 °C) is not superconducting [1, 2], for example, YBCO quenched from 900 °C to room temperature is a nonsuperconductor. A long post-anneal is proven still to be an effective method to make such a thin film with a large area and to obtain superconductivity. However, it sometimes introduces mutual element diffusion between the films and the substrates, and changes properties of the film. Can the high-temperature phase become superconducting in a relatively short time? The work of Feng *et al* and Shi *et al* [2, 3] gave some clues to the above question. They reported that the T_c of YBCO quenched from 900 °C to room temperature could be raised to 88 K by doping 3 wt% WO_3 into it. Moreover, they revealed that the oxygen contents were different for the undoped and

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WO_3-doped samples through Raman scattering spectra analyses, and confirmed the increase of oxygen content in the WO_3-doped samples. However, it was proven by x-ray powder diffraction (XRD) analyses that W did not enter the lattice of YBCO. An unidentified phase existed in the superconductor, of which peaks appeared at $2\Theta = 30.1^\circ$, 35.7° and 43.0° in the (XRD) pattern. There were two kinds of possibility to explain the increase of the oxygen content. (i) The existence of the unidentified phase might improve the oxygen environment of YBCO and accelerate its oxygen absorption. (ii) It might reduce the effect of quenching on the whole sample, giving YBCO in the doped sample time to obtain oxygen and become superconducting. Here, an interesting problem arises. Of the two assumptions, which one is nearer to the truth?

To answer the above question, in this work, the second phase was first identified. The microstructure and the thermal diffusivity of the samples were carefully investigated. Our experimental results supported the second hypothesis strongly. It has been reported by Kuwabara and Kusaka [4] that the critical current density J_c of YBCO could also be improved by proper addition of WO_3, and no harmful influence on electrical conduction had been found. Therefore, through proper doping and appropriate controlling of preparing temperature, high-quality and large-area YBCO thin film which need not be post-annealed may be expected to be achieved. In other words, explanations in this paper are not only novel but also instructive to the improvement of the preparation technique of YBCO superconducting thin film.

2. Experimental details

YBCO ceramics (with 0 and 3 wt% WO_3 addition) studied in this work were obtained by a conventional solid state reaction method. After sintering at 900 °C for 30 h in flowing oxygen, the samples were quenched in air to room temperature. It was found by ac susceptibility measurement that the undoped sample was a nonsuperconductor, while the superconducting transition of the doped one occurred above 88 K. A second phase was detected by x-ray powder diffraction in the doped sample besides the main phase YBCO. The difference of the oxygen content between the two samples was determined by Raman scattering spectra analyses. Details of the samples' processing, as well as the mentioned analyses, can be found in our previous report [2, 3].

In this research, the x-ray diffraction patterns were obtained on a D/MAX-rA rotated target x-ray diffractometer with Cu Kα radiation. The specimens for transmission electron microscope (TEM) observation were ground in an agate mortar with alcohol for a few minutes, then several drops of the resulting powder suspension were placed on a carbon film supported by an Mo grid. The H-800 TEM used here was operated at 200 kV and was equipped with a carbon specimen holder as well as an x-ray energy dispersive spectroscope (EDS) which has to be calibrated strictly before the acquisition of the spectra. The fresh fracture surfaces examined by scanning electron microscope (SEM) were obtained by breaking off a part of the sample. The X-650 SEM used here was equipped with an x-ray wavelength dispersive spectroscope (WDS) and was operated at 25 kV. The data of thermal diffusivity were obtained using the photothermal deflection conductivity measurement system which was developed according to the principle of photothermal deflection spectroscopy (PTDS) [5]. Many standard samples had been measured and the results agreed well with the reference data in the literature.

3. Results and discussion

To identify the unknown second phase, nearly pure phase $YBa_2Cu_2WO_{9-\delta}$ (YBCWO) was prepared separately by sintering the stoichiometric mixture of the oxides and carbonates at 1080 °C for 24 h, and was characterized by XRD (as shown in figure 1(a)). By comparing the peaks with that of the doped sample (denoted by black dots in figure 1(b)), the unknown phase could be identified as YBCWO [6]. However, all the crystalline grains examined in TEM gave typical electron diffraction patterns of YBCO. Their average content ratio of Y, Ba, Cu and W in at.% was Y:Ba:Cu:W = 22.5:35.2:42.3:0.0 according to the EDS results. In other words, WO_3 did not enter into the lattice of YBCO which was still dominant in the quenched sample [7], in very good agreement with the previous report obtained by XRD [2, 3].

More detailed information concerning the micrographs of YBCO and YBCWO was revealed by SEM/WDS investigation, as described below.

(i) In the matrix of YBCO were dispersed some clusters of the second phase of which the crystalline state was much worse than that of the main phase, as evidenced in figure 2(b), labelled with the letter C. The clusters were composed of YBCWO small grains. The shapes of the clusters were not regular. Their dimensions ranged from a few to forty micrometres.

(ii) The existence of YBCWO clusters exerted considerable influence on the grain morphology of YBCO, as evidenced in figure 2: the sizes of YBCO grains in the doped sample were obviously larger than those in the undoped one.

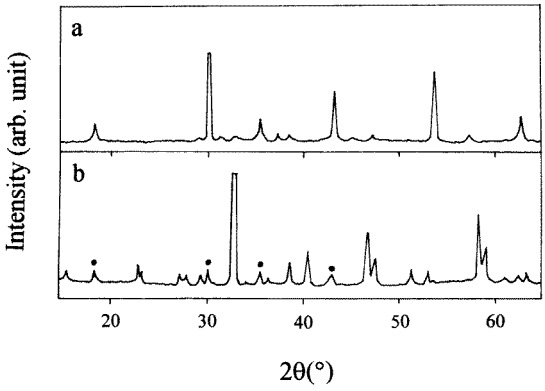

Figure 1. X-ray diffraction patterns for samples: (a) $YBa_2Cu_2WO_{9-\delta}$; (b) the quenched $YBa_2Cu_3O_{7-x}$ with 3 wt% WO_3 addition. The unknown phase is denoted with black dots; the main phase is $YBa_2Cu_3O_{7-x}$.

The SEM/WDS experimental results provided a reasonable explanation of why the second phase failed to be identified by XRD in our previous research and by SAED in this work. Being in a different chemical environment and at the relatively low sintering temperature (900 °C), the crystal of YBCWO in the doped sample did not develop sufficiently, and, therefore, could not be identified directly by the diffraction method. However, the larger size of the YBCO grains implied that the clusters of YBCWO might have some influence on the heat transportation as a whole.

To confirm the above assumption, the two samples were studied by the photothermal deflection conductivity measurement system under the same condition. A small difference

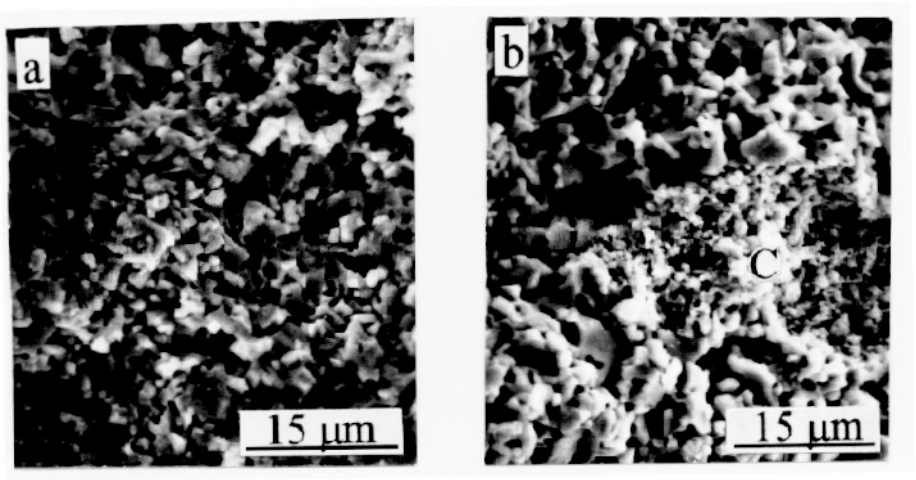

Figure 2. SEM images of the samples: (a) the quenched $YBa_2Cu_3O_{7-x}$; (b) the quenched $YBa_2Cu_3O_{7-x}$ with 3 wt% WO_3 addition. The area labelled by the letter C refers to the $YBa_2Cu_2WO_{9-\delta}$ small-grain clusters.

between them in the data of the thermal diffusivity was observed. The thermal diffusivity of the undoped sample was 0.025 ± 0.001 cm^2 s^{-1}, while that of the 3 wt% WO_3-doped one was 0.015 ± 0.001 cm^2 s^{-1}. Since all the conditions (including the sample preparation, heat treatment and the measurement) were the same, the difference must be introduced by the existence of the clusters of YBCWO in the doped sample. Due to its small amount, the difference was reasonably not large. However, it suggests that heat diffused more slowly in the doped sample than in the undoped one. In other words, although both of the samples were quenched in air from 900 °C to room temperature, they actually experienced different processes. YBCO in the undoped sample cooled faster than that in the doped sample.

Since the valence state of W remains +6 in $YBa_2Cu_2WO_{9-\delta}$, there seems to be no improvement in the oxygen environment in the doped sample. It is more convincing to consider the reduction of the effect of quenching on the whole sample to be the main cause of the recovery of superconductivity. This conclusion was supported by the experimental results in both microstructure investigation and thermal diffusivity measurement quite well. Therefore, the recovery of the quenched YBCO with 3 wt% WO_3 addition can be explained as follows: the clusters of YBCWO stored some heat and released them slowly than the YBCO surrounding them, enabling YBCO in the doped sample to cool more slowly than expected. Thus, they had time to absorb enough oxygen at 600–700 °C and to grow. Consequently, they appeared larger in the SEM images and showed superconductivity above 88 K. In contrast, YBCO in the undoped sample cooled faster than that in the doped sample; having no chance to acquire sufficient oxygen and to grow, it was reasonably composed of grains which were not only smaller but also nonsuperconducting.

In the work of Kuwabara and Kusaka [4], no harmful influence of WO_3 addition on T_c was observed. Moreover, the J_c of the doped sample showed a significant increase compared with that of the undoped one. They also proved that W did not enter the lattice of YBCO but formed an unknown phase. In this work, the unknown phase has been identified as $YBa_2Cu_2WO_{9-\delta}$. Therefore, regardless of the still unclear mechanism, it appears worthwhile to consider WO_3 addition as an effective method to improve the

preparation technique of YBCO superconducting thin films. Through proper doping and appropriate control of preparation temperature, high-quality and large-area YBCO thin film which need not be post-annealed may be expected to be achieved.

4. Conclusion

In summary, W was proved not to have entered into the lattice of YBCO, but combined with Y, Ba and Cu to form YBCWO. The small grains of YBCWO in the 3 wt% WO_3-doped sample existed mostly in the form of clusters which dispersed in the matrix of YBCO. It is suggested by present experimental results in both microstructure observation and thermal diffusivity measurement that the reduction of the cooling rate due to the existence of YBCWO clusters is responsible for the recovery of superconductivity in the quenched YBCO system.

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