Superconducting Property and Structure Studies of YBa₂Cu₃O₇-Ag₂O Composites

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We have studied the superconducting property and the structure of YBa₂Cu₃O₇ added with Ag₂O, with the weight ratios of YBa₂Cu₃O₇ to Ag equal to 4, 6, 8, and 10. Resistance and magnetization measurements show that the normal-state transport behavior and the superconducting transition temperature, T_c , are insensitive to the amount of Ag added. The normal-state resistance decreases linearly with temperature, reaching a large value of ≈ 3 for the ratio $R(300\text{ K})/R(100\text{ K})$. This value is evidently larger than that (≤ 2.5) generally observed in polycrystalline YBa₂Cu₃O₇, and is ascribed to the improved grain growth behavior resulting from Ag addition. X-ray diffraction and scanning electron microscopy studies have also been performed. X-ray diffraction study indicates the Ag peaks appear as a separate phase. Scanning electron microscopy study reveals large YBa₂Cu₃O₇ grains ($\approx 20\text{--}60\text{ }\mu\text{m}$). Finally, we point out that the microstructures of the samples depend much on the subtle preparation conditions.

KEYWORDS: high- T_c superconductor, YBa₂Cu₃O₇ system, Ag addition, electrical resistance, scanning electron microscopy

§1. Introduction

The superconducting properties and the structure of the high temperature cuprate superconductor YBa₂Cu₃O₇ with Ag addition have recently been studied.¹⁻⁵ The reasons for this interest, among others, are: (1) the added "Ag" appears as a separate phase, without being incorporated into the superconducting YBa₂Cu₃O₇ phase,¹⁻⁴ and (2) Ag addition results in interesting magnetic properties such as suspension of the sample below a permanent magnet.^{1,6} The most direct and convincing manifestation of the unique properties of these samples is that the superconducting transition temperature, T_c , is not at all suppressed even in the presence of sizeable amount of Ag.¹⁻³ This phenomenon is extremely different from that observed in samples "doped" with (transition) metal atoms, M. Doping with M usually results in substitution of Cu by M, and hence causes a significant suppression of T_c .^{7,8} However, despite these interesting phenomena, a few puzzles of this system remain unanswered. For example, whether or not the flux pinning force, and/or critical current density, J_c , has been enhanced due to Ag addition remains unclear.^{4,6} Besides, the Ag addition has been introduced by several different ways, including mixing YBa₂Cu₃O₇ with metallic Ag (refs. 4 and 5), AgO (ref. 1), or Ag₂O (refs. 2-4). Different preparation methods can result in different sample morphologies and physical properties. In this work, we use YBa₂Cu₃O₇ and Ag₂O as the starting materials.

In this paper we report our results on the resistance, magnetization, X-ray diffraction, and scanning electron microscopy studies on the YBa₂Cu₃O₇-Ag₂O composites. In particular, we show clearly (1) that the normal-state transport behavior, including the room-temperature resistivity, $\rho(300\text{ K})$, and the temperature dependence of the

normalized resistance, $R(T)/R(300\text{ K})$, and the superconducting transition temperature, T_c , are insensitive to the amount of Ag added, and (2) that the resistance ratio, $R(300\text{ K})/R(100\text{ K})$, shows a large value of ≈ 3 , which has never been addressed before. This paper is organized as follows. In §2 we discuss the experimental details. In §3 our results and discussions are presented. §4 contains our conclusion.

§2. Experimental Method

Samples were prepared by standard solid state reaction method under nominally identical conditions. Appropriate amounts of stoichiometric YBa₂Cu₃O₇ and Ag₂O were mixed and heated at 910°C in air for 48 hours. The amount of the starting material was chosen so that, after Ag₂O decomposed,* the weight ratio of YBa₂Cu₃O₇ to Ag was equal to 4, 6, 8, and 10.** The fired mixtures were then reground and pelletized. The pellets were then fired at 935°C for 1 day and subsequently were annealed at 470-480°C in flowing O₂ for 24 hours and then slowly cooled to ambient in O₂. One silver-free YBa₂Cu₃O₇ sample (#3-1) was also prepared and studied for comparison. The values for the relevant parameters of the samples are listed in Table I.

Samples were sliced from each pellet for resistance, magnetization, X-ray diffraction, and scanning electron microscopy (SEM) studies. The ac resistance was measured by standard four-probe technique, with a

*Ag₂O was found to decompose to metallic Ag releasing oxygen at around 300-500°C. See ref. 4.

**We had also attempted to synthesize samples with weight ratios of 3, 2, 1, and 0.5, but those samples melted at our firing temperature of 935°C. This result is consistent with that by Tiefel *et al.* (ref. 4). They have recently reported that Ag₂O addition causes partial melting of YBa₂Cu₃O₇ phase.

Table I. Values for the relevant parameters of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and four $\text{YBa}_2\text{Cu}_3\text{O}_7\text{-Ag}_2\text{O}$ composites with different compositions.

Sample	Weight ratio	$\rho(300\text{ K})$ (m Ω -cm)	Meissner fraction (%)	$\chi(100\text{ K})$ (emu/g)
#3-1	∞	—	17	—
#9-1	10	1.6	31	2.1×10^{-6}
#9-2	8	6.7	23	8.6×10^{-6}
#9-3	6	1.7	22	2.3×10^{-6}
#9-4	4	2.5	23	2.2×10^{-6}

calibrated platinum thermometer as the temperature sensor. Zero-field-cooled and field-cooled magnetizations at 20 G and normal-state magnetizations at 5 kG were determined using a vibrating sample magnetometer. SEM photographs were taken from a Phillips SEM-515.

§3. Experimental Results and Discussions

X-ray diffraction data for silver-free $\text{YBa}_2\text{Cu}_3\text{O}_7$ as well as for $\text{YBa}_2\text{Cu}_3\text{O}_7\text{-Ag}_2\text{O}$ composites were obtained from a Rigaku powder diffractometer with filtered copper radiation. Inspection of diffraction patterns showed that metallic Ag with 2θ at about 38.25, 44.37, and 77.50 was present in the samples #9-1 through #9-4. In addition, there was no sign of composition-dependent and systematic shift in the series of X-ray diffraction pattern measured. These observations show, as previously reported,¹⁻⁴⁾ that the added Ag appeared not to substitute for Cu in $\text{YBa}_2\text{Cu}_3\text{O}_7$; instead, it presumably filled into grain boundaries, and in particular, played an important role in determining J_c and the grain growth behavior. Shown in Table II are the cell parameters for both silver-free and silver-containing orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$ determined from at least twelve peaks in the individual X-ray diffraction pattern using a least-squares refinement program LATT.* No significant changes in the cell dimensions were observed if a 3σ correction was considered in the comparisons.

Figure 1 shows the normalized resistance, $R(T)/R(300\text{ K})$, as a function of temperature for samples #9-1, #9-3, and #9-4. Above T_c , the resistance is linear in temperature, as is in the silver-free parent compound. This linearity has been observed essentially in all the newly found high temperature cuprate superconductors. At $91.5 \pm 0.5\text{ K}$, all the samples undergo a superconducting transition (with a width $\approx 1.0\text{--}1.5\text{ K}$), being independent of the amount of Ag added. This transition temperature is the

Fig. 1. Normalized resistance, $R(T)/R(300\text{ K})$, as a function of temperature for samples #9-1 (open circles), #9-3 (solid line), and #9-4 (open squares). The resistance above T_c is linear in temperature, reaching a value of 3 for the ratio $R(300\text{ K})/R(100\text{ K})$. Some data points have been removed for clarity.

same as that in our silver-free sample (#3-1) measured simultaneously. Therefore, this figure shows clearly that the T_c of $\text{YBa}_2\text{Cu}_3\text{O}_7$ does not change upon Ag addition. This behavior has been reported previously,¹⁻³⁾ and is characteristic to Ag (and Au, ref. 9) addition alone. Pavuna *et al.*²⁾ have observed no sign of suppression of T_c in this system provided that the Ag added does not exceed about 30 wt.%.

Interestingly enough, not only the transition temperature T_c is the same for all the samples shown in Fig. 1, but the normal-state transport property is the same. First we note that the room-temperature resistivity, $\rho(300\text{ K})$, of our samples are scarcely dependent on the amount of Ag added, see Table I. This observation does not seem to be in line with that reported previously by Pavuna *et al.*,²⁾ and by Plechack *et al.*,³⁾ in the same composite system. Further work is underway to clarify this issue. Second, as the temperature is reduced from room temperature, the normalized resistance for the samples overlaps closely. The normalized resistance ratio, $R(300\text{ K})/R(T)$, for the samples increases steadily, reaching a value of ≈ 3 at 100 K. This similarity suggests that the transport behavior be barely affected by the different amounts of Ag added. This is consistent with the X-ray diffraction results, i.e. the Ag peaks appear as a separate phase discussed above. The resistance ratio of ≈ 3 deserves special attention. This value of $R(300\text{ K})/R(100\text{ K})$ is larger than that (in general in the range 2.0–2.5) usually found in well-prepared polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_7$ samples.¹⁰⁻¹²⁾ This is ascribed to the improved sample morphologies and enlarged grain sizes (Fig. 2) resulting from improved grain growth behavior in the presence of Ag. Apart from the larger grain sizes, the grain boundary resistance has greatly been diminished in these samples, and as a result, a large resistance ratio is achieved. The improved grain growth behavior is likely to play a key role in the future applications of the new cuprate superconductors. Work to study the mechanisms of the improved grain growth behavior is underway.

Table II. The cell parameters of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and four $\text{YBa}_2\text{Cu}_3\text{O}_7\text{-Ag}_2\text{O}$ composites with different compositions (the number in the parenthesis indicates standard deviation).

Sample	a(Å)	b(Å)	c(Å)	Volume(Å ³)
#3-1	3.835(8)	3.880(2)	11.74(2)	174.7(8)
#9-1	3.829(3)	3.887(6)	11.74(1)	174.7(4)
#9-2	3.818(6)	3.890(8)	11.74(2)	174.7(5)
#9-3	3.826(3)	3.890(6)	11.73(1)	174.6(4)
#9-4	3.830(4)	3.903(10)	11.73(1)	174.4(5)

*F. Takusagawa, Ames Laboratory, Iowa State University, Ames, Iowa, USA, (1981), unpublished.

Fig. 2. SEM photographs of (a) sample #9-4, and (b) sample #9-2. The grain size in (a) is in the range 20–60 μm , while in (b) is 100–200 μm .

Figures 2(a) and 2(b) show the SEM data for two (#9-4 and #9-2) of the samples. Figure 2(a) shows a spread of the grain size for sample #9-4 in the range 20–60 μm . This size is about four times that ($\approx 10 \mu\text{m}$ on average) in silver-free $\text{YBa}_2\text{Cu}_3\text{O}_7$.^{4,13} Similar grain sizes have also been found for samples #9-1 and #9-3. Therefore, it is clear that Ag addition has resulted in enlarged grains. The reasons why and how such enlargement occurs require further study, however. Similar observation has recently been reported in $\text{YBa}_2\text{Cu}_3\text{O}_7\text{-AgO}$ composites.^{4,14}

Figure 2(b) shows the SEM data for sample #9-2. The grain size of this sample is distinctively large, reaching 100–200 μm . This larger grain size is believed to be closely connected with the larger normal-state susceptibility for this sample (Table I). Recently, Huang *et al.*¹⁴ reported that the microstructure, and therefore presumably the transport and magnetic properties, of Ag added $\text{YBa}_2\text{Cu}_3\text{O}_7$ depended much on the preparation conditions. They concluded that the microstructure de-

pended more on the preparation conditions than on the relative weight ratio of $\text{YBa}_2\text{Cu}_3\text{O}_7$ to Ag. Our result is in line with theirs, although, instead of starting with Ag_2O , their samples were prepared from mixing $\text{YBa}_2\text{Cu}_3\text{O}_7$ with AgO. The anomalous properties and structure of sample #9-2 may result from fluctuations in preparation conditions, *e.g.* differential temperature variations during long-term annealing or a minor temperature gradient present in the furnace. This indicates that some subtle aspect of the sample processing of this potentially important system has yet to be mastered.

§4. Conclusion

We have studied the transport properties and the structure of the high temperature cuprate superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ added with Ag_2O . We find that Ag addition results in enlargement of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ grains with sizes of 20–60 μm , while leaving T_c intact. We also find that due to improved grain growth behavior the resistance ratio $R(300 \text{ K})/R(100 \text{ K})$ is very large, being equal to 3 at 100 K.

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