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Resistivity-Temperature Characteristics of Sol Gel $YBa_2Cu_3O_y$ Samples Synthesized in Flowing Oxygen Atmosphere

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The relationship of resistivity versus synthesizing temperature of sol gel $YBa_2Cu_3O_y$ samples was studied while prepared under flowing oxygen conditions. A set of high-temperature ρ −T curves was obtained for the whole process. After the sample finished the test measuring, its resistivity was $\rho_{300} = 9.83 \times 10^{-3}$ Ω • cm at room temperature. The ρ-T curve also showed that the orthorhombic-tetragonal phase transformation of sol-gel $YBa_2Cu_3O_y$ sample occurred at 581℃ as the sample in the rising temperature process, but at 613℃ in the cooling process, lower than that of the samples made by using the conventional powder metallurgy methods.

Key words: sol gel $YBa_2Cu_3O_y$ sample, ρ-T curve, resistivity, phase transformation**.**

PACC: 7470, 7470R, 7430

1. Introduction

Many normal and superconducting properties of high Tc superconductors have been investigated and discussed，[1,2] such as the crystallographic structure，[3] oxygen deficiency，[4] defects，[5]anisotropy，[6] magnetic properties，[7] and the transport properties[8] etc. However, the properties of high-temperature (HT) ρ －T curve have rarely been studied at temperatures higher than 800 ℃ or in the synthesis process．[9-15]

Freitas et al[9] measured the temperature dependence of the resistivity under several oxygen partial pressures Po_2 for $YBa_2Cu_3O_y$ samples from room temperature to 800℃. From these results they found that the HT order-disorder phase transition in the superconductor $YBa_2Cu_3O_y$ sample occurred at 685℃ as it was heated and cooled at a rate of 0.1K/min in $Po_2=10^5$Pa. Cooke et al．[10] found that the sulfur incorporation into $YBa_2Cu_3O_y$ was possible by diffusion in gaseous state according to their HT resistivity measurement of $YBa_2Cu_3O_y$. We found that the HT resistivity measurement of superconductors is a useful means for assessing the progress, success of any kind of ceramic superconductors, and researching the properties and the phase formation．[11-16]

From our previous results[11] it is known that the orthorhombic-tetragonal phase transition

(O-T phase transition) of $YBa_2Cu_3O_y$ samples observed by using the HT ρ −T curves only after its resistivity decreased during the whole cooling process. If the O-T phase transition phenomena can be observed under the above condition, we can predict that the sintering process has ended.

We have also measured the HT ρ −T curves of MgB_2 sample to investigate the phase formation while sintering under different atmosphere conditions and using different sizes of magnesium powders as the raw materials.[12-15] We found that not only the sintering atmosphere may affect the phase formation of MgB_2,[12,13,16] but also the size of magnesium powders can have strong influence on the features of the phase.[14,15] For example, if MgB_2 sample is prepared with nanometer magnesium powders as the raw materials, the temperature of phase formation of MgB_2 will range from 430 to 490℃,[14] i.e. 100℃ lower than that by using ordinary off-the shelf magnesium powders and sintering in flowing argon atmosphere,[12]and 220℃ lower than that by using ordinary off-the shelf magnesium powders and sintered in vacuum.[19] Therefore, it will be very interesting to study: if we use the sol gel method to prepare the $YBa_2Cu_3O_y$ raw powders, and sinter it in flowing oxygen, what will be the temperature of the O-T phase transition appearing on the HT ρ −T curves?

In this paper we present the results of measurements of the resistivity against temperature of the sol gel $YBa_2Cu_3O_y$ (hereafter refer to as SG-YBCO) sample synthesized in flowing oxygen. The temperature range of the O-T phase transition occurring in the SG-$YBa_2Cu_3O_y$ superconductor is also discussed.

2. Experiment

Samples were prepared in two steps. First, the primary SG-YBCO powders were prepared by the sol gel method.[17,18]Then, the solid-state reaction technique was used to sinter the primary SG-YBCO samples at about 920℃ for the first sintering cycle. The sample was pulverized and reground after it finished the first sintering process. The samples were then sintered at 950℃ in the second cycle. Four gold wires of Φ=0.4 mm diamter were used as the electric leads and pressed into the rectangular sample with a size of 2.5×1.0×（0.28～0.32) cm^3 by using a special mould. Then the sample was heated in a tube furnace, at the same time its resistivity was measured in-situ by the dc four-probe method. A computer was used to collect the experimental data. All of the sintering processes were carried out in flowing oxygen. The heating rate in each sintering process was 475℃/h; the sample was cooled down within the tube furnace with power off to room temperature.

The x-ray diffraction patterns were obtained using the Philips diffractometer with Cu K_α radiation, from which we found that the SG-YBCO sample changs into $YBa_2Cu_3O_y$ only after sintering twice, that is at around 920℃ in the first sintering process, and at 950℃ in the second sintering process.

3. Results and discussion

In each sintering cycle, the sample undergoes three processes: heating (rising temperature) process, constant (holding) temperature process, and cooling process. The corresponding HT ρ–T curve was measured in each process. The experimental curves are shown in Figs. 1 and 2.

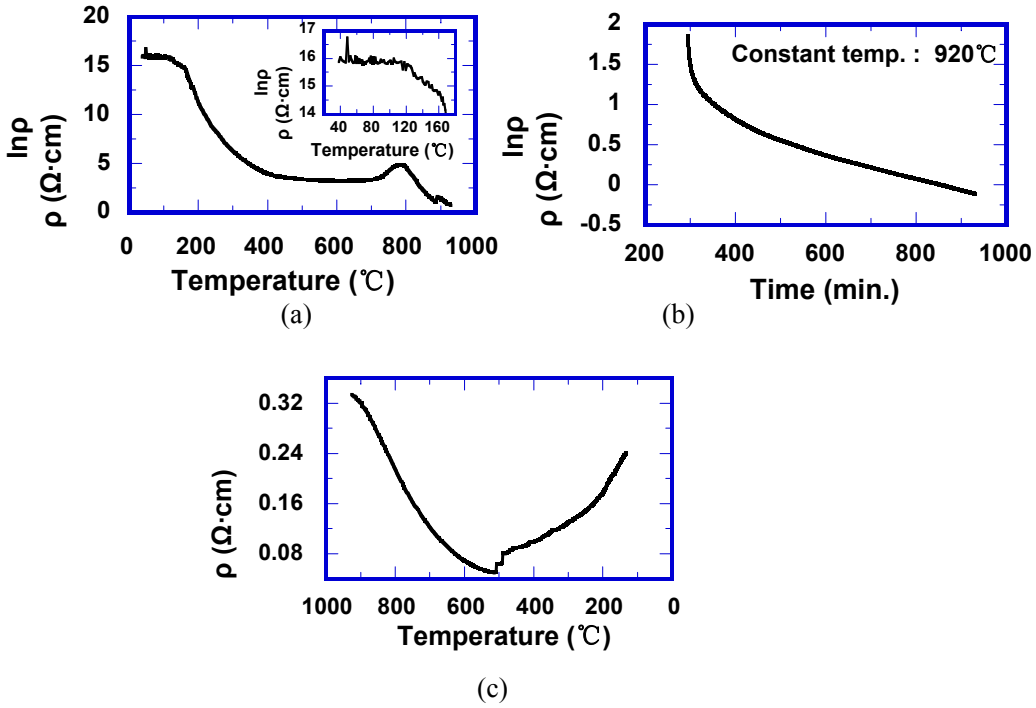


Fig. 1 The in-situ HT ρ-T curves of SG-YBCO sample sintered in the first cycle： (a) heating, (b) constant temperature at 920℃, and (c) cooling in the furnace.

Figures 1(a), (b), and (c) show the heating , keeping constant temperature at 920℃ and cooling processes respectively of the HT ρ–T curves of the SG-YBCO sample sintered in the first cycle. From Fig. 1(a) it can be seen that the SG-YBCO sample is initially an insulator at room temperature. Its resistivity is about $2\times10^{7}\ \Omega\cdot$cm with some jitter observed till the temperature reaches 110℃ during the heating process. The resistivity of the SG-YBCO sample is decreased gradually with increasing temperature, but it reduces rapidly at temperatures higher than 200℃. This may be caused by some kind of chemical reaction occurring in the heating process. For example, some residual nitrate and citrate decompose, and send off some kinds of gases, such as NO_x, CO_2, and NH_3 to produce $BaCO_3$, Y_2O_3, CuO, and CuO_2 etc. [18] The thermogravity curve also shows that the SG-YBCO sample has a high weight loss at temperatures of 200～300℃. [18]

There are two special temperature points T_v and T_p, where the YBCO sample changes its conductivity for every HT ρ−T curve in the heating process: at T_v the YBCO sample changes from semiconducting to conducting and presents a minimum resistivity value ρ_v; while at T_p the YBCO sample changes from conducting to semiconducting again, and presents a maximum resistivity value ρ_p. In different sintering processes, the temperatures T_v and T_p are different. In order to compare the sintering processes between the SG-YBCO samples and the YBCO samples sintered in ambient air (hereafter refer to as A-YBCO sample), we must compare their HT ρ−T curves in each sintering process.

The curve shape in Fig.1(a) is similar to that obtained from the second cycle to sixth cycle of the A-YBCO samples in the heating process. [11]

We believe that the SG-YBCO samples produced using sol gel method have already undergone an active chemical reaction during the preparation, which corresponds to the first

sintering in the solid reaction process of the A-YBCO sample. This is why the first sintering cycle of the SG-YBCO samples is equivalent to the second sintering cycle of the A-YBCO samples; the second sintering cycle of the SG-YBCO samples is corresponding to the sixth sintering cycle of A-YBCO samples.

The points T_v and T_p for ρ_v and ρ_p appear at 534 and 871℃ respectively for the A-YBCO samples in the second cycle. However, the T_v and T_p for the SG-YBCO samples appear at 609 and 785℃ in the first sintering cycle. The T_v and T_p for the A-YBCO samples appear at 487 and 871℃ respectively in the sixth cycle, but the T_v and T_p for the SG-YBCO samples appear at 597 and 721℃ in the second sintering cycle. The comparison of these characters between the SG-YBCO and the A-YBCO samples are listed in Table 1.

Table 1. The comparison between the resistivities of SG-YBCO and A-YBCO samples

Process	1st round of SG-YBCO and 2nd round of A-YBCO				2nd round of SG-YBCO and 6th round of A-YBCO				End testing measuring
Parameters	T_v (℃)	ρ_v (Ω•cm)	T_p (℃)	ρ_p (Ω•cm)	T_v (℃)	ρ_v (Ω•cm)	T_p (℃)	ρ_p (Ω•cm)	ρ_{end} (Ω•cm)
SG-YBCO	609	67.79	785	388.8	597	2.59	721	2.772	0.0098
A-YBCO	534	0.1425	871	0.554	487	0.1124	871	0.341	0.0047

The SG-YBCO and the A-YBCO samples have the same variation trend in resistivity. But the difference of T_p and T_v is different. In the second cycle of the A-YBCO samples, the temperature difference is ΔT =337℃, but in the 1st cycle of the SG-YBCO samples, the temperature difference is ΔT =176℃. In the sixth cycle of the A-YBCO, ΔT =384℃, but in the second cycle of the SG-YBCO sample, ΔT =124℃.

The above results reveal that it is easier for the SG-YBCO samples to finish the transition from semiconducting to conductiving at T_v and then from conducting to semiconducting at T_p than for the A-YBCO samples. The reasons for this are: 1. the SG-YBCO samples are sintered in a flowing oxygen atmosphere, but the A-YBCO samples are in ambient air; 2. the raw materials of the SG-YBCO samples of nanometer powders are easier to get into solid reaction than those of the A-YBCO samples of micrometer powders. This also can be confirmed from the sintering process of MgB_2 samples by using nanometer magnesium powders as the raw material. [14]

While keeping the SG-YBCO sample at 920℃ for about 11.5 h in the first cycle, the resistivity decreased continuously. This is similar to the behaviour of the A-YBCO samples kept at constant temperature in the second sintering process.

In the cooling process of the SG-YBCO samples, the resistivity continuously decreases from 920 to 505℃, then suddenly turns to increase from 505℃ down to room temperature. The A-YBCO samples in the cooling process from the first cycle to the fifth cycle show the same variation trend. This indicates that oxygen content is still not enough to keep the YBCO samples in the conducting state in higher temperature. Obviously, such a kind of YBCO sample is certainly not in the superconducting state at low temperatures.

Figure 2 shows the in-situ HT ρ–T curves of the SG-YBCO sample which underwent the first cycle of sintering process, and then pulverized, reground, and the gold wires re-pressed into

the rectangular sample for performing the second cycle of sintering. Figures 2 (a), (b), and (c) correspond to the heating process, constant temperature process at 950℃, and cooling process respectively. The three curves in the figures are nearly the same as the corresponding curves of the A-YBCO sample which was sintered in the 6th cycle in ambient air. [11]

It also can be seen that the room temperature resistivity is much lower, about 88 Ω • cm. The resistivity decreases to about 0.12 Ω • cm after the heating process is finished. The resistivity of the SG-YBCO shows a shoulder of 2. 77 Ω at 725℃ from the fig. 2 (a). This means that the metal-semiconductor transition occurs in the SG-YBCO sample again. This temperature is lower than the A-YBCO sample as shown in Table 1. For the A-YBCO sample this temperature appears at about 800℃ in every rising temperature process. This indicates that the transition temperature ranges from semiconducting-metallic to metallic-semiconducting of the SG-YBCO sample is narrower than that of the A-YBCO sample. This also indicates that the YBCO crystal grain formation of the SG-YBCO sample is easier than that of the A-YBCO sample.

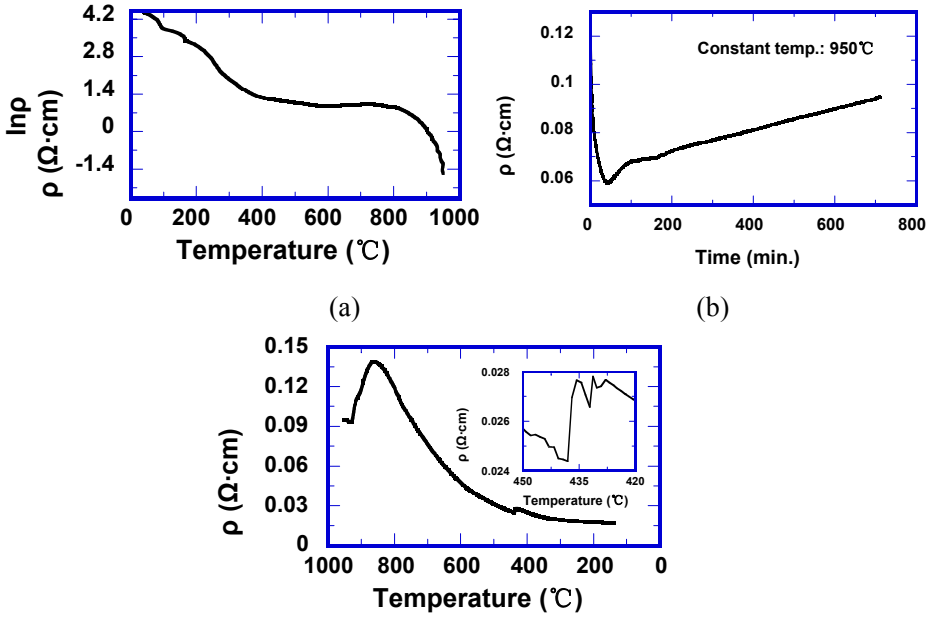
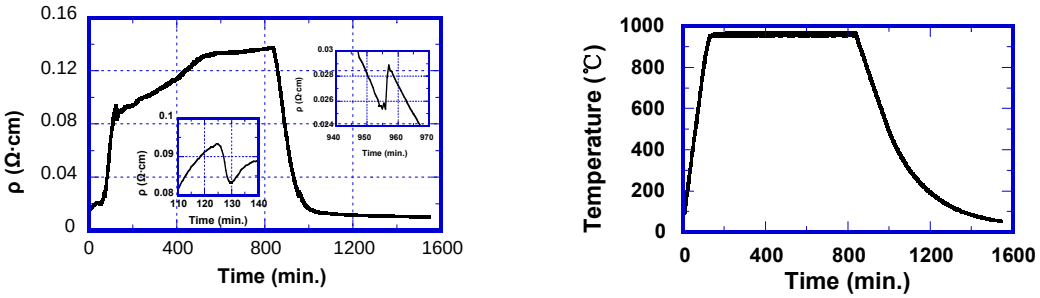


Fig. 2. The in-situ HT ρ-T curves of SG-YBCO sample sintered in the second cycle in the (a) heating process, (b) holding process at 950℃ and (c) cooling process.

These figures further indicate that the SG-YBCO sintering process is similar to the A-YBCO sintering process. In the heating process, the sample exhibits semiconducting at the temperatures lower than T_v. It shows a metallic character at heating temperatures higher than T_v. If the temperature rises above T_p, it becomes to semiconducting again. In the constant temperature process (950℃) the range of resistivity variation is smaller than the heating or cooling process. In the cooling process, the resistivity of the SG-YBCO sample shows an obvious small peak. For the A-YBCO sample it appears at 690℃ in the 6th sintering cycle, but for the SG-YBCO sample it appears at 437℃ as seen in Fig. 2 (c). This indicates that the SG-YBCO sample is different from the A-YBCO sample at the O-T phase transition. For our A-YBCO sample the O-T phase

transition occurred at 690℃[5], which is different from the results of 685℃[9], and 700℃.[19,20]



(a) (b)

Fig. 3 The in-situ HT ρ-T curves for SG-YBCO sample after the two sintering cycle. The sample tested in the whole process (a) for the resistivity – testing time ρ-t curve; (b) for the temperature – testing time T-tcurve.

In order to confirm that the small peak of HT ρ -T curve appearing at 437℃ in the cooling process of the second sintering cycle, the ρ –t and T–t curves of the SG-YBCO samples are measured in the whole process, as shown in fig.3. The structures repeat themselves very well. The small peaks in the ρ –t curve or ρ –T curve are not different from the second sintering process. All the 3 characteristic temperatures of the SG-YBCO sample are lower than those of the A-YBCO sample. This could be ascribed to the smaller grain sizes of the SG-YBCO samples. We will discuss it in more detail later.

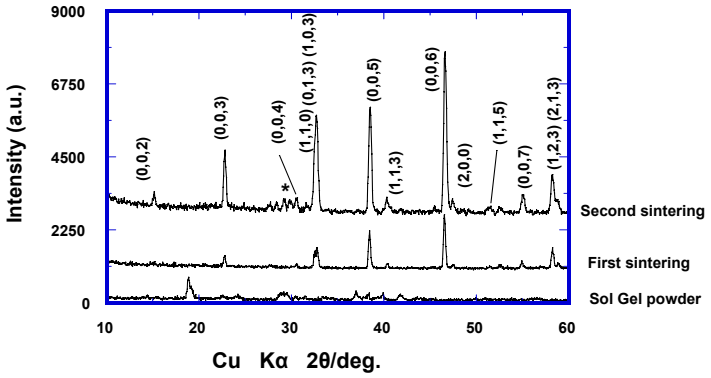


Fig.4 The x-ray patterns of sol gel YBCO sample before sintered and sintered for the first and second cycle. "*" Impurity phase.

Figure 4 shows the XRD patterns obtained after the SG-YBCO sample finishes the two sintering cycles. There are not any diffraction peaks of the $YBa_2Cu_3O_y$ can be seen in the XRD

pattern of sol-gel powders. After the SG-YBCO sample finished the first sintering cycle, the main diffraction peaks of the $YBa_2Cu_3O_y$ appeared as shows in the x-ray pattern index of the first sintering. After the second cycle sintering, not only the intensity of those main diffraction peaks enhanced, but also the (0, 0, 2) peak appeared. This indicates that the SG-YBCO sample has changed into real $YBa_2Cu_3O_y$ sample although there are still some impurity peaks.

4. Conclusion

We have measured the in-situ HT ρ –T curves of the sol-gel $YBa_2Cu_3O_y$ samples sintered in various temperature range. The resulting curves are shown in figures 1, 2, and 3 for the 3 consecutive runs of the sintering cycles. The resistivities of SG-$YBa_2Cu_3O_y$ $\rho_{300} = 9.8\times10^{-3}$ Ω •cm in the room temperature and $\rho_{1223} = 6.68\times10^{-2}$ Ω •cm at 950℃ can be seen from these figures. According to these results, the O-T phase transformation process can also be studied. The transformation temperature of the SG-YBCO sample is lower than that of the A-YBCO sample which has not been reported previously to our knowledge. This could be due to the fine particles of the SG-YBCO chemically active, leading to an easier solid reaction sintering process. The present work suggests that the technology of the in-situ HT ρ –T measurement is an effective probe in the superconducting research. By this method, the O-T phase transition temperature has been shown to be lower for the SG-YBCO than the A-YBCO samples.

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溶胶-凝胶法制备的 $YBa_2Cu_3O_y$ 样品电阻随温度的变化特性研究

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摘要

采用凝胶法制备的并且在氧气气氛之中烧结 $YBa_2Cu_3O_y$，同时对样品的系列温度与电阻的关系进行研究。常温电阻率 $\rho_{300}=9.83\times10^{-3}$ Ω·cm。ρ-T 曲线表明凝胶法 $YBa_2Cu_3O_y$ 样品的从正交向四方晶系的转变的温度在升温和降温时分别是 581℃和 613℃，比通常采用粉末冶金方法制备的样品转变温度低。

关键词：溶胶-凝胶法 $YBa_2Cu_3O_y$ 样品， ρ-T 曲线，O-T 相变，烧结过程