HIGH-TEMPERATURE HEAT CAPACITIES OF THE PHASES IN Y-Ba-Cu-O SYSTEM①

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ABSTRACT TG and DSC techniques were used to investigate the phases and the reaction behavior at elevated temperatures of the oxygen-nonstoichiometric compounds $YBa_2Cu_3O_{7-x}$ and $BaCuO_{2+x}$. Based on the results of TG and DSC experiments, appropriate procedures were found for heat capacity measurements of the phases with DSC method. Combined with the drop method, the heat capacities of the phases $YBa_2Cu_3O_{6.90}$, $Y_2Cu_2O_5$, Y_2BaCuO_5 and $BaCuO_{2.42}$ were measured from room temperature to 973 K. The results for these phases are represented respectively as follows:

$$C_p(\mathrm{J/mol\cdot K}) = 333.97 - 454.43\times10^{-3}T + 41.836\times10^{5}T^{-2} + 794.18\times10^{-6}T^{2}$$

$$C_p(\mathrm{J/mol\cdot K}) = 149.82 + 113.02\times10^{-3}T$$

$$C_p(\mathrm{J/mol\cdot K}) = 329.09 - 361.56\times10^{-3}T - 42.745\times10^{5}T^{-2} + 341.43\times10^{-6}T^{2}$$

$$C_p(\mathrm{J/mol\cdot K}) = 77.628 - 14.018\times10^{-3}T + 18.141\times10^{5}T^{-2} + 130.85\times10^{-6}T^{2}$$

Key words heat capacity high-temperature DSC TG superconductor Y-Ba-Cu-O system

1 INTRODUCTION

Previous studies on $YBa_2Cu_3O_{7-x}$ and its superconducting-related phases in the Y-Ba-Cu-O system have been mainly devoted to the measurements of low-temperature heat capacities in order to detect the heat capacity jump at the superconducting transition point. The results were reviewed in Ref. [1, 2]. But very few measurements of high-temperature capacities of the phases have been made, with the only available reports from Maiorova *et al*[3] on $BaCuO_{2+x}$ in the temperature range of 40～400 ℃ and that from Matsui *et al*[4] on $YBa_2Cu_3O_{7-x}$ (x = 0.18, 0.35 and 0.60) in several temperature ranges. Accurate heat capacities of the related phases in Y-Ba-Cu-O system are required for further thermodynamic analyses of the system using enthalpy data determined experimentally[5]. In the present work, both the DSC and drop methods are used to measure the heat capacities of the phases in the system in the temperature range of 298～973 K.

2 EXPERIMENTAL

2.1 *Samples and Equipment*

A heat-flow type differential scanning calorimeter DSC111 (SETARAM, FRANCE) and a Calvet-type microcalorimeter HT1000 (SETARAM, FRANCE) were used to determine the heat capacities. The temperature measurement systems of these two calorimeters were calibrated with the melting points of high purity In, Sn, Bi, Pb, Zn and Al, and the sensitivities were calibrated with the Joule effect at various temperatures and at various heating rates.

The sensitivities were checked further with the melting enthalpy changes of the above metallic standards. It was confirmed

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that the instrument employed were all of good reproducibility and high accuracy.

The phases of $YBa_2Cu_3O_{7-x}$ ($7-x=6.60$, 6.77, 6.90 and 6.99), $Y_2Cu_2O_5$, Y_2BaCuO_5 and $BaCuO_{2+x}$ ($2+x=2.33$ and 2.42) were prepared by direct solid reactions at high temperatures[5] and examined using XRD. The drop method was used to determine the heat capacities of the phases in the vicinity of room temperature with the HT1000 calorimeter. Samples used here were compressed into small tablets.

The program-controlled scanning method (DSC method) was employed to determine the heat capacities at elevated temperatures with the DSC111 calorimeter. Samples were ground to fine powders with an agate mortar and then were put into alumina boats for the DSC measurements. All of the measurements were carried out in an open dehumidified air atmosphere.

2.2 *Measurement of Heat Capacities*

2.2.1 $YBa_2Cu_3O_{7-x}$

$YBa_2Cu_3O_{7-x}$ is an oxygen-nonstoichiometric compound, whose oxygen index ($7-x$) varies with the oxygen potential in the atmosphere as well as the temperature. Therefore, when measuring the heat capacities, at an increased temperature in a specified atmosphere such as air, the composition of the phase changes.

In order to choose appropriate samples for measuring the heat capacities by DSC method, DSC and TG studies were performed for the phases $YBa_2Cu_3O_n$ of different oxygen indexes ($n=6.60$, 6.77, 6.90 and 6.99), at the heating rate of 7 ℃/min for DSC and 7.5 ℃/min for TG. The TG apparatus used has been described previously[6]. The results are shown in Fig. 1.

The TG curve of the low-oxygen phase $YBa_2Cu_3O_{6.60}$ in Fig. 1 shows that, at first, the phase absorbed oxygen and was oxidized, and thus gained weight initially; then it was reduced and released oxygen, and thus lost weight finally. In the DSC curve, a corresponding exothermic peak of oxidation was observed. The phase of $YBa_2Cu_3O_{6.77}$ behaved similarly. In contrast, the high-oxygen index phase $YBa_2Cu_3O_{6.99}$ released oxygen and lost weight gradually, and an endothermic peak of reduction was observed in its DSC curve. Only the phase $YBa_2Cu_3O_{6.90}$ was observed having no remarkable endothermic peak or exothermic peak during DSC scanning under the experimental conditions. Therefore, the phase $YBa_2Cu_3O_{6.90}$ was chosen for heat capacity determinations with the DSC method. Similar TG and DSC curves were also observed by Beyers *et al*[7], Niinisto *et al*[8], and by Johnson *et al*[9], and all of them gave similar explanations.

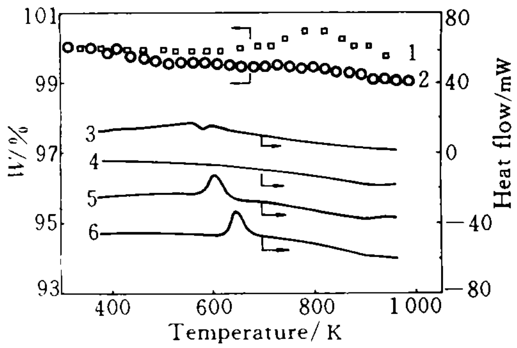

Fig. 1 TG and DSC experimental results for the compound $YBa_2Cu_3O_n$

(W —mass fraction)

1— $n=6.60$, 159.51 mg; 2— $n=6.99$, 97.85 mg; 3— $n=6.99$, 296.39 mg; 4— $n=6.90$, 290.96 mg; 5— $n=6.77$, 302.94 mg; 6— $n=6.60$, 306.70 mg

The high-temperature heat capacity measurement for the phase $YBa_2Cu_3O_{6.90}$ was made between 100～700 ℃ with DSC method, and the heat capacities in vicinity of room temperature were measured with drop method using HT1000 calorimeter. Experimental procedures were described in detail previously[5]. Results are shown in Fig. 2. Curve 1 shows that the measured heat capacity of one standard sample Al_2O_3 (points) agrees with the literature data (solid line)[10, 11] fairly well. Points in curve 2 represent the results of the heat capacities of the phase $YBa_2Cu_3O_{6.90}$. A regression equation is obtained based on the experimental data (solid line):

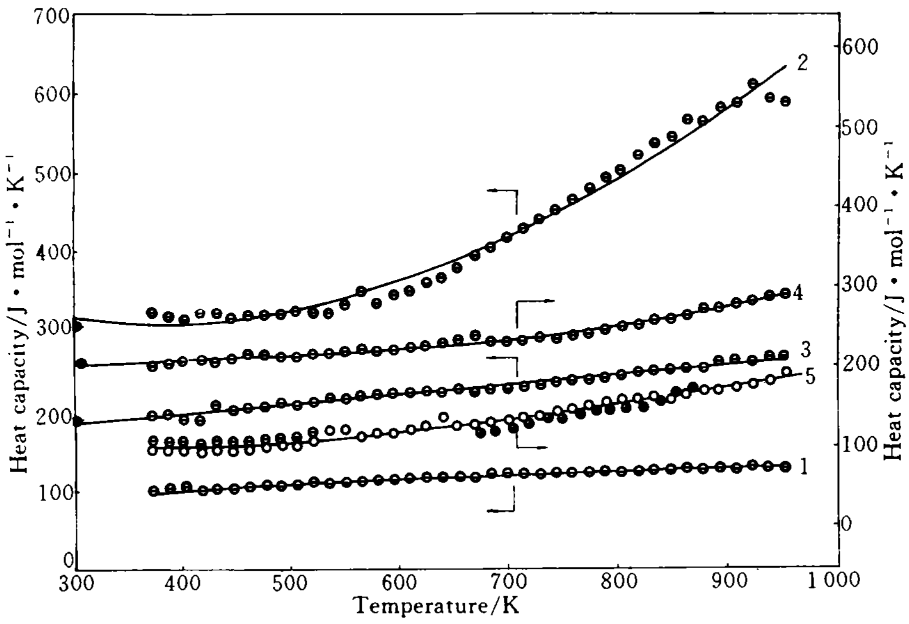

Fig. 2 Experimental heat capacities of related phases in Y-Ba-Cu-O system

●—with drop method; other points—with DSC method;

1—Al_2O_3; 2—$YBa_2Cu_3O_{6.9}$; 3—$Y_2Cu_2O_5$; 4—Y_2BaCuO_5; 5—$BaCuO_{2.42}$

$$C_p(J/mol \cdot K) = 339.97 - 454.43 \times 10^{-3}T + 41.836 \times 10^5 T^{-2} + 794.18 \times 10^{-6} T^2 \quad (298 \sim 973K) \qquad (1)$$

where T denotes the temperature in K.

2.2.2 $Y_2Cu_2O_5$ and Y_2BaCuO_5

The heat capacities of the phases $Y_2Cu_2O_5$ and Y_2BaCuO_5 were measured using DSC method and drop method.

The results are shown in Fig. 2; the regression equations for these two phases are as follows:

For $Y_2Cu_2O_5$

$$C_p(J/mol \cdot K) = 149.82 + 113.02 \times 10^{-3}T \quad (298 \sim 973K) \qquad (2)$$

For Y_2BaCuO_5

$$C_p(J/mol \cdot K) = 329.09 - 361.56 \times 10^{-3}T - 42.745 \times 10^5 T^{-2} + 341.43 \times 10^{-6} T^2 \quad (298 \sim 973K) \qquad (3)$$

2.2.3 $BaCuO_{2+x}$

$BaCuO_{2+x}$ is also an oxygen-nonstoichiometric compound, and its oxygen index $(2+x)$ varies with the experimental conditions, i.e., the oxygen partial pressure $P(O_2)$ and temperature T. The oxygen index may range from 1.8 to 2.5[3]. Consequently, the oxygen index also changes in the determination of the heat capacities using DSC, as that of $YBa_2Cu_3O_{7-x}$ does.

Fig. 3 shows the results of the DSC and the TG experiments for the phases $BaCuO_{2.33}$ and $BaCuO_{2.42}$. The DSC scanning rate and the TG heating rate were the same as those used for $YBa_2Cu_3O_{7-x}$ samples. In the DSC curve of $BaCuO_{2.42}$, an endothermic peak exists, while in that of $BaCuO_{2.33}$ an exothermic peak exists. The TG curve of $BaCuO_{2.42}$ illustrates that there was slight mass loss when it was heated in air. The mass loss of the sample $BaCuO_{2.42}$ was about 0.2%~0.3% when the temperature reached 600 ℃ at which the corresponding oxygen index changed from 2.42 to about 2. 39, and after which there were no more obvious losses.

In order to eliminate the errors due to the change in the oxygen index and the absorbing of the energy from the surroundings at about 280 ℃, the heat capacity determinations for the phase of $BaCuO_{2.42}$ were done with DSC within the temperature ranges of 100 to 250 ℃, 400 to 600 ℃ and 100 to 700 ℃, respectively, Results are shown in Fig. 3.

The regression equation for the experimental data is:

$$C_p(J/mol \cdot K) = 77.628 - 14.018 \times 10^{-3}T + 18.141 \times 10^{5}T^{-2} + 130.85 \times 10^{-6}T^{2} \quad (373 \sim 973K) \qquad (4)$$

where T represents the temperature in K. Equation (4) may be extrapolated to 298 K for application at room temperature.

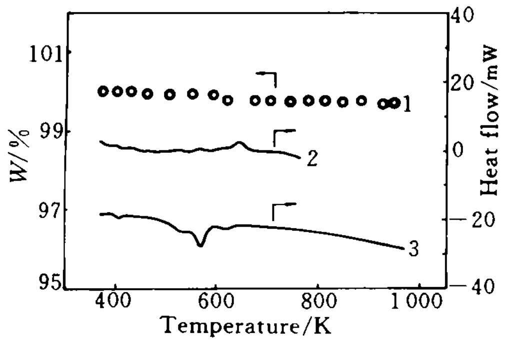

Fig. 3 TG and DSC experiments for the compound $BaCuO_n$

(W—mass fraction)

1—n = 2. 42, 91. 96 mg;

2—n = 2. 33, 124. 29 mg;

3—n = 2. 42, 170. 53 mg

3 DISCUSSION

Matsui *et al*[4] measured the heat capacities of $YBa_2Cu_3O_{7-x}$ (x = 0. 18, 0. 35 and 0. 60) in the range from room temperature to 806 K with an adiabatic scanning calorimeter. According to Fig. 1 of their paper[4], at all temperatures:

$C_p(7 - x = 6.65) >$

$C_p(7 - x = 6.40) >$

$C_p(7 - x = 6.82)$

This seems unreasonable, because the existence of the oxygen atoms in the phase $YBa_2Cu_3O_{7-x}$ should contribute to the C_p of the compound.

The more oxygen atoms in the phase, the greater its C_p, therefore, the sequence of C_p for these phases should be:

$C_p(7 - x = 6.82) >$

$C_p(7 - x = 6.65) >$

$C_p(7 - x = 6.40)$

This is confirmed by our theoretical derivation to be published later. The changeable oxygen index during DSC scanning may account for their odd results.

Further more, their analytical representation for C_p of these phases conflicts with their figure presentation, which restricts our further analyses.

Maiorova *et al*[3] determined the heat capacity of $BaCuO_{2+x}$ ($2.00 < 2 + x < 2.11$) for 40 ℃ < t < 400 ℃. The following equation was used to present their results:

$$C_p(J/g \cdot ℃) = 0.405 + 1.05 \times 10^{-4}t$$

In their work they actually used DTA instead of DSC as they claimed. The calibrated coefficients of the instrument they used could only apply to samples of mass of 35 ~ 90 mg and beyond whose the linear dependence of signal on sample mass no longer held, and the coefficients were only checked with standard samples at 70 ℃.

In the present work, the sensitivity of the DSC instrument was calibrated from ambient temperature up to 700 ℃, and were checked further with the metallic standards at their melting temperatures. Thus the heat capacity data determined in the present work might be more accurate and precise than those of Maiorova *et al.* Comparing the results of Maiorova *et al* with those of the present work (equation (4), converted to J/g·K), it appears that their data are lower by 0. 02 to 0. 1 J/g·K within 100~400 ℃. The deviation becomes larger at high temperatures since the high-temperature sensitivity of their apparatus was not checked further.

4 CONCLUSIONS

Prior to heat capacity measurements, TG and DSC experiments were proceeded for the samples of the oxygen-nonstoichiometric compounds $YBa_2Cu_3O_{7-x}$ ($7-x=6.60$, 6.77, 6.90 and 6.99) and $BaCuO_{2+x}$ ($2+x=2.33$ and 2.42) in order to find appropriate samples and experimental procedures for heat capacity measurements. For the samples of low-oxygen indexes, exothermic peaks were observed in DSC scanning due to the increasing oxygen content, and for the samples of high-oxygen indexes, endothermic peaks were observed due to the loss of oxygen. Some approaches were adopted to eliminate the detection errors in C_p measurements caused by the above aspects for oxygen-nonstoichiometric compounds. Heat capacities in the range from room temperature to 973 K were measured for the phases $YBa_2Cu_3O_{6.90}$, $Y_2Cu_2O_5$, Y_2BaCuO_5 and $BaCuO_{2.42}$. The heat capacity data obtained here may be combined with the enthalpy data determined by calorimetry to predict the thermodynamic behavior of the system Y-Ba-Cu-O at elevated temperatures[12].

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