Phase Relation and Heat Capacities of $Ba_2YCu_3O_{7-x}$ at High Temperature

TSUNEO MATSUI[1], TOORU FUJITA, AND KEIJI NAITO

Department of Nuclear Engineering, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

AND TAKUO TAKESHITA

Central Research Institute, Mitsubishi Metal Corporation, Kitabukuro-cho, Omiya, Saitama 330, Japan

The heat capacities of $Ba_2YCu_3O_{7-x}$ ($x = 0.18, 0.35$, and 0.60) were measured in the range from room temperature to 860 K by an adiabatic scanning calorimeter. X-ray diffraction analyses were also performed on the quenched and annealed samples. No heat capacity anomaly was seen in either orthorhombic(I) $Ba_2YCu_3O_{6.82}$ or tetragonal $Ba_2YCu_3O_{6.40}$. For $Ba_2YCu_3O_{6.65}$, the heat capacity anomaly was observed above 700 K, which was correlated with the phase transition from orthorhombic(I) to orthorhombic(II) structure. The phase relations among orthorhombic(I), orthorhombic(II), and the tetragonal phases were also clarified. © 1990 Academic Press, Inc.

1. Introduction

We have reported the occurrence of a phase transition from the orthorhombic to the tetragonal structure in $Ba_2YCu_3O_{7-x}$ in the range $x = 0.35$–0.40 at temperatures of 773–973 K, based both on the oxygen partial pressure dependence of oxygen nonstoichiometry x and on the compositional dependence of the chemical diffusion coefficient of oxygen (*1*). The phase transition from the orthorhombic to the tetragonal structure in $Ba_2YCu_3O_{7-x}$ was also observed by high temperature X-ray (*2–4*) and neutron (*5*) dif-

¹ To whom correspondence should be addressed.

fractometry, but the phase boundary determined by these methods did not agree well since these experiments were carried out on the samples held under constant oxygen partial pressure, so that the composition could change with temperature. Moreover several investigators described a new orthorhombic phase(II) with a somewhat lower critical temperature T_c (50–70 K) and larger x in addition to the orthorhombic phase(I) with a higher T_c (~90 K) and smaller x value in $Ba_2YCu_3O_{7-x}$ by X-ray diffractometry (*6, 7*), electron diffractometry (*8*), diamagnetic magnetization measurement (*9*), resistivity measurement (*10*), and thermogravimetry (*11*). However, the phase boundary be-

tween the orthorhombic(I) phase and the
orthorhombic(II) phase determined by the
previous investigators (6–11) was not in
good agreement.

The heat capacity of $Ba_2YCu_3O_{7-x}$ at high
temperatures above room temperature,
which is an important thermodynamic prop-
erty, has not yet been measured for correla-
tion with the phase transition between the
orthorhombic phase(I) and the orthorhom-
bic phase(II).

In the present study, the heat capacity
measurements of $Ba_2YCu_3O_{7-x}$ (x = 0.18,
0.35, and 0.60) at high temperatures (room
temperature—860 K), the electrical resist-
ivity measurements of the samples (x =
0.35) at low temperatures below 230 K, and
the X-ray diffraction analyses of the samples
(x = 0.18, 0.25, 0.33, 0.35, 0.36, 0.39, 0.60)
were made in order to elucidate the phase
relation among three phases of orthorhom-
bic(I), orthorhombic(II), and tetragonal
structures in $Ba_2YCu_3O_{7-x}$.

2. Experimental

Sample preparation from Y_2O_3, $BaCO_3$,
and CuO powders and the analytical meth-
ods for the determination of Ba, Y, and Cu
have been described in our previous paper
(1).

Three samples of $Ba_2YCu_3O_{7-x}$ with dif-
ferent values of oxygen composition $7 - x$
(x = 0.18, 0.35, and 0.60) used for the heat
capacity measurements were prepared by
annealing the specimens at a selected tem-
perature (T) in a selected oxygen partial
pressure (P_{O_2}) for 16 hr based on the relation
among temperature–oxygen partial pres-
sure–oxygen nonstoichiometry which was
obtained by the present authors (1): i.e., T
= 873 K and P_{O_2} = 10^5 Pa for x = 0.18; T
= 923 K and P_{O_2} = $10^{4.32}$ Pa for x = 0.35;
and T = 1073 K and P_{O_2} = $10^{4.32}$ Pa for x =
0.60; the samples were then quenched in a
dry-ice–ethanol bath. The quenched sample
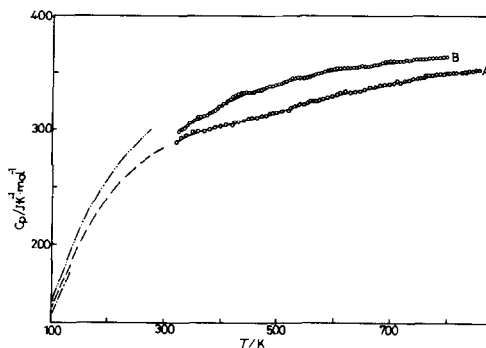powder (~12 g) was sealed in a small quartz

FIG. 1. Heat capacity of $Ba_2YCu_3O_{7-x}$. A, (O) Ba_2Y-Cu_3O_{7-x} (x = 0.18) in this study. B, (O) $Ba_2YCu_3O_{7-x}$ (x = 0.60) in this study. —, Heat capacity curves by the least-squares method for $Ba_2YCu_3O_{7-x}$ (x = 0.18 and 0.60) in this study; —·—, $Ba_2YCu_3O_{7-x}$ (x ≈ 0.07) by Kitazawa et al. (13); —··—, $Ba_2YCu_3O_{7-x}$ (x ≈ 0.1) by Braun et al. (14); ———, $Ba_2DyCu_3O_7$ by Atake et al. (15).

vessel to avoid significant compositional
changes during heat-capacity measure-
ments. Helium gas (~20 kPa) was added to
aid in thermal equilibration within the quartz
vessel. The sample in the quartz vessel was
then annealed at 573 K for 48 hr prior to
measuring the heat capacity of Ba_2Y-Cu_3O_{7-x} in an adiabatic scanning calorime-
ter (12).

Electrical resistivity measurements were
made on the quenched and annealed sam-
ples with x = 0.35 at low temperature below
230 K.

X-ray diffraction analyses were per-
formed for the quenched and annealed sam-
ples with several x values (x = 0.25, 0.33,
0.36, 0.39) in addition to three samples used
in the heat-capacity measurements; all sam-
ples were prepared based on the known T
$- P_{O_2} - x$ relations (1).

3. Results and Discussion

The heat capacity of $Ba_2YCu_3O_{7-x}$ (x =
0.18) measured from 325 to 860 K in this
study is shown in Fig. 1, together with those
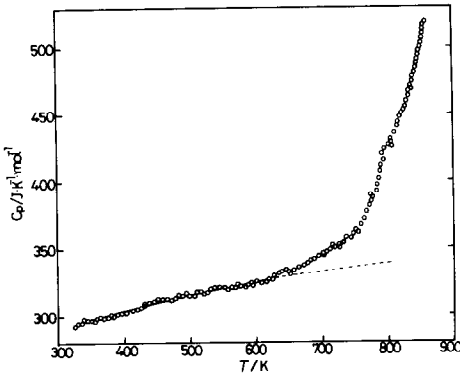
FIG. 2. Heat capacity of $Ba_2YCu_3O_{7-x}$ ($x = 0.35$). —, Heat capacity curve below about 600 K by the least-squares method.

of $Ba_2YCu_3P_{7-x}$ ($x \simeq 0.07$, as estimated by the present authors from the reported preparation condition of the sample) as published by Kitazawa et al. (13), those of Ba_2Y-Cu_3O_{7-x} ($x \simeq 0.1$, an assumed value) measured by Braun et al. (14), and those of $Ba_2DyCu_3O_7$ by Atake et al. (15), all of which were measured below 300 K. As is seen in the figure, no heat-capacity anomaly is observed above 325 K. X-ray diffraction analyses indicated that both powdered samples of $Ba_2YCu_3O_{7-x}$ ($x = 0.18$) after quenching from 873 K and after annealing at 573 K for 48 hr were only in the orthorhombic phase(I), according to the diffraction pattern reported by Chen et al. (6). It is, therefore, concluded that there is no phase transition in $Ba_2YCu_3O_{7-x}$ ($x = 0.18$) between 325 and 873 K. The equation for the heat capacity of $Ba_2YCu_3O_{7-x}$ ($x = 0.18$) is determined by the least-squares method as Eq. (1) and shown by a solid line in Fig. 1.

$$C_p/J \ K^{-1} \ mole^{-1} = 3.7848 \times 10^2$$
$$+ \ 3.0977 \times 10^{-2}(K/K) - 5.1902$$
$$\times \ 10^2 \ (T/K)^{-1} + 6.6601 \times 10^6(T/K)^{-2},$$
$$(325 \leqq T \leqq 860 \ K). \quad (1)$$

The heat capacity of $Ba_2YCu_3O_{7-x}$ ($x = 0.35$) measured from 325 to 860 K in the present study is shown in Fig. 2. An increase

of the heat capacity was observed at the temperatures above about 700 K. By comparing the X-ray diffraction patterns of $Ba_2YCu_3O_{7-x}$ ($x = 0.35$) obtained in this study to those reported by Chen et al. (6), it was found that the sample powder annealed at 573 K for 48 hr (as used for the heat capacity measurement) formed a single orthorhombic(I) phase, while the sample powder quenched from 923 K formed a single orthorhombic(II) phase. The occurrence of the phase transition from orthorhombic(I) to orthorhombic(II) structure in Ba_2Y-Cu_3O_{7-x} has also been suggsted by X-ray diffractometry (6, 7), electrical resistivity measurements (10), magnetic measurements (8, 9), and thermogravimetry (11). It is, therefore, believed that the increase in the heat capacity above 700 K is related to the phase transition from the orthorhombic(I) to the orthorhombic(II) structure. The transition temperature from orthorhombic(I) to orthorhombic(II) structure, however, is considered to lie between 860 and 923 K, from the fact that the heat capacity peak probably appeared above the experimental temperature range ($T > 860$ K) and that the orthorhombic(II) phase was observed in the sample quenched from 923 K by X-ray diffraction. The equation for the heat capacity of $Ba_2YCu_3O_{7-x}$ ($x = 0.35$) in the temperature range from 325 to 650 K determined by the least-squares method is expressed by Eq. (2) and shown in Fig. 2:

$$C_p/J \ K^{-1} \ mole^{-1} = 3.7371 \times 10^2$$
$$+ \ 1.2230 \times 10^{-2}(T/K) - 4.1022$$
$$\times \ 10^2 \ (T/K)^{-1} + 4.4694 \times 10^6(T/K)^{-2},$$
$$(325 \leqq T \leqq 650 \ K). \quad (2)$$

The electrical resistivities of the quenched and annealed samples of Ba_2Y-Cu_3O_{7-x} ($x = 0.35$) measured in this study are shown in Fig. 3 as a function of temperature. The different temperature dependences of these two samples also provide evidence for the phase transition.
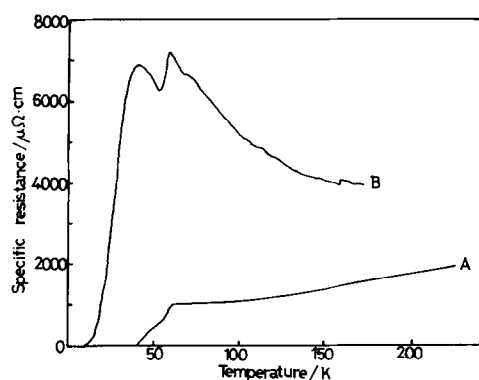
FIG. 3. Low temperature resistivity of $Ba_2YCu_3O_{7-x}$ ($x = 0.35$). A, quenched from 923 K in air. B, annealed for 3 days at 573 K in a sealed quartz glass.
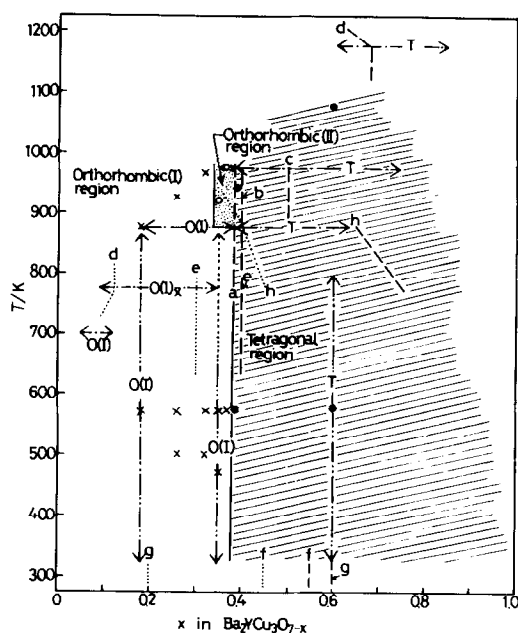

FIG. 4. Phase diagram of the $Ba_2YCu_3O_{7-x}$ system. —, Phase boundaries determined in this study. Phase boundaries reported by various investigators: a(1); b(2); c(5); d(6); e(7); f(8); g(9); h(10); ···, orthorhombic(I) (O(I))/orthorhombic(II) (O(II)); ————, orthorhombic (I or II)/tetragonal (T).

◄···►, temperature range investigated by the heat capacity measurement in this study; ◄—►, compositional range of the single orthorhombic or tetragonal phase previously determined from the relations between log x and log P_{O_2} and also between log x and log $\bar{D}$ by the present authors (1). ×, O(I); ○, O(II); and ●, T phases determined by X-ray diffraction analyses in this study. □, orthorhombic (I) phase region; ▨, orthorhombic (II) phase region; ▨, tetragonal phase region.

The heat capacity of $Ba_2YCu_3O_{7-x}$ ($x = 0.60$) is shown in Fig. 1 in comparison with that of $Ba_2YCu_3O_{7-x}$ ($x = 0.18$). The difference in the heat capacity is probably caused by the difference in the crystal structure (the former is in the tetragonal and the latter is in the orthorhombic structure). No heat capacity anomaly is seen in the temperature range between 325 and 800 K. X-ray diffraction analysis indicated that both sample powders of $Ba_2YCu_3O_{7-x}$ ($x = 0.60$) quenched from 1073 K and annealed at 573 K for 48 hr after quenching from 1073 K formed a single tetragonal phase. It is concluded that there is no phase transition in $Ba_2YCu_3O_{7-x}$ ($x = 0.60$) and that the tetragonal structure is maintained up to 1073 K. The equation of the heat capacity of Ba_2Y-Cu_3O_{7-x} ($x = 0.60$) determined by the least-squares method is given as Eq. (3) and shown in Fig. 1:

$$C_p/J\ K^{-1}\ mole^{-1} = 4.6605 \times 10^2$$

$$- 5.4034 \times 10^{-2}(T/K) - 4.9671$$

$$\times 10^2\ (T/K)^{-1} + 1.7776 \times 10^5(T/K)^{-2},$$

$$(325 \leqq T \leqq 800\ K). \quad (3)$$

In Fig. 4 the phase relations among orthorhombic(I), orthorhombic(II), and tetragonal phases are summarized on the basis of the results reported so far (1, 2, 5–10), and the present result including the X-ray diffraction data for the samples with various x values ($x = 0.25, 0.33, 0.36, 0.39$), in addition to three samples ($x = 0.18, 0.35, 0.60$) for the heat capacity measurement. It is seen in the figure that the orthorhombic(I) to tetragonal phase transition occurs close to x = 0.38 below about 900 K, and that the

orthorhombic(I) to orthorhombic(II) phase transition and the orthorhombic(II) to tetragonal phase transition occur near $x = 0.35$ and 0.38, respectively, in the range between roughly 900 and 1000 K.

Acknowledgment

References

1. T. MATSUI, K. NAITO, AND S. HAGINO, "Proceedings of NATO Advanced Research Workshop on Nonstoichiometric Compound-Surfaces, Grain Boundaries and Structural Defects," p. 471, (Kluwer Pub. Co., FRG (1989).

2. E. D. SPECHT, C. J. SPARKS, A. G. DHERE, J. BRYNESTAD, O. B. CAVIN, AND D. M. KROEGER, *Phys. Rev. B* **37,** 7426 (1988).

3. K. YUKINO, T. SATO, S. ODA, M. OHTA, F. P. FUJIO, AND A. ONO, *Japan. J. Appl. Phys.* **26,** L869 (1987).

4. A. C. MOMIN, M. D.MATHEW, V. S. JAKKAL, I. K. GOPALAKRISHNAN, J. V. YAKHMI, AND R. M. IYER, *Solid State Commun.* **64,** 329 (1987).

5. J. D. JORGENSEN, M. A. BENS, D. G. HINKS, L. SODERHOLM, K. J. VOLIN, R. L. HITTERMAN, J. D. GRACE, AND IVAN K. SCHULLER, *Phys. Rev. B* **36,** 3608 (1987).

6. I-W. CHEN, S. J. KEATING, C. Y. KEATING, X. WU, J. XU, P. E. REYES-MOREL, AND T. Y. TIEN, *Solid State Commun.* **63,** 997 (1987).

7. R. J. CAVA, B. BATLOGG, C. H. CHEN, E. A. RIETMAN, S. M. ZAHURAK, AND D. WERDER, *Nature (London)* **329,** 423 (1987).

8. Y. KUBO, T. ICHIHASHI, T. MANAKO, K. BABA, J. TABUCHI, AND H. IGARASHI, *Phys. Rev. B* **37,** 7858 (1988).

9. M. TOKUMOTO, H. IHARA, T. MATSUBARA, M. HIRABAYAHI, N. TERADA, H. OYANAGI, K. MURATA, AND Y. KIMURA, *Japan. J. Appl. Phys.* **26,** L1565 (1987).

10. S. YAMAGUCHI, K. TERABE, A. IMAI, AND Y. IGUCHI, *Japan. J. Appl. Phys.* **27,** L220 (1988).

11. K. SWAMINATHAN, J. JANAKI, G. V. N. RAO, O. M. SREEDHARAN, AND T. S. RADHAKRISHNAN, *Mater. Lett.* **6,** 261 (1988).

12. K. NAITO, H. INABA, M. ISHIDA, Y. SAITO, AND H. ARIME, *J. Phys. E* **7,** 464 (1974).

13. K. KITAZAWA, T. ATAKE, H. ISHII, H. SATO, H. TAKAGI, S. UCHIDA, Y. SAITO, K. FUEKI, AND S. TANAKA, *Japan. J. Appl. Phys.* **26,** L748 (1987).

14. E. BRAUN, G. JACKEL, B. RODEN, J. G. SERENI, AND D. WOHLLEBEN, *Z. Phys. B: Condens. Matter* **72,** 169 (1988).

15. T. ATAKE, Y. TAKAGI, T. NAKAMURA, AND Y. SAITO, *Phys. Rev. B* **37,** 552 (1988).