Thermal Behavior of Melt-Quenched Products of YBa₂Cu₃O_{7- δ} Compound

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YBa₂Cu₃O_{7- δ} 化合物の融体急冷生成物の熱的挙動

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The melt-quenched products of the orthorhombic YBa₂Cu₃O_{7- δ} compound from 1200° and 1400°C were characterized by X-ray powder diffraction and DTA-TG methods. It was found that crystalline phases in the quenched samples from 1200°C were Y₂BaCuO₅ (major phase) and BaCuO₂, while those in the quenched samples from 1400°C were Y₂O₃ (major phase) and BaCuO₂. The products showed the weight gain and the exothermic peaks in the range of 200° to 300°C, corresponding to the oxidation of Cu(I) in BaCuO_{2-x} and amorphous compounds to Cu(II), and the endothermic peaks due to the partially melting in the range of 900° to 950°C. In addition, it was confirmed that superconducting YBa₂Cu₃O_{7- δ} compound began to form by annealing the melt-quenched products at 900°C.

[Received November 30, 1987; Accepted January 22, 1988]

Key-words : Superconductivity, YBa₂Cu₃O_{7- δ} , Phase diagram, Thermal behavior, Melt-quenching, Y₂BaCuO₅

1. Introduction

The superconducting YBa₂Cu₃O_{7- δ} compound with a T_c above 90 K was discovered by Wu et al.¹⁾ and defined to have orthorhombic oxygen-deficient perovskite-derived structure.^{2),3)} As its superconductivity is very sensitive to the oxygen vacancies and the composition, it is necessary to establish the proper processing conditions according to its stability. The determination of the phase stability and compatibilities surrounding the superconducting compounds is also important, because liquid melt within the Y-Ba-Cu-O system is very critical for crystal growth and liquid phase sintering. Preliminary and tentative compatibility triangles in the system YO_{1.5}-BaO-CuO at 950° to 1000°C have been reported by several researchers.⁴⁾⁻⁶⁾ In the system, YBa₂Cu₃O_{7- δ} , Y₂BaCuO₅ and YBa₃Cu₂O_x phase are known as a ternary phase. The YBa₂Cu₃O_{7- δ} films were prepared through a liquid phase by a plasma spray⁷⁾ and a melt-quenching method.⁸⁾ In this paper, we report the preliminary results on the characterization of the thermal behavior of quenched products of YBa₂Cu₃O_{7- δ} compound from 1200° and 1400°C by X-ray powder diffraction and DTA-TG analysis.

2. Experimental

A sample with a nominal composition YBa₂Cu₃O_{7- δ} was prepared by mixing the pow-

ders of BaCO₃, Y₂O₃ and CuO (~99.9% Purity). The mixed powder was calcined at 900°C for 12 h in air. The calcined powder was ground and reheated at 900°C for 12 h in a flow of O₂. Subsequently, the powder thus prepared was ground and pressed into pellets and then sintered at 950°C for 24 h in O₂, followed by annealing at 450°C for 12 h. The product was black and identified as an orthorhombic YBa₂Cu₃O_{7- δ} compound. YBa₂Cu₃O_{7- δ} powders thus prepared were melted in a Pt crucible at 1200° and 1400°C for 1 h and then quenched into liquid nitrogen. Quenched samples were characterized by X-ray powder diffraction and DTA-TG method. DTA-TG analysis was performed in air or O₂ atmosphere at a heating rate of 10°C/min.

3. Results and discussion

A melt-quenched product of orthorhombic YBa₂Cu₃O_{7- δ} compound from 1200°C was green material, while a quenched product from 1400°C was dark-brown glassy material. **Figure 1** shows X-ray powder diffraction patterns of prepared orthorhombic YBa₂Cu₃O_{7- δ} compound and quenched products from 1200° and 1400°C. Crystalline phases in the product quenched from 1200°C were Y₂BaCuO₅ (major phase) and BaCuO₂ (minor phase), and those in the product quenched from 1400°C were Y₂O₃ (major phase) and BaCuO₂ (minor phase). BaCuO₂ phase, which is reported

Fig. 1. X-ray diffraction patterns of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound (A) and melt-quenched products of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound from 1200°C (B) and 1400°C (C).

to melt congruently at about 1000°C⁵¹, has to be liquid at 1200°C, but may be easily crystallized from the liquid melt on quenching. The results revealed that $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound melts incongruently to Y_2BaCuO_5 phase and a liquid phase. As BaCuO_2 was crystallized metastably on quenching, the composition of the liquid phase tended to approach toward the eutectic composition in the pseudo-binary $\text{BaCuO}_2\text{-CuO}$ system. In order to examine the approximate eutectic composition in the BaO-CuO system, the samples with the compositions of $3\text{BaO} \cdot 5\text{CuO}$ and $\text{BaO} \cdot 3\text{CuO}$ were prepared both at 950°C for 12 h and by quenching from 1200°C. The products of $3\text{BaO} \cdot 5\text{CuO}$ and $\text{BaO} \cdot 3\text{CuO}$ samples prepared at 950°C were composed of $\text{BaCuO}_2 \gg \text{CuO}$, unknown phase and $\text{CuO} > \text{BaCuO}_2$, respectively. On the other hand, quenched samples of $3\text{BaO} \cdot 5\text{CuO}$ and $\text{BaO} \cdot 3\text{CuO}$ from 1200°C were composed of $\text{BaCuO}_2 \gg \text{Cu}_2\text{O}$ and $\text{Cu}_2\text{O} > \text{CuO}$, respectively. The results indicate that the eutectic composition exists between $3\text{BaO} \cdot 5\text{CuO}$ and $\text{BaO} \cdot 3\text{CuO}$ and is close to the eutectic composition ($\sim 63\%$ CuO) of postulated phase diagram in the $\text{BaCuO}_2\text{-CuO}$ system proposed by Roth et al.⁵¹ The peak intensity of XRD profiles of BaCuO_2 increased and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ began to form by the heat-treatment at 900°C for 2 h of the melt-quenched samples of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ com-

Fig. 2. DTA and TG curves of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound (A) and quenched products of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound from 1200°C (B) and 1400°C (C).

pound. $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound did form as a single phase by the solid state reaction among Y_2BaCuO_5 , BaCuO_2 and liquid phase at 950°C for 12 h. Figure 2 shows DTA-TG curves of original orthorhombic and quenched samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound. Only a strong endothermic peak was observed in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound at about 1020°C, which corresponds to the incongruent melting to form Y_2BaCuO_5 and liquid phase. In the quenched sample from 1200°C, characteristic weight gains of about 0.9% at two steps were observed between 200° and 300°C, and then slight loss occurred around 400°C and further weight gain of 0.4% between 550° and 700°C. A weight loss began again at about 700°C and became remarkable above 900°C. Strong and weak exothermic peaks in the DTA curve, which corresponds to the weight gain in TG curve, were observed at about 210° and 260°C, respectively. These peaks were very similar to those of the quenched sample of $3\text{BaO} \cdot 5\text{CuO}$ from 1200°C, as shown in Fig. 3. In the quenched sample of BaCuO_2 from 1200°C, an exothermic peak was observed at about 220°C, while no exothermic peak was observed in the range of 200° to 300°C in the sample heated at 950°C and followed by annealing at 450°C (Fig. 3). Hence, these two exothermic peaks can be attributed to the oxidation of Cu(II) in

Fig. 3. DTA curves of quenched products of $3\text{BaO} \cdot 5\text{CuO}$ sample (A) and BaCuO_2 compound (B) from 1200°C .

BaCuO_{2-x} and in an amorphous substance to $\text{Cu}(\text{II})$, respectively. At temperatures above 1200°C , the system is not within the stable regime of $\text{Cu}(\text{II})$ and close to the $\text{Cu}(\text{II})$ - $\text{Cu}(\text{I})$ stability boundary even in an oxygen atmosphere. Therefore, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound is considered to be intensively reduced to $\text{Cu}(\text{I})$ at the temperatures above 1200°C . BaCu_2O_2 and $\text{BaCuO}_{2.5}$ compounds have also been reported,⁵⁾ but seem to be not apparently stable in air. In addition, two endothermic peaks were observed at about 900° and about 940°C in the quenched sample from 1200°C . These may be attributable to the melting of a glassy phase and a reaction product of BaCuO_2 and the liquid, respectively. The thermal behavior of the quenched sample from 1400°C is very similar to that from 1200°C . In the quenched sample from 1400°C , an exothermic peak at about 220°C is more intense than that from 1200°C , suggesting that the greater reduction of $\text{Cu}(\text{II})$ in BaCuO_x to $\text{Cu}(\text{I})$ takes place at a higher melting temperature of 1400°C .

Based on the present results, a postulated phase diagram of a portion in the system $\text{YO}_{1.5}\text{-BaO-CuO}$ was proposed in Fig. 4. More detail work on the phase stability is in progress in relation to the crystallization and the microstructure control of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramics. The pre-

Fig. 4. Postulated phase diagram of a portion in the system $\text{YO}_{1.5}\text{-BaO-CuO}$.

sent result also revealed that the melt-quenched product from 1400°C consisted of Y_2O_3 and glass phase, indicating that Y_2BaCuO_5 might be incongruently decomposed.

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