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# The Phase Transition of Bismuth(III) Oxide Prepared by the Thermal Decomposition of Bismuth Sulfate

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**Synopsis.** The phase transitions of $\alpha$-$Bi_2O_3$ prepared by the thermal decomposition of $Bi_2(SO_4)_3$ on heating and cooling are revealed. The phase transition on cooling is remarkably affected by the existence of a small amount of $SO_4$, such as 0.05%, in the $Bi_2O_3$.

The phase transition of $\alpha$-$Bi_2O_3$ (monoclinic[1]), prepared by the thermal decomposition of $Bi_2(SO_4)_3$, has been examined with special attention paid to the effect of a small amount of $SO_4$ in the $Bi_2O_3$ on its phase transition.

The $Bi_2(SO_4)_3$ used as the starting material was prepared by dissolving high-purity commercial bismuth (Bi: 99.9999%) in $HNO_3$, followed by treatment with an excess of $H_2SO_4$.[2] Two samples of $\alpha$-$Bi_2O_3$ were obtained as follows.

Sample A: According to a previous report of the present authors,[2] $\alpha$-$Bi_2O_3$ was prepared by heating 15 g of $Bi_2(SO_4)_3$ placed in a platinum boat at 950 °C for about 130 hr in an argon stream. The $SO_4$ in the product was not detected by the indirect determination of a small amount of $SO_4^{2-}$ using solid barium chromate.[3]

Sample B: $Bi_2O_3$ was prepared by heating $Bi_2(SO_4)_3$ at 950 °C for about 110 hr. The $SO_4$ content in the product was 0.05%. X-Ray analysis showed it to be $\alpha$-$Bi_2O_3$.

The phase transitions of $Bi_2O_3$ on heating and cooling were examined by DTA. The heating and cooling rates of 5 °C/min were employed. Sample holders made of platinum were used, and $\alpha$-$Al_2O_3$ was used as a reference. The accuracy of the temperature measurements was ±4 °C. The experimental results of DTA were followed by high-temperature X-ray diffractometry in order to examine the phase transition of $Bi_2O_3$. Ni-filtered Cu radiation was used, and the scanning speed of 2°/min was employed. The details of the techniques of DTA and high-temperature X-ray diffractometry were described in a preceding paper.[4]

The phase transitions of Samples A and B on heating were examined. The experimental results showed that both samples transformed to $\delta$-$Bi_2O_3$ (cubic[5]) at 730 °C, which then melted at 827 °C. The phase transitions of Samples A and B on heating were the same as those of the $\alpha$-$Bi_2O_3$ prepared by the thermal decompositions of $Bi(NO_3)_3 \cdot 5H_2O$, $(BiO)_2CO_3$, and bismuth nitrate oxide.[4]

The phase transitions of Samples A and B on cooling from temperatures of 740—890 °C were examined. The results for Sample A are shown in Table 1. The peak temperature of the DTA curve is shown as the transition temperature. When the DTA curve showed a supercooling effect and the peak temperature became higher than the temperature at which the exotherm started, the latter is shown as the transition temperature and is marked with an asterisk.

TABLE 1. PHASE TRANSITION OF SAMPLE A ON COOLING (Cooling rate: 5 °C/min)

| Temperature before cooling (°C) | Phase transition |
|---|---|
| 740 | $\delta \xrightarrow{702^\circ C} \alpha$ |
| 750 | $\delta \xrightarrow{695^\circ C} \alpha$ |
| 760 | $\delta \xrightarrow{648^\circ C*} \alpha$ |
| 770 | $\delta \xrightarrow{650^\circ C} \beta \xrightarrow{545^\circ C*} \alpha$ |
| 800 | $\delta \xrightarrow{648^\circ C} \beta \xrightarrow{545^\circ C*} \alpha$ |
| 810 | $\delta \xrightarrow{650^\circ C} \beta \xrightarrow{547^\circ C*} \alpha$ |
| 840 | $\text{melt} \longrightarrow \delta \xrightarrow{637^\circ C} \beta \xrightarrow{503^\circ C*} \alpha$ |
| 860 | $\text{melt} \longrightarrow \delta \xrightarrow{635^\circ C} \beta \xrightarrow{500^\circ C*} \alpha$ |
| 880 | $\text{melt} \longrightarrow \delta \xrightarrow{635^\circ C} \beta \xrightarrow{500^\circ C*} \alpha$ |
| 890 | $\text{melt} \longrightarrow \delta \xrightarrow{625^\circ C*} \alpha$ |

Note: Temperature accuracy, ±4 °C

The experimental results given in Table 1 show that the variation in the phase transition of Sample A with the temperature before cooling was similar to those of $Bi_2O_3$ prepared from $Bi(NO_3)_3 \cdot 5H_2O$, $(BiO)_2CO_3$, and bismuth nitrate oxide.[4,7]

The results for Sample B, which are shown in Table 2, were compared with those for Sample A shown in Table 1. The phase transitions of Sample B on cooling from

TABLE 2. PHASE TRANSITION OF SAMPLE B ON COOLING (Cooling rate: 5 °C/min)

| Temperature before cooling (°C) | Phase transition |
|---|---|
| 740 | $\delta \xrightarrow{698^\circ C} \alpha$ |
| 760 | $\delta \xrightarrow{650^\circ C*} \alpha$ |
| 770 | $\delta \xrightarrow{640^\circ C} \beta \xrightarrow{525^\circ C*} \alpha$ |
| 780 | $\delta \xrightarrow{640^\circ C} \beta \xrightarrow{525^\circ C*} \alpha$ |
| 800 | $\delta \xrightarrow{642^\circ C} \beta \xrightarrow{523^\circ C*} \alpha$ |
| 810 | $\delta \xrightarrow{645^\circ C} \alpha$ |
| 840 | $\text{melt} \longrightarrow \delta \xrightarrow{630^\circ C} \alpha$ |
| 860 | $\text{melt} \longrightarrow \delta \xrightarrow{632^\circ C} \alpha$ |
| 890 | $\text{melt} \longrightarrow \delta \xrightarrow{630^\circ C} \alpha$ |

Note: Temperature accuracy, ±4°C

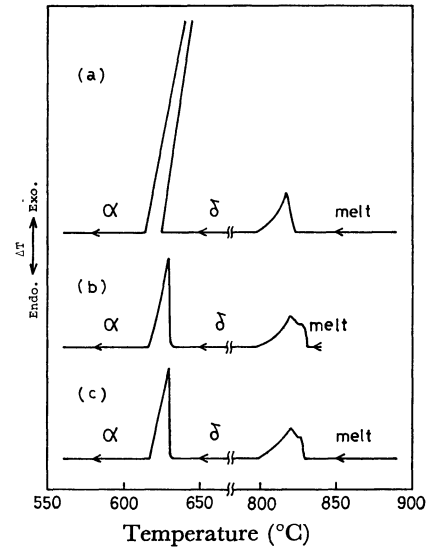

Fig. 1. DTA curves for the melt→δ→α transitions of Samples A and B
(a): Sample A on cooling from 890 °C
(b): Sample B on cooling from 840 °C
(c): Sample B on cooling from 890 °C

temperatures below 800 °C were the same as those of Sample A. However, the transition temperatures of δ→β and β→α for Sample B were lower than those for Sample A. When Sample B was allowed to cool from temperatures above 810 °C, δ-$Bi_2O_3$ transformed directly to α-$Bi_2O_3$ without passing through β-$Bi_2O_3$, regardless of the temperature before cooling. On the other hand, the phase transition of Sample A was dependent on the temperature before cooling, and the melt→δ→α transition occurred when Sample A was allowed to cool from 890 °C. This is the most remarkable difference between the phase transitions of Samples A and B.

The DTA curves observed when the melt→δ→α transitions occurred in Samples A and B are shown in Fig. 1.

By comparing the observations of Sample A (Fig. 1 (a)) with those of Sample B(Fig. 1(b), (c)), it was found that the DTA curve for the δ→α transition of Sample A showed a marked supercooling effect, which caused the sample temperature to increase remarkably. On the other hand, no such supercooling effect was observed in the DTA curve for the δ→α transition of Sample B. It was roughly estimated that the area of the exothermic peak due to the δ→α transition of Sample B was about one-fourth of that of Sample A. Also, the exothermic peak representing the solidification of Sample B had a shoulder. These differences may be due to the existence of $SO_4$ in Sample B.

The above-mentioned experimental results revealed that the phase transition of $Bi_2O_3$ on cooling was remarkably affected by the existence of a small amount of $SO_4$, such as 0.05%, in the $Bi_2O_3$.

## References

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