Bismuth Molybdate: The γ''-Bi$_2$O$_3$ · MoO$_3$ Polymorph

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An equimolar mixture of γ-Bi$_2$O$_3$ · MoO$_3$ and α-Bi$_2$O$_3$ · 3MoO$_3$ was prepared by the coprecipitation method. When heated at 550°C, this mixture was changed into β-Bi$_2$O$_3$ · 2MoO$_3$. Then single crystals of γ''-Bi$_2$O$_3$ · MoO$_3$ were obtained by heating β-Bi$_2$O$_3$ · 2MoO$_3$ in air at 750°C (1020 K). The crystal unit cell of γ''-Bi$_2$O$_3$ · MoO$_3$ is tetragonal with $a = 11.880(4)$ Å and $c = 10.778(1)$ Å. Possible space groups are $P4_2/nmc$, $P4/nmn$, $P4/n$, or $P4_2/n$. The structure is of a fluorite type. Comparison with the unit cells of β-Bi$_2$O$_3$ · 2MoO$_3$ and γ'-Bi$_2$O$_3$ · MoO$_3$ is made.

INTRODUCTION

The thermal stability of the various bismuth molybdates used as catalysts is still not exactly known, especially in the middle- and high-temperature ranges. Many authors have studied the Bi$_2$O$_3$–MoO$_3$ system and the Bi : Mo = 2 : 1 domain is a rather complicated area in the diagram. Good reviews were published in Gmelin's Handbook (*1*) and in the paper by Watanabe and Kodama (*2*), and several articles give accurate details of the behaviour of these compounds (*3, 4*).

Nevertheless, as stated by Watanabe and Kodama (*2*), the lack of a unified notation "adds unnecessary confusion." Following their choice we will use the Erman and Gal'perin notation (*5*) for γ, γ', and γ'' bismuth molybdates. These authors have written several papers but their 1968 one defines the γ'' phase with least ambiguity: the cell is said to be orthorhombic with two parameters (*a* and *b*) very close to each other: $a = b = 11.90(1)$ Å. The c parameter equals $5.450(5)$ Å or a multiple of it. The cell has close similarities with β-Bi$_2$O$_3$ · 2MoO$_3$.

γ'' bismuth molybdate changes reversibly

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into γ unless it is stabilized at room temperature, depending on the cooling scheme and the presence of microimpurities (*5*). γ'' is not seen in the phase diagram published later (*3*) and Watanabe and Kodama (*2*) although able to detect it by DTA measurement were not able to prepare it. Thus, there remained doubt as to whether γ'' could be prepared or not. As the cell parameters of all these fluorite-type structures are related, it is rather difficult to distinguish their reciprocal space; only accurate diffraction measurements can solve the problem.

EXPERIMENTAL

Preparation of γ-Bi$_2$O$_3$ · MoO$_3$ and β-Bi$_2$O$_3$ · 2MoO$_3$

The method was similar to that used by Erman and co-workers (*6*) which had enabled them to prepare γ'-Bi$_2$O$_3$ · MoO$_3$.

There were two steps, namely, coprecipitation and heating in a furnace. Coprecipitation was performed by adding (NH$_4$)$_6$Mo$_7$O$_{24}$,4H$_2$O in NH$_4$OH solution to Bi(NO$_3$)$_3$ · 5H$_2$O in HNO$_3$ solution. The pH was adjusted to 6–7 by ammonia. However, the experiment was then conducted in a slightly different way. We did not wash the precipitate because we believed that a reaction develops when the mixture is heated

with the liquid at 100°C. This may be seen by observing the change of the colour of the mixture. Hence, the whole beaker was heated gradually at 50, 100, 150, and 200°C. The water evaporated; NH_4NO_3 then sublimed and this made the catalyst quite friable.

When the powder was dry, it was ground and heated in a silica vessel in air at increasing temperature by 50°C steps until 450°C. At higher temperatures, it was heated either in the open air or in sealed silica tubes. Cooling was carried out at a rate of 100°C/h.

Thermal Decomposition of β-Bi$_2$O$_3$ · 2MoO$_3$: Preparation of γ''-Bi$_2$O$_3$ · MoO$_3$

Catalysts having the composition $Bi_2O_3 \cdot 2MoO_3$ and obtained by coprecipitation were mixtures of γ(koechlinite)-$Bi_2O_3 \cdot MoO_3$ and α-$Bi_2O_3 \cdot 3MoO_3$, as shown by neutron diffraction powder diagrams. When heated gradually the mixture changed into β-$Bi_2O_3 \cdot 2MoO_3$ at 550°C.

The sample was then laid in a thin layer in a silica crucible and was heated gradually in air up to 750°C for 24 h; after cooling it to room temperature, needle-shaped crystals were found. The crystals ground into a powder exhibited an X-ray diffraction spectrum which agreed with Erman's γ'' spectrum (also reproduced on PDF card No. 22-113 (14)).

Preparation of γ' Crystals from Koechlinite

When the Bi:Mo ratio equals 2:1, koechlinite (Zemann (7), van den Elzen and Rieck (8)) is formed during the coprecipitation process; it remains unchanged at least until 550°C. If the sample is heated at more than 650°C in sealed silica tubes, it is changed into a different phase with an X-ray powder diffraction spectrum similar to Erman's phase II described in 1964, to the Blasse phase reported in 1966 (9), to the spectrum of a compound obtained at 750°C by Batist et al. (10) in 1968, and to the

spectrum published as γ by Chen and Smith (4) in 1975, but which is actually the γ' (high temperature) form.

Heated at 800°C, and cooled down at 100°C/h, the sample gave tiny crystals less than 0.1 mm in length, the crystallographic cell of which proved to be identical to that found by Chen and Smith (4). Unfortunately, all these crystals were twinned. No evidence of the γ'' phase was shown. All the results on the behaviour of the $Bi_2O_3 \cdot MoO_3$ sample at high temperature agreed with Watanabe and Kodama's paper (2).

CHARACTERIZATION OF γ''

Crystal Cell of γ''-Bi$_2$O$_3$ · MoO$_3$

A single crystal (0.1 × 0.03 × 0.03 mm) was examined by Weissenberg and Buerger techniques. A tetragonal cell was observed: 11.8 × 11.8 × 10.8 Å^3. This result was confirmed by automated measurements on a Nonius CAD 4 diffractometer. After using the "searching program" the following cell was found: $a = b = 11.880(5)$ Å; $c = 10.778(1)$ Å; $\alpha = 90.00(2)°$; $\beta = 90.02(2)°$; $\gamma = 89.94(3)°$, but as the program may fail to find some very weak reflections, a larger cell was examined ($a' = a + b$; $b' = a - b$; $c' = c$) in order to ascertain that no weak reflection had been missed at the first attempt: the new intensities measured in this way were smaller than the average error on intensities so the use of the larger cell is not justified.

Weissenberg and precession photographs did not contain any diffuse or extra spots not belonging to the cell determined by the automatic diffractometer. The space group is rather difficult to ascertain due to the weakness of most of the reflections. Nevertheless, systematic absences were observed for $h k 0: h + k$ odd. Rules for $h h 1$ and $0 0 1$ were dubious. According to this observation, possible space groups are: $P4_2/nmc$, $P4/nmn$, $P4/n$, or $P4_2/n$.

Comparison with the Cell of the γ' Phase

In the γ''-Bi$_2$O$_3$ · MoO$_3$ spectrum there

are very strong reflections contrasting with very weak (superlattice) ones. The very strong reflections belong to the fluorite lattice subcell (a_F) and these are very similar to the strong reflections produced by the γ′-Bi$_2$O$_3$ · MoO$_3$ given to us by Chen. This is one reason why the comparison of powder data of γ′ and γ″ is difficult.

Comparison with the Cell Found by Erman et al. (5, 6)

The relation between the cell of the γ″ phase found here and the cell found by Erman (index 1) is simple: $c = 2c_1 \simeq 2a_F$ $b = a = a_1 \simeq 3a_F/2^{1/2}$.

Comparison with the β Phase

The cell content of the β phase was demonstrated by van den Elzen and Rieck (11). As pointed out by Erman and Gal'perin (5) there is a great similarity between both cells, because the angle β in β-Bi$_2$O$_3$ · 2MoO$_3$ is almost a right angle.

Figure 1 shows how the β, γ, γ′, and γ″ cells derive from the cubic fluorite cell. Attention is drawn to the fact that the actual relative orientation of the cells in a reaction involving two of them is not necessarily the one in the figure. Nevertheless, the similarities between these cells make it quite possible that a topotactic relation exists between the phases during the reaction of β into γ″ or of γ into γ″.

Cell Content

In the cell of γ″-Bi$_2$O$_3$ · MoO$_3$ there are 36 sites available for heavy atoms (Bi and Mo), i.e., 24 Bi atoms and 12 Mo atoms.

DISCUSSION

Kumar and Ruckenstein (12) have studied the thermal behaviour of β-Bi$_2$O$_3$ · 2MoO$_3$ in air at 400°C and under vacuum at 350°C and observed that it was decomposed into γ-Bi$_2$O$_3$ · MoO$_3$ (koechlinite) and MoO$_2$. Previously Sleight and Jeitschko (13) had shown that in several reactions performed in the air and involving MoO$_3$, this compound sublimed and as a
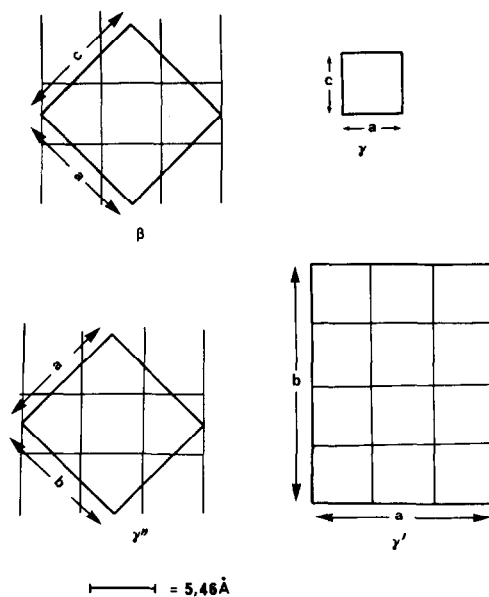
	γ (8)	γ′ (4)	γ″	β (11)
a (Å)	5.487(2)	17.251(1)	11.880(5)	11.946(2)
b (Å)	16.226(6)	22.422(2)	11.880(5)	10.795(2)
c (Å)	5.506(2)	5.581(2)	10.778(1)	11.876(2)
$β$ (°)		89.50 (1)		90.15 (2)

FIG. 1. Correspondence between elementary cells (direct cells) of β, γ, γ′, and γ″.

consequence the composition of the sample was changed.

Our results are therefore easy to understand: MoO$_3$ sublimes and the composition of the remaining sample shifts from Bi : Mo = 1 : 1 to Bi : Mo = 2 : 1. However, we obtain γ″ in place of γ (koechlinite) because we operate at a higher temperature: $β \xrightarrow{750°C}$ γ″. Thus, our results are complementary to those of Kumar and Ruckenstein (12) $β \xrightarrow{400°C}$ γ and also to Erman and Gal'perin's γ $\xrightarrow{600-650°C}$ γ′.

Several presumptions can be made concerning factors which might influence the stability of the γ″ phase, thus enabling it to be observed at room temperature, for instance:

—the presence of silicon in the sample, due to the fact that it has been prepared in a silica vessel;

—γ″ may be nonstoichiometric because the sample has been heated in the open air.

No measurements to check these presumptions have yet been made.

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