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Polymorphic Transformations of Bi_2MoO_6

A. WATANABE AND H. KODAMA

National Institute for Research in Inorganic Materials, 1-1 Namiki, Sakura-mura, Niihari-gun, Ibaraki 305 Japan

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The polymorphism of Bi_2MoO_6 has been studied by differential thermal analysis, differential dilatometry, and differential scanning calorimetry with γ form specimens having the koechlinite structure prepared by sintering the oxides Bi_2O_3 and MoO_3. Two stable γ and γ' forms and one metastable γ'' form were observed. The relative thermal stability of the γ form compared with the γ' form has been examined by isothermal heating of a mixture of the two forms under hydrothermal conditions. Thus the low-temperature stable γ form transformed reversibly to the γ'' form at 604 ± 3°C, and on subsequent heating, the γ'' form transformed irreversibly to the high-temperature stable γ' form in the range 640 to 670°C, depending on heating rates; however, an isothermal treatment at a temperature above 604 ± 3°C brought the gradual transition of the γ'' form into the γ' form.

Introduction

The modifications of bismuth molybdate, Bi_2MoO_6, have been reported by several investigators (*1–6*). Figure 1 summarizes the phase relations of this compound together with the results of the present study. It is obvious that inconsistencies exist in the number of the modifications, in the relative stabilities of them, and in the transition temperatures; furthermore, no unified notation corresponding to the various modifications adds unnecessary confusion. Three modifications were labeled γ, γ', and γ'' by Kohlmuller and Badaud (*4*) as well as by Erman and Gal'perin (*3*), but these assignments do not agree. The γ form of the former workers corresponds actually to the γ' form of the latter authors, who reported that the γ phase was the metastable form, the γ' phase the high-temperature stable one, and the γ'' phase the form intermediate between them. Likewise, the γ form designated by Chen and Smith (*6*) corresponds to the γ' form of Erman and Gal'perin (*3*). Thus, in order to avoid confusion, the notation of Erman and Gal'perin (*3*) will be used for γ, γ', and γ'' in the following as a matter of convenience.

The γ form is found in natural deposits as the mineral koechlinite, and can usually be synthesized by coprecipitation from solutions (*7, 8*). As for the γ' form, it is readily prepared by sintering the oxides Bi_2O_3 and MoO_3 at 750°C for several hours (*2*); large single crystals can also be grown by the flux method or top-seeded method (*6*). That is, both γ and γ' phases exist in the apparently stable form at room temperature.

In the present paper, the polymorphic transformations of Bi_2MoO_6 compound were studied by differential thermal analysis (DTA), differential dilatometry, and differential scanning calorimetry (DSC) with the γ form specimens prepared by sintering the oxides; the relative stability of

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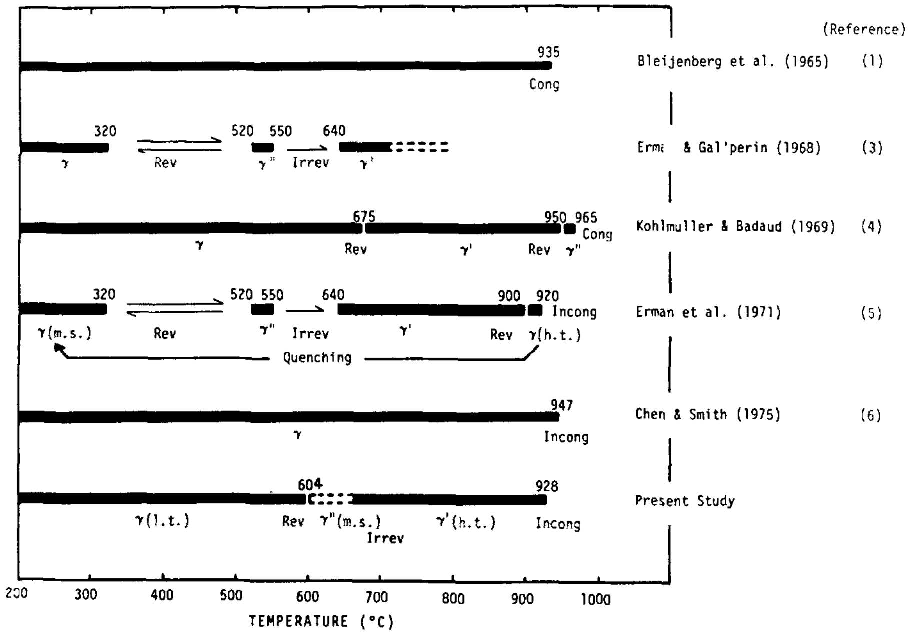

FIG. 1. Summary diagram of previous works for Bi_2MoO_6. Rev, Reversible transition; irrev, irreversible transition; l.t., low-temperature stable form; m.s., metastable form; h.t., high-temperature stable form; cong, congruent melting point; and incong, incongruent melting point.

the γ form compared with the γ′ form was examined by isothermal heating of a mixture of these two forms under hydrothermal conditions.

Experimental

Polycrystalline γ-Bi_2MoO_6 was readily fabricated in the following procedures. The starting materials Bi_2O_3 and MoO_3, both 99.9% pure, were thoroughly mixed in stoichiometric proportion (Bi_2O_3 : MoO_3 molar ratio of 1 : 1) under ethanol. After drying, the mixture was heated in a covered Pt crucible at 530°C for 20 hr. The compound prepared in this way was greenish yellow. It was characterized as the γ form by X-ray powder diffraction method using Ni-filtered Cu*K*α radiation; namely, the diffraction data were identical to those of the synthetic koechlinite (i.e., the γ form) of Aykan (*8*), and the lattice parameters correspond well with those (a = 5.487, b = 16.226, and c = 5.506 Å) of the mineral koechlinite refined by van den Elzen and Rieck (*9*).

So as to check whether the γ phase has solid solubility, samples with composition $Bi_{2x}Mo_{1-x}O_3$ ($x = 0.475$–0.525) were prepared by sintering the oxides in the same way as mentioned above. A small amount of another phase (i.e., the β or ε phase (*6*)) was found in X-ray diffraction patterns in this composition region except the γ phase with $x = 0.5$. Therefore, no solid solubility exists in the γ phase; it is a line compound.

The DTA measurements were made to detect the phase transitions for Bi_2MoO_6 and to confirm the presence and the regions of existence of the modifications. The apparatus (Rigaku-Denki Standard Unit) was calibrated against the α–β transition of K_2SO_4 at 585°C and the melting point of NaCl at 800°C using Al_2O_3 as a reference material. The temperature accuracy was ±2°C. The rates of heating and cooling were 1.25, 2.5, 5, 10, or 20°C min^{-1}. The transition temperatures were determined from peaks on DTA curves during the heating cycle.

Dilatometry with Rigaku-Denki Standard Type was employed to measure linear dimensional changes of a bar sample of Bi_2MoO_6 near the transition points. The rates of heating and cooling were 10°C min^{-1}. The bar of Bi_2MoO_6 was prepared as follows: the powder obtained by sintering the oxides was isostatically pressed at 900 kg cm^{-2} into a rod 5 mm in diameter and 15 mm long, followed by a second sintering at 580°C for 8 hr.

The heats of transformations in Bi_2MoO_6 were determined by means of DSC (Rigaku-Denki Standard Unit). A calibrant was powdered crystalline K_2SO_4 with a heat of transition of 2.14 kcal mol^{-1}. Scanning speeds of 5 and 10°C min^{-1} were employed.

In order to examine the relative stability of polymorphs, a mixture of the γ and γ' modifications was sealed in a Pt capsule together with aqueous NH_4F solution. The sample weight was about 50 mg. The capsule was placed in a cold-seal pressure vessel, and then heated isothermally in a vertical tube furnace. One mixture was treated at 500°C and 750 kg cm^{-2} for 6 d in 2 mol dm^{-3} NH_4F solution, and the other at 404°C and 650 kg cm^{-2} for 3 d in 0.5 mol dm^{-3} NH_4F solution. After being quenched, the products were identified by X-ray powder diffraction method.

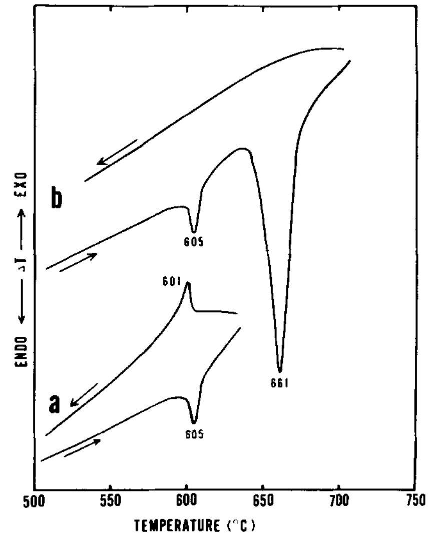

FIG. 2. DTA curves for Bi_2MoO_6 measured at a rate of 10°C min^{-1} below the melting point: (a) the first heating and cooling cycle, maximum temperature 640°C; (b) the second cycle, maximum temperature 705°C. The first peak shows a reversible transition and the second an irreversible one.

Results and Discussion

The present study confirmed that the γ form was a line compound. On the other hand, Chen and Smith (*6*) made sure of no solid solubility in the γ' form, although discrepancies were found with regard to the range of composition of it (*1*, *4*, *5*, *10*).

Figure 2 shows representative DTA curves. When the γ form is heated up to 640°C and then cooled to room temperature, only one peak appeared reversibly at about 600°C (Fig. 2a). This peak corresponds to the $\gamma \rightarrow \gamma''$ transition. On heating above 700°C, two endothermic peaks were observed; neither the first peak nor the second one was observed in the subsequent cooling curve as indicated in Fig. 2b. The second transition is irreversible, and therefore this peak is related to the $\gamma'' \rightarrow \gamma'$ transition. When the samples underwent this irreversible transition and were cooled to room temperature, their X-ray powder data coincided with those (*6*) of the γ' form. This irreversible transition is not a peritectoid reaction but a polymorphic transformation, because both the γ and γ' forms are line compounds.

Results of differential dilatometry also showed two phase changes in the heating. Figure 3 represents a typical dilatometric curve for heating and cooling cycle. The first small inflection at the lower tempera-

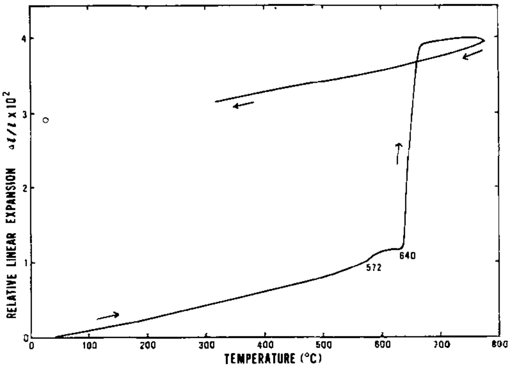

FIG. 3. Change of relative linear expansion $\Delta l/l$ for Bi_2MoO_6 with temperature at a rate of 10°C min^{-1}; open circle represents the final $\Delta l/l$ value of 0.029 for a sample cooled to room temperature.

ture changed reversibly, if the sample was cooled before the second change which gives rise to a sizable, irreversible expansion. The first and the second changes are related to the $\gamma \rightarrow \gamma''$ and the $\gamma'' \rightarrow \gamma'$ transitions, respectively. The transition temperatures are somewhat lower than those measured by the DTA method, because the changes in thermal expansion may not be themselves part of the transition but may be premonitory symptoms (*11*).

A series of DTA runs was carried out at various heating rates to check the dependence of the transition points on the heating rate. The results showed that the $\gamma \rightarrow \gamma''$ transition was always observed at 604 ± 3°C irrespective of heating rates employed, and the temperature of the $\gamma'' \rightarrow \gamma'$ transition ranged from 640 to 670°C, depending markedly upon heating rates.

The γ'' form seems to be in a metastable state, because the temperature region of existence of it varies with the heating rate. According to Erman and Gal'perin (*3*), the γ'' form could be stabilized at room temperature, depending on the cooling scheme. However, after various heat treatments of the γ form samples at temperatures between 605 and 640°C, the material we observed by X-ray diffraction at room temperature consisted of a mixture of the γ and γ' forms. This indicates that, above the transition temperature of 604°C, part of the γ'' form transforms gradually to the γ' form, as suggested by Erman and Gal'perin (*3*), while the rest of it returns inevitably to the γ form on cooling. Therefore, the γ'' form could not exist at a temperature below 604°C. The gradual transformation process of the γ'' form into the γ' form was easily detected using the dilatometer because of the marked volume change. When a temperature was maintained in the region of existence of the γ'' form, a bar sample expanded gradually as a function of time, as shown in Fig. 4. It seems that the initial, appreciable shrinkage is due to the occurrence of grain growth in the γ'' phase. Such a gradual transition proved the γ'' form to be metastable.

As shown in Fig. 1, the two transition-temperature ranges reported by Erman and Gal'perin (*3*) differ markedly from the

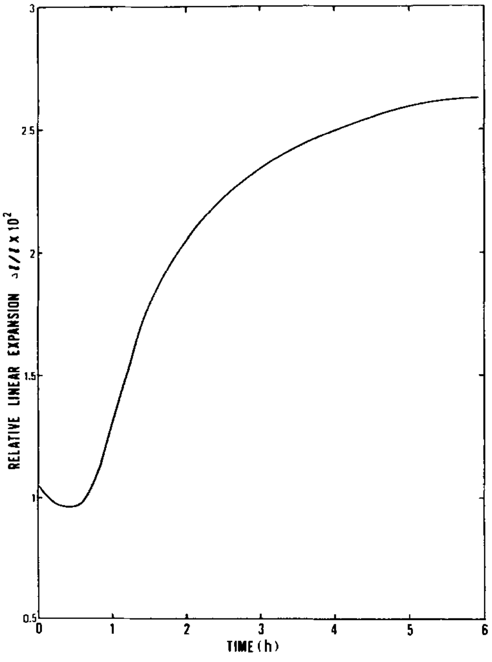

FIG. 4. Change of relative linear expansion for Bi_2MoO_6 as a function of time at 608°C.

present. These investigators inferred from their high-temperature X-ray diffraction studies that the $\gamma \rightarrow \gamma''$ transition began as low as 320°C; however, no heat effects were detected in their DTA curves. In fact, the reversible transition at 604°C was also not observed in their DTA measurements, and Erman and Gal'perin (*3*) inferred that the heat of the transition was too small to be detected. Cross (*12*) has also found only the irreversible transition at 610°C in the DTA curves. At the high temperatures, our DTA curve agreed well with that reported by Chen and Smith (*6*); however, our value for the melting point is somewhat lower. In agreement with Chen and Smith (*6*), we find no evidence for the further transition at about 900°C reported by Erman *et al.* (*5*).

The transition enthalpies obtained in DSC experiments were about 0.1 kcal mol^{-1} for the $\gamma \rightarrow \gamma''$ transition and about 3.2 kcal mol^{-1} for the $\gamma'' \rightarrow \gamma'$ transition. The enthalpy of the $\gamma \rightarrow \gamma''$ transition was so small that this transition was not observed by the previous investigators.

Experimental results of the relative thermal stability of the polymorphs revealed that the γ phase was the low-temperature stable form and the γ' phase the high-temperature stable one, because only the γ phase was observed in X-ray powder patterns obtained from all the products treated isothermally at 404 or 500°C under hydrothermal conditions; however, further work is needed to examine the effect of pressure on the relative stability, because we neglected the effect in the present work.

In order to obtain the pure γ-Bi_2MoO_6 phase by means of solid-state reaction, a stoichiometric mixture of Bi_2O_3 and MoO_3 should be heated at a temperature below 600°C as a precaution against occurrence of the gradual, irreversible $\gamma'' \rightarrow \gamma'$ transition; nevertheless, a heat treatment at a temperature below 500°C showed rather sluggish reaction of the component oxides or no solid-state reaction of them. In fact, the reaction was incomplete even after the heat treatment for 300 hr at 400°C. Consequently, a temperature range 520 to 590°C was most favorable for obtaining the pure γ phase by heat treatment for 10 to 20 hr. A single-crystal growth of the γ phase also succeeded under hydrothermal conditions below 600°C (*13*).

Recently, Ismailzade *et al.* (*14*) have reported the ferroelectricity in γ-Bi_2MoO_6 for ceramic samples. These samples were prepared as follows: a mixture of the oxides was heated at 700°C for 3 hr and sintered finally at 850°C for 1.5 hr. In view of our results, there is considerable doubt about their results; namely, it would seem that their samples consist of the γ' form. If γ-Bi_2MoO_6 is a ferroelectric substance, the transition temperature at 604°C may be a Curie temperature. Consequently, the ferroelectricity in γ-Bi_2MoO_6 will be the future subject.

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