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Structural and Thermal Characterization of the γ'' Polymorph of Bi_2MoO_6

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Among the different polymorphic phases of the Bi_2MoO_6 system, the intermediate γ'' compound has been characterized within a metastable state by high temperature X-ray diffraction and Raman spectroscopy. The transition $\gamma \rightleftarrows \gamma''$ is found to be partially displacive and partially reconstructive. In the context of the ferroelectricity of γ, the nature of the paraelectric phase is discussed with the help of space group considerations and Buerger's theory of phase transitions.

Introduction

Many contradictory results have been published during the past 20 years concerning the physicochemical properties of Bi_2MoO_6, a well known active component in mild oxidation or ammoxidation of olefins to unsaturated aldehydes or nitriles. This compound, often lying on the surface of multicomponent catalysts, is very sensitive to temperature calcination. A minimum of four different phases have been found to exist from 20°C to the incongruent melting point (930°C) at atmospheric pressure. The nature of the phase transitions—especially concerning the molybdenum environment—is still obscure. The role of bismuth on the crystalline field of Mo seems to be fundamental as in the case of Fe, Co, Ni in the $CoMoO_4$ structure type (*1*); this might explain the substantial promoting effect of this ion in catalysis.

A knowledge of physicochemical properties of mono- or multiphasic systems is necessary to understand the mechanisms involving the surface and the bulk during the reaction of the adsorbed phase.

Only the structure of the γ, low temperature form—the mineral koechlinite—has been determined with precision (*2*): there exist four equivalent Mo in a very distorted octahedral environment, with site symmetry C_1, in an orthorhombic $Pca2_1$ (C_{2v}^5) lattice. This highly lamellar compound along (010) belongs to the Aurivillius series of bismuthyl compounds of the general formula

$$(BiO)_2\,(A_{n-1}B_nO_{3n+1})$$

where the perovskite structural unit $(A_{n-1}B_nO_{3n+1})^{2-}$ is reduced to MoO_4^{2-} (*3*).

Recently, the phenomenon of ferroelectricity of Bi_2MoO_6 was discovered (*4*) by dielectric measurements on ceramics. This property was well known previously for many crystals of this type (*5*). The shift by 0.21 Å of the molybdenum atom towards an edge of the octahedra is the main cause of the resultant polarization of the lattice in the ⟨100⟩ direction (Fig. 1).

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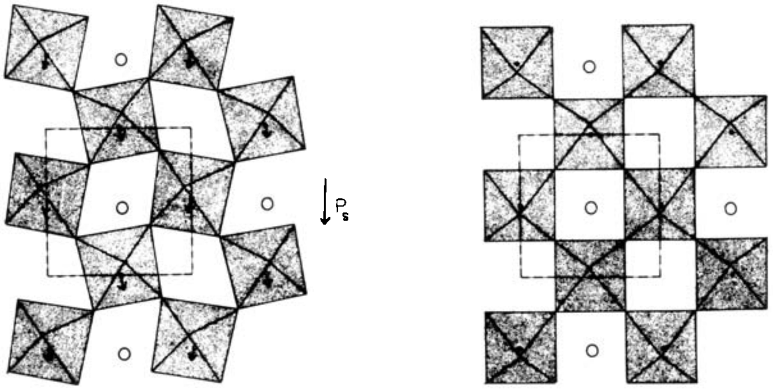

Bi_2MoO_6 [0,1,0] Bi_2TeO_6 [0,1,0]

FIG. 1. Cleavage plane of the molybdate and tellurate of bismuthyl: the displacement of Mo atoms in the first structure leads to an electric dipole P_s. The collapsed structure (left) is a distortion of the open structure (right).

Thus, one may ask what is the paraelectric phase and where does the corresponding transition occur?

The "Blasse structure" (*6*) named γ' by Erman (*7*) is obtained either by solid–solid reaction between Bi_2O_3 and MoO_3 or by calcination of γ, both above 600°C. It is stable at room temperature and has been thought to be the stable form, γ being metastable up to the irreversible and sluggish transition $\gamma \rightarrow \gamma'$, whose kinetics have been studied by Egashira *et al.* (*8*). Initially considered as isotypic to La_2MoO_6 (quadratic) (*6*), its symmetry has been found to be much lower (monoclinic $P2_1/c$–C_{2h}^5) (*9*). All the authors agree with the tetrahedral configuration of Mo.

A very slight endothermic transition has been observed in DTA experiments by Watanabe (*10*) at 604°C; this was confirmed by us. This corresponds to the reversible formation of the γ'' Erman phase. In this paper we try to clarify the nature of this phase by high temperature measurements of structural properties.

Finally, a high temperature structure, obtained between 850°C and the melting point, named γ_{HT} by Erman, yields the γ' phase on slow cooling, and the γ phase on quenching at room temperature.

Experimental Procedure

The method of Batist *et al.* (*11*) was used to prepare γ Bi_2MoO_6 from $BiONO_3$ (Merck) and $(NH_4)_6$ MO_7O_{24}, $4H_2O$ (Labosi) by reacting for 24 hr, in boiling water. The slurry was then filtered, washed with hot distilled water, and calcined at 450°C for a few hours. Electron microscopy of the powder reveals square single crystals 0,1 μ in width, the (010) plane being perpendicular to the beam.

X-ray diffraction was performed on a "type F" Siemens Goniometer equipped with a high temperature vacuum "HTK 10" in the 300–1500° K range, the sample being fastened on a platinum ribbon.

Raman spectra were recorded on the Raman microprobe (*12*) in the 30–950 cm^{-1} range, with an incident 514.5-nm line of an argon-ion laser.

Infrared spectra were recorded at room temperature on a Perkin–Elmer double-beam spectrophotometer with KBr as solvent.

DTA was performed on a Setaram "micro ATD M5"; a temperature rise of 10°C/mn was chosen. The sample weight was less than 1 mg. Quartz was added in the Al_2O_3 reference for calibrating the temperature which is measured on a third, empty, platinum crucible.

Results

High Temperature X-ray Diffraction

The whole spectrum of Bi_2MoO_6 was analyzed from room temperature to 700°C; the lines associated with the γ'' phase appeared reversibly in addition to those of the γ phase near 600°C. The γ' spectrum appeared a little later in competition with that of γ'', but was not considered here. The slope of the d_{hkl} vs temperature lines is steeper for (202) than for (060). The coexistence of the two phases γ and γ'' was due to the heterogeneity of the sample temperature and prevented possible confusion between the two similar spectra near the transition point.

The indexing of γ'' at 600°C was then performed on the same lattice as γ, and the least square method was used to optimize the parameters (Table I). The same extinctions were observed in the high temperature spectra, and all the doublets of the orthorhombic distortion of γ are still present in γ''.

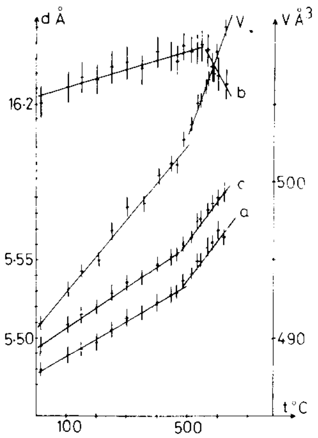

FIG. 2. Variation of the parameters and cell volume of the γ and γ'' structures with temperature.

TABLE I

X-RAY DIFFRACTION LINES OF γ'' AT 600°C

hkl	d_{obs}	d_{cal}	I_{obs}	*hkl*	d_{obs}	d_{cal}	I_{obs}
111	3.836	3.834	10	062	1.944	1.943	18
140	3.282	3.278	2	260	1.940	1.940	16
131	3.192	3.187	100	222	1.919	1.917	4
002	2.797	2.795	27	320	1.810	1.810	1
200	2.791	2.785	20	113	1.758	1.757	<1
060	2.706	2.703	20	311	1.753	1.752	<1
022	2.646	2.643	4	172	1.698	1.699	4
220	2.638	2.634	3	133	1.681	1.680	15
151	2.508	2.505	9	331	1.676	1.675	14
211	2.464	2.464	1	280			<1
122	2.389	2.388	1	191	1.640	1.639	12
042	2.304	2.301	1	262	1.594	1.594	11
240	2.296	2.296	2	153	1.552	1.552	<1
080	2.029	2.027	<1	351	1.549	1.548	<1
152	1.973	1.973	<1				
202			18				

Note. $a = 5.570 \pm 0.005$, $b = 16.219 \pm 0.011$, $c = 5{,}591 \pm 0.005$, $V = 505.03$ Å^3, $Z = 4$.

The parameters a and c of γ exhibit a linear expansion up to 500°; thereafter the slope increases markedly. By contrast, b exhibits a contraction at 600°C, followed by a negative expansion parameter (Fig. 2).

The cell volume (Fig. 2) shows a variation ΔV consistent with the endothermicity of the DTA according to Clapeyron's law:

$$L = T.\Delta S = T.\Delta V \left(\frac{dP}{dT}\right) > 0.$$

DTA Experiments

The transition $\gamma \rightleftarrows \gamma''$ is observed in DTA, provided the sample is sufficiently crystalline and the programming rate sufficiently high to accelerate the formation of γ'' before the slow transformation into γ'. Reversibility on cooling was encountered only when the second transition was avoided, in accordance with Watanabe's results (*10*). No supercooling seems to occur, and the thermal peak, near 600°C, is narrow, suggesting a fast, second-order type transition.

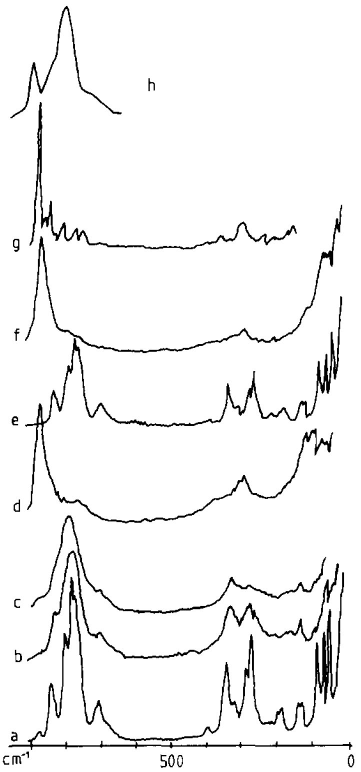

FIG 3. Raman spectra: (a) ambient; (b) 300°C; (c) 550°C; (d) 600°C (γ''); (e) cooling back to ambient (γ); (f) 750°C (γ'); (g) cooling back to ambient (γ'); (h) 1 hr near 900°C ($\gamma_{HT} + \gamma'$).

High Temperature Raman Scattering

The room temperature Raman spectra are similar to those obtained by Matsuura (*15*) and Blasse (*16*) (for Bi_2WO_6) who interpreted their results, respectively, on the basis of tetrahedral and octahedral coordination for the transition cation. In fact, the distortion of the Mo environment (octahedra C_1 in factor groups C_{2v}) is greater than that of W (octahedra C_2 in factor group C_{2v}), and the A_{1g} mode splits up into four modes (instead of two for Bi_2WO_6). Moreover, the shift of the stretching modes towards the upper frequencies, despite the lower weight of Mo, is due to the weaker Mo–O bonds, according to the formula

$$\nu = \frac{1}{2\pi} \sqrt{\frac{\mu}{K}}$$

where K is the force constant and μ the reduced mass.

The thermal shift of the mean frequency of the ν_1 mode is very small as compared to the reversible jump near 600°C, leading to a nearly perfect tetrahedral structure (A_{1g} at 860 cm^{-1}) (Fig. 3).

The further transformation into γ' could not be followed, the Mo configuration seeming identical; but above 700°C, the reversibility could no longer be observed (Fig. 4).

Finally, the transition $\gamma' \rightleftarrows \gamma_{HT}$ was obtained slowly (in 1 hr) at 900°C. The ν_1 vibration at 792 cm^{-1} of γ_{HT} appeared and is characteristic of nearly perfect octahedra (it would be at 770 cm^{-1} by extrapolating to 20°C). The reproducibility of this result could not be ascertained because of the vicinity of the melting point. A better characterization of this transition should be attainable by high temperature DTA and RX measurements.

Discussion

The $\gamma \rightleftarrows \gamma''$ transition has been characterized by three effects:

(1) a reversible change in Mo coordination (from 6 to 4) at 600°C;

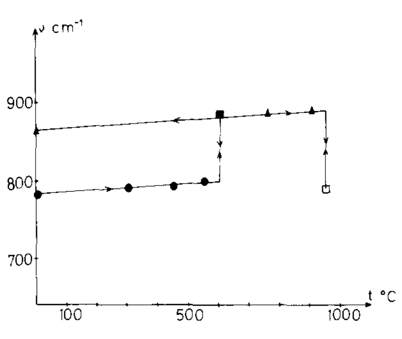

FIG. 4. Variation of the $\nu_1(A_{1g})$ mode with temperature: ●, γ; ■, γ''; ▲, γ'; □, γ_{HT}.

(2) a reversible thermal effect at the same temperature;

(3) a progressive evolution of a and c lattice parameters starting from 500°C, followed by contraction of b at 600°C.

The isostructural Bi_2WO_6 (space group $Aba2$–C_{2v}^{17}) undergoes a ferroelectric transition at 935°C (*13*). The low temperature polar phase involves only a slight distortion of the octahedral high temperature phase obtained by a displacive, progressive transition. The space group of the paraelectric phase is one of the D_{2h} supergroups of C_{2v}^{17}, this phase being probably similar to Bi_2TeO_6 ($Cmca$–D_{2h}^{18}) (Fig. 1).

An octahedral, nonpolar phase was also anticipated in the case of Bi_2MoO_6. According to Raman spectra, it might be of the γ_{HT} type (no polar structure is known at such an elevated temperature). In fact, well sintered ceramics of γ can be obtained by quenching from 900°C, fast enough to prevent the slow formation of γ'. According to Ismaïlzade (*4*) these ceramics are ferroelectric: this means that the spontaneous polarization of the structure is reversible under a high electrical field.

What happens during formation of γ''? The progressive dilatation of a and c may be interpreted as the beginning of the depolarizing transition leading to γ_{HT}. The deformation stops abruptly at 600°C, when a reconstructive, first-order transition sets in. Probably only two bonds are broken to produce the tetrahedral coordination of Mo, and a sixth BiO bond is formed between the Bi and Mo layers. The transition would be only partially reconstructive because of the absence of supercooling, suggesting a low activation barrier.

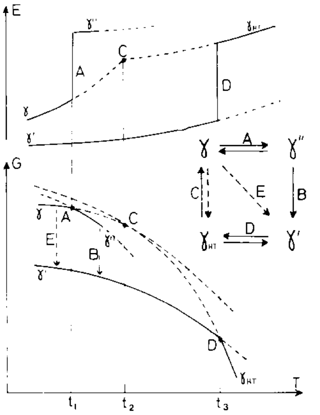

FIG. 5. Thermodynamic scheme: internal energy E and free energy G versus temperature. Non observed phases are represented in dotted lines, t_1 is approximately 600°C, t_2 is unknown, and t_3 is close to 900°C.

Figure 5 sums up the situation at a glance. The internal energy E and Helmholz (or Gibbs) free energy $E - TS$ ($+ PV$) of each polymorph is drawn. The slope of the free energy curve yields the entropy $S = -(\partial G/\partial T)$. A stable phase has a lower value of G than an unstable one. A reversible phase transition is represented by the crossing of two G curves. A discontinuity of internal energy occurs when the transition is reconstructive. However, in the case of a true Curie point, the G curves osculate, and E is continuous.

An irreversible transition is shown as a vertical relaxation from a metastable state to a stable one.

In this context, the quenched specimens of γ have been obtained via a "stranded phase" in the Buerger's terminology (*14*) between D and C, the activation energy of the $\gamma_{HT} \rightleftarrows \gamma'$ (point D) transition probably being very large.

The $\gamma \rightleftarrows \gamma''$ transition shown as a progressive increase of E, followed by a jump, is seen to occur within a metastable state. This explains its competition with the $\gamma \rightarrow \gamma'$ transition.

Conclusion

We propose a model consistent with all the data published so far. The details still have to be checked (the "E" transition at atmospheric pressure, with the help of a nucleation agent, for example), and the Curie point to be pinpointed. Dielectric studies under both high frequency–low field and low frequency–high field are projected.

Note. Two recent publications have appeared concerning the structure of γ''. The first (*17*) deals with a quadratic phase obtained from $Bi_2MO_2O_9$ by thermal decomposition, and is perhaps a metastable structure not obtained by us. The second (*18*) is in agreement with our interpretation, but the transition $\gamma \rightleftarrows \gamma''$ is found to be very gradual, in disagreement with the latent heat observed in DTA.

Acknowledgments

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