Structural aspects of bismuth molybdate (Bi2MoO6)

Solid State Chemistry 1982, Proceedings of the Second European Conference, Veldhoven, The Netherlands, 7—9 June 1982, R. Metselaar, H.J.M. Heijligers and J. Schoonman (Eds), *Studies in Inorganic Chemistry*, Volume 3

STRUCTURAL ASPECTS OF Bi_2MoO_6

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ABSTRACT

The change of the structure of the metastable, catalytic active γ-Bi_2MoO_6 was followed by x-ray diffraction techniques. The γ-Bi_2MoO_6 phase transforms via an intermediate phase in the temperature region 400-600°C irreversibly to the γ'-Bi_2MoO_6 phase. The positions of the metal-ions in this phase were determined.

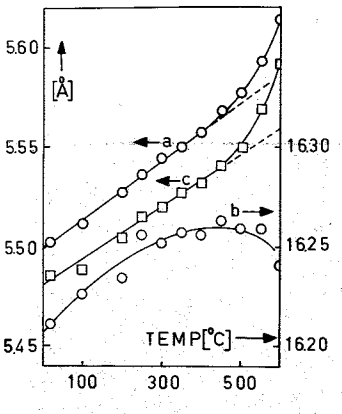
INTRODUCTION

According to different authors the compound Bi_2MoO_6 is a line compound or has a narrow existence area. Several modifications have been reported in literature (ref. 1,2,3). In this study we have followed both x-ray diffraction patterns and electrical conductivity from room temperature up to the melting point at 938°C.

STRUCTURE OF THE γ-PHASE

The γ-phase (Koechlinite structure) is of special interest because of its catalytic activity in oxidation reactions of alkenes. The space group is $Pca2_1$, with cell dimensions a = 5.487, b = 16.226 and c = 5.506 Å (Rhombic symmetry). The structure consists of alternating $[MoO_4^{2-}]_N$ and $[BiO^+]_{2N}$ layers perpendicular to the b-axis (ref. 4)*. The γ-phase is metastable and gradually transforms to the catalytic inactive γ'-phase at temperatures above 600°C. An intermediate phase is reported to occur in the temperature region 400-600°C [1]. Celparameters, as calculated from the positions of six simple and three composed peaks, under which two reflections coincided, are shown as a function of the temperature in Fig. 1. The celvolume increases linearly with the temperature (β = 6.0 10^{-5} $°C^{-1}$) up to 400°C, as shown in fig. 2. Above this temperature there is a much steeper increase and finally we obtain the γ'-phase.

* Recent investigations [5] indicate that the structure also can be described with the spacegroup Pbca. However the resulting changes in the atomic coordinates do not influence the conclusions of this paper.



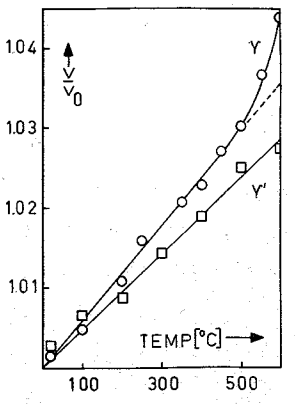


Fig. 1. Celparameters of the γ-phase as function of the temperature [left].

Fig. 2. Relative cel volume of the γ and γ'-phase as function of temperature [right].

These structural changes are reflected by changes in the electrical conductivity.

STRUCTURE OF THE γ'-PHASE

The spacegroup is $P\frac{2_1}{c}$ with cell dimensions a = 17.250, b = 22.426, c = 5.586 Å and $\beta = 90.50^{o}$ (Monoclinic symmetry), as determined by refinement of powder diffraction data. For the indices of the strongest reflections one could recognize the diffraction pattern of a face-centered cell with dimensions $1/3a=a^{*}=5.75$ Å, $1/4b=b^{*}=5.61$ Å, $c=c^{*}=5.59$ Å and $\beta = 90.50^{o}$. The elementary cel of γ'-Bi_2MoO_6 then consists of 12 of such cells. The structure of the γ'-Bi_2MoO_6 phase can be derived from the fluorite structure by replacing three Ca^{2+}-ions by two Bi^{3+}-ions and one Mo^{6+}-ion; the fluorine ions are replaced by oxygen ions. The dependence of the cell parameters, as calculated from the positions of three simple and two composed peaks, is shown as a function of the temperature in Fig. 2. The cubic dilatation coefficient is $4.5\ 10^{-5}\ {}^{o}C^{-1}$. It is impossible to determine the exact positions of the oxygen-ions from the

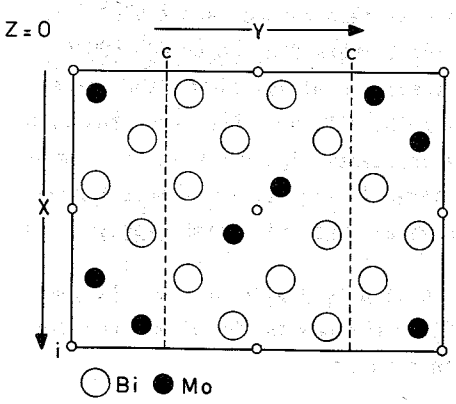
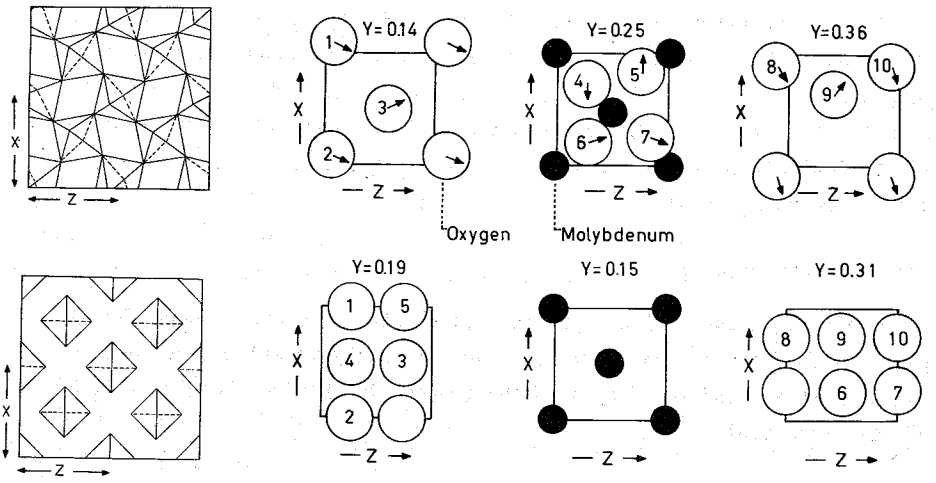


Fig. 3. A cross-section through the elementary cel of γ'-Bi_2MoO_6. Only the positions of the metal-ions are shown.



Figs. 4 and 5. [left] MoO_4^{2-}-layer perpendicular to the b-axis of the γ-phase (above). MoO_4^{2-}-layer of the γ"phase (under).
Fig. 6. Cross-sections perpendicular to the b-axis through the MoO_4^{2-}-layer of γ-phase (above) and the γ"-phase (below). Arrows in the big circles (oxygen-ions) represent the displacement in the xz-plane. The numbers of the oxygen ions in the different structures correspond [right].

powder diffraction data. A cross section through the elementary cel is given in Fig. 3. The large values of the cel-parameters of the a- and b-axis is caused by ordering in the distribution of bismuth and molybdenum-ions over the cation-sublattice.

TRANSFORMATION OF THE γ TO THE γ"-PHASE

Lanthanummolybdate, La_2MoO_6, has like koechlinite a layer structure and is constructed of alternating layers with the compositions $[LaO^+]_{2N}$ and $[MoO_4^{2-}]_N$. The $[LaO^+]$-layers are identical with the $[BiO^+]$-layers in koechlinite. The $[MoO_4^{2-}]$-layer in lanthanummolybdate consists of separate MoO_4^{2-}-tetrahedrons, whereas the MoO_4^{2-}-octahedrons in koechlinite are interconnected at the corners. With increasing temperature the layer with interconnected molybdenum-oxygen-octahedrons gradually transforms into a layer with separate MoO_4^{2-}-tetrahedrons as shown in Figs. 4 and 5.
The oxygen ions in the (MoO_4^{2-})-layer of the γ-phase only need to be displaced about 0.9 Å in the xz plane and about 0.9 Å in the y-direction and the tetragonal La_2MoO_6 structure arises. This is illustrated in Fig. 6, in which a number of cross sections perpendicular to the b-axis through the (MoO_4^{2-})-layers is given. The change of celparameters as a function of the temperature can be explained by the formation of a closed-packed plane of oxygen-ions above and

below the molybdenum plane. Parallel to the b-axis the distance of the oxygen-ions to the molybdenum ions decreases, which explains the temperature dependence of the b-axis. The irreversible transformation to the γ'-phase apparently involves a reordering in the distribution of metal ions over the cationsublattice. This transformation is accomplished in 24 hours at 600°C and in a few hours at 700°C.

ELECTRICAL CONDUCTIVITY

As mentioned above, all changes in crystal structure are accompanied by changes in electrical conductivity. We are presently investigating, whether these changes are due to changes in the transportmechanism. Results will be published separately.

CONCLUSIONS

The reversible character of the $\gamma \rightarrow \gamma''$ transition can be understood on the basis of the small changes in the atomic positions of the oxygen ions. The loss of the catalytic activity of Bi_2MoO_6 after transformation to the γ'-phase seems to be due to a drastic change in crystal structure, resulting in the loss of the layer structure of the γ-phase.

REFERENCES

1 L. Erman, E. Gal'perin and B. Sobolev, Russ. J. of Inorg. Chem. 16, (1971) 258-261.
2 R. Kohlmuller, J.P. Badaud, Bull. Soc. Chim. France 10, (1969), 3434-3439.
3 M. Egashira, K. Matsuo, S. Kagawana and T. Seiyama, J. Catal. 58, (1979), 409-418.
4 A.F. van den Elzen and G.D. Rieck, Acta Cryst. B29, (1973), 2436-2438.
5 F. Pertlik and J. Zemann, to be published in "Fortschritte der Mineralogie", 1982.