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Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

Abstract

Full Text

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Crystallography

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On the Crystal Structure of Bi-Molybdate $Bi_2[MoO_4]_3$

Single-crystal specimens of $Bi_2[MoO_4]_3$ suitable for X-ray structural analysis were isolated from a melt of the corresponding oxides.

From rotation photographs obtained with Cu radiation, as well as from X-ray goniometric sweeps, the parameters of the monoclinic cell were again established: $a = 7.89$ Å, $b = 11.70$ Å, $c = 12.24$ Å, with angle $\beta = 116°20'$. In accordance with the specific gravity 5.90 g/cm^3, a cell with these parameters contains $Z = 4$ formula units $Bi_2Mo_3O_{12}$. In comparison with the data of work (^{1}), the parameters given here have been substantially refined.

Fig. 1. $Bi_2[MoO_4]_3$. Principal peaks of the Patterson projection $P(yz)$

Fig. 2. Isolation of the primitive monoclinic cell of $Bi_2[MoO_4]_3$ from the centered cell of tetragonal scheelite

Unambiguous indexing of the X-ray goniometric sweeps and the observed systematic extinctions made it possible, with a high degree of confidence, to assign the crystals of Bi-molybdate to the Fedorov group

$$C_{2h}^5 = P2_1/c.$$

The intensities of the reflections were estimated from blackening marks, and from them, after exclusion of the LP-factor, arrays F_{0kl}^2 and F_{h0l}^2 were obtained; on their basis the principal projections of interatomic vectors $P(yz)$ and $P(xz)$ were constructed.

On the Patterson projection $P(yz)$ (in the direction of the shortest axis a), along with incompletely resolved and blurred maxima, there appears a series of peaks that are well resolved and regularly distributed over the entire area of the projection, so that the latter is divided into similar subcells. This is shown schematically in the squared Fig. 1. This characteristic feature of the projection suggests that in the structure under investigation there is a sharply expressed "sublattice" with shorter periods, which is converted into the final motif only by a superposed "additional" structure (according to Buerger (2)) ("superstructure").

A similar regularity (with subcells) is also characteristically manifested in the other Patterson projection, $P(xz)$. Analysis of both projections, together with crystallochemical considerations, made it possible to conclude that the structure sought for Bi-molybdate should be regarded as derived from scheelite, and that its cell may be "constructed" from several cells of the scheelite structure $CaWO_4$. For both Patterson projections, if the irregular maxima are excluded, all the remaining ones can be explained (identified—

···as vectors between specific atoms), starting from the scheelite structure.

It is not difficult to establish also the relationship between the cells of the derivative structure and the "parent" scheelite structure. In Fig. 2 this is shown graphically. The basic feature of derivative structures according to Buerger (2) is present, which requires that in the new cell one of the edges be tripled. Next, the minimal cell is singled out with an area 3 times greater than that of the original scheelite square.

The relations (covariant) between the parameters of the two cells are

$$a_{\mathrm{M}} = a_{\mathrm{sh}} + a'_{\mathrm{sh}},$$
$$b_{\mathrm{M}} = c_{\mathrm{sh}},$$
$$c_{\mathrm{M}} = -a_{\mathrm{sh}} + 2a'_{\mathrm{sh}}.$$

In the scheelite cell complicated in this way—tripled—there are 12 formula units of $CaWO_4$, i.e., 12 Ca cations per 12 WO_4 orthotetrahedra, whereas in the now primitive Bi molybdate cell of the same dimensions, with 12 MoO_4 groups, there are only 8 Bi atoms. Thus there can be no complete analogy between the two structures, but it is quite probable that Bi molybdate repeats the scheelite structure with omissions (vacancies) of some cation positions, in the same way as the structure of Ga_2S_3 repeats the ZnS structure with omission of one third of the cation positions. In the gallium compound the trivalence of Ga undoubtedly plays the decisive role; in the bismuth compound, perhaps, a certain tendency of Bi toward metallicity plays a role, allowing it at the initial stage to use all vacancies and subsequently to release them in the order of self-purification (autolysis).

Fig. 3. $Bi_2[MoO_4]_3$. **Distribution of the principal peaks in the projection of the electron density** $\rho(yz)$

Fig. 3. $Bi_2[MoO_4]_3$. Distribution of the principal peaks in the projection of the electron density $\rho(yz)$

Figure 2: Fig. 3. $Bi_2[MoO_4]_3$. Distribution of the principal peaks in the projection of the electron density $\rho(yz)$

Analogous vacancies have already been observed in the structure of $Eu_2(WO_4)_3$, the determination of which has been completed ⁽³⁾, with specific division of the 12 vacancies in the scheelite structure into 8 occupied and 4 empty ones. However, in europium tungstate (and, apparently, in analogous tungstates of other rare-earth elements) the Fedorov symmetry group is higher: $C_{2h}^6 = C\,2/c$, i.e., base-centered. Both this group and the one we establish for $Bi_2[MoO_4]_3$ are subgroups of the tetragonal scheelite group $C_{4h}^6 = I\,4_1/a$ that characterizes scheelite.

The first syntheses of the electron density confirmed the correctness of the basic proposition concerning the repetition in $Bi_2[MoO_4]_3$ of the scheelite motif (Fig. 3 with a squared cell). All attempts to distribute the Bi atoms over the Ca positions in scheelite in an ordered manner were unsuccessful, and a satisfactory discrepancy factor $R = 25\%$ is obtained only with statistical occupation of all cation positions in the structural motif of $CaWO_4$.

Work on refining the coordinates is continuing. It should be noted that an analogous Bi–Mo phase appears in ⁽⁴⁾, and the cell parameters given there are close (within the accuracy of the measurements) to ours.

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