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Scheelite Bismuth Molybdate?

In a recent paper by Kumar and Ruckenstein (*1*) (hereafter, K&R) on thin films in the bismuth molybdate system, the existence of a new scheelite phase was reported. However, I conclude that this scheelite was not a bismuth molybdate but was actually a phase in the $Na_{0.5-3x}Bi_{0.5+x}MoO_4$ system which resulted from reaction with the NaCl substrate.

The general formula for oxides with the scheelite structure is AMO_4. The only established large deviations from this ideal stoichiometry are of the type $A_{1-x}MO_4$, and such phases are of interest for their catalytic properties (*2–6*). The only phase in the bismuth molybdate system which is known to be structurally related to scheelite is $Bi_2(MoO_4)_3$. This is an $A_{1-x}MO_4$ phase with x equal to $\frac{1}{3}$, and the A cation vacancies are ordered. As recognized by K&R, this is not the scheelite phase they obtained in thin films. Neither did they obtain $BiMoO_4$. Although $AMo^{5+}O_4$ scheelites are known (*7*), the cell dimensions of $a = 5.26$ Å and $c = 11.52$ Å given by K&R are much too small for hypothetical $BiMoO_4$.

The scheelite cell dimensions given by K&R are in fact those observed in the $Na_{0.5-3x}Bi_{0.5+x}MoO_4$ system (*3*). The obvious source of Na would be from the NaCl substrate used by K&R. The reaction between bismuth molybdate and rock salt may have occurred when these intimately contacted phases were heated in air. I find that NaCl readily reacts with $Bi_2Mo_2O_9$ in the temperature range 250 to 500°C used by K&R. A major product of this reaction is a $Na_{0.5-3x}Bi_{0.5+x}MoO_4$ scheelite.

There is little reason to suppose that the electron diffraction experiments described by K&R will provide information about surface structure which differs from bulk structure. Certainly, the scheelite structure observed by K&R is not the result of the thin film nature of their sample but is rather due to gross contamination by sodium.

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