Ternary Molybdenum Sulfides of the Heavy Alkali Metals

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Z. Naturforsch. 35b, 929–930 (1980); received April, 1980

Ternary Molybdenum Sulfides, Molybdenum Disulfide

Two series of ternary molybdenum sulfides, A\textsubscript{2}Mo\textsubscript{4}S\textsubscript{6} (A = K, Rb, Cs) and A\textsubscript{2}Mo\textsubscript{15}S\textsubscript{20} (A = K, Rb), were prepared by reduction of molybdenum disulfide with alkali metals in alkali halide melts at 1100–1300 K. All compounds are hexagonal and show electronic conductivity; structural characteristics suggest isolated [Mo\textsubscript{5}S\textsubscript{2}]\textsuperscript{2-} chains as lattice elements for A\textsubscript{2}Mo\textsubscript{4}S\textsubscript{6}.

Ternary molybdenum sulfides A\textsubscript{2}Mo\textsubscript{4}S\textsubscript{6} with the oxidation state of molybdenum < +6 are of actual interest with respect to their structural features and their unusual physical properties [1–3]. Whereas compounds with transition and post transition elements have been studied rather thoroughly, the information on ternary molybdenum sulfides with strongly electropositive elements is much less satisfactory. Metastable alkali phases A\textsubscript{2}Mo\textsubscript{4}S\textsubscript{6} with layered structures [2, 4, 5] and A\textsubscript{2}Mo\textsubscript{4}S\textsubscript{8} with framework structure [6] can be obtained at ~300 K via chemical or electrochemical intercalation. Compounds prepared at high temperatures have been described by several authors [7–9]; their detailed structures are, however, unknown so far. We report here on the formation and characterization of two new series of ternary molybdenum chalcogenides which were obtained from alkali halide melts.

The reduction of Mo\textsubscript{4}S\textsubscript{6} with the corresponding alkali metal in molybdenum autoclaves at 1100 to 1300 K under argon atmosphere in KCl, RbCl and CsCl melts results in the formation of whisker-like grey needles with metallic appearance up to 5 mm in length. They are stable towards air and H\textsubscript{2}O and were isolated from the salt matrix by washing with water; the analytical composition corresponds to Mo\textsubscript{5}S\textsubscript{2} per unit cell. The rubidium phase was brittle grey needles with hexagonal cross section and metallic lustre. The stoichiometry of the potassium compound (electron microprobe data using K\textsubscript{2}Pd\textsubscript{3} as reference sample) was found to correspond to K\textsubscript{5}Mo\textsubscript{15}S\textsubscript{20}. X-ray powder diagrams can be indexed hexagonally; lattice parameters are given in Table I. The density observed for K\textsubscript{5}Mo\textsubscript{15}S\textsubscript{20} is equivalent to \( \rho = 3.89 \text{ g/cm}^3 \); the calculated value amounts to \( \rho = 4.11 \text{ g/cm}^3 \) with \( Z = 5 \), i.e. a stoichiometry of K\textsubscript{5}Mo\textsubscript{15}S\textsubscript{20} per unit cell. The rubidium phase was found to be isomorphous with the potassium compound (Table I). Although symmetry and lattice

Table I. Hexagonal lattice parameters of alkali molybdenum sulfides A\textsubscript{2}Mo\textsubscript{4}S\textsubscript{6} and A\textsubscript{2}Mo\textsubscript{15}S\textsubscript{20}.

<table>
<thead>
<tr>
<th>Ternary phase</th>
<th>( a ) [pm]</th>
<th>( c ) [pm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>K\textsubscript{2}Mo\textsubscript{4}S\textsubscript{6}</td>
<td>873.8</td>
<td>441.3</td>
</tr>
<tr>
<td>Rb\textsubscript{2}Mo\textsubscript{4}S\textsubscript{6}</td>
<td>895.9</td>
<td>441.2</td>
</tr>
<tr>
<td>Cs\textsubscript{2}Mo\textsubscript{4}S\textsubscript{6}</td>
<td>928.8</td>
<td>441.0</td>
</tr>
<tr>
<td>K\textsubscript{5}Mo\textsubscript{15}S\textsubscript{20}</td>
<td>922.7</td>
<td>1181.0</td>
</tr>
<tr>
<td>Rb\textsubscript{5}Mo\textsubscript{15}S\textsubscript{20}</td>
<td>923.6</td>
<td>1174.1</td>
</tr>
</tbody>
</table>

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0340–5087/80/0700–0929/$ 01.00/0

From Fig. 1 it can be seen that the \( a \) axis varies linearly with the cation diameter, while the \( c \) axis remains almost constant. This fact along with the observation of strongly anisometric crystal morphology, high elasticity and perfect cleavage of the crystals parallel to the hexagonal \( c \) axis suggests a structure consisting of isolated rigid (Mo\textsubscript{5}S\textsubscript{2})\textsuperscript{2-} one-dimensional matrix units held together by the alkali cations. All single crystals investigated so far exhibited specific structure defects, however, and a complete structure determination will have to wait for crystals of better quality by improved growth techniques. Preliminary studies on the physical properties of these phase indicate a rather high electronic conductivity which is likely to be due to metal-metal bonding.

Extended reaction times at 1300 K led to the formation of additional molybdenum rich phases in KCl and RbCl melts which crystallize as compact brittle grey needles with hexagonal cross section and metallic lustre. The stoichiometry of the potassium compound (electron microprobe data using K\textsubscript{2}Pd\textsubscript{3} as reference sample) was found to correspond to K\textsubscript{5}Mo\textsubscript{15}S\textsubscript{20}. X-ray powder diagrams can be indexed hexagonally; lattice parameters are given in Table I. The density observed for K\textsubscript{5}Mo\textsubscript{15}S\textsubscript{20} is equivalent to \( \rho = 3.89 \text{ g/cm}^3 \); the calculated value amounts to \( \rho = 4.11 \text{ g/cm}^3 \) with \( Z = 5 \), i.e. a stoichiometry of K\textsubscript{5}Mo\textsubscript{15}S\textsubscript{20} per unit cell. The rubidium phase was found to be isomorphous with the potassium compound (Table I). Although symmetry and lattice
parameters suggest a structural similarity to the well-known ternary molybdenum sulfides \( T_x\text{Mo}_S_2 \) [1], intensity values and systematic extinctions do not agree with this assumption. It is more likely that these sulfides are structurally related to \( \text{In}_3\text{Mo}_i_{5}\text{Se} \) which shows both \( \text{Mo}_6\text{Seg} \) and \( \text{Mo}_6\text{Sen} \) building blocks [10]. The minor quality of single crystals isolated so far prevented a complete X-ray structure analysis.

With decreasing reaction temperature the appearance of layered alkali molybdenum sulfides \( \text{A}_x\text{MoS}_2 \) is observed which exhibit a distorted \( \text{MoS}_2 \) sublattice with considerable stacking disorder. As described by us earlier these compounds easily undergo topotactic solvation [9]. Electron diffraction studies on hydrated samples of improved crystal quality now indicate that their symmetry is not hexagonal as reported originally but orthorhombic (Table II) with the following correlation:

\[
a_0 = 2a_1; \quad b_0 = 2a_1 \sqrt{3}; \quad c_0 = c_1.
\]

The orthorhombic distortion of the \( \text{[MoS}_2\text{]}^{2-} \) sublattice is supposedly due to the formation of metal-metal chains similar to those found for a series of related layered binary and ternary dichalcogenides [3, 11].

According to electron diffraction and X-ray powder data the hydrogen bronze \( \text{H}_0.3\text{MoS}_2 \) [9] was found to exist in two modifications: (i) orthorhombic, \( a = 647 \text{ pm}, b = 1120 \text{ pm}, c = n \cdot 599 \text{ pm} \) \( (n = 1, 2, 3) \); (ii) hexagonal, \( a = 550 \text{ pm}, c = n \cdot 599 \text{ pm} \). Both phases show considerable stacking disorder.

The authors are grateful to Dr. G. A. Wiegers, Groningen, for discussions on defect structure problems.

### Table II. Orthorhombic lattice parameters of hydrated layered alkali molybdenum sulfides \( \text{A}_x\text{(H}_2\text{O})_z\text{[MoS}_2\text{]}^{2-}. \)

<table>
<thead>
<tr>
<th>( \text{A} )</th>
<th>( a \text{ [pm]} )</th>
<th>( b \text{ [pm]} )</th>
<th>( c \text{ [pm]} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Na} )</td>
<td>655.1</td>
<td>1137.2</td>
<td>2492.9</td>
</tr>
<tr>
<td>( \text{K} )</td>
<td>648.4</td>
<td>1122.9</td>
<td>1842.3</td>
</tr>
<tr>
<td>( \text{Rb} )</td>
<td>648.7</td>
<td>1124.1</td>
<td>1875.7</td>
</tr>
<tr>
<td>( \text{Cs} )</td>
<td>649.4</td>
<td>1125.3</td>
<td>1915.3</td>
</tr>
</tbody>
</table>

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