

THE FORMATION OF SINGLE CRYSTALS OF THE SALTS OF HETEROPOLYACIDS IN THE FUSED SALT

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The Bridgman method was employed to prepare single crystals of $\text{Na}_{24}\text{As}_2\text{Mo}_{22}\text{O}_{83}$ and $\text{Na}_{24}\text{As}_2\text{W}_{22}\text{O}_{83}$, the conditions for their formation were characterized and X-ray analysis carried out.

This work is based on information on the formation of the salts of heteropolyacids of a new kind either in nitrate melt medium^{1,2} or directly from the components of the given salts^{2,3}. The heteropolyanions of these substances have the composition $[\text{X}_2\text{Z}_{22}\text{O}_{83}]^{24-}$, where $\text{X} = \text{P(V)}, \text{As(V)}, \text{V(V)}$ and $\text{Z} = \text{Mo(VI)}$ or W(VI) . So far, both salts have been prepared in the pure form for $\text{X} = \text{As}$, i.e. compounds with the empirical composition $\text{Na}_{24}\text{As}_2\text{Mo}_{22}\text{O}_{83}$ and $\text{Na}_{24}\text{As}_2\text{W}_{22}\text{O}_{83}$. These substances melt congruently at a temperature of 597°C ($\text{Z} = \text{Mo}$) and 691°C ($\text{Z} = \text{W}$). It follows from their formation mechanism and from the IR spectra that, in contrast to heteropolyanions formed in aqueous solutions⁴, their structure is based on diarsenate anions with an As—O—As bond. They can be prepared in the pure form by prolonged tempering of a mixture of the pure components, i.e. $\text{Na}_4\text{As}_2\text{O}_7 + \text{ZO}_3 + \text{Na}_2\text{ZO}_4$ weighed in the exact molar ratio 1 : 12 : 10. Tempering must be carried out at a temperature of about 10°C higher than their melting point. The molybdenum compound is formed after tempering for about 30 hours and the tungsten compound for about 50 hours for a total amount of 2 g of the mixture. The compound is then formed in the liquid state. Slow cooling (in a cooling oven) yields the polycrystalline substance, while rapid cooling (pouring into a cold platinum or quartz dish) yields a glassy substance.

This work was carried out in order to prepare the two given compounds as single crystals suitable for determining the crystal structure.

EXPERIMENTAL

The initial chemicals, i.e. $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, MoO_3 , WO_3 , $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ were of *p.a.* purity (Lachema, Brno, Czechoslovakia). They were employed to prepare $\text{Na}_4\text{As}_2\text{O}_7$, Na_2MoO_4 , and Na_2WO_4 by thermal dehydration at temperatures of 130–300°C for a period of 1–3 hours. Samples of the studied compounds, $\text{Na}_{24}\text{As}_2\text{Mo}_{22}\text{O}_{83}$ and $\text{Na}_{24}\text{As}_2\text{W}_{22}\text{O}_{83}$.

$W_{22}O_{83}$ were prepared in polycrystalline form by tempering of a mixture of the solid components³.

Attempts were made to prepare the single crystals by the Bridgman-Stockbarger method in a vertical arrangement⁵. The tubular furnace employed was 100 mm long with an opening diameter of 20 mm. The samples were placed in a cylindrical quartz crucible with a pointed bottom, suitable for crystal growth from a single nucleus. The outer diameter of the crucible was 15 mm. The crucible and sample were fitted to the end of a long screw with very fine thread. The screw was turned by a very slowly rotating motor in a fixed nut. The adjustable rotation rate permitted vertical movement of the crucible at velocities of 2 to 100 mm *per* 10 h.

The formation of single crystals was followed both by observing a fragment under a microscope and also by the X-ray method with an oscillating and rotating single crystal. The crystal X-ray patterns were recorded using a Weissenberg goniometer (Freiberger Präzisionsmechanik, G.D.R.). CuK_{α} radiation with a voltage of 35 kV and current of 24 mA was employed. The exposure time was 60 min in the oscillation method and 180 min in the crystal rotation method.

RESULTS AND DISCUSSION

Several attempts were made to prepare a single crystal of $Na_{24}As_2Mo_{22}O_{83}$ at various rates of passage of the crucible through the oven. The maximum temperature in the oven was 630°C, about one third of the way from the top. The temperature gradient in the oven and the rate of sample temperature change can be seen in Fig. 1. While a polycrystalline material was still formed at a crucible velocity of 70 mm *per* 10 h, a single crystal was formed at velocities of 50 mm *per* 10 h and slower. It can be seen from Fig. 1 that the sample remained in a zone above its melting point for about 3.4 hours at the former velocity and for about 5.2 h at the latter.

This effect of the crucible velocity on the quality of the material obtained can be explained in terms of the fact that a period of 5.2 h of sample heating above the melting point is quite sufficient for complete disappearance of crystallization nuclei

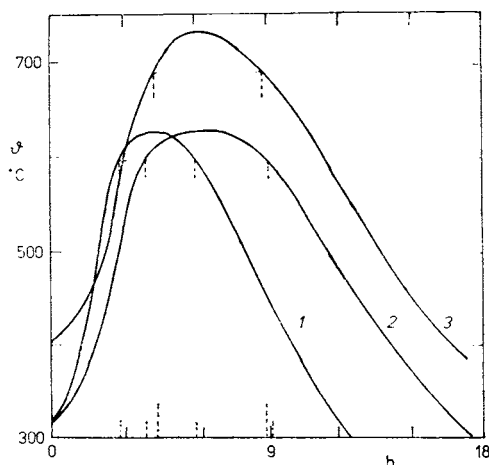


FIG. 1

The dependence of the sample temperature during passage through the oven on time.
 1 $Na_{24}As_2Mo_{22}O_{83}$, 70 mm *per* 10 h;
 2 $Na_{24}As_2Mo_{22}O_{83}$, 50 mm *per* 10 h;
 3 $Na_{24}As_2W_{22}O_{83}$, 50 mm *per* 10 h

in the liquid melt, while 3-4 h is not a sufficiently long period of time. A further factor that can limit single crystal formation is the development of parasitic crystallization nuclei on the inner wall of the crucible during fast and uneven cooling as a result of a faster velocity. The crucible walls can then have a lower temperature than the crystal/melt interface. The first factor could be distinguished from the latter by testing various sample heating and cooling rates. During slower cooling the growing single crystal can absorb the increasing supersaturation, while this is not possible at faster cooling rates and new nuclei are formed in an uncontrolled manner. These factors require further study before attempts are made to grow larger single crystals. A further factor that could lead to the formation of parasitic crystal nuclei could involve chemical interaction between the crucible and the sample of studied substance, *i.e.* the formation of different chemical compounds at some sites on the surface of the crucible wall. These chemical interactions could include exchange of arsenic atoms in the compound for silicon atoms. This reaction, is not, however, very probable, as the crucible walls were not visibly etched after crystal formation and, under these conditions, the temperature and retention time of the substance in the liquid state would have the opposite effect on the formation of single crystals to that observed. Nonetheless, X-ray studies were carried out using single crystal fragments from the inner part of the sample.

Only an experiment at the optimum velocity of the crucible determined for the molybdenum compound was carried out using the tungsten compound, $\text{Na}_{24}\text{As}_2 \cdot \text{W}_{22}\text{O}_{83}$, *i.e.* 50 mm *per* 10 h.; however, appropriately higher temperatures were employed, corresponding to the melting point of the tungsten compound. It can be seen from Fig. 1 that the sample was exposed to a temperature above its boiling point for a period of 4-6 h. This experiment was successful and a fragment was removed from the single crystal formed for X-ray study. For this purpose, the quartz crucibles were broken and quartz fragments were separated mechanically from the single crystal. The fragments of the single crystal are prismatic in shape, probably either rhombohedral or monoclinic.

X-ray patterns were also recorded for both substances by the rotating and oscillating crystal method. After suitable crystal orientation was found, layers characteristic for single crystals were recorded. For both compounds, the average identity period in the direction of the rotation axis of the crystal is 720 pm.

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