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Note

DIMORPHISM OF THE ANHYDROUS SELENITES OF ZINC, CADMIUM AND MERCURY

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The oxidation of selenides and tellurides is a subject of great interest both in connection with the oxidizing calcination of copperelectrolytic slimes in whose composition the selenides and tellurides of various metals take part, and in connection with the choice of heating conditions for the activation of semi-conducting photoresistors in which many selenides and tellurides are used. More accurate data about the composition of the solid and gaseous products formed during operation may be obtained from data in the metal–halcogen–oxygen diagrams. To draw these diagrams, however, it is necessary to know the thermal and thermodynamic properties of all possible compounds in these three-member systems.

Data concerning the selenides of Zn, Cd and Hg are scarce. The studies of Markovsky et al. [2,3] show that the anhydrous selenites of Zn, Cd and Hg can exist in the form of two allotropic modifications, i.e. α and β. In refs. 2–4, however, there are no data concerning the conditions needed to obtain, for example, the effect of the concentration of H_2SeO_3 and temperature. Data concerning the thermal and thermodynamic properties of the modifications are also scarce.

This work presents results of a study of the melting points, melting heats, temperatures and heats of polymorphic transitions, and the specific heats of these substances.

EXPERIMENTAL

Our study showed that when the oxides or hydroxides of Zn, Cd and Hg react with selenious acid at 100°C and upon continued crystallisation of the selenites by the technique described in [1], β-forms of these selenites are obtained in the concentration range 2.42–43.69 mass% of H_2SeO_3 for $ZnSeO_3$; 2.81–46.66 mass% of H_2SeO_3 for $CdSeO_3$; and 0.41–62.11 mass% of H_2SeO_3 for $HgSeO_3$. The α-modification of anhydrous $ZnSeO_3$ may be obtained by dehydration of $ZnSeO_3 \cdot H_2O$ and $ZnSeO_3 \cdot 2\ H_2O$. The α-mod-

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ification of $CdSeO_3$ is formed when $CdCO_3$ is dissolved in H_2SeO_3 at 100°C, the favourable concentration of selenious acid being from 5 to 30% in excess of the stoichiometric amount. The α-modification of $HgSeO_3$ results from the precipitation reaction between mercuric acetate or nitrate and selenious acid. Its formation is favoured by the selenite remaining in the mother solution for a longer period (up to 1 month). Our results concerning the formation of α-modifications of the anhydrous selenites of Zn, Cd and Hg are in good agreement with the literature data [2–4].

TABLE 1

Chemical analysis of the selenites of Zn, Cd and Hg

Compound	Calcd. (%)		Found (%)	
	MO	SeO_2	MO	SeO_2
α-$ZnSeO_3$	42.29	57.71	42.37, 42.28, 42.41	57.80, 57.74, 57.68
β-$ZnSeO_3$	42.29	57.71	42.19, 42.30, 42.36	57.71, 57.83, 57.63
α-$CdSeO_3$	53.64	46.36	53.57, 53.70, 53.69	46.38, 46.11, 46.35
β-$CdSeO_3$	53.64	46.36	53.83, 53.60, 53.69	46.32, 46.47, 46.36
α-$CdSeO_3$	66.12	33.88	66.00, 66.19, 66.13	33.80, 33.91, 33.87
β-$CdSeO_3$	66.12	33.88	66.06, 66.17, 66.10	33.79, 33.81, 33.90

TABLE 2

Melting point and melting heat of the anhydrous selenites of Zn, Cd and Hg (β-modification)

Compound	Present data		Literature data		Ref.
	Melting point (°C)	ΔH of melting (kcal $mole^{-1}$)	Melting point (°C)	ΔH of melting (kcal $mole^{-1}$)	
$ZnSeO_3$	640	7.46 ± 0.03	615–620	11.1 ± 1.4	2,5
$CdSeO_3$	701	6.94 ± 0.03	677 ± 10	14.1	3,6
$HgSeO_3$	466	3.54 ± 0.03	465 ± 10	4.0 ± 2.0	4,5

TABLE 3

Temperature and heat of α → β polymorphic transitions of the anhydrous selenites of Zn, Cd and Hg

Compound	Present data		Literature data		Ref.
	Temperature (°C)	ΔH (kcal $mole^{-1}$)	Temperature (°C)	ΔH (kcal $mole^{-1}$)	
$ZnSeO_3$	327	3.16 ± 0.03	290		2
$CdSeO_3$	394	1.46 ± 0.03	660	0.7 ± 0.3	6
$HgSeO_3$	376.6	0.41 ± 0.03	360 ± 10	0.6 ± 0.4	4,8

TABLE 4

Coefficients for the temperature dependence of the heat capacities of the anhydrous selenites of Zn, Cd and Hg (β-modification) in the equation $C_p = a + bT + cT^2$

Compound	Coefficients in the equation $C_p = f(T)$			Temperature range of measurement (K)
	a	b	c	
$ZnSeO_3$	-43.07	27.87×10^{-2}	-20×10^{-5}	350–500
$CdSeO_3$	21.28	1.91×10^{-2}	-1.39×10^{-5}	350–700
$HgSeO_3$	37.1	-5.36×10^{-2}	9.52×10^{-5}	420–550

The substances obtained were subjected to chemical and X-ray phase analysis. The chemical analysis for the concentration of Zn^{2+}, Cd^{2+} and Hg^{2+} was made complexometrically, the indicator being Eriochrome Black T. Analysis for the concentration of SeO_3^{2-} was made iodometrically. The results are presented in Table 1.

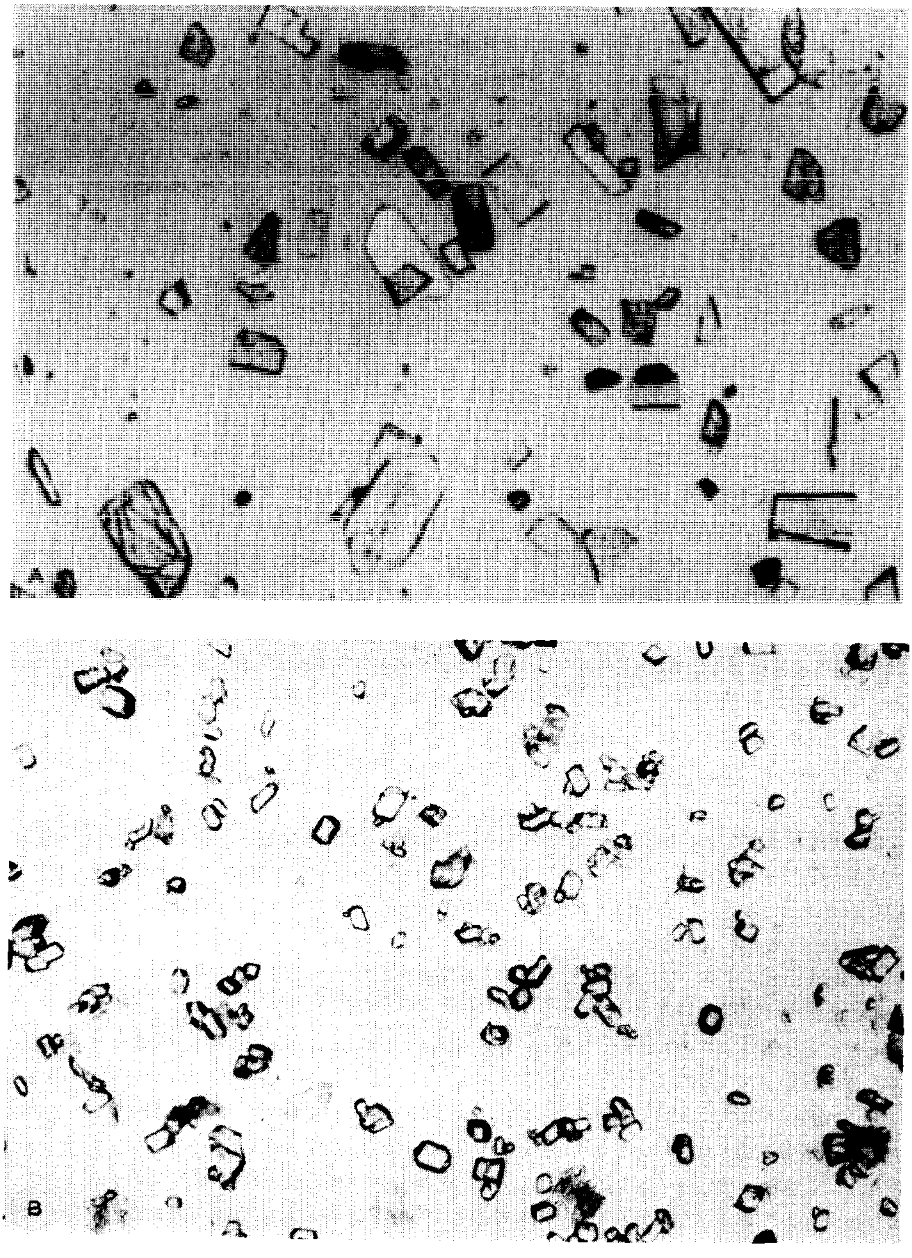
As is seen from Table 1, the composition of the compounds is identical with the theoretical composition of the corresponding selenites. X-Ray phase analysis was made using a TURM-61M apparatus with a Cu anode and K_α emission. The results obtained, when compared with the literature data, prove that the products formed are the α- and β-phases of the corresponding selenites.

Microscopy studies using a Dokuwal microscope (Karl Zeiss Jena, DDR) were also carried out. The thermal and thermodynamic properties were studied using a DSC-111 differential scanning calorimeter (Seteram, France). The samples were placed into hermetically sealed capsules which were inactive towards the products. The temperature was raised from room temperature to 820°C at a rate of 10° min^{-1}.

The anhydrous selenites of Zn, Cd and Hg are white crystalline compounds, which are slightly soluble in water and spirit. At room temperature they are quite stable and do not change in air. In moist air, however, zinc selenite adsorbs up to 4–5% of moisture which is easily removed by drying. $ZnSeO_3$, $CdSeO_3$ and $HgSeO_3$ are soluble in mineral acids, acetic acid, ammonia and in a solution of alkaline cyanide. They are less soluble in bases.

Microscopy photos (Fig. 1) indicate that the crystals of the β-modification of $ZnSeO_3$ (Fig. 1A) are rectangular plates of size 40–400 mkm; the β-$CdSeO_3$ crystals are well-shaped of size 5–25 mkm (Fig. 1B); and the β-$HgSeO_3$ crystals are polygonal and comparatively large ($>$ 100 mkm).

The polymorphic transition temperatures and the melting points were determined according to the temperatures of the corresponding DSC peaks. Our values for the melting points (Table 2) are higher than the literature



data. This is accounted for by the fact that other authors determined the melting points in open crucibles, and it is quite possible that this leads to partial dissociation of the compound, contamination of the selenites with dissociation products, and a decrease in the melting point. The melting heats presented in Table 2 have lower values than those in the literature since the latter were determined indirectly and, as was reported, they were mostly tentative.

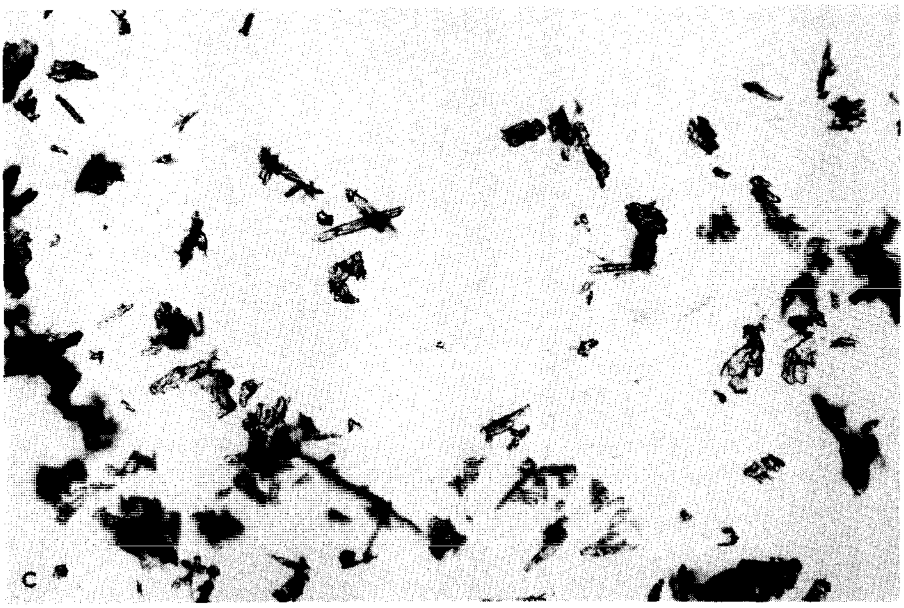


Fig. 1. Microphotographs of the anhydrous selenites of zinc, cadmium and mercury. A, β-$ZnSeO_3$ ($\times 80$); B, β-$CdSeO_3$ ($\times 210$); C, β-$HgSeO_3$ ($\times 210$).

Table 3 presents data on the temperatures and heats of polymorphic transitions in comparison with the literature data. Some of them were first determined by us. As is seen from the table, moving downwards from $ZnSeO_3$ to $HgSeO_3$, the heats of polymorphic transitions decrease.

The specific heats of the products under study were determined by the technique described in ref. 7, using a heating rate of 1° min^{-1} in the temperature range shown in Table 4. Al_2O_3 was used as the reference compound. The results obtained were worked up by the least-squares method and the coefficients were found for the equation $C_p = a + bT + cT^2$, expressing the dependence of C_p of the selenites upon temperature (Table 4).

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