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Abstract

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ON GERMANIUM ARSENATE

Arsenic-acid compounds of germanium have not been described in the literature. Meanwhile, the close similarity of H_3PO_4 and H_3AsO_4 and of many of their derivatives makes it possible to assume the existence of a germanium arsenate analogous to the described phosphate $\text{Ge}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (^{1,2}).

Saturation of a solution of H_3AsO_4 with germanium dioxide did not lead to the formation of a metastable solution, as occurred in the interaction of GeO_2 and H_3PO_4 . As a result of two weeks' stirring of a mixture of GeO_2 and H_3AsO_4 (4 mol/kg), a paste-like mass was formed. In the liquid phase, separated by suction on a porous filter No. 4, no germanium was found. Analysis of the solid phase, thoroughly washed with alcohol and ether and dried at 70° , established the following composition (in %): Ge 18.4; As 39.5; H_2O 9.5. For $\text{GeO}_2 \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ the calculated values are (in %): Ge 19.0; As 39.4; H_2O 9.7. Germanium was determined by the tannin method, arsenic iodometrically. The water content was determined directly from the loss in weight upon heating to 600° . As can be seen, the compound obtained has a composition analogous to that of the germanium phosphate separated from a metastable solution of GeO_2 in H_3PO_4 .

(Figure: Fig. 1. Thermogram of $\text{GeO}_2 \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$)

Fig. 1. Thermogram of $\text{GeO}_2 \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$

$\text{GeO}_2 \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ is a finely crystalline powder, readily decomposed by water. Its thermogram is shown in Fig. 1. A series of successive endoeffects at 168° , 224° , and 275° corresponds to the removal of the first molecule of water; the crystalline structure changes hardly at all. At a temperature of 450° the remaining water is split off and the compound $\text{GeO}_2 \cdot \text{As}_2\text{O}_5$ is formed, which we designate as $\text{GeAs}_2\text{O}_7\text{-}\alpha$.

The exothermic effect at 700° , as established by X-ray diffraction, is a consequence of a change in the crystalline structure. The compound formed at 700° , which we designate as $\text{GeAs}_2\text{O}_7\text{-}\beta$, is characterized by lower symmetry than $\text{GeAs}_2\text{O}_7\text{-}\alpha$. Thermal decomposition of germanium pyroarsenate begins immediately after the exoeffect.

The endothermic effects at 835° and 925° are associated with the intense evolution of As_2O_5 and melting of the products formed. The composition of the product

formed at 925° corresponds to the formula $4\text{GeO}_2 \cdot \text{As}_2\text{O}_5$. Complete splitting off of As_2O_5 occurs after prolonged heating at $\sim 1000^\circ$. Analysis showed that the final product of heating is GeO_2 .

Figure 2 gives the schemes of the X-ray diffraction patterns of $\text{GeO}_2 \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, $\text{GeAs}_2\text{O}_7\text{-}\alpha$, and $\text{GeAs}_2\text{O}_7\text{-}\beta$. The values of the interplanar spacings d , the intensities I , and $\sin^2\theta$ are given in Table 1. The X-ray diffraction patterns were obtained with $\text{CuK}\alpha$ radiation in a camera 57.3 mm in diameter. The line intensities were estimated visually according to a nine-point system. Comparison of the X-ray diffraction pattern of $\text{Ge}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{GeP}_2\text{O}_7\text{-}\alpha$ with the X-ray diffraction patterns of $\text{GeO}_2 \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ and $\text{GeAs}_2\text{O}_7\text{-}\alpha$ indicates their similarity (there is no isomorphism), which is possibly connected with the isostructural nature of the compounds being compared. Mixing

lines toward smaller angles θ (and, consequently, the increase in lattice periods), observed in the X-ray patterns of arsenic-acid compounds, is due to the increase in the radius of AsO_4^{3-} as compared with the radius of PO_4^{3-} .

In Fig. 3A the IR absorption spectrum of $\text{GeO}_2 \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ is shown (wave numbers of the maxima and inflections: 740, 780, 800, 815, 850, 890, 900, 935, 1260, 1635 cm^{-1}). The absorption band at 1635 cm^{-1} belongs to deformation vibrations of water. In the spectrum of the compound of composition $\text{GeO}_2 \cdot \text{As}_2\text{O}_5 \cdot \text{H}_2\text{O}$, obtained by heating to 250° , this absorption band is absent. Thus,

Fig. 2. Schemes of X-ray diffraction patterns of $\text{GeO}_2 \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ (1), $\text{GeAs}_2\text{O}_7\text{-}\alpha$ (2), $\text{GeAs}_2\text{O}_7\text{-}\beta$ (3)

one of the two water molecules in $\text{GeO}_2 \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ is chemically bound and, evidently, enters into the composition of the compound in the form of two HAsO_4^{2-} ions.

The character of the IR spectrum of $\text{GeO}_2 \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ does not contradict the statement made, since it is known from the literature ⁽³⁾ that in the spectra of acid arsenates, alongside the most intense band at 920–800 cm^{-1} , weaker bands are present to the left and to the right of it. On the basis

Table 1

$\text{GeAs}_2\text{O}_7\text{-}\alpha$						
$\text{GeO}_2 \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$						
I	$\sin^2 \theta, \text{\AA}$	I	$\sin^2 \theta, \text{\AA}$	I	$\sin^2 \theta, \text{\AA}$	I
8	0.00978104	0.334.3326	0.01741806	0.017418 4	0.173.85 1	0.430.17
3	0.03242804	0.361.2829	0.0373.9764	0.0146.45 4	0.182.80 1	0.434.16
4	0.036110481	0.377.2565	0.0331.2253	0.023.17 2	0.189.77 1	0.465.13
8	0.0493.4804	0.392.2314	0.0503.4334	0.032.28 3	0.201.72 1	0.481.11
1	0.0593.1632	0.399.2205	0.072.8799	0.038.94 3	0.212.67 2	0.505.08
5	0.083.6685	0.442.1598	0.097.4751	0.039.84 3	0.228.61 3	0.530.06
9	0.092.4932	0.475.1185	0.112.3135	0.043.54 1	0.234.59 1	0.540.05

GeAs ₂ O ₇ - GeO ₂ · As ₂ O ₅ · 2H ₂ O									
1	0.102.4222	0.497.0944	0.132.0987	0.043.46 4	0.242.56 2	0.576.02			
3	0.102.3611	0.531.0591	0.166.8904	0.063.15 4	0.248.55 1	0.591.003			
2	0.112.2373	0.539.0502	0.209.6885	0.062.98 3	0.259.52 2	0.607.990			
3	0.132.1071	0.599.9955	0.233.5964	0.072.83 3	0.272.48 2	0.630.966			
5	0.142.0182	0.626.9753	0.269.4855	0.082.64 1	0.283.45 1	0.659.950			
4	0.162.9123	0.638.9657	0.292.4266	0.092.55 5	0.291.43 1	0.694.926			
3	0.181.8124	0.687.9304	0.307.3916	0.092.48 2	0.299.44 2	0.721.909			
4	0.201.7232	0.694.9265	0.389.2346	0.102.34 2	0.309.39 1	0.750.891			
1	0.211.6773	0.758.8854	0.429.1763	0.112.27 1	0.317.37 1	0.859.832			
2	0.231.6071	0.795.864		1 0.122.16 3	0.341.32 1	0.883.821			
6	0.244.5611	0.837.843		4 0.112.23 4	0.352.30 1	0.935.796			
3	0.261.5101	0.848.837		4 0.142.05 2	0.379.25				
3	0.278.4634	0.885.819		3 0.151.99 3	0.392.23				
7	0.291.4273	0.921.803		1 0.161.93 3	0.407.21				
5	0.301.4063	0.935.797		3 0.168.88 1	0.417.19				

From the foregoing, the compound $\text{GeO}_2 \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ should be regarded as $\text{Ge}(\text{HAsO}_4)_2 \cdot \text{H}_2\text{O}$. It was established by X-ray diffraction that removal of the water molecule leads only to a slight distortion of the crystal lattice, which makes it possible to assume the presence in the structure of the compound of channels or voids occupied by water.

(Figure: Fig. 3. IR spectra of $\text{GeO}_2 \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ (A) and $\alpha\text{-GeAs}_2\text{O}_7$ (B))

Fig. 3. IR spectra of $\text{GeO}_2 \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ (A) and $\text{GeAs}_2\text{O}_7\text{-}\alpha$ (B)

Figure 3B gives the IR spectrum of $\text{GeAs}_2\text{O}_7\text{-}\alpha$, obtained by dehydration of $\text{Ge}(\text{HAsO}_4)_2$ at 500° . (Wave numbers of the maxima: 853, 910, and 1010 cm^{-1} .)

The IR spectra of $\text{Ge}(\text{HPO}_4)_2\text{H}_2\text{O}$ (?) and $\text{Ge}(\text{HAsO}_4)_2 \cdot \text{H}_2\text{O}$ are very similar in form, which, together with the similarity of the X-ray diffraction patterns of the indicated compounds, attests to the identity of their structures.

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