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STUDY OF THE GERMANIUM–SULFUR SYSTEM

Germanium sulfides GeS and GeS_2 were first obtained preparatively by Winkler ([1]). Germanium monosulfide crystallizes in a rhombic lattice, which is a distorted sodium chloride structure, and has identity periods: $a = 4.29$ Å; $b = 3.64$ Å; $c = 10.42$ Å ([2], [3]) (space group D_{2h}^{16}—$Pcmn$). Germanium disulfide also crystallizes in the rhombic system with parameters: $a = 11.66 \pm 0.05$ Å; $b = 22.34 \pm 0.10$ Å; $c = 6.86 \pm 0.03$ Å (space group $Fdd2$) ([4]). The melting point of germanium monosulfide is 625° ([1], [5]), that of germanium disulfide 825° ([6]). Both germanium monosulfide and disulfide possess semiconductor properties ([7], [8]). Despite the fact that germanium sulfides have been studied rather well, the literature contains no data on the germanium—sulfur phase diagram. We have studied the germanium—sulfur system by methods of thermal and X-ray phase analysis.

For preparing alloys, single-crystal germanium with a specific resistance of approximately 1 ohm · cm and sulfur of 99.997% purity were used. We obtained germanium monosulfide by direct fusion of germanium and sulfur at 1000° in an evacuated quartz ampoule. During synthesis of GeS_2 from the components, the ampoules ruptured; therefore, to obtain germanium disulfide we fused germanium monosulfide and sulfur, taken in stoichiometric amounts, at 1000°. In order for the reaction to proceed to completion, vibrational mixing was employed ([9]).

For preparing alloys containing 3–48 at.% sulfur, a mixture of Ge and GeS was used; for alloys containing 55–70 at.% sulfur, a mixture of GeS and GeS_2; and for 70–95 at.% sulfur, a mixture of GeS_2 and sulfur. Fusion of the indicated substances, taken in calculated amounts, was carried out in sealed quartz ampoules for thermal analysis with frequent mixing. Alloys containing 3–48 at.% sulfur were heated to 950° and held at this temperature for 3 hours, which was sufficient for homogenization of alloys of such composition. This series of alloys was then annealed at 500–550° for 60 hours. Alloys containing 50–70 at.% sulfur were heated to 850°, held for 3 hours at this temperature, and then annealed

Fig. 1. Ge—S system. *I*—melt, *II*—melt$_1$ + melt$_2$, *III*—melt + Ge, *IV*—melt + βGeS, *V*—Ge + βGeS, *VI*—Ge + αGeS, *VII*—GeS + melt, *VIII*—melt + GeS$_2$, *IX*—βGeS + GeS$_2$, *X*—αGeS + GeS$_2$, *XI*—GeS$_2$ + melt, *XII*—GeS$_2$ + S

Figure 1: Fig. 1. Ge—S system. *I*—melt, *II*—melt$_1$ + melt$_2$, *III*—melt + Ge, *IV*—melt + βGeS, *V*—Ge + βGeS, *VI*—Ge + αGeS, *VII*—GeS + melt, *VIII*—melt + GeS$_2$, *IX*—βGeS + GeS$_2$, *X*—αGeS + GeS$_2$, *XI*—GeS$_2$ + melt, *XII*—GeS$_2$ + S

for 100 hours at 500-550°.

When the sulfur content exceeded 70 at.%, equilibrium in the system was established very slowly. We used the following regime for homogenization and annealing of alloys in this region of the system. Ampoules with alloys of the indicated composition were heated to 850-900° and held at this temperature for 2-3 hours until complete homogenization. The alloy was then slowly cooled over 9-10 hours to room temperature. Microscopic examination of the alloys obtained in this way showed that they consisted of crystalline and glassy phases uniformly mixed with one another. The alloys with 75, 80, 83, 90, and 95 at.% sulfur obtained by the described method were annealed for 200 hours at 250° and then annealed at 100-110° for 100 hours. Annealing at 100° was undertaken for the purpose of better crystallization of sulfur.

Differential thermal analysis was carried out on an N. S. Kurnakov PK-52 pyrometer with platinum-platinum-rhodium thermocouples. Tem-

temperature was determined with an accuracy of ±5°. Aluminum oxide was used as the reference substance; the usual sample weight was 2-2.5 g. The average heating rate was 7-9 deg/min, and the average cooling rate was 5-6 deg/min. X-ray diffraction patterns were obtained by the powder method using Fe—K radiation in RKD cameras 57.3 mm in diameter. The intensity of the lines in the diffraction patterns was estimated visually on a five-point scale.

The phase diagram of the germanium—sulfur system, obtained on the basis of thermal and X-ray phase analysis data, is shown in Fig. 1. The melting temperatures of the components germanium and sulfur determined by us were, respectively, 956° and 120°. In the system on the germanium side there is a wide region of liquid immiscibility (3-45 at.% sulfur) in the liquid state into a phase rich in germanium and a phase close in composition to germanium sulfide GeS; the monotectic horizontal lies at 920 ± 5°. We quenched an alloy containing 30 at.% sulfur, heated to 1000°. We were able to observe visually two layers—a dark one at the edges of the specimen and a lighter one in the center of the specimen.

Fig. 1. Ge—S system. *I*—melt, *II*—melt$_1$ + melt$_2$, *III*—melt + Ge, *IV*—melt + βGeS, *V*—Ge + βGeS, *VI*—Ge + αGeS, *VII*—GeS + melt, *VIII*—melt + GeS$_2$, *IX*—βGeS + GeS$_2$, *X*—αGeS + GeS$_2$, *XI*—GeS$_2$ + melt, *XII*—GeS$_2$ + S

Two compounds were found in the system—monosulfide GeS and germanium disulfide GeS_2. The compound Ge_2S_3, the preparation of which was reported in ([10]), was not found by us. In work ([11]) it was also reported that the compound Ge_2S_3 is not formed. Germanium monosulfide melts congruently at 665° and forms a eutectic with germanium at 650° and 48 at.% sulfur. At 590° germanium monosulfide undergoes a polymorphic transformation. The effect corresponding to the polymorphic transformation of germanium monosulfide is clearly manifested on the heating curves after annealing for 60 h at 500-550°. On the cooling curves this effect is less noticeable and is clearly manifested only near the GeS composition. In the composition range GeS—GeS_2, the polymorphic transformation is recorded only on cooling curves for compositions near GeS (55 at.% sulfur). By analogy with tin sulfide and selenide ([12,13]), we believe that the 590° effect corresponds to a second-order transformation.

Germanium disulfide melts congruently at 840°, which is in good agreement with the data ([6]). Owing to stable glass formation, the two-phase region GeS_2—S is the most difficult part of the system to study. This part of the diagram was constructed only from heating curves. The effects corresponding to the solidus line appeared on the heating curves only for compositions with 80-95 at.% sulfur. Because of glass formation, the effects are not manifested on the cooling curves. We believe that this part of the system has a pronounced eutectic, practically indistinguishable in composition and temperature from the melting point of pure sulfur.

The specific electrical conductivity of germanium disulfide was measured; at room temperature it is of the order of 10^{-15} $\Omega^{-1} \cdot \mathrm{cm}^{-1}$. The temperature dependence of the conductivity has a semiconductor character.

It was also shown that germanium monosulfide crystallizes in a rhombic cell with identity periods: $a = 4.29 \pm 0.02$ kX; $b =$

$= 3.64 \pm 0.01$ kX; $c = 10.42 \pm 0.01$ kX, which is in good agreement with the literature data ([3]).

We carried out a more detailed X-ray study of germanium disulfide. In addition to the usual X-ray phase study, in the course of investigating the system we obtained an X-ray pattern of germanium disulfide with a Guinier-type camera. The results of indexing the X-ray pattern are given in Table 1.

Table 1

Indexing of the X-ray pattern of germanium disulfide

I	d_{exp}, kX	$1/d^2_{\mathrm{exp}}$	$1/d^2_{\mathrm{calc}}$	hkl	I	d_{exp}, kX	$1/d^2_{\mathrm{exp}}$	$1/d^2_{\mathrm{calc}}$	hkl
2	8.055	0.0154	0.0154	012*	2	3.4344	0.0848	0.0850	020
2	7.363	0.0185	0.0180	003	4	3.3374	0.0898	0.0896	131
3	6.597	0.0230	0.0233	101*	2	3.1520	0.1007	0.1008	116
2	6.241	0.0257	0.0254	013*	2	3.0809	0.1053	0.1056	133

I	d_{exp}, kX	$1/d^2_{\text{exp}}$	$1/d^2_{\text{calc}}$	hkl
5	5.719	0.0306	0.0307	111
3	5.553	0.0324	0.0321	004
2	5.157	0.0376	0.0375	022
3	5.021	0.0397	0.0393	103*
2	4.647	0.0463	0.0467	113
3	4.1905	0.0570	0.0575	015*
1	4.0276	0.0616	0.0616	024
2	3.8331	0.0681	0.0683	031*
2	3.7325	0.0718	0.0721	006
2	3.5560	0.0791	0.0788	115
3	2.9545	0.1145	0.1145	220
3	2.9105	0.1180	0.1179	040
2	2.8620	0.1221	0.1225	222
2	2.8162	0.1261	0.1259	042
3	2.7956	0.1280	0.1283	008
3	2.7477	0.1324	0.1325	223
4	2.6966	0.1375	0.1377	135
2	2.5785	0.1504	0.1501	044
2	2.5173	0.1579	0.1577	028
3	2.4256	0.1699	0.1697	019*

The following values of the lattice periods were obtained: $a = 6.86 \pm 0.01$ kX; $b = 11.65 \pm 0.01$ kX; $c = 22.34 \pm 0.04$ kX; $z = 24$; $d_{\text{X-ray}} = 3.05$ g/cm^3; $d_{\text{exp}} = 3.01$ g/cm^3.

The structure of germanium disulfide is analogous to the structure of germanium diselenide (^{14}) and, apparently, is a strongly deformed structure of the eight-layer cadmium iodide type. This assumption is supported by the fact that all strong lines and lines of medium intensity obey the extinction rules for a body-centered cell.

The deformation of the germanium disulfide structure leads to a certain deviation from the body-centered cell; the lines marked with an asterisk (see Table 1) are forbidden in the body-centered cell. The parameters of germanium disulfide are related to the parameters of the ideal structure of the CdJ_2 type as follows: $a = a_{\text{id}}\sqrt{3}$; $b = 3a_{\text{id}}$; $c = 4c_{\text{id}}$.

In accordance with the extinction rules, we assume that germanium disulfide belongs to the Fedorov group *Pmtn* or *Pmn*.

We obtained single crystals of germanium disulfide by interaction in the gas phase between germanium monosulfide and hydrogen sulfide. A rotation X-ray pattern (RKU-86 camera) along the a axis of a GeS_2 single crystal confirmed our results obtained from powder photographs. It should also be noted that Debyegrams of germanium disulfide obtained by synthesis in the gas phase and by fusion are identical to one another.

The data we obtained on the structure of germanium disulfide differ from those available in work (^{4}) in the type of Bravais lattice and the space group. The germanium disulfide single crystal used for the study in work (^{4}) was obtained by distilling disulfide from a germanium concentrate containing large amounts of arsenic trisulfide and sulfur (^{15}). Therefore, we believe that the GeS_2 single crystal studied in (^{4}) contained a small amount of some impurity (possibly As_2S_3), which led to a change in its crystal structure.

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