# LIU TSYUN-HUA, A. S. PASHINKIN,

Corresponding Member of the Academy of Sciences of the USSR A. V. NOVOSELOVA

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## Abstract

## Full Text

## Chemistry

**LIU TSYUN-HUA, A. S. PASHINKIN,**
**Corresponding Member of the Academy of Sciences of the USSR A. V. NOVOSELOVA**

# INVESTIGATION OF THE GERMANIUM–SELENIUM SYSTEM

The germanium–selenium system has not been studied. Germanium monoselenide and diselenide have been obtained by preparative methods ([1]). Germanium monoselenide is isostructural with germanium sulfide ([2,3]) (Fedorov group $Pcmn$) and has identity periods $a = 4.38$; $b = 3.82$; $c = 10.79$ kX ([2]). This compound possesses semiconducting properties ([4]). Germanium diselenide also crystallizes in the rhombic system ([1]) and, in contrast to germanium disulfide, has a layered structure; the identity periods of germanium diselenide are $a = 6.939 \pm 0.001$; $b = 12.196 \pm 0.005$; $c = 22.99 \pm 0.03$ kX ([5]). In its electrical properties germanium diselenide is close to insulators ([5]). In the germanium–selenium system an extensive glass-formation region has been found ([6,7]), investigated within the range 75–96 at. % selenium ([7]). We have investigated the germanium–selenium system by methods of thermal and X-ray phase analysis.

To prepare the alloys, selenium of the grade "selenium for rectifiers" and germanium with a specific resistance of approximately 1 $\Omega^{-1} \cdot \text{cm}^{-1}$ were used. Fusion of the components, taken in calculated amounts, was carried out in sealed ampoules with frequent stirring. Alloys containing 5–35 at. % selenium were heated to 850–950°, while those containing more than 35 at. % selenium were heated to 750°. The alloys were held at these temperatures for 20 h. The presence of an equilibrium state was checked radiographically. To achieve equilibrium in the system in the range 0–50 at. % selenium, no additional annealing was required. Equilibrium in the concentration range 50–70 at. % selenium was established after 40–50-hour annealing at 500–550°. At selenium contents of more than 70 at. %, in agreement with the literature data ([7]), we found a stable glass-formation region in the system. Differential thermal analysis was carried out on an N. S. Kurnakov PK-52 pyrometer with platinum–platinum-rhodium thermocouples. The 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 6–8 deg/min, and the average cooling rate 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 intensities of the lines in the X-ray diffraction patterns were estimated visually on a five-point scale.

Fig. 1. Ge–Se system.

Figure 1: Fig. 1. Ge–Se system.

The phase diagram of the germanium–selenium system, obtained on the basis of data from thermal and X-ray phase analysis, is shown in Fig. 1. The melting temperatures of the components germanium and selenium determined by us proved to be, respectively, 956 and 218°. In the system two compounds were found–monoselenide GeSe and germanium diselenide $GeSe_2$. Monoselenide GeSe decomposes at 670° by the peritectic reaction

$$GeSe \rightleftarrows \text{melt} + GeSe_2$$

and forms with germanium a eutectic at 650° and 40 at. % Se. Evidently, the difficulty of synthesizing GeSe by fusion of the components ([8]) is associated with retardation–

with the occurrence of the indicated peritectic reaction on cooling. At 620° germanium monoselenide undergoes a polymorphic transformation. The effect corresponding to the polymorphic transformation of germanium monoselenide is clearly manifested on the cooling curves of alloys of composition Ge–GeSe. On the heating curves this effect is resolved much less well. In the composition range GeSe–$GeSe_2$ the polymorphic transformation of the monoselenide is recorded only on the cooling curves for compositions near GeSe, since equilibrium in this composition range is established much more with difficulty because of the tendency of germanium diselenide to glass formation ([6], [7]). It is interesting to note that a polymorphic transformation was observed for tin sulfide and selenide ([9], [10]), which are isostructural with germanium selenide.

**Fig. 1.** Ge–Se system. *I* –melt; *II* –melt + Ge; *III* –melt + GeSe; *IV* –Ge + GeSe ($\beta$); *V* –Ge + GeSe ($\alpha$); *VI* –melt + $GeSe_2$; *VII* –GeSe ($\chi$) + $GeSe_2$; *VIII* –melt + $GeSe_2$; *IX* –$GeSe_2$ + Se; *X* –GeSe ($\beta$) + $GeSe_2$

Germanium diselenide melts congruently at 740°. The two-phase region $GeSe_2$ –Se remained the least studied. In this part of the system the glassy state is stable. Only after a 250-hour annealing at 180–190° (below the possible solidus line) were we able to obtain, on the heating curves, effects corresponding to the liquidus points of the corresponding compositions. Effects corresponding to the solidus line were not manifested on the heating 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 selenium, as has been noted for most binary systems containing selenium ([11]). On the X-ray diffraction patterns of alloys containing more than 70 at. % selenium, only a few diffraction lines corresponding to germanium diselenide were recorded, which also indicates that a considerable fraction of the substance of the alloys of this part of the system is in the glassy state. A satisfactory X-ray diffraction pattern

of selenium was obtained after 150–200 hours of annealing at 170°. It was found that germanium monoselenide crystallizes in a rhombic cell with identity periods $a = 4.375 \pm 0.005$, $b = 3.825 \pm 0.005$; $c = 10.80 \pm 0.02$ kX, which agrees well with the literature data ([2], [3]). Debyegrams of germanium diselenide had sharp lines only near the 1st zero. Indexing of these X-ray diffraction patterns with the periods indicated above gave quite satisfactory results.

Moscow State University
named after M. V. Lomonosov

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*Note: Figure translations are in progress. See original paper for figures.*