

The germanium-selenium phase diagram¹

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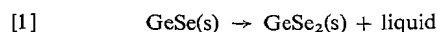
The Ge-Se phase diagram was determined in the composition range 0–66.67 at. % Se by the method of differential thermal analysis. The diagram differs totally from the one reported by Liu *et al.* (1) but is in good agreement with the diagram recently reported by Karbanov *et al.* (13). In its broad features the Ge-Se phase diagram is quite similar to the diagrams of the Ge-S, Sn-S, and Sn-Se systems.

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Introduction

Liu *et al.* (1) investigated the germanium-selenium system over the whole composition range. The main features of the reported phase diagram are

(a) The existence of two selenides of germanium, GeSe and GeSe₂; the diselenide melts congruently at 740 °C while the monoselenide melts incongruently at 670 °C according to the reaction



(b) The existence of a Ge-GeSe eutectic at 650 °C (40 at. % Se).

(c) The existence of a polymorphic transformation at 620 °C in GeSe. The thermal arrest corresponding to this transition was detectable readily on the cooling curves of the GeSe-Ge alloys. Resolution of this effect was considerably worse on the heating curves. In the GeSe-GeSe₂ region, the transformation of the monoselenide was recorded only on cooling curves, for compositions close to GeSe.

The three IV-VI compounds GeS, SnS, and SnSe are isostructural with GeSe (black-phosphorus-type structure) (2). Furthermore, the Ge-S (3, 4), Sn-S (5), and Sn-Se (6) phase diagrams show strong similarities; they are characterized by the presence of a monotectic reaction on the metal-rich side, by the presence of a eutectic in the MX-MX₂ region (X = chalcogen), and a degenerate eutectic in the MX₂-X region.

The Ge-Se phase diagram, as reported by the above investigators, is quite different from the phase diagrams of the Ge-S, Sn-S, and Sn-Se systems. Because of this discrepancy and because

of the fact, also, that results obtained during the course of electrical conductivity measurements on liquid GeSe could not be reconciled entirely with the reported Ge-Se diagram, the latter was re-examined to the composition of GeSe₂ (66.67 at. % Se); the method of differential thermal analysis (d.t.a.) was used in the study of this diagram.

Experimental

Preparation of the Ge-Se Alloys

Alloys corresponding to the different compositions were prepared in 2 g quantities by fusing together weighed amounts of the elements in evacuated and sealed quartz vials. The germanium used (Sylvania Corporation) was of electronic grade with a minimum resistivity, at 27 °C, of 40 Ω cm. High purity selenium shot containing at least 99.99% selenium was obtained from Canadian Copper Refiners. To prevent the loss of selenium during sealing of the vials and to ensure a minimum vapor space, the following procedure was used.

Quartz tubes (12 cm long, 0.5 cm internal diameter) were constricted at two different levels. Germanium and selenium, ground to pass a 10 mesh sieve, were weighed directly in the tubes; the rough grinding prevented sticking of germanium or selenium powder to the tubes during weighing. The tubes were then evacuated (10⁻³ mm Hg) and sealed at the upper constriction. The samples were contracted to a point below the lower constriction by heating just above the melting point of selenium (220 °C); during this operation, a small quantity of selenium sublimed to the top of the tube. The sublimed selenium was returned below the constriction by placing the upper part of the tube in a small furnace heated at approximately 700 °C while the lower part of the tube was surrounded by a water-cooled brass block. After all the selenium had returned to the bottom of the tube, the latter was sealed at the lower constriction. It is believed that the percentage compositions were known to better than 0.03%. Each vial was then enclosed in a second quartz tube also sealed under vacuum; this last precaution was taken to avoid oxidation of the samples in case of inner vial breakage during cooling.

The germanium-rich samples (Ge > 50 at. %) were homogenized in the liquid state at a temperature of 960 °C i.e. just above the melting point of germanium; the selenium-rich samples were homogenized in the

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liquid state at a temperature of 850 °C for a period of 1 h. All samples were baked at 765 °C for 2 days and at 690 °C for 5 h; they were then annealed at 650 °C for 17 h, at 600 °C for 8 h, and at 550 °C for 24 h, in a controlled furnace with a 13 cm constant temperature zone. Since preliminary work had indicated the possible existence of a monotectic reaction on the germanium-rich side, all samples containing between 2–50 at. % Se were mixed thoroughly, by rocking the furnace vigorously during the entire period that they were in the liquid state; this precaution was taken in order to prevent separation of two liquid phases which would increase the necessary equilibration time at the lower temperatures. After annealing, all the samples were cooled to room temperature, in the furnace, at the rate of approximately 10 °C/min. The samples were then ground to a fine powder as a preparation for d.t.a.

Some samples corresponding to the overall compositions GeSe and GeSe₂ were prepared as described above. The selenides were also obtained by subliming stoichiometric alloys; the GeSe was sublimed at 425 °C under vacuum while the GeSe₂ was sublimed at 550 °C under an atmospheric pressure of helium. Germanium diselenide disproportionates to some extent during sublimation. This is evidenced by the presence of three rather sharply defined sections in the sublimate which correspond to Se, GeSe, and GeSe₂. The monoselenide has a bright metallic appearance while the diselenide is orange-yellow.

Differential Thermal Analysis

The d.t.a. instrument and the technique used for preparing the samples have been described in a previous publication (4). All the thermograms were obtained from undiluted samples (2–3 mg), sealed in quartz under vacuum, at a heating rate of 4–5 °C/min and at a cooling rate of 4–6 °C/min. Platinel thermocouples were used. The calibration curves of the thermocouples provided by the manufacturer of the d.t.a. instrument were used as such. It is believed that the temperatures reported are precise to ± 2 °C. The temperatures given are those of the maximum of the peaks since they proved to be the most reproducible. An empty quartz capsule was used as reference material. The measured melting points of pure germanium and pure selenium were 950 and 220 °C, respectively.

X-Ray Diagrams

The X-ray diagrams were taken with a Philips instrument (Cu K α radiation, Ni filter) using a Guinier camera; exposure time varied between 4–14 h depending on the particular information required. Diffractograms also were obtained by means of a Norelco diffractometer.

Results

The germanium-selenium phase diagram as determined in this investigation is shown in Fig. 1. The diagram was traced from the data obtained during heating cycles; small Ge-Se samples are subject to severe supercooling and for this reason, not much information on equilibrium freezing temperatures can be obtained from

cooling curves. The points obtained during cooling are shown on the diagram. All transformations observed during heating cycles were endothermic, and during cooling cycles all were exothermic. It should perhaps be emphasized that the pressure over the samples was not 1 atm but rather the equilibrium vapor pressure at a particular temperature-composition.

The Ge-GeSe Region

The addition of selenium depresses the melting point of germanium to a minimum of 900 °C, the temperature of the monotectic reaction; the thermal effect corresponding to this reaction was large and easily detectable during both heating and cooling cycles. Further evidence for this monotectic reaction was obtained by visual examination of samples held vertically in the furnace, at 960 °C, for a period of 2 h and quenched to room temperature. Two layers could be distinguished: one layer was hard and had the physical aspect of germanium; the d.t.a. trace of this layer showed two small peaks at 660 and 666 °C and a rather large one at 900 °C. The other layer was flakier and resembled GeSe; the thermogram showed two large peaks at 660 and 666 °C and a small one at 900 °C. The approximate compositions of the two liquid phases in equilibrium at the monotectic temperature are respectively 11–12 at. % Se on the germanium-rich side and 40–42 at. % Se on the selenium-rich side.

The temperature limits of immiscibility in the two-liquid region could not be determined by d.t.a. because of small heat effects. Between 900 and 666 °C the liquidus is quite steep. By successive heating and cooling of samples, approximate points on the liquidus curve could be obtained for some compositions. The point at 710 °C which corresponds to the GeSe composition was obtained during the course of electrical conductivity measurements on liquid GeSe (7); this point was obtained under equilibrium conditions and can be regarded with some degree of confidence.

The two thermal effects at 661 and 666 °C were detectable easily on heating curves of all samples of composition between 2–50 at. % Se; these arrests were also very sharp on cooling curves but they occurred at lower temperatures. No evidence was found that would indicate the existence of a Ge-GeSe eutectic.

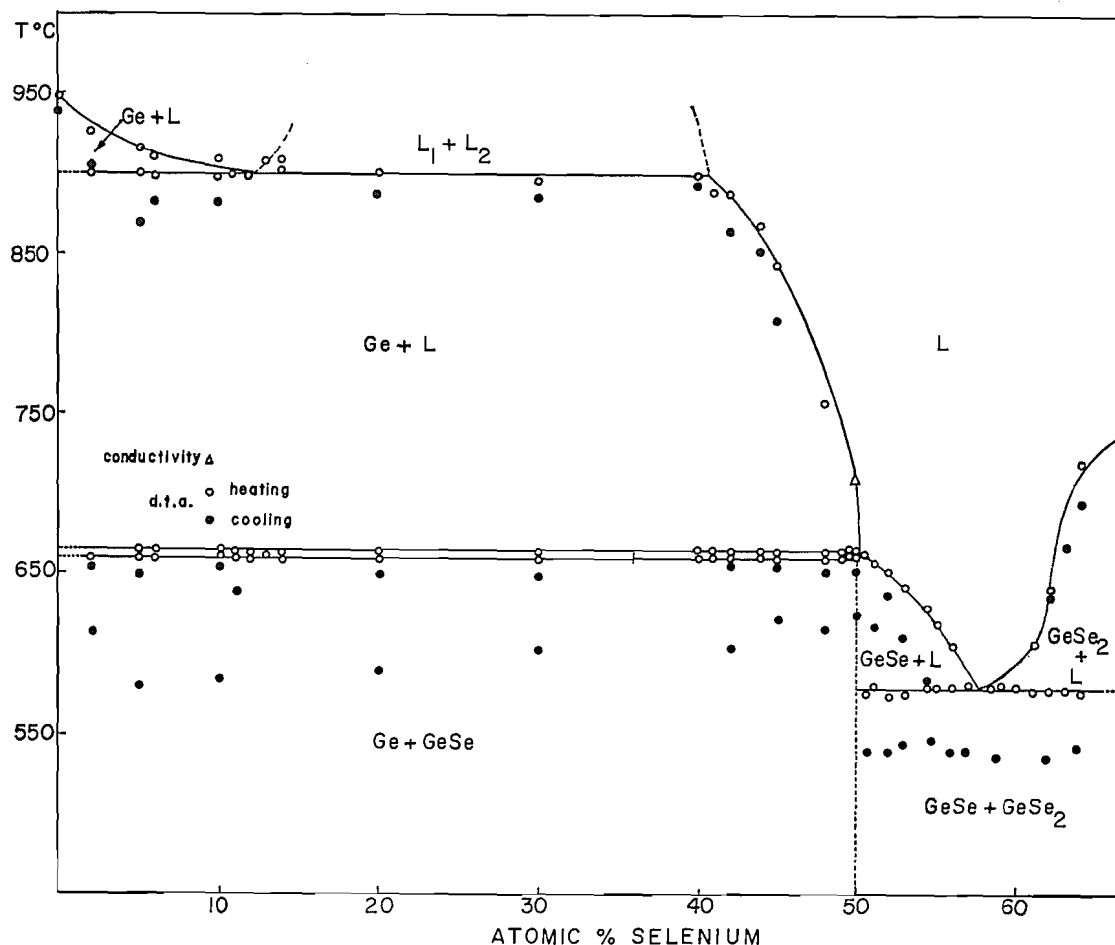


FIG. 1. The germanium-selenium phase diagram.

The Compounds GeSe_2 and GeSe

Congruent melting of GeSe_2 at 740°C is confirmed in the present investigation; the same melting point was obtained from annealed samples prepared by weighing and from sublimed samples. X-Ray diagrams were obtained from sublimed GeSe_2 samples; the calculated spacings of the lattice planes were identical with those reported by Pashinkin *et al.* (8). According to these investigators, the structure of germanium diselenide is apparently a highly deformed version of an eight-layered cadmium iodide type.

All GeSe samples, sublimed or annealed and quenched, gave identical X-ray diagrams. The diagrams of the quenched samples showed a regular increase in the unit cell parameters as a function of temperature of annealing due, pre-

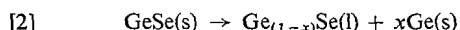
sumably, to dilation of the lattice or to the changing stoichiometry of GeSe on heating. The symmetry of the lattice and the parameters of the unit cell were determined from the X-ray diagrams of samples annealed at 350°C and quenched; all the lines could be accounted for on the basis of a unit cell of orthorhombic symmetry, space group $Pcmm$, of parameters: $a = 4.38 \text{ \AA}$, $b = 3.83 \text{ \AA}$, $c = 10.78 \text{ \AA}$. These results are in substantial agreement with those of the literature (2, 9, 10).

The peak at 661°C which appears on the thermograms of all samples on the germanium-rich side of the diagram is due presumably to a solid-state transition which occurs in GeSe ; this transition could not be detected on the selenium-rich side of the diagram. The importance of the

peak is more indicative of a first-order transition. Transformations of the second order are known to exist in the compounds SnS (11) and SnSe (12) which are isostructural with GeSe: in both these cases, however, the thermal effects are very small and barely detectable on a d.t.a. trace. Attempts were made to fix the high temperature crystalline form of GeSe by quenching; this proved to be impossible.

No extensive study of the homogeneity region of GeSe was made; preliminary results seem to indicate, however, that this region is very narrow.

All the evidence accumulated during the course of this investigation leads to the conclusion that germanium monoselenide melts incongruently because of the peritectic disproportionation



where the phase $\text{Ge}_{(1-x)}\text{Se}$ can be considered as a solution of GeSe_2 in GeSe. Germanium lines could not be detected on the X-ray diagrams of GeSe samples annealed at 690 °C and quenched; this is an indication that the peritectic point lies quite close to the composition GeSe.

The GeSe-GeSe₂ Region

The GeSe-GeSe₂ region of the phase diagram is of the simple eutectic type; the eutectic has the composition 57-58 at. % Se and melts at 578 °C. The thermal effect corresponding to melting of the eutectic was detectable readily at all compositions between GeSe and GeSe₂. The liquidus temperatures were determined without difficulty at compositions lying to the left of the eutectic point; the phase reactions which correspond to crossing of the liquidus at compositions to the right of the eutectic point were, however, very sluggish and the temperatures were determined with more difficulty. It should be mentioned that samples prepared by different methods gave essentially the same results. Some alloys were prepared as described above, others were prepared by weighing the necessary quantities of sublimed GeSe and GeSe₂ with or without annealing.

X-Ray diffractograms obtained from samples in the selenium-rich region consistently showed the presence of both the GeSe₂ and the GeSe peaks; the GeSe₂ peaks were more intense to the right of the eutectic point while the GeSe peaks were more intense to the left of the eutectic point.

Discussion

The phase diagram as determined in this work is quite different from the one obtained by Liu *et al.* (1). These investigators did not detect the monotectic reaction on the germanium-rich side of the diagram. Furthermore, the thermal arrests which they observed on the thermograms of germanium-rich samples occurred at lower temperatures than the ones that were observed in this work; a possible explanation is that they determined these points from cooling curves. Their results on the selenium-rich side of the diagram are in direct contradiction with our results; no explanation for this discrepancy can be suggested; no single piece of evidence was found that would agree with reaction [1].

The very recent work of Karbanov *et al.* (13) on the Ge-Se phase diagram is in close agreement with the present work although the two diagrams differ in some details. Their diagram was plotted from d.t.a. data, using 2 g samples. The liquidus line was plotted from heating data (3 °C/min) and only the region between the GeSe-GeSe₂ eutectic and GeSe₂ was plotted from cooling data (3 °C/min). Karbanov *et al.* made the following observations.

(a) The melting points of Ge and Se were found to be 941 and 218 °C respectively. GeSe melts incongruently at 675 °C according to reaction [2]; the peritectic point was found to lie at 50.5 at. % Se. GeSe₂ melts congruently at 740 °C.

(b) A region of immiscibility was found to exist in the liquid at 17-40 at. % Se; the monotectic reaction occurs at 905 °C.

(c) Heating and cooling curves indicated an endothermic effect, corresponding to a polymorphic transformation of GeSe, at 664 °C. Effects, related to changes in the crystal structure of GeSe, were observed on cooling curves at 645 °C, in the region of 20-50 at. % Se. (In the present work, the transition was observed at 661 °C on heating curves only. The first arrest, on cooling curves, occurred in the vicinity of 650 °C while a second arrest was observed at temperatures between 580 and 620 °C, depending on composition.)

(d) In the GeSe-GeSe₂ region, the GeSe transformation was detected on heating and cooling curves at 579 °C while a eutectic, of composition 56.5 at. % Se, was found to melt at 587 °C. (In the present work, one peak only was

found on heating curves at 578 °C; during cooling this peak occurred in the vicinity of 540–550 °C and it was observed that this temperature decreased if the rate of cooling was increased.)

The Ge–Se phase diagram as determined in this work and in the work of Karbanov *et al.* is more consistent with the phase diagrams of the Ge–S (3, 4) and the Ge–Te (14) systems. Regular trends can be observed in these diagrams.

(a) The width of the two-liquid region decreases on going from the Ge–S system to the Ge–Te system; in fact, this two-liquid region has disappeared in the Ge–Te system; this is consistent with the increasing metallic character of the melt on going from the Ge–S to the Ge–Te system.

(b) The melting point of the dichalcogenide decreases from GeS₂ to GeSe₂ and in the Ge–Te system the ditelluride does not exist.

(c) A solid-state transition exists in GeTe at 430 °C; at this temperature the rhombohedral structure changes to the NaCl structure. As discussed above, a solid-state transition seems to exist in the Ge–Se system, but at a higher temperature. There is no evidence for the existence of a polymorphic transformation in GeS (4).

(d) The peritectic point approaches the composition 50 at. % chalcogen on going from GeS to GeTe; in fact, it is not definitely known whether melting of GeTe is congruent or incongruent. Also, the melting point of the monochalcogenide increases on passing from GeS to GeTe.

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