

PHASE DIAGRAM OF THE TERNARY SYSTEM Ge—Te—Se

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ABSTRACT

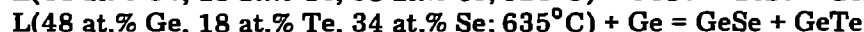
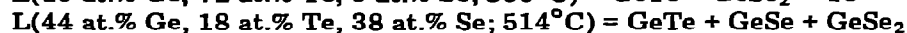
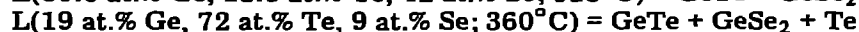
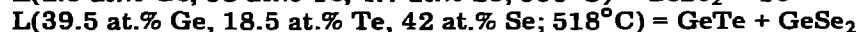
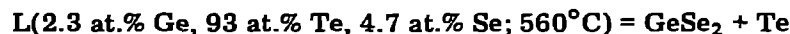
The ternary system Ge—Te—Se was investigated by differential thermal analysis, thermogravimetry, X-ray diffraction and scanning electron microscopy. The quasi-binary systems, various isoplethal sections and the liquidus surface of the system were constructed. The liquid—liquid miscibility gaps have been obtained.

The principal results are summarized as follows.

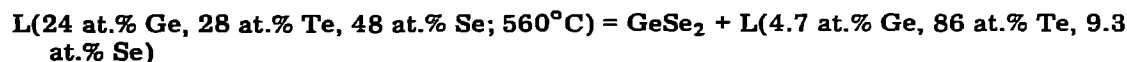
(1) No ternary compound appears in the system.

(2) The GeSe₂—Te and GeTe—GeSe₂ junctions form true quasi-binary systems.

(3) The reactions at the main invariant points are



(4) Three liquid—liquid miscibility gaps exist: the first is situated entirely in the ternary system giving the monotectic reaction



in the GeSe₂—Te quasi-binary system. The other liquid—liquid miscibility gaps are based on those occurring in the GeSe₂—Ge system.

INTRODUCTION

Chalcogenide alloy glasses have been studied for a long time as materials with particularly interesting properties. Knowledge of the equilibrium phase diagram is very instructive for the understanding of the role of chemical bonding and of the kinetics of glass formation from the metastable liquid phase in rapid-quenching techniques.

The study of the equilibrium ternary phase diagram in the Ge—Te—Se system is part of a survey of glass formation in chalcogenide alloy systems [1], the study of the glass-forming ability being the subject of a later paper [2].

Phase diagrams of the binary systems have been studied by several authors. The Ge—Te system contains one compound, GeTe, and two eutectics containing 49.85 and 85 at.% Te, respectively [3–5]. The Ge—Se system has two compounds, GeSe₂, which melts congruently, and GeSe with incongruent melting. There are two liquid immiscibility regions around GeSe and several invariant transformations [6,7]. The Te—Se system is very simple and shows complete miscibility in liquid and solid phases [8].

EXPERIMENTAL

The experimental details on sample preparation are given in ref. 9. Simultaneous differential thermal analysis (DTA) and thermogravimetry (TG) were performed at a heating rate of 5°C min⁻¹, using an STA 429 Netzsch thermal analyzer, on ~200 mg powdered and annealed samples kept in a dynamic argon atmosphere. The samples were referenced against carborundum. The temperature scale and instrument sensibility were calibrated by running heating-rate curves of known quantities of ICTA-recommended materials [10]. DTA results on liquid—liquid immiscibility were complemented by quenching experiments followed by scanning electron microscopic investigations. X-Ray diffraction studies were carried out using the CuK α radiation in a Guinier—de Wolff camera.

RESULTS

The sub-solidus regions of the system are shown in Fig. 1. The two compounds GeTe and GeSe₂ divide the ternary system into three parts, the ternary systems GeSe₂—Te—Se, GeTe—GeSe₂—Te and Ge—GeTe—GeSe₂.

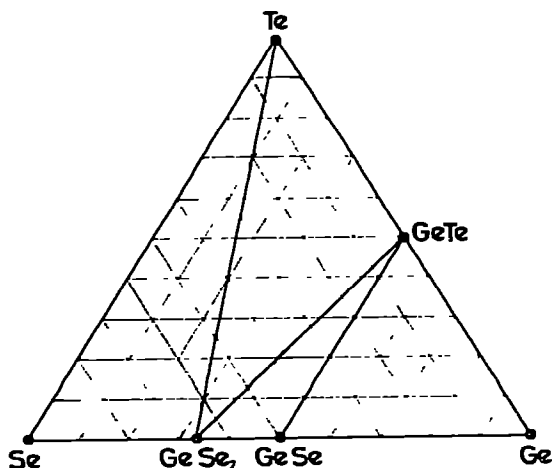


Fig. 1. Subsolidus regions of the Ge—Te—Se system.

Quasi-binary systems and isoplethal sections

GeSe₂—Te system

The phase diagram, derived from DTA and microstructure studies, is shown in Fig. 2 [9]. There is a liquid—liquid immiscibility region which extends from 28 ± 1 to 86 ± 1 at.% Te, and gives the monotectic reaction



The invariant line between GeSe₂ and Te at $440 \pm 3^\circ \text{C}$ corresponds to the eutectic e₁ at 93 ± 1 at.% Te. Study of some samples near the eutectic located on one side or the other of the line showed that the eutectic is a saddle point and, as both GeSe₂ and Te melt congruently, we conclude that this line corresponds to a quasi-binary section of the ternary Ge—Te—Se system.

GeTe—GeSe₂ system

There is no ternary compound in this system. The phase diagram, estab-

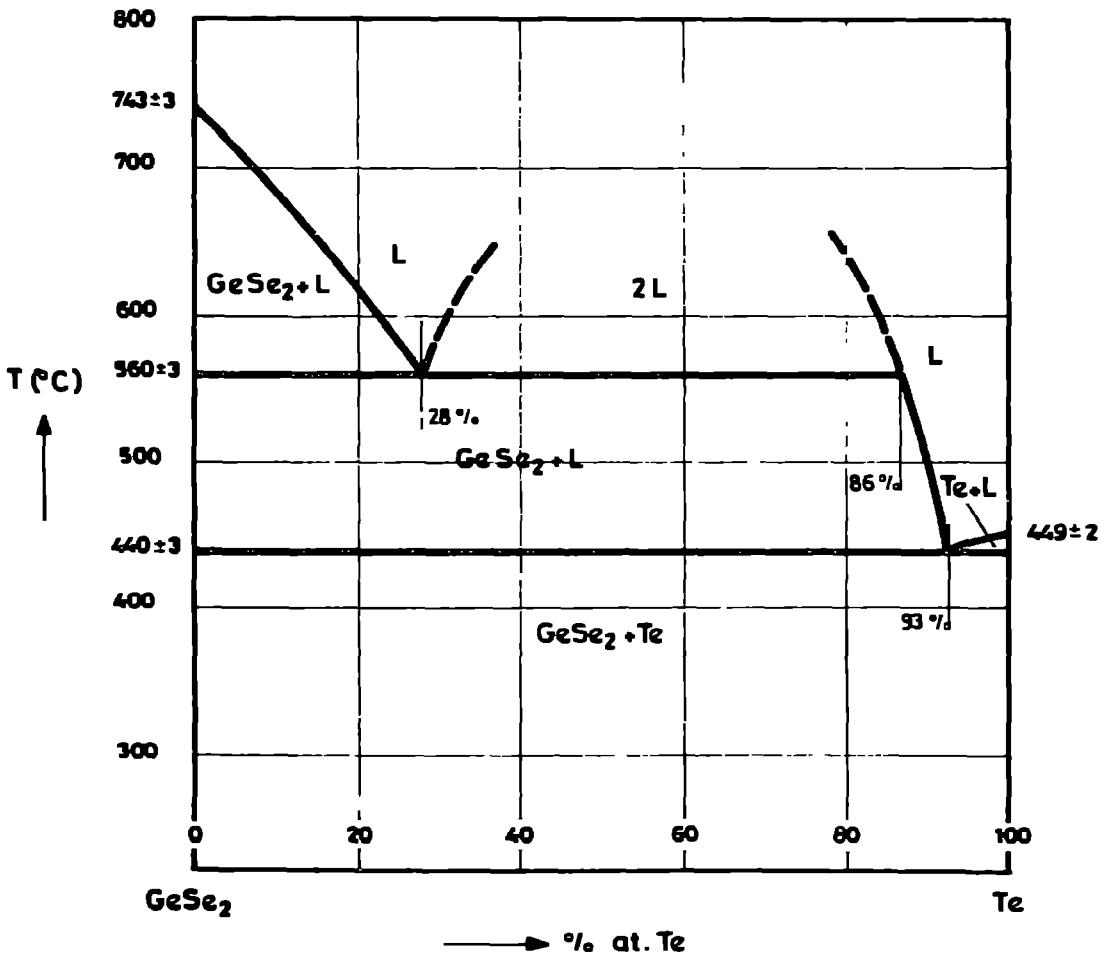


Fig. 2. Phase diagram of the GeSe₂—Te system.

lished by thermal analysis, is shown in Fig. 3 and is of the eutectic type with mutual solubility in the liquid state. The eutectic e_2 occurs at 18.5 ± 1 at.% Te and $518 \pm 4^\circ\text{C}$. For the same reasons as those given for the $\text{GeSe}_2\text{—Te}$ line, this invariant line is also a quasi-binary system. We have not studied solid solubility systematically but it seems to be a small solubility of GeTe in GeSe_2 .

GeTe—GeSe isopleth

Polymorphic phase transformations occur in both GeSe and GeTe compounds near 620 and 370°C , respectively. The low temperature form of GeSe has an orthorhombic lattice whilst the high temperature form is hexagonal [11]. At low temperature, GeTe crystallizes in a rhombohedral lattice, which represents a slight distortion of the corresponding high temperature cubic NaCl-type structure [3–5]. The various studies undertaken on this line present several discrepancies [11–13]. It cannot be a quasi-binary system because GeSe is formed by a peritectic reaction, but forms an invariant line. The low stability of the alloys, detected by TG, hindered the DTA study of this line. However, taking into account the Ge—

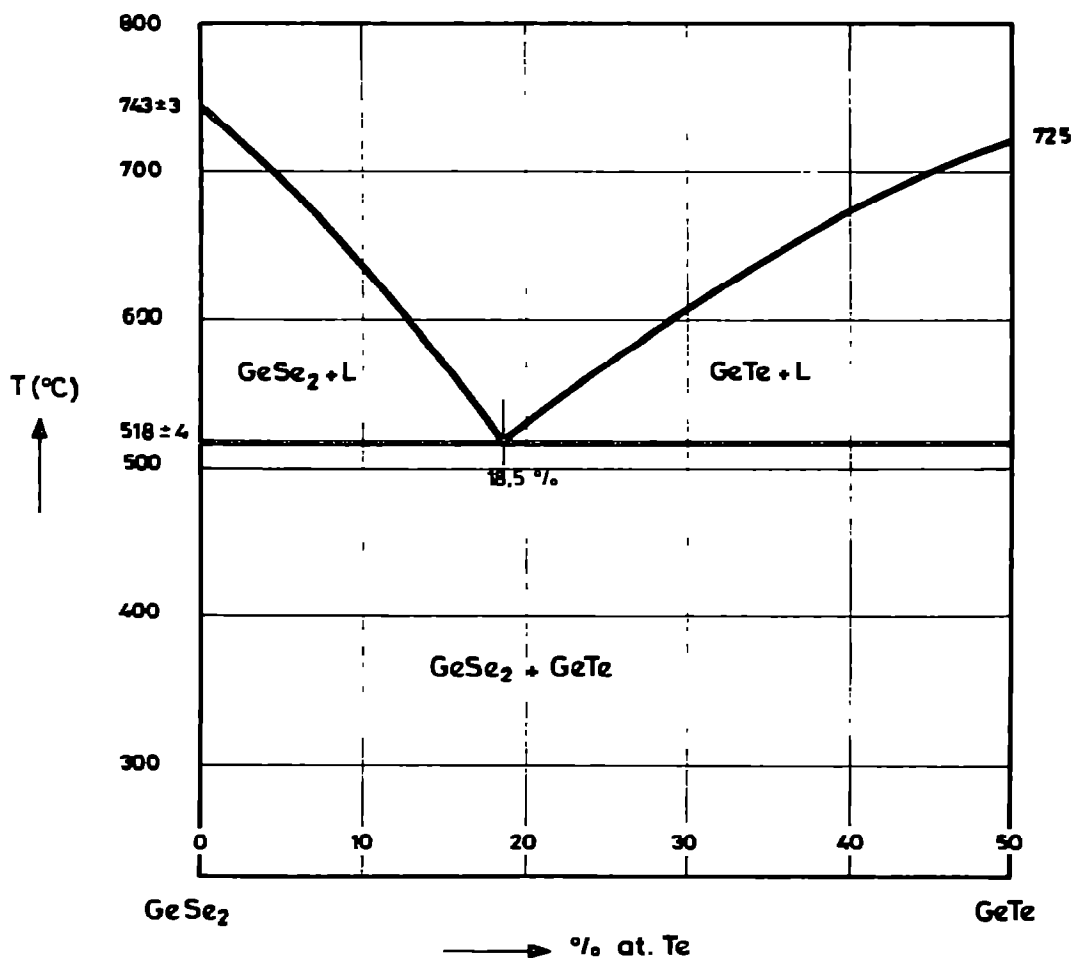


Fig. 3. Phase diagram of the GeTe—GeSe₂ system.

Se phase diagram, our results are not consistent with those published [13]. We obtained a minimum in the liquidus temperature at 38 ± 2 mole% GeTe and $635 \pm 4^\circ\text{C}$. We assume in the following that this line resembles the GeTe—GeS line [14] because of the similarity between GeS and GeSe.

Isoplethal section at 50 at.% Te

This section presented in Fig. 4 reveals the existence of a liquid immiscibility gap situated entirely in the ternary system that leans on that existing in the GeSe_2 —Te system. The liquidus and solidus profiles show the separation in two regions caused by the GeSe_2 —Te quasi-binary system. In the region defined by large selenium content, the liquidus and solidus curves decrease monotonically with increasing selenium content. The continuous depression of the solid transformations indicates that there is some kind of solid solution. X-Ray diffraction showed that it is to be attributed to the Te—Se solid solution, α .

In the Ge-rich region, an invariant reaction at $360 \pm 3^\circ\text{C}$ was obtained which corresponds to the existence of a ternary eutectic ξ_1 (Fig. 7) and excludes solid solubility in this region. The minimum in the liquidus curve

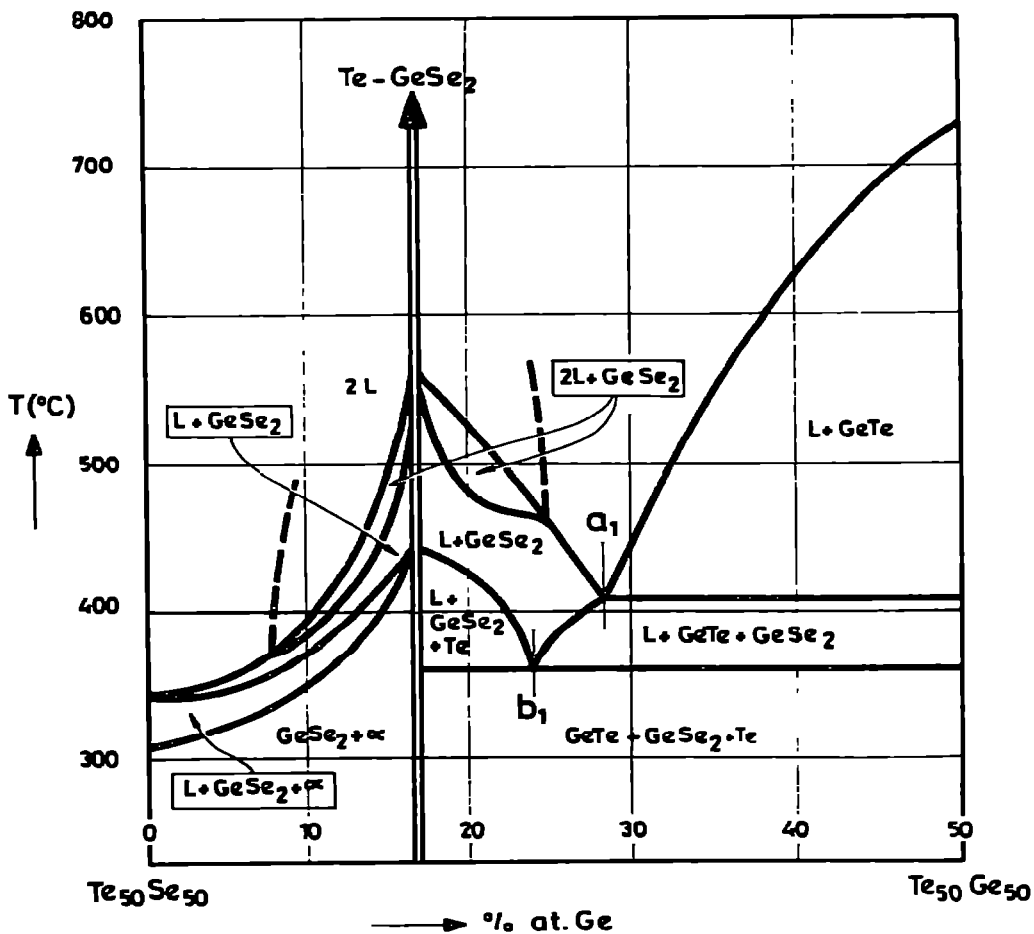


Fig. 4. Isoplethal section at 50 at.% Te.

at about 28 at.% Ge (point a_1) corresponds to the intersection of the vertical section with the binary eutectic line going down from the GeSe_2 — GeTe binary eutectic e_2 towards the GeTe — GeSe_2 — Te ternary eutectic ξ_1 . Point b_1 corresponds to the intersection with the minimal conodal line going from GeSe_2 to the ternary eutectic ξ_1 .

Isoplethal section at 60 at.% Te

Figure 5 shows the phase transformations observed in this section. Phase boundaries are similar to those encountered in the former vertical section. There appear again the invariant reaction at 360°C as also the liquid immiscibility gap. Points a_2 and b_2 have the same meaning as points a_1 and b_1 . Point b_3 corresponds to the intersection of this section with the minimal conodal line going from GeTe to the ternary eutectic ξ_1 .

GeSe—Te isopleth

The GeTe — GeSe_2 quasi-binary system divides this line into two parts (Fig. 6), one rich in GeSe_2 and the other rich in Te , that show the respective solidus invariants at 514 ± 4 and $360 \pm 3^\circ\text{C}$. In the region defined by large

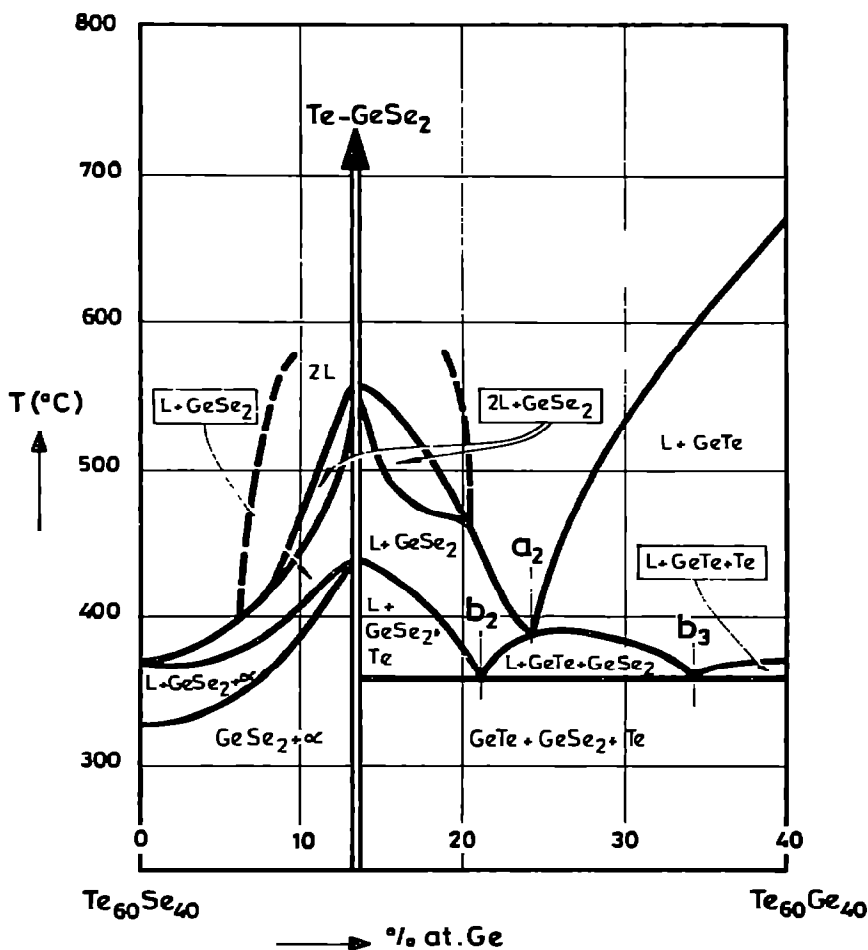


Fig. 5. Isoplethal section at 60 at.% Te.

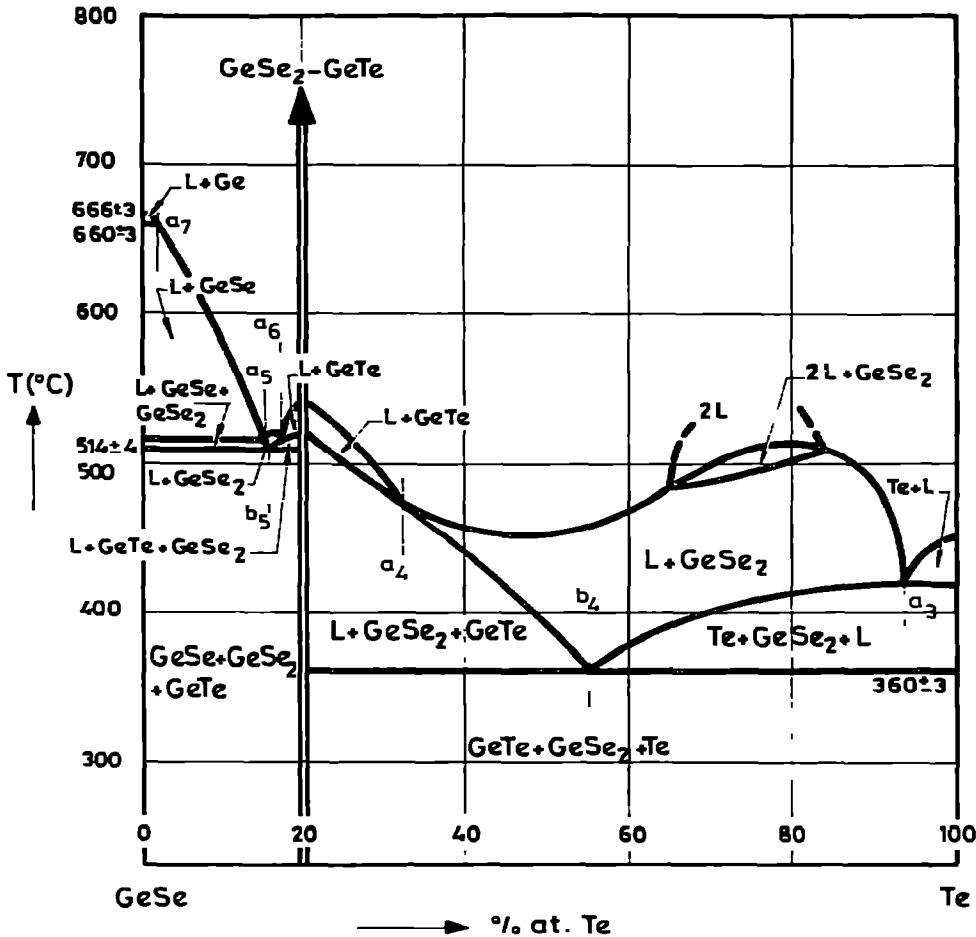
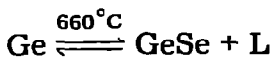


Fig. 6 GeSe—Te isopleth.

selenium content, the invariant at 514°C corresponds to the ternary eutectic ξ_2 of the GeTe—GeSe₂—Ge system (Fig. 7). Points a_5 and a_6 are the trace of the intersection of this line with the eutectic lines going down from the Ge—Se binary eutectic E_4 and the GeSe₂—GeTe eutectic e_2 , respectively, towards the ternary eutectic ξ_2 . Point a_7 corresponds to the peritectic reaction



and point b_5 is the intersecting point with the minimal conodal line from GeSe₂ to the eutectic ξ_2 .

In the rich Te part of Fig. 6, point a_4 corresponds (as a_1 and a_2 , previously encountered) to the binary valley descending from the GeSe₂—GeTe eutectic e_2 to the ternary eutectic ξ_1 . Point a_3 is the trace of the binary line ascending from ξ_1 to the GeSe₂—Te eutectic e_1 , and b_4 is the intersecting point with the minimal conodal drawn from GeSe₂ to ξ_1 . This section also intercepts the liquid immiscibility gap, as shown in Fig. 6.

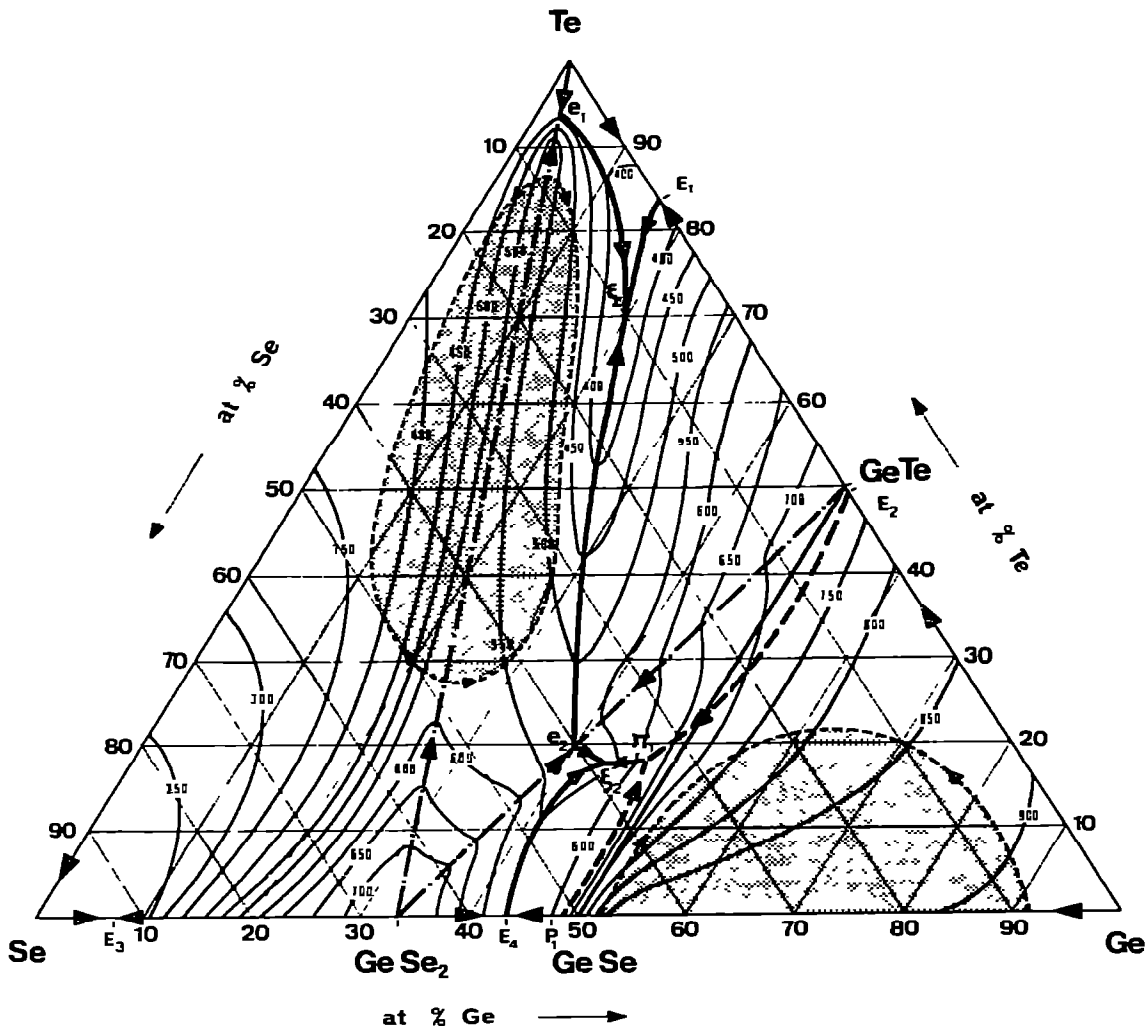


Fig. 7. Ternary phase diagram of the Ge—Te—Se system.

Ternary subsystems

The liquidus isotherms, main invariant points, monovariant lines and liquid immiscibility regions of the Ge—Te—Se system are shown in Fig. 7.

The GeSe_2 —Te—Se system shows liquidus profiles which decrease in temperature with increasing Se content and touch themselves at Se, Te, GeSe_2 —Se eutectic E_3 and GeSe_2 —Te eutectic e_1 . The form of the solidus surface confirms the solid solubility established by X-ray diffraction. As can be shown from the analysis of the data reported in Table 1, the thermal stability of the alloys increases with the Te content and decreases with the GeSe_2 content. Thermal decomposition begins near 300°C for large Se content and near 450 – 500°C for large Te or GeSe_2 content. Alloys with composition in the liquid immiscibility gap have lower stability than the surrounding ones.

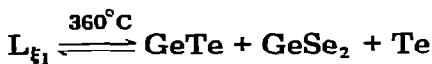
The GeTe — GeSe_2 —Te system has an invariant solidus surface at $360 \pm 3^\circ\text{C}$

TABLE 1

Composition, solidus and liquidus temperatures, and temperature at which decomposition starts for ternary subsystems

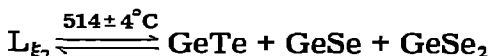
Composition (at.%)			T_{solidus} (°C)	T_{liquidus} (°C)	Start of decomposition (°C)
Ge	Te	Se			
5	85	10	440	562	478
10	10	80	220	265	373
10	20	70	225	274	375
10	30	60	240	316	390
10	40	50	271	348	411
10	50	40	368	397	327
10	60	30	380	485	452
10	70	20	439	560	490
10	80	10	358	510	473
15	55	30	440	559	450
20	10	70	290	450	410
20	20	60	315	470	412
20	30	50	342	512	435
20	40	40	442	555	470
20	50	30	362	540	485
20	60	20	364	462	466
20	70	10	359	365	476
25	25	50	437	576	464
30	10	60	435	680	464
30	20	50	365	595	468
30	30	40	360	545	495
30	40	30	360	475	482
30	50	20	360	456	500
30	60	10	360	515	500
35	5	60	435	715	450
40	10	50	515	570	489
40	20	40	520	525	510
40	30	30	365	560	526
40	40	20	360	596	492
40	50	10	358	620	532
45	35	20	514	663	512
50	10	40	645	700	516
50	20	30	655	668	519
50	30	20	665	685	530
50	40	10	685	716	536
60	10	30	635	820	465
60	20	20	635	785	500
60	30	10	640	790	560
70	10	20	634	860	505
70	20	10	645	845	600
80	10	10	640	880	610

that corresponds to the eutectic reaction

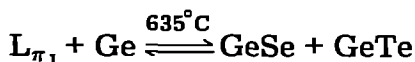


The composition of the eutectic point ξ_1 is 19 at.% Ge, 72 at.% Te, 9 at.% Se. Thermal stability increases generally with Te content and is also high near the ternary eutectic. Temperatures for the beginning of thermal decomposition are in the range 460–520°C.

The GeTe—GeSe—GeSe₂ system has a ternary eutectic point ξ_2 of composition 44 at.% Ge, 18 at.% Te, 38 at.% Se, which corresponds to the invariant reaction



and a peritectic reaction



The approximate composition of point π_1 is 48 at.% Ge, 18 at.% Te, 34 at.% Se.

In the Ge—GeTe—GeSe triangle there is a large liquid immiscibility region based on that existing in the Ge—Se system. Thermal stability is very low for these alloys; the decomposition begins at 500–600°C and, once initiated, is very rapid. For this reason, the determination of the univariant equilibrium curves extending from the peritectic π_1 to both the Ge—Te binary eutectic E_2 and the Ge—Se peritectic P_1 (dotted lines in Fig. 7) is approximate.

CONCLUSIONS

From the study of the ternary system, we conclude that here is no ternary compound. The following quasi-binary systems are found.

GeSe₂—Te system, the phase diagram of which is similar to that reported in ref. 15 but contradicts that reported in ref. 16.

GeTe—GeSe₂ system, the phase diagram of which is of the eutectic type and similar to that reported in ref. 16.

Three liquid—liquid miscibility gaps exist. The first is situated entirely in the ternary system and the other two are based on those occurring in the GeSe—Ge system and between GeSe₂ and GeSe.

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