PHASE DIAGRAM OF THE TERNARY SYSTEM Ge-Sb-Te. II. THE SUBTERNARY Ge-GeTe-Sb₂Te₃-Sb

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ABSTRACT

The phase diagram of the ternary subsystem $Ge-GeTe-Sb_2Te_3-Sb$ was investigated using differential thermal analysis, differential scanning calorimetry, thermogravimetry powder X-ray diffraction and metallographic techniques. Five isoplethal sections were constructed. Seven transition reactions (U type) and a melting point minimum of the liquidus surface were characterized. Eight isothermal sections have been constructed in order to follow the reaction path for any composition of the subsystem.

INTRODUCTION

This study follows a previous investigation [1] of the phase diagram of the GeTe-Sb₂Te₃-Te ternary subsystem, and is part of a more general study on the phase diagrams of some chalcogenide systems [2,3]. The phase diagram of the Ge-GeTe-Sb₂Te₃-Sb subternary has already been reported by Abrikosov and Danilova-Dobryakova [4], who made a general study, but incomplete, of the equilibria in this system. Nevertheless, some contradictory results given by these authors prompted a deeper study that is presented in this paper.

The study was performed by differential thermal analysis (DTA), differential scanning calorimetry (DSC), X-ray diffraction and metallography. Special care has been taken to identify the temperatures and compositions of the ternary invariants of the system. In that sense, the use of DSC with slow heating rates has allowed us to distinguish between reactions that are very close in temperature and have small heats associated with them.

EXPERIMENTAL

168 samples were prepared with compositions shown in Fig. 1. The preparation method and thermal treatment were specified in a recent paper [1]; most alloys were annealed at 500°C for eight months. The experimental equipment used for the measurement is the following: a DTA Netzsch 404 and 429, a Perkin-Elmer DSC-2, a Setaram DSC 111, a Guinier de Wolff camera and a Reichert metallographic microscope.

CONSTITUENT BINARY SYSTEMS

System Ge–Te

The Ge-Te system (see Fig. 2) contains one compound GeTe, and two eutectics, with 15 and 50.15 at% Ge, at 385°C (e_2) and 720°C (e_3), respectively [5,6]. The GeTe compound melts congruently at 724°C and has two polymorphic varieties: α -GeTe at low temperature and β -GeTe at high temperature. There is a peritectoid reaction corresponding to the formation of α -GeTe at 430°C [7,8].

Subsystem $Sb-Sb_2Te_3$

The Sb_2Te_3 congruently melting compound divides the Sb-Te system into two parts, that have been studied by Abrikosov et al. [9] and taken for



Fig. 1. Location in the ternary system of the samples studied.



Fig. 2. Phase diagram of the Ge-Te system.

granted by Elliot [10] in his compilation. 19 samples have been prepared in the Sb-Sb₂Te₃ subsystem. They were annealed for eight months at 500°C before being analysed. The results of the analysis are given in Fig. 3, and they agree with the results of Abrikosov et al. Two solid solutions, γ and δ , appear which are formed by peritectic reactions. They are:

$$L_{P_1} + \langle Sb_2Te_3 \rangle \rightleftharpoons \gamma \text{ at } 558^{\circ}C$$
$$L_{P_2} + \langle Sb \rangle \rightleftharpoons \delta \text{ at } 550^{\circ}C$$
$$L_{P_3} + \gamma \rightleftharpoons \delta \text{ at } 548^{\circ}C$$

with L_{P_1} at 38 at% Te, L_{P_2} at 25 at% Te and L_{P_2} at 34 at% Te.

The solubility region at 500°C of the δ phase ranges from about 17 to 37 at% Te and that of the γ phase from about 41 to 54 at% Te.

There is one difference with Abrikosov's results which refers to the temperature of the melting point minimum (located at 31 at% Te): 544°C in this study and 533°C from Abrikosov.

System $GeTe-Sb_2Te_3$

The GeTe-Sb₂Te₃ line is a quasi-binary system that has been described by Abrikosov and Danilova-Dobryakova [11] and the present authors [1]. The phase diagram is presented in Fig. 4. There are three compounds, $Ge_2Sb_2Te_5$, $GeSe_2Te_4$ and $GeSb_4Te_7$, with incongruent melting at 630, 616



Fig. 3. Phase diagram of the Sb-Sb₂Te₃ system.

and 606°C, respectively. The peritectic reactions are: $L_{P_1} + \beta \rightleftharpoons Ge_2Sb_2Te_5$ at 630°C $L_{P_2} + Ge_2Sb_2Te_5 \rightleftharpoons \langle GeSb_2Te_4 \rangle$ at 616°C $L_{P_1} + \langle GeSb_2Te_4 \rangle \rightleftharpoons \langle GeSb_4Te_7 \rangle$ at 606°C with L_{P_1} at 19 at% Ge, L_{P_2} at 12 at% Ge and L_{P_1} at 6 at% Ge. The $\langle GeSb_4Te_7 \rangle$ compound has a limited solubility range.



Fig. 4. Phase diagram of the quasi-binary system GeTe-Sb₂Te₃.

System Ge–Sb

The phase diagram of this system is of the eutectic type and is shown in Fig. 5. The eutectic, e_4 , occurs at 17 at% Ge and 590°C [12]. The solubility of both elements is 2.5 at% Ge for $\langle Sb \rangle$ and 2.4 at% Sb for $\langle Ge \rangle$, after annealing at 540°C for four months [12]. As seen in Fig. 5, our few measurements agree with those compiled by Hansen and Anderko [12].

THE SUBSYSTEM Ge-GeTe-Sb₂Te₃-Sb

This study has been carried out by means of five isoplethal sections, from which eight isothermal sections have been constructed. In Table 1 are summarized the reactions that take place in the constituent binaries and in the ternary subsystem, ordered according to the temperature at which they occur.



Fig. 5. Phase diagram of the Ge-Sb system.

Isoplethal sections

We will first discuss the isopleths. They are plotted in Figs. 6–10 together with the experimental points by DTA and DSC measurements.

The first, and simplest, isoplethal section is the one joining the melting point minimum $(Sb_{0.69}Te_{0.31})$ of the Sb-Sb₂Te₃ binary with germanium, and it is shown in Fig. 6. The solid solution δ of the Sb-Sb₂Te₃ binary enters into the ternary. The liquidus curves corresponding to the L + δ and L + $\langle Ge \rangle$ equilibria meet at point *a* which lies on the monovariant line between the ternary transition reactions U₁₁ and U₁₂. The experimental determination of the composition of point *a* is made easy by the relative slopes of the liquidus curves and we obtained it at 15 at% Ge. The temperature of that point can be obtained easily from the line dividing the regions L + $\langle Ge \rangle$ and L + δ + $\langle Ge \rangle$. The general description of the isopleth agrees with ref. 4, in particular the composition of point *a* is approximately the same but the temperature is 529°C instead of 520°C in ref. 4. This must be related to the

Ge - Sb GeTe - Ge Ge-GeTe-SbzTe3-Sb Sb-Sb 7 Te 1 Sb₂Te₃-Gere e₃ 720°C L 2 a+<Ge> P1 630°C L + a ‡ Ge, Sb, Te, P2 616°C + Ge₂Sb₂Te₅⁺ GeSb₂Te U₅ 615°C + α ‡ Ge₂Sb₂Te₅ + <Ge P, 606°C . + GeSb₂Te₄ Z∠GeSb₄Te7 U₂ 600°C + Ge2Sb Te5 ≠ GeSb2Te4 + <Ge> E₁ 595°C L <u>+</u> <GeSb₄Te₇>+ <Sb₂Te₃> e, 590°C L ‡ <Ge>+<*S*b> Ug 562°C ∙L+GeSb2Tet ≵ <GeSb4Te7>+ <Ge> == p₁ 558°C L + <Sb₂Te₃> 7 γ ₽₂ 550°C L + <5b> ≠ δ ™3 548°C L + 1 2 8. U₉ 542°C L +<GeSbyTe*>≠ <Sb2Te3> + <Ge> U₁₁536°C -L+<Sb₂Te₃>‡ Y+<Ge> ™ 5250 Melting point minimum U12 529°C <5b> ‡ δ+<Ge>

The reaction path in the Ge-GeTe-Sb₂Te₃-Sb system

TABLE 1

difference in temperature we obtained for the melting point minimum on the binary $Sb-Sb_2Te_3$, as previously discussed.

Figure 7 corresponds to the isoplethal section Sb_2Te_3 -Ge. The samples of this section present thermal effects at 615, 600, 562 and 542°C that we attribute to the ternary transition reactions U_6 , U_7 , U_8 and U_9 , respectively, given in Table 1. Below 542°C we found the solidus line that limits the three-phase region $L + \langle Sb_2Te_3 \rangle + \langle Ge \rangle$ from the two-phase region $\langle Sb_2Te_3 \rangle + \langle Ge \rangle$. This line is not necessarily a horizontal line, but it must run at most between 542 (U_9) and 536°C (U_{10}). The limits of the solid solutions $\langle Sb_2Te_3 \rangle$ and $\langle Ge \rangle$ have not been accurately determined, as a consequence they are estimated.

In Fig. 8 is shown the isoplethal section $Te_{0.50}Sb_{0.50}$ -GeTe constructed from the experimental data. Apart from the transition reactions U_6 , U_7 , U_8 and U_9 we observe another invariant at 536°C that has been atributed to the transition reaction U_{10} given in Table 1. The complexity of this isopleth is greater than that of Fig. 7 because of the presence of the γ phase, which



Fig. 6. Isoplethal section Sb_{0 69}Te_{0.31}-Ge.

enters into the ternary in a limited composition interval, not accurately determined.

The isoplethal section GeTe-Ge_{0.50}Sb_{0.50} is presented in Fig. 9 and shows all the invariant reactions of the subsystem Ge-GeTe-Sb₂Te₃-Sb. Apart from the reactions already present in Fig. 8 there are those occurring at 531°C (point U_{11}) and at 529°C (point U_{12}) located on each side of the two-phase region $\delta + \langle Ge \rangle$. The extent of this two-phase region and also of the $\gamma + \langle Ge \rangle$ region emphasises the essential role the phases δ and γ (of the Sb_2Te_3 -Sb system) play in the characteristics of the phase diagram of the ternary subsystem Ge-GeTe-Sb₂Te₃-Sb. The thermal effects corresponding to the liquidus are clearly apparent in the DTA curves but the other transformations give rise to small thermal effects so to construct this isoplethal section we have taken into account the results obtained in other vertical sections, mainly those corresponding to the $Ge_{0.10}Sb_{0.90}$ $Ge_{0.10}Sb_{0.32}Te_{0.58}$ section. This isoplethal section is presented in Fig. 10 and the broadness of both the $\gamma + \langle Ge \rangle$ two-phase and the δ single-phase can be seen, the latter one entering deeply into the regions Ge-GeTe-Sb₂Te₃-Sb system. Also the liquidus curve is very like that of the Sb₂Te₃-Sb system. The invariants at 529 and 531°C and the solidus line dividing the L + δ and δ regions have been accurately determined using very sensitive DSC measurements at 0.625 and 1.25°C min⁻¹ scanning rates.

A striking feature of the Ge–GeTe–Sb₂Te₃–Sb ternary subsystem is that it shows no ternary eutectic invariant but a melting point minimum located

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Fig. 7. Sb₂Te₃-Ge isopleth.



Fig. 8. Isoplethal section Te_{0.50}Sb_{0.50}-GeTe.

at 15 at% Ge and 61.5 at% Sb and at a temperature of 525°C. In fact this is a consequence of the introduction into the ternary of the δ phase. At 525°C the two L + $\langle Ge \rangle$ + δ phase regions coalesce into a critical tie-line with



Fig. 9. Isoplethal section $GeTe-Ge_{0.50}Sb_{0.50}$.





Fig. 10. Isoplethal section $Ge_{0.10}Sb_{0.90}-Ge_{0.10}Sb_{0.32}Te_{0.58}$.

liquid L_{cr} (15 at% Ge, 61.5 at% Sb) in equilibrium with δ_{cr} and $\langle Ge_{cr} \rangle$. Below 525°C, equilibrium is between δ and $\langle Ge \rangle$.

Isothermal sections

Apart from the five isoplethal sections described in Figs. 6-10 a limited study was undertaken for small portions of the sections corresponding to

6.6, 30 and 40 at% Te and to 16.6 and 26.6 at% Ge (see Fig. 1) This study allowed us to obtain the boundaries of the different regions in which each invariant reaction takes place.

From these results and those presented in Figs. 6-10 several isothermal sections have been constructed to obtain a better description of the reaction path for the different compositions of the subsystem.

In the following we will describe schematically the seven isothermal sections presented in Figs. 11-17. They are arranged from high to low temperature. Each of them shows the equilibrium of the different phases present at a temperature slightly above that corresponding to a specified invariant reaction and also the phase equilibrium occurring at a temperature slightly below that of the reaction, with the purpose of showing how the different multi-phase regions change with temperature. Figure 11 shows an isothermal section at 615°C. One of the broken straight lines represents the boundary between regions $L + \beta + A$ and $L + \beta + \langle Ge \rangle$ that would exist in an isothermal section drawn at a temperature slightly above 615°C while the other broken line shows the boundary between the $L + A + \langle Ge \rangle$ and $\beta + A + \langle Ge \rangle$ regions occurring at temperatures slightly below 615°C. The same procedure of drawing broken lines to show how the phase equilibrium is modified on varying the temperature around that of a particular invariant reaction will be used for the other isothermal sections presented.

The next isothermal section, presented in Fig. 12, corresponds to a temperature of 600°C, which is the temperature of the transition reaction U_7 . Some uncertainty exists both in the location of the composition and the temperature of U_7 because the thermal effects due to the reaction are very small. Smaller thermal effects are associated with the transition reaction U_8 . The temperature of this reaction has been taken as 562°C with an uncertainty of ± 3 °C. The isothermal section at 562°C is shown in Fig. 13. Following the same procedure, Fig. 14 is the isothermal section at 542°C that corresponds to the transition reaction U_9 . This reaction is clearly apparent by DTA; that is, the temperature and composition of U_9 are quite accurate. Also some parts of the isothermal sections are constructed from an assessment of indirect experimental determinations.

Figures 15, 16 and 17 represent the isothermal sections at 536, 531 and 529°C, respectively. Comparison of these figures shows that the liquid region shrinks very rapidly with a small temperature drop. This reflects the fact that the liquidus surface is very flat in the neighbourhood of the U_{10} , U_{11} and U_{12} transition reactions and also around the ternary melting point minimum, located at 525°C.

The isothermal section shown in Fig. 18, drawn at 525°C, shows the phase equilibria associated with the critical tie-line between liquid + δ + $\langle Ge \rangle$. Just below 525°C all alloys are completely solid.

















Polythermal projection

From the study of the five isoplethal sections and eight isothermal sections we propose the polythermal projection and the liquidus isotherms of the phase diagram presented in Fig. 19. Generally speaking, this figure shows a shallow valley going through the quadrilateral around one of its diagonals; that is, joining the binary eutectic e_3 (near GeTe) to the other binary eutectic e_4 (near Sb), and meeting at point U₉ another valley going down from the quasi-binary eutectic E_1 .

Also, monovariant lines leave both the P_1 , P_2 and P_3 peritectics of the GeTe-Sb₂Te₃ system and the p_1 , p_2 and p_3 peritectics of the Sb-Sb₂Te₃ system and intersect the main valley at points U_6 , U_7 , U_8 and U_{10} , U_{11} , U_{12} , respectively. The melting point minimum of the ternary subsystem occurs between points U_{11} and U_{12} . The composition and temperature of all the relevant points inside the quadrilateral are given in Table 2.

In Fig. 20 is plotted a perspective of the liquidus surface in the composition-temperature coordinates. This figure shows, better than Fig. 19, that the slope of the liquidus surface is quite steep in the Ge primary crystallization region, and rather shallow elsewhere.

The present work is complementary to the previous study [1] on the GeTe-Sb₂Te₃-Te subsystem. Figure 21 presents the overall polythermal projection of the Ge-Sb-Te system, which is a summary of the results given here and those published before.

It is necessary to compare our results to those published by Abrikosov and Danilova-Dobryakova [4]. In general there is agreement between our results and those of these authors, and their previous study has been very useful as a starting point and as a guide to try to get a better knowledge of the system.

If we consider the polythermal projection we propose and that given by Abrikosov we can make some comments: we have obtained the path of lines P_2U_7 and P_3U_8 , that were indicated by dashed lines in Abrikosov's work; we obtain a composition of the transition points U_6 , U_7 and U_8 , richer in antimony than indicated in fig. 6 of ref. 4. Also, we have been able to determine the temperatures of the seven transition reactions. This has been possible by using apparatus of great sensitivity and a low heating rate. Our projection of the liquidus isotherms differs from that of Abrikosov in some areas. One reason for the difference may be that the liquidus measurements made by Abrikosov were done on cooling curves by DTA, giving probably lower points than our measurements, made only with heating curves. In particular there is a large difference for the isotherms at 650 and 700 °C near the Sb₂Te₃-GeTe quasi-binary system, but we notice that these isotherms of Abrikosov do not agree with his earlier publication of the quasi-binary [11].

Another point of disagreement comes from the results on the isoplethal section Sb_2Te_3 -Ge. Abrikosov proposes the existence of a three-phase region





	L _{U6}	L_{U_7}	L_{U_8}	L _U ,	L _{U10}	$L_{U_{11}}$	L _{U12}	Melting point minimum
Ge	28	25	20	16	15	15	14	15
Sb	32	36	43	52	55	58	66	61.5
Te	40	39	37	32	30	27	20	23.5
T (°C)	615	600	562	542	536	531	529	525

The compositions (at%) and temperatures (°C) of the relevant ternary invariant reactions

(liquid, Ge and GeSb₄Te₇) between 537 and 630°C. We think that it is not possible for GeSb₄Te₇ to exist above 606°C, which is the temperature we measured for the reaction L + GeSb₂Te₄ \rightleftharpoons GeSb₄Te₇. Also, Abrikosov proposed a unique horizontal line at 537°C which delimits the three-phase area liquid + Ge + GeSb₄Te₇, and the binary area Sb₂Te₃ + Ge. We consider that this is very unlikely to happen, so we assume that this is a simplification of the phase equilibria occurring in this isoplethal section. To better visualize the situation, we have drawn a space model in temperature-composition coordinates around the Sb₂Te₃-Ge line (Fig. 22). The upper part of this



Fig. 20. Perspective of the liquidus surface in composition-temperature coordinates.

TABLE 2



Fig. 21. Polythermal projection of the Ge-Te-Sb phase diagram.

figure corresponds to a portion of the isothermal section at 542°C, see Fig. 14, in which there are the two-phase $\langle Sb_2Te_2 \rangle$ and $\langle Ge \rangle$. In the middle there is a part of the isothermal section at 536°C, see Fig. 15, and the lower part corresponds to another isothermal section at a lower temperature, for example at 531°C, see Fig. 16. The two-phase area $(Sb_2Te_3) + (Ge)$ is contained in the volume delimited by the surfaces cb"c"c, df "d"d and the ruled surfaces cb"f"dc and cc"d"dc. The interpretation given by Abrikosov demands the surface cc"d"dc to be a vertical plane contained in the vertical section Sb₂Te₃-Ge. This author estimated that no ternary solid solution around pure Ge existed, so the surface df "d"d would reduce to the vertical line in the Ge vertex of the composition quadrilateral. Nevertheless, there is a relatively large solid solution around Sb₂Te₃. This means that the surface cb"c"c cannot be reduced to a line and then it is very unlikely that the vertical section Sb₂Te₃-Ge contains the line cc". The interpretation we propose in Fig. 7 is that the vertical section Sb₂Te₃-Ge crosses the lines cb', b"c", df' and f"d".



Fig. 22. Space model of temperature-composition around the Sb₂Te₃-Ge line.

CONCLUSION

On considering the foregoing results, the following points are notable.

(a) The liquidus surface has a melting point minimum associated with a critical tie-line and located at 525°C with a composition of 15 at% Ge and 61.5 at% Sb.

- (b) As a consequence of the ternary compounds $Ge_2Sb_2Te_5$, $GeSb_2Te_4$ and $GeSb_4Te_7$ which form peritectically in the quasi-binary system Sb_2Te_3 -GeTe and also of the extended solid solutions γ and δ of the binary subsystem Sb_2Te_3 -Sb, there are several ternary transitions reactions in the ternary.
- (c) The liquidus surface has quite a steep slope in the Ge primary crystallization region (which extends over about two-thirds of the composition quadrilateral) and a rather shallow slope elsewhere.
- (d) The solid solution regions of γ and δ of the binary subsystem Sb₂Te₃-Sb enter into the ternary to a large extent.
- (e) Eight isothermal sections have been constructed from the experimental results. They allow the reactions that occur during solidification to be followed for any alloy composition.
- (f) The temperatures and compositions of all the invariant reactions of the ternary have been determined and they are presented and connected with the binary invariants in Tables 1 and 2.

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