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Study of the ternary system cadmium–germanium–tellurium: phase equilibria in the ternary system

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Abstract

The ternary system Cd–Ge–Te has been studied by differential thermal analysis, differential scanning calorimetry and X-ray powder diffraction analysis. No definite ternary compound has been found. Two isoplethic sections are quasi-binaries. So, the ternary system is divided in three subternaries. The establishment of the ternary phase diagram of four isoplethic sections has made it possible to determine the layout of the eutectic and peritectic valleys and thus to delimit the different primary crystallization areas. Four ternary invariants have been determined, two of which are ternary eutectics and one is a peritectic ternary corresponding to the three subternaries and a ternary metatectic invariant.

Keywords: Thermal analysis; Phase equilibria; Cadmium; Tellurium; Germanium

1. Introduction

The study of the ternary system Cd–Ge–Te was part of the systematic examination of the glass system X–Ge–Te (X = Ga, In, Tl, Sb, ...) with X = Cd for this work.

The formation and the thermal behaviour of these glasses can be explained from the ternary phase diagram. So it has been first established. We specified the ternary invariants and delimited all fields of crystallization.

Furthermore, the choice of this ternary system is justified by the fact that it constitutes the continuation of work undertaken by Morgant et al. [1,2] concerning the establishment of the ternary phase diagram Cd–Te–X (X = Sn, Pb).

2. Experimental details

The samples were prepared from cadmium and germanium, both 99.999% pure, and tellurium, 99.9999% pure. The synthesis was carried out in evacuated (10^{-3} Torr) and sealed-off silica ampoules. The annealing procedure of the alloys was gradual: 6 h at 400 °C, 500 °C, and final annealing at 1100 °C and then the temperature was slowly reduced. The mass of the alloys investigated was about 0.3 g.

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In order to check the calibration of the apparatus (differential thermal analysis (DTA) and differential scanning calorimetry (DSC)), the Pt–(Pt–10%Rh) thermocouples were calibrated at the melting points of high purity Sn (99.9999%), Te (99.9999%) and Ge (99.999%) [3].

The study was performed using the following.

- The DTA apparatus (DTA Netzsch®) was sensitive to temperature differences greater than ±0.5 K and the absolute temperature measurement was accurate to ±2 K. The data reported in this paper were obtained at heating rates of 2 K min^{-1}.
- The DSC apparatus (DSC 111 Setaram® with a HP 86 calculator) was sensitive to temperature differences greater than ±0.5 K. The data reported in this paper were obtained at heating rates of 1 K min^{-1}.
- X-Ray powder patterns were obtained with a Philips® PW1840 diffractometer, at room temperature using Cu Kα radiation. Alloy powders were prepared by crushing the solidified samples after thermal analysis.

3. The boundary systems

3.1. *The Germanium–Cadmium system*

The assessed equilibrium phase diagram for the Ge–Cd system given by Olesinski and Abbaschian [4]

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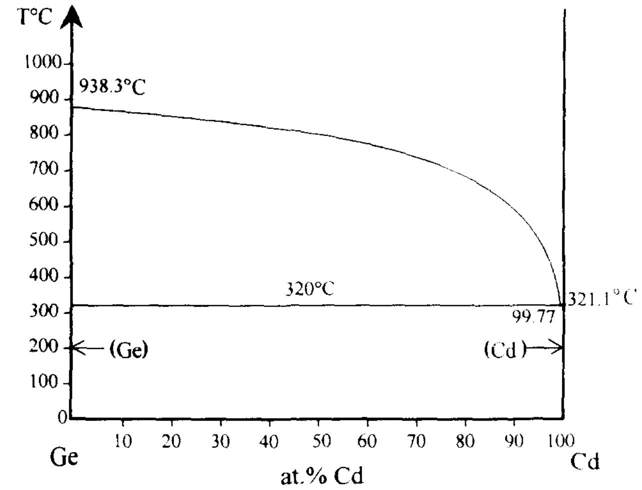


Fig. 1. Phase diagram of the germanium–cadmium system according to Olesinski and Abbaschian [4].

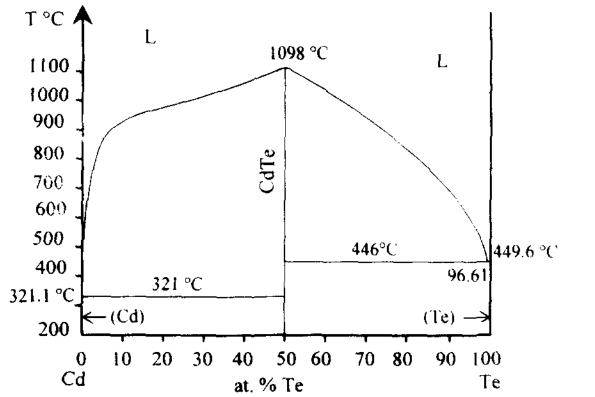


Fig. 2. Phase diagram of the cadmium–tellurium system according to Sharms and Chang [5].

is presented in Fig. 1. It shows a eutectic reaction at a temperature close to the melting point of Cd. The eutectic reaction is

$$L \rightleftharpoons Ge + Cd \qquad 320\ °C$$

Mutual solid solubilities of germanium and cadmium are negligible.

3.2. The Cadmium–Tellurium system

The assessed equilibrium phase diagram for the system Cd–Te given by Sharms and Chang [5] is shown in Fig. 2. There is a congruently melting intermediate phase, CdTe, that forms at 50 at.% Te, and the deviation from stoichiometric composition in CdTe is negligible. Two eutectic reactions occur in each of the Cd–CdTe and CdTe–Te regions of the phase diagram:

$$L \rightleftharpoons CdTe + Cd \qquad 321\ °C$$

$$L \rightleftharpoons CdTe + Te \qquad 446\ °C$$

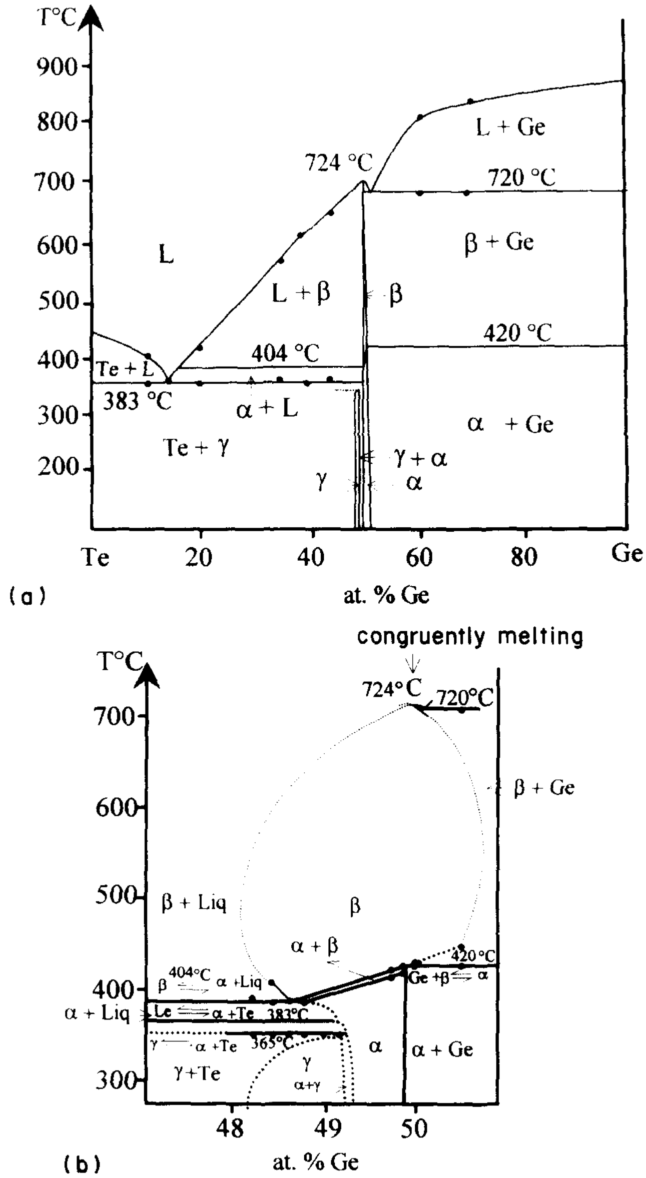


Fig. 3. Phase diagram of the germanium–tellurium system according to Legendre and co-workers [6–8].

3.3. The Germanium–Tellurium system

The Ge–Te equilibrium diagram (Fig. 3) determined by Legendre and co-workers [6–8] contains a single compound, GeTe, and two eutectics, with 15 at.% Ge and 50.15 at.% Ge respectively at 383 °C and 720 °C. The compound GeTe melts congruently at 724 °C and has two polymorphic varieties: α-GeTe at low temperature ($T < 420$ °C) and β-GeTe at high temperature ($T > 405$ °C). The $\alpha \rightarrow \gamma$ transition requires prolonged annealing (more than 6000 h) [8].

There is a peritectoid reaction corresponding to the formation of α-GeTe at 420 °C.

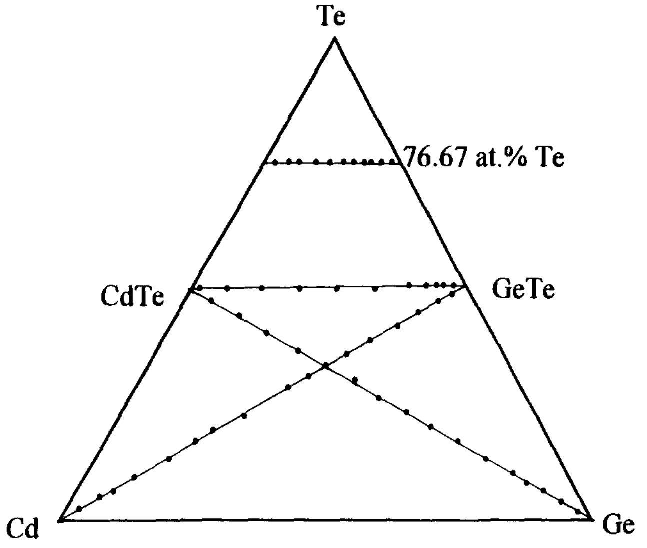


Fig. 4. Location in the ternary system Cd–Ge–Te of the samples studied in this investigation.

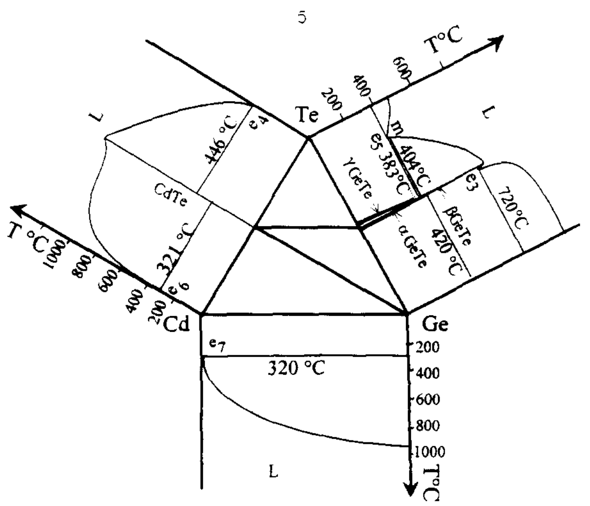


Fig. 5. Triangulation of the Cd–Ge–Te system.

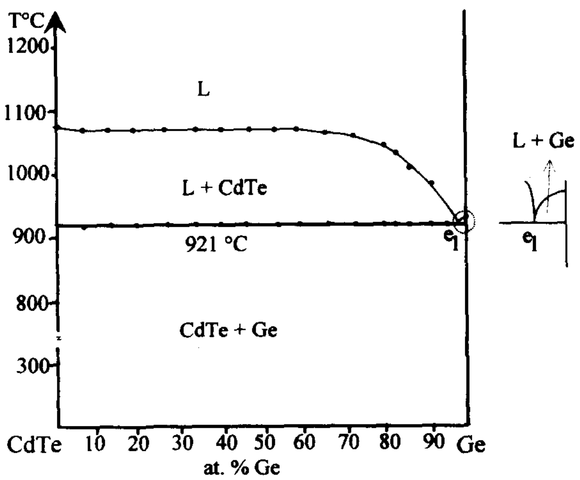


Fig. 6. Phase diagram of the CdTe–Ge section.

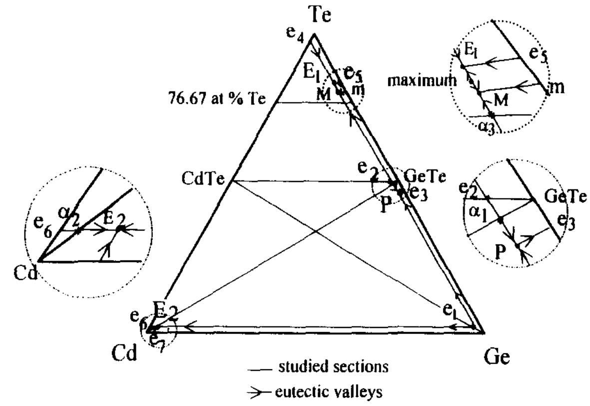


Fig. 7. Diagram of the Cd–Ge–Te system: e_i (i = 1–7), binary eutectics; E_1 and E_2, ternary eutectics; M_1, ternary metatectic; P_1, ternary peritectic.

Table 1
Thermal data for the CdTe–Ge section

Composition (mol.%)			T (°C), invariant	T (°C), liquidus
Cd	Ge	Te		
47	6	47	920	1074
43	14	43	921	1074
40	20	40	921	1074
37	26	37	920	1074
33	33	33	920	1074
30	40	30	920	1074
27	46	27	920	1070
23	54	23	920	1070
20	60	20	921	1070
17	66	17	921	1067
13	74	13	921	1065
10	80	10	920	1064
8.3	84	8.3	921	1064
7	86	7	921	1041
5	90	5	921	996
3	94	3	921	973
2	96	2	921	

$$L \rightleftharpoons Ge + \beta\text{-}GeTe \quad 720\ °C$$
$$Ge + \beta\text{-}GeTe \rightleftharpoons \alpha\text{-}GeTe \quad 420\ °C$$
$$\beta\text{-}GeTe \rightleftharpoons \alpha\text{-}GeTe + L \quad 404\ °C$$
$$L \rightleftharpoons \alpha\text{-}GeTe + Te \quad 383\ °C$$
$$Te + \alpha\text{-}GeTe \rightleftharpoons \gamma\text{-}GeTe \quad 365\ °C$$

4. The ternary system Cadmium–Germanium–Tellurium

4.1. Triangulation of the ternary system Cadmium–Germanium–Tellurium

The preparation included over 60 alloys divided equally over four sections (CdTe–Ge, CdTe–GeTe, Cd–GeTe and the section with 76.67 at.% Te), which

Table 2
Thermal data for the CdTe–GeTe section

Composition (mol.%)			T °C, phase transition	T (°C), invariant	T (°C), liquidus
Cd	Ge	Te			
48	2	50	403	723	1064
43	7	50	403	723	1059
37	13	50	401	723	1031
30	20	50	403	723	998
23	27	50	402	723	982
17	33	50	401	722	937
10	40	50	401	722	884
7	43	50	400	722	810
5	45	50	400	722	785
4	46	50	401	722	
3	47	50	399	720	
1	49	50	402	720	

Table 3
Thermal data for the Cd–GeTe section

Composition (mol.%)			T (°C), phase transition	T (°C), invariant	T (°C), liquidus	
Cd	Ge	Te				
96	2	2		320	483	656
94	3	3		320	541	841
86	7	7		320	620	889
82	9	9		320	658	917
74	13	13		320	687	956
66	17	17		320	745	994
60	20	20		320	768	1018
54	23	23		320	805	1035
42	29	29		320	878	1060
38	31	31		320	902	1075
33	33	33		921	1075	
28	36	36	403	720	903	1052
24	38	38	403	721	900	1032
18	41	41	403	721	890	1006
12	44	44	402	721	855	935
6	47	47	402	721	761	855
2	49	49	401	721	772	

made it possible to investigate the ternary system Cd–Ge–Te. The compositions of the investigated samples are listed in Fig. 4. The triangulation of the system is based on two binary compounds CdTe and GeTe (Fig. 5). No ternary compound was observed. So the ternary system is divided into three subternaries (Te–CdTe–GeTe, CdTe–Ge–GeTe and CdTe–Cd–Ge), each of which is characterized by a ternary invariant. The former which were observed in the four sections made the establishment of the ternary equilibria phases diagram possible.

Table 4
Thermal data for the 76.67 at.% Te section

Composition (mol.%)			T (°C), invariant		T (°C), liquidus	
Cd	Ge	Te				
23		77	444		843	
21	2	77	381		435	825
19	5	77	380		424	819
16	7	77	380		415	802
13	10	77	380		402	777
12	13	77	380		395	752
9	14	77	380		723	
8	15	77	380	398	421	698
7	16	77	380	397	421	688
5	18	77	380	397	450	658
2	21	77	380	398	476	
1	22	77	380	398	483	
	23	77	383		405	505

4.2. Phase equilibria in the ternary system Cd–Ge–Te

4.2.1. The equilibrium diagram of the CdTe–Ge section

This section is limited by CdTe, a compound which melts congruently, and Ge. The equilibrium diagram (Fig. 6) has a eutectic at a temperature of 921 °C. The reaction of type e is the following (921 °C, e_1):

$$L \rightleftharpoons CdTe + Ge$$

Liquidus temperatures (Table 1) and the shape of the liquidus curve showed that the eutectic is degenerated to Ge. It was difficult to determine the temperatures of the liquidus of alloys close to germanium. During the heating of the thermal analysis, the two thermal peaks (invariant and liquidus) were not correctly distinguishable, because the liquidus was masked by the invariant. Nevertheless, these two exothermic peaks could be observed during the cooling. So, the eutectic was found between 98 at.% Ge and Ge.

On either side of the isoplethic section, the eutectic valley, in the form of a saddle, goes to the ternary eutectic E_2 at 320 °C (invariant in the subternary CdTe–Ge–Cd) on one side and goes to the ternary peritectic P at 721 °C (invariant in the subternary CdTe–GeTe–Ge) (Fig. 7) on the other side. So, this diphased isopleth section is a quasibinary.

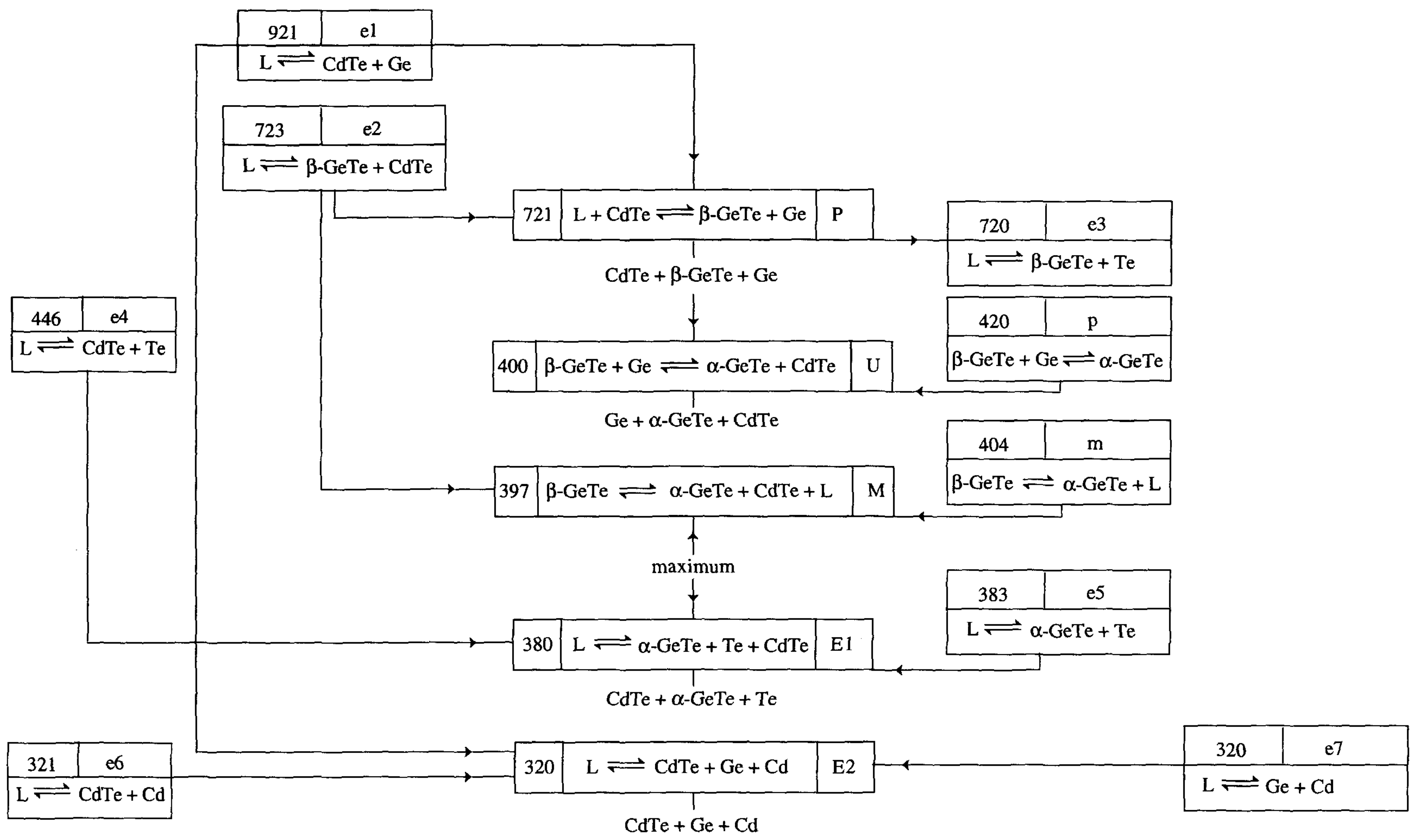
4.2.2. The equilibrium diagram of the CdTe–GeTe section

This section, limited by the compounds CdTe and GeTe which melt congruently, presents two phases in the solid state. The equilibrium diagram shows a eutectic (Fig. 8). The eutectic liquid, composition 3.5 at.% Cd, 50 at.% Te and 46.5 at.% Ge, determined by the Tammann curve, crystallizes at 723 °C according to the reaction of type e (723 °C, e_2):

$$L \rightleftharpoons \beta\text{-}GeTe + CdTe$$

Table 5
The reaction path in the Cd–Ge–Te system

Binary system Cd–Te	Ternary system Cd–Te–Ge	Binary system Te–Ge	Binary system Cd–Ge



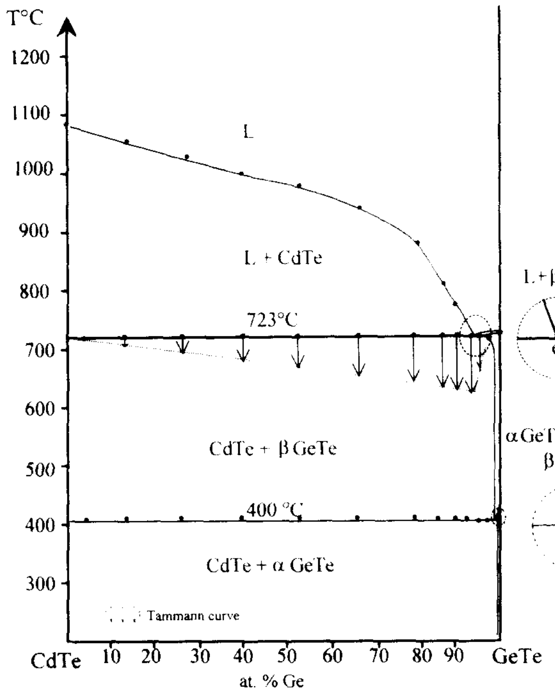


Fig. 8. Phase diagram of the CdTe–GeTe section.

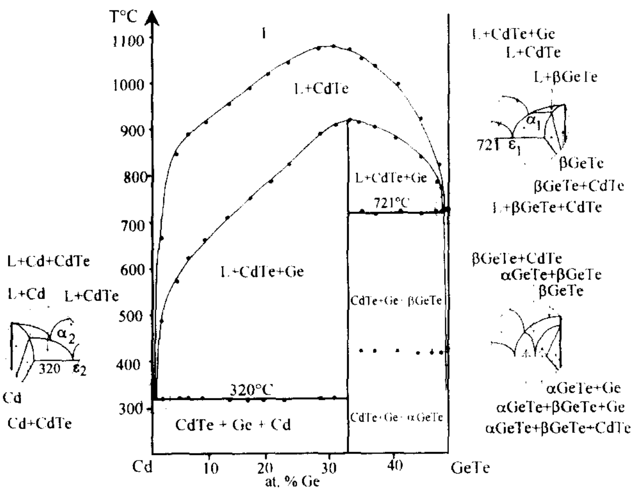


Fig. 9. Phase diagram of the Cd–GeTe section.

Temperature measurements of the liquidus (Table 2) and the Tammann curve show that the eutectic e_2 degenerated to GeTe.

Disregarding the phenomenon in the vicinity of GeTe, this section is a quasi-binary. The eutectic valley, in the form of a saddle, points either to the ternary invariant P (ternary peritectic of the subternary CdTe–GeTe–Ge) or the ternary invariant M (ternary metatectic of the invariance triangle α-GeTe–β-GeTe–Te) (Fig. 7).

This section loses its quasi-binary character in the vicinity of the GeTe solid solution. Indeed, the plateau at 400 °C characterizes the phase transition of GeTe according to the reaction of type U as follows:

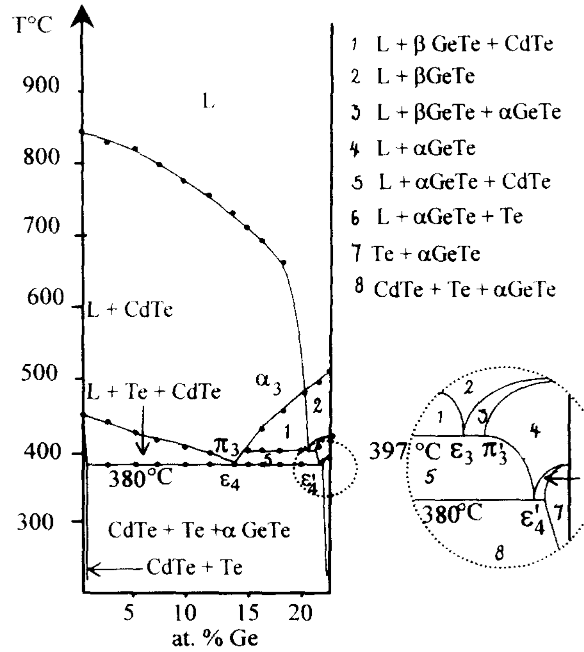


Fig. 10. Phase diagram of the 76.67 at.% Te section.

$$\beta\text{-GeTe} + \text{Ge} \rightleftharpoons \alpha\text{-GeTe} + \text{CdTe}$$

We did not observe solid solutions based on CdTe and Ge.

4.2.3. Comparison with previous publications

The CdTe–GeTe section was described by Quenez and Khodadad [9]. Their study differs from the present according to their finding. The invariant at 724 °C would correspond to the peritectic formation of a solid solution at a high temperature based on GeTe (β). We are also in disagreement with the juxtaposition of the two primary crystallization areas L + β and L + CdTe, that is to say the two juxtaposition diphased areas.

4.2.4. Equilibrium diagram of Cd–GeTe and 76.67 at.% Te sections

The two sections GeTe–Ge and CdTe–GeTe are quasi-binaries. So, the ternary system is divided into three subternaries. We have therefore chosen to study
(a) the Cd–GeTe section and
(b) the 76.67 at.% Te section,
which enable us to determine the three ternary invariants and a metatectic invariant. The latter results from the binary metatectic reaction based on GeTe.

4.2.4.1. Equilibrium diagram of the CdTe–Ge section (Fig. 9). The Cd–GeTe section crosses two subternaries CdTe–Ge–GeTe and CdTe–Cd–Ge (Fig. 7). The valley starting from the binary eutectic e_2 at 723 °C (on the CdTe–GeTe section) moving towards the ternary invariant P (721 °C) crosses this section at the point α_1 (Fig. 7). The ternary peritectic P of the subternary

CdTe–GeTe–Ge is marked by the plateau at 721 °C along which the following reaction develops (721 °C, P):

$$L + CdTe \rightleftharpoons \beta\text{-}GeTe + Ge$$

The point ϵ_1 is the mark of the minimal tie line, in the invariant quadrilateral GeTe–CdTe–Ge–P, coming from CdTe and going to P.

The primary crystallization areas (L + Cd) and (L + CdTe) meet in α_2 (Fig. 7). This point corresponds also to the passage of the eutectic valley coming from the eutectic e_6 (in the binary system CdTe–Cd at 321 °C) and going to E_2 (Fig. 7). The ternary eutectic E_2 of the subternary CdTe–Ge–Cd is characterized by the following reaction of type E (320 °C, E_2):

$$L \rightleftharpoons CdTe + Ge + Cd$$

This ternary invariant E_2 is degenerated, because its temperature is close to the two binary eutectics e_6 (321 °C) in the system CdTe–Cd and e_7 (320 °C) in the system Ge–Cd. The point ϵ_2 is the trace of the minimal tie line, in CdTe–Cd–Ge, coming from CdTe and going to E_2.

4.2.4.2. Equilibrium diagram of 76.67 at.% Te section. The 76.67 at.% Te section crosses the subternary Te–CdTe–GeTe (Fig. 7). The equilibrium phase diagram (Fig. 10) of this section shows the passage of the valley starting from the binary eutectic e_2 at 723 °C (on the CdTe–GeTe section) to the point α_3 and going to the ternary metatectic invariant M (Fig. 10). This invariant is marked in this section by the plateau at 397 °C. The following reaction of type M (397 °C, M) is found:

$$\beta\text{-}GeTe \rightleftharpoons \alpha\text{-}GeTe + CdTe + L$$

The points π_3, ϵ_3 and π'_3 correspond to traces of the minimal tie lines, in the invariance metatectic triangle α-GeTe–β-GeTe–M, coming from respectively CdTe, β-GeTe and α-GeTe and going towards the metatectic invariant M.

The plateau at 380 °C is the result of the ternary eutectic E_1 of subternary α-GeTe–Te–CdTe. The reaction of type E is the following (380 °C, E_1):

$$L \rightleftharpoons \alpha\text{-}GeTe + Te + CdTe$$

The minimal tie lines CdTe–E_1 and α-GeTe–E_1 in the subternary α-GeTe–Te–CdTe meet the section respectively at the points ϵ_4 and ϵ'_4.

Invariants and liquids thermal accident temperatures of the alloys studied in these two last sections are listed in Tables 3 and 4.

5. Conclusions

The ternary system Cd–Ge–Te has been investigated by the establishment of the equilibrium diagram of four isoplethic sections. Two of them are quasi-binary sections. The ternary system can therefore be divided in three subternaries. Two ternary eutectics and one ternary peritectic have been found. A ternary metatectic reaction has been observed owing to the occurrence of the phase transition in the compound GeTe. We have determined the boundaries of the primary crystallization fields.

All of these results are summarized in Table 5 which indicates the evolution of the liquid–solid and solid–solid equilibria in the ternary system.

This work is currently being continued with the study of the vitreous area that we have observed in this ternary system. It covers largely the subternary CdTe–GeTe–Te. A correlation between this vitreous area and the phase diagram will furnish a possible explanation of the thermal behaviour of these glasses.

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