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Study of the ternary system germanium–antimony–tin: experimental phase diagram☆

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Abstract

The phase diagram of the ternary system Ge–Sb–Sn was established by X-ray powder diffraction and differential scanning calorimetry. No ternary compound was found. Two vertical sections were studied in order to follow the reaction path. Four ternary reactions were characterised: three transition peritectic (U-type) reactions and one eutectoid (E-type) reaction. Moreover, from all equilibrium temperatures, a description of liquidus surface in the whole composition range is proposed.

Keywords: Germanium; Antimony; Tin; Phase equilibrium; Ternary system, Thermal analysis

1. Introduction

Germanium based alloys receive the greatest attention because of their semiconducting properties and applications in the electronic industry. This study was undertaken in order to investigate the phase equilibria in the Ge–Sb–Sn ternary system. Both Ge–Sb [7] and Ge–Sn [14] binary systems are simple eutectics while in the Sb–Sn system two intermediate phases and extended solid solutions are formed [3]. So in the Ge–Sb–Sn ternary system more complex phase equilibria might be expected including the formation of a new compound.

To our knowledge, the only information on the phase equilibria in the Ge–Sb–Sn ternary system were reported by Gubenko and Miller [2] and by Kuznetsov et al. [4]. Gubenko and Miller [2] gave few points of the liquidus of the sections Ge–(Sn+2 wt% Sb) and Ge–(Sn+5.4 wt% Sb). Kuznetsov et al. [4] have shown the section Ge–(Sn+29.5 at.% Sb), a part of the Ge-side solidus surface (to 1 at.% Sn and 0.06 at.% Sb) and the liquidus surface. Their results, however, are not always consistent with the recently optimised data in the respective binary phase diagrams. For this reason a new study of the ternary Ge–Sb–Sn phase diagram seemed useful and is described in the present paper.

2. Experimental details

The samples were prepared from 99.9999% pure germanium, antimony and tin. The elements were introduced into the silica ampoules and sealed under vacuum (10^{-3} Torr). The thermal treatment of the alloys was gradual: 2 h at 250°C, 2 h at 700°C and 1 h at 1050°C. Then, the temperature was slowly reduced and the alloys were maintained at a annealing temperature for several weeks.

The alloys were studied using:

- a differential scanning calorimetry apparatus (D.S.C.121. Setaram). The experiments were performed at a heating rate of 1°C/min. For the invariant temperature, the rates used were 0.02°C/min or 0.1°C/min.
- a differential thermal analysis apparatus (DTA Netzsch) for the alloys which have a melting point higher than the limit temperature of the DSC121 calorimeter. The analysis were carried out at a rate of 2°C/min.

In order to check the calibration of the apparatus (DTA Netzsch and DSC Setaram), the Pt/Pt-10% Rh thermocouples were calibrated at the melting point of high purity In

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156.634°C, Sn 231.9681°C, Pb 327.502°C, Sb 630.755°C and Ge 938.3°C (only for DTA) [6].

X-ray powder patterns were obtained with a Philips PW1840 diffractometer at room temperature using CuKα radiation. The apparatus was calibrated with Si.

3. The boundary systems

3.1. The antimony–tin system

The Sb–Sn system was the subject of numerous investigations. Revised forms of the diagram were presented by Hansen and Anderko [1] and Predel and Schwermann [3]. Both agreed for the existence of limiting solid solutions based on Sb and Sn as well an intermediate phase (SbSn) with an extended homogeneity range around the 1:1 composition. The second intermediate phase was assigned alternatively as a high temperature polymorphic modification of the (SbSn) phase [1] or as a stoichiometric Sb_2Sn_3 phase [3].

Later investigations [9,10] showed no evidence of a polymorphic transition of the SbSn phase up to 375°C and in the phase diagram calculation of the binary and ternary systems involving the Sb–Sn equilibrium (e.g. [5,11–13]) the version proposed by Predel and Schwermann [3] is taken into account in most cases.

Recently, the existence of a number of stoichiometric phases: SbSn, $Sb_{13}Sn_{12}$, Sb_3Sn_2 and Sb_2Sn [15] or Sb_3Sn_4 and Sb_4Sn_3 [16] has been suggested.

In this work, we have adopted the Sb–Sn phase diagram optimised by Jönsson et al. [5], which is consistent with our experimental results. We have verified that three peritectic reactions and one eutectoid reaction occur (Fig. 1):

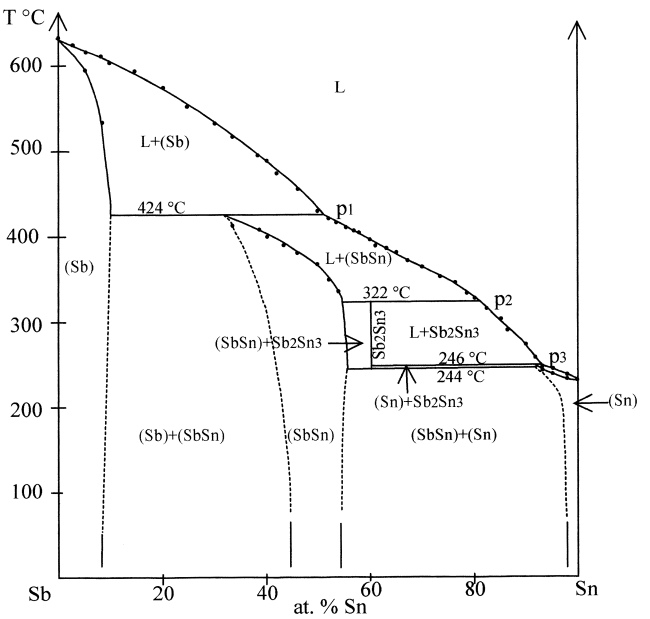

Fig. 1. Phase diagram of the antimony–tin system.

p_1 at 424°C, l + (Sb)↔(SbSn)
p_2 at 322°C, l + (SbSn)↔Sb_2Sn_3
p_3 at 246°C, l + Sb_2Sn_3↔(Sn)
e_3 at 244°C, Sb_2Sn_3↔(SbSn) + (Sn)

The corresponding phase compositions are reported in Table 1.

3.2. The germanium–antimony system

The Ge–Sb phase diagram (Fig. 2) was assessed by Olesinski and Abbaschian [7] and Chevalier [8]. It shows a eutectic (e_1). Our experimental values agree with Olesinski and Abbaschian [7].

Table 1
Invariant equilibria in the Sb–Sn system

Reaction	*T* (°C)	Type	Phase	Composition (at.%)	
				Sb	Sn
l+(Sb)⇔(SbSn)	424	p_1	(Sb)	90	10
			(SbSn)	67	33
			lp	49	51
l+(SbSn)⇔(Sn)	322	p_2	(SbSn)	46	54
			Sb_2Sn_3	40	60
			lp_2	20	80
l+Sb_2Sn_3⇔(Sn)	246	p_3	Sb_2Sn_3	40	60
			(Sn)	9	91
			lp_3	7	93
Sb_2Sn_3⇔(SbSn)+(Sn)	244	e_3	Sb_2Sn_3	40	60
			(SbSn)	45	55
			(Sn)	8	92

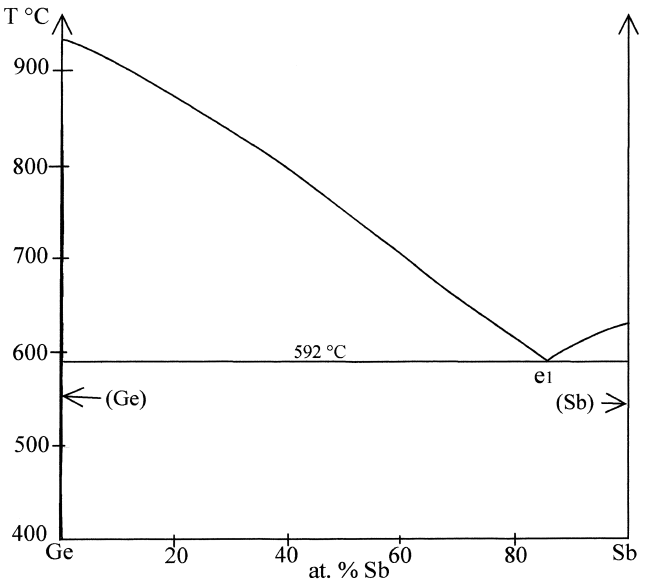

Fig. 2. Phase diagram of the germanium–antimony system.

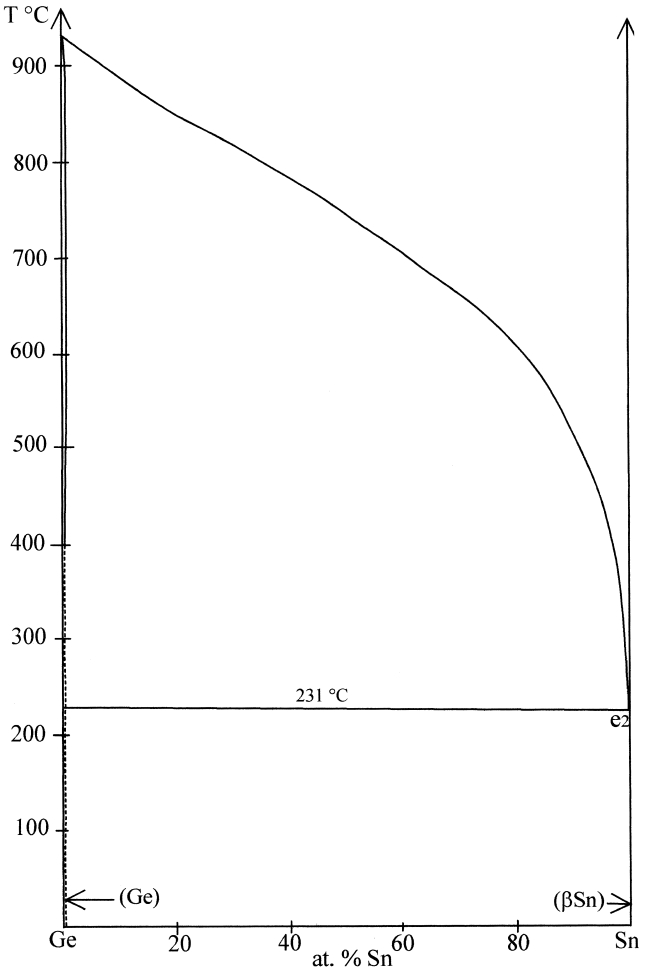

Fig. 3. Phase diagram of the germanium–tin system.

The eutectic reaction is: $l \leftrightarrow (Sb)+(Ge)$ $T=592°C$

The composition of the eutectic (e_1) is 85.5 at.% Sb.

The solid solution (Ge) has a retrograde character with a maximum solubility of ~0.035 at.% Sb at 800°C. At the eutectic temperature, the solid solution (Ge) is 0.01 at.% Sb. The solid solution (Sb) is negligible.

3.3. The germaniun–tin system

The Ge–Sn system was assessed and optimised by Feutelais et al. [14]. Our results agree with the presented phase diagram. It shows a eutectic (e_2) at the temperature close to the melting point of Sn (Fig. 3).

The eutectic reaction is: $l \leftrightarrow (Ge)+(Sn)$ $T=231°C$

The solid solution (Ge) has a retrograde character with a maximum solubility of ~1.1 at.% Sn at 400°C. At the eutectic temperature, the solid solution (Ge) is 1 at.% Sn.

4. The ternary system germanium–antimony–tin

The phase diagram was studied by Kuznetsov et al. [4], but these authors have taken into account the binary system Sb–Sn proposed by Hansen [1].

In order to determine the ternary invariant and to delimit the primary crystallisation, 136 alloys have been prepared. Two vertical sections have been constructed. The composition of the investigated samples are listed in Fig. 4.

4.1. Vertical section 10 at.% Ge

In this section (Fig. 5), the primary crystallisation areas L+(Sb) and L+(Ge) meet in α (Fig. 6). This point shows the passage of the valley starting from the binary eutectic e_1 in the binary system Ge–Sb to the ternary invariant U_1 at 419°C (Fig. 6).

The vertical section at 10 at.% Ge shows four invariant equilibria:

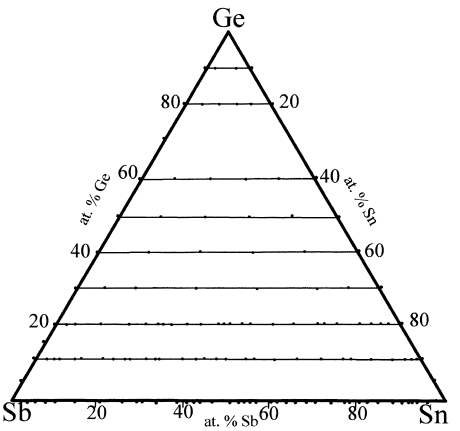

Fig. 4. Location in the ternary system Ge–Sb–Sn of the samples studied.

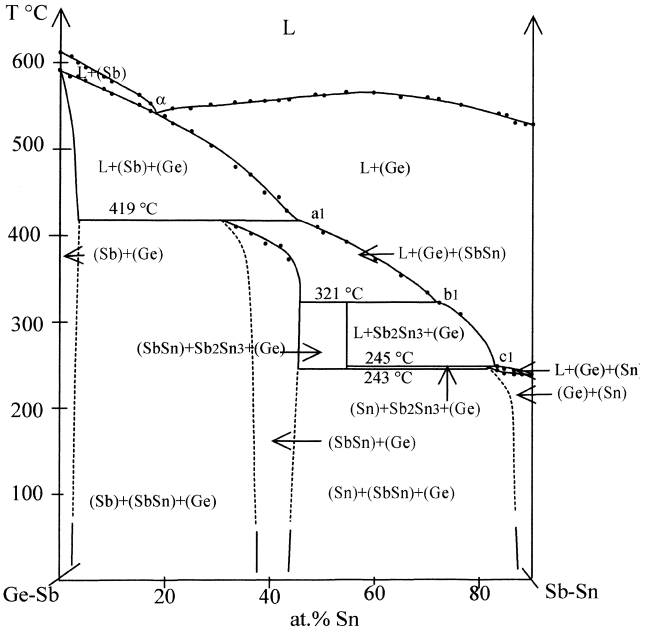

Fig. 5. Vertical section at 10 at.% Ge.

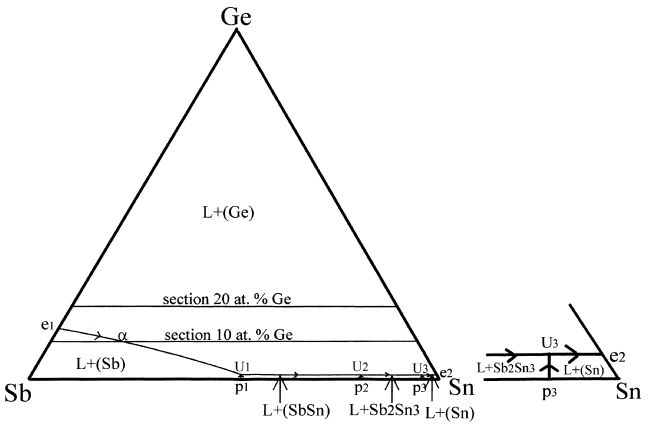

Fig. 6. Polythermal projection of the Ge–Sb–Sn phase diagram [e_i ($i=1,2$), binary eutectics; p_i ($i=1,2,3$), binary peritectic; U_i ($i=1,2,3$), ternary transition peritectic].

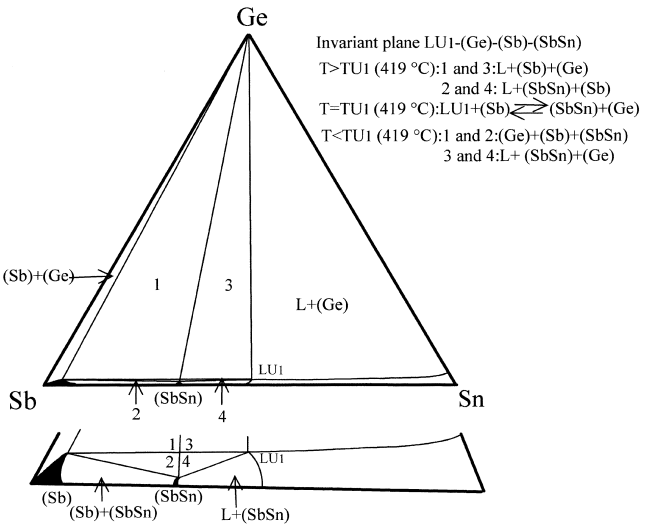

Fig. 7. Isothermal section at 419°C.

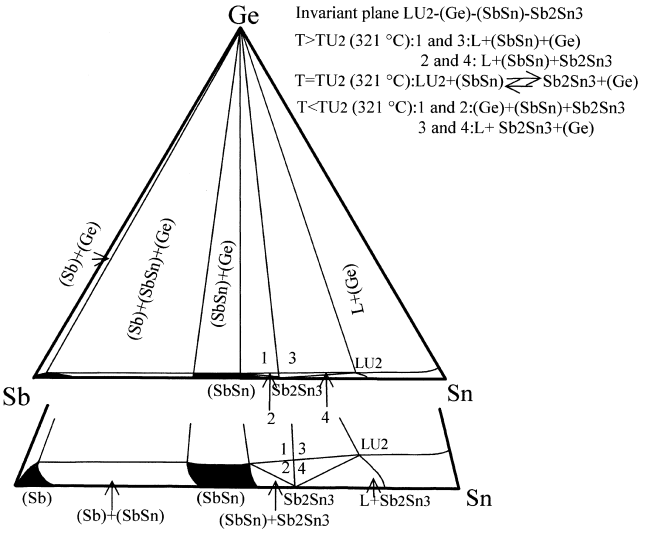

Fig. 8. Isothermal section at 321°C.

- At 419°C the transition peritectic equilibrium U_1, $L+(Sb)\leftrightarrow(Ge)+(SbSn)$. Point a_1 is the mark of the tie line from (Ge) to L_{U_1} in the invariant plane (Ge)–(Sb)–(SbSn)–L_{U_1} (Fig. 7).
- At 321°C the transition peritectic equilibrium U_2, $L+(SbSn)\leftrightarrow(Ge)+Sb_2Sn_3$. Point b_1 is the mark of the tie line from (Ge) to L_{U_2} in the invariant plane (Ge)–(SbSn)–Sb_2Sn_3–L_{U_2} (Fig. 8).
- At 245°C the transition peritectic equilibrium U_3, $L+Sb_2Sn_3\leftrightarrow(Ge)+(Sn)$. Point c_1 is the mark of the minimal tie line from (Ge) to L_{U_3} in the invariant plane (Ge)–Sb_2Sn_3–(Sn)–L_{U_3} (Fig. 9).
- At 243°C the eutectoid equilibrium E, $Sb_2Sn_3\leftrightarrow(Sn)+(SbSn)+(Ge)$.

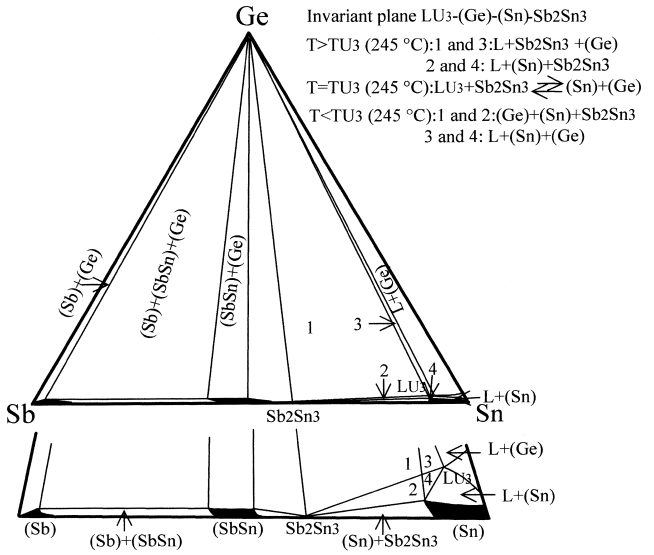

Fig. 9. Isothermal section at 245°C.

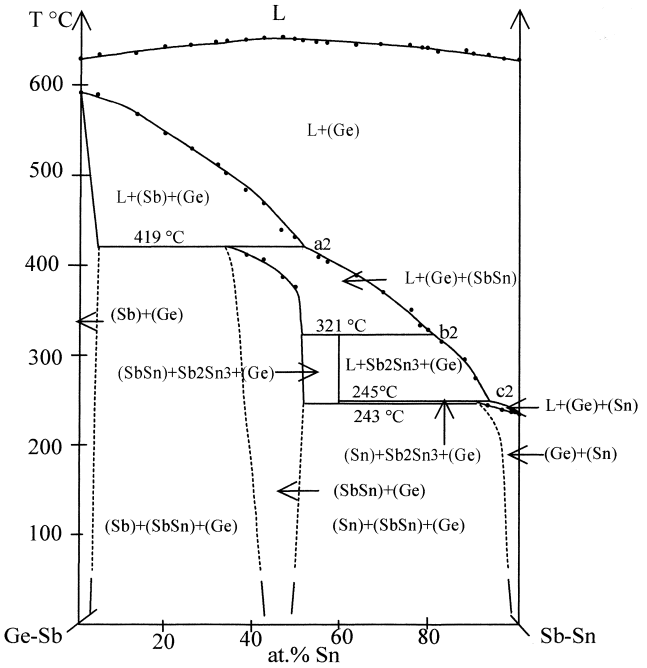

Fig. 10. Vertical section at 20 at.% Ge.

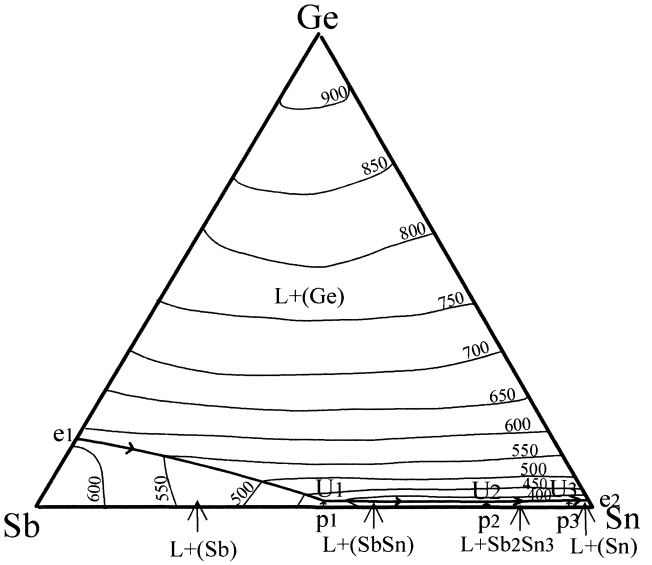

Fig. 11. Liquidus surface.

Table 2
Reaction scheme

Binary system Ge - Sn	Binary system Ge - Sb	Ternary system Ge - Sb - Sn	Binary system Sb - Sn
	592 e_1: l ⇄ (Ge) + (Sb)		
		419 L + (Sb) ⇄ (Ge) + (SbSn) U_1	424 p_1: l+(Sb) ⇄ (SbSn)
		321 L+(SbSn) ⇄ (Ge)+Sb_2Sn_3 U_2	322 p_2: l+(SbSn) ⇄ Sb_2Sn_3
		245 L+Sb_2Sn_3 ⇄ (Ge)+(Sn) U_3	246 p_3: l+Sb_2Sn_3 ⇄ (Sn)
		243 Sb_2Sn_3 ⇄ (Ge)+(Sn)+(SbSn) E	244 e_3: Sb_2Sn_3 ⇄ (SbSn)+(Sn)
231 e_2: l ⇄ (Ge)+ (Sn)			

L+(Ge)+(SbSn) (Ge)+(Sb)+(SbSn)
L+(Ge)+Sb_2Sn_3 (Ge)+(Sb)+Sb_2Sn_3
L+(Ge)+(Sn)
(Ge)+ (Sn)+Sb_2Sn_3
(Ge)+ (Sn)+(SbSn)

4.2. Vertical section at 20 at.% Ge

The vertical section at 20 at.% Ge is shown in Fig. 10. The high temperature part is completely recovered by the primary crystallisation area L+(Ge) (Fig. 10).

The interpretation of the four invariant equilibria is the same as the vertical section 10 at.% Ge.

4.3. Liquidus surface

The polythermal projection is shown in Fig. 11. It has been determined in the entire composition range by investigating the alloys whose compositions were located along sections 30, 40, 50, 60, 80 and 90 at.% Ge (Fig. 4). Five areas of primary crystallisation can be observed. There are limited by monovariant lines (e_1 U_1, U_1 U_2, U_2 U_3, U_3 e_2, p_1 U_1, p_2 U_2 and p_3 U_3).

The reaction scheme showing the successive liquid–solid and solid–solid equilibria found in the Ge–Sb–Sn system is given in Table 2.

5. Conclusion

In this work, the equilibrium phase diagram of the Ge–Sb–Sn ternary system was constructed by using differential thermal analysis (DTA), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). Four ternary invariant reactions have been determined: three transition peritectics and one eutectoid. Moreover, all interpolated liquidus temperatures were used to propose the polythermal projection of the liquidus surface.

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