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PHASE EQUILIBRIA IN THE GeSe$_2$–SnTe SYSTEM

V. Vassilev[*], *L. Aljihmani and V. Parvanova*

University of Chemical Technology and Metallurgy, 8 Kliment Ohridski blvd.,1756 Sofia, Bulgaria

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Abstract

The phase diagram of the system GeSe$_2$–SnTe is studied by means of X-ray diffraction, differential thermal and measurements of the microhardness and the density of the material. The unit-cell parameters of the intermediate phases α-3GeSe$_2\cdot$SnTe (phase A) and GeSe$_2\cdot$2SnTe (phase B) are determined as follows for phase A: a=0.7955 nm, b=0.6969 nm, c=0.6064 nm, α=91.47°, β=85.90°; for phase B: a=0.6063 nm. The phase α-3GeSe$_2\cdot$SnTe melts congruently at 500°C and a polymorphic transition of the phase takes place at $T_{\alpha\leftrightarrow\beta}$=400°C and the phase GeSe$_2\cdot$2SnTe at 385°C decomposes to the peritectoidal reaction at α-3GeSe$_2\cdot$SnTe+SnTe.

Keywords: phase diagram, phase equilibria, unit-cell parameters

Introduction

The system GeSe$_2$–SnTe has not been still investigated in relation with the phase equilibria and with the possibility for forming chalcogenide glasses as well. It is of scientific and practical interest because its building components (GeSe$_2$, SnTe) are typical semiconductors with quite opposite properties.

GeSe$_2$ is a wide gap semiconductor with an energy gap ΔE=2.3 eV [1] and is included in a large group of prospective materials – germanium chalcogenide glasses and crystal compounds $A_2^{I}GeSe_3$, $A_2^{II}GeSe_4$, $A^{II}GeSe_3$, $A_2^{III}GeSe$ [1] and other. GeSe$_2$ melts congruently at 740°C [1], crystallises in a diamond lattice with parameters a=0.694 nm, b=1.298 nm, c=2.213 nm (coordination number z =24) and shows a resistivity $\rho=10^{10}$ Ω m [2]. GeSe$_2$ is good for forming glasses and is used basically for obtaining multicomponent oxychalcogenide, chalcohalide and oxychalcohalide glasses. The latter are used for the production of electrographic coatings, photoresists and X-ray resists, electronic switches and memory cells, ion-selective electrodes, optical components for the IR optics, passive and active components and systems for the fiber and integrated optics, systems for reversible optical data storage with capacity of several billions of bytes per disk.

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[*] Author for correspondence: E-mail: venciv@uctm.edu

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SnTe is the only compound within the system Sn–Te that melts congruently at 790°C. The maximum melting temperature (805.9±0.3°C) corresponds to an alloy containing 50.8 at% Te [3]. SnTe has a NaCl-type structure (a=0.63 nm) and coordination number $z=4$. SnTe is a semimetal with energy gap $\Delta E=0.18$ eV [1] and conductivity 8000–9000 S cm^{-1} in the temperature range 140–800 K [4, 5]. At normal conditions SnTe is always a p-type semiconductor with high hole concentration. This concentration is increased with increasing the Te content and varies from $2\cdot10^{20}$ up to $1.5\cdot10^{21}$ cm^{-1} [4]. The maximum mobility measured at 300 K is $\mu_p \cong 1\cdot10^3$ cm^2 V^{-1} s^{-1} [1]. Monocrystal and polycrystal layers of SnTe [6, 7] are used for fabrication of epitaxial heterostructures $Pb_{1-x}Sn_xTe$ [8, 9], SnTe–Cd(S,Se) [6] and others on substrates of PbTe, Si, $A^{II}B^{IV}$, $A^{III}B^{V}$ and others, which are used in the optoelectronics.

Detailed knowledge about the phase diagram of the system $GeSe_2$–SnTe with its phasic fields, non-variant equilibria and intermediate phases (compounds) is critical for definition of the area of glass formation and the stability of the chalcogenide glasses in multicomponent systems with formula $(GeSe_2)_x(SnTe)_yA_zB_{100-x-y-z}$, where *A, B*=chalcogenide, chalcogenide or oxide resp.($0\leq z<100$).

The main goal; of this work is the definition of the phase equilibria in the system $GeSe_2$–SnTe by the means of the conventional differential thermal analysis (DTA) and X-ray powder difraction (XRD) [10–12] and building of its phase diagram in order: 1 – to investigate the properties of the solid solutions and intermediate phases (if such exist) and 2 – to estimate the feasibility of obtaining multicomponent glasses making use of the pair $GeSe_2$–SnTe and to determine the area of glass formation in systems with formula $GeSe_2$–SnTe–A, where *A*=chalcogenide, halide or oxide.

Experimental

The system $(GeSe_2)_{100-x}(SnTe)_x$ was studied over 17 compositions within the concentration range 0–100 mol% SnTe. The compositions were prepared through a direct mono-temperature synthesis [1] in evacuated and sealed quartz ampoules. For the synthesis of the compositions rich of SnTe the internal surface of the ampoules was preliminary covered with graphite. The maximum temperature and the duration of the synthesis were 1050°C and 1 h resp. A vibrational stirring of the melt was applied. As a final step the melts were homogenized at 350°C for 3 h.

The phase transformations in the samples were investigated by means of several methods as follows: DTA (equipment of the system Paulik–Paulik–Erdey made by MOM Hungary) at heating rate of 10°C min^{-1}; reference substance (calcinated γ-Al_2O_3) and the studied substance weighed 0.3 g and was placed in evacuated and sealed quartz ampoules at pressure equal to 0.1 Pa; XRD (equipment TUR-M61) with CuK_α irradiation and Ni-filter, θ=5–40°; microstructure analysis (microscope MIM-7). Measurements of the microhardness (instrument PMT-1 at loading 10 and 20 g) and of the density of the material (hydrostatic technique with toluene as reference liquid) were carried out as well.

Results

The data obtained from the X-ray diffraction analyses are summarized in a schematic diagram (Fig. 1). They are in a complete agreement with the results reported previously in [13, 14].

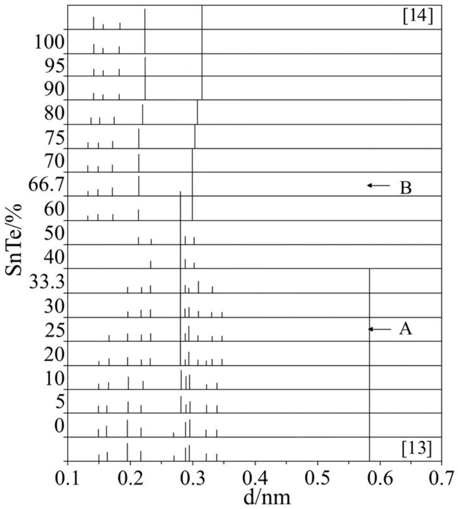

Fig. 1 Schematic diagram of the X-ray diffraction lines for the system $GeSe_2$–SnTe

Within the range of concentrations 0–100 mol% SnTe new lines are observed, different from those of $GeSe_2$ and SnTe. They are of maximum intensity and best pronounced for compositions containing 25 and 66.7 mol% SnTe resp. These data suggest the existence of two intermediate phases with compositions $3GeSe_2\cdot SnTe$ (phase A) and $GeSe_2\cdot 2SnTe$ (phase B).

The unit-cell parameters of the phases α-$3GeSe_2\cdot SnTe$ (phase A) and $GeSe_2\cdot 2SnTe$ (phase B) are determined by the Ito's method [15] as follows: for phase A: a=0.7955 nm, b=0.6969 nm, c=0.6064 nm, α=91.47°; for phase B: a=0.6063 nm.

The indexing data of these phases are given in Tables 1 and 2, respectively.

From the heating curves and the observed endoeffects of the curves the maximum temperatures of the different phase transformations were determined. They are given in Table 3.

The effects observed in thermal curves are endothermal. The thermoeffects from the 1st up to 6th column (including) are of relatively small area but well pronounced. An exception are the effects for the composition containing 25.0 mol% SnTe (at 400 and 450°C) and 66.7 mol% SnTe (at 385°C). These peaks are of significantly greater area and probably correspond to non-variant points or to phase transitions. The thermoeffects represented in columns 3–6 (including) of Table 3 are at equal temperature i.e. they are related with different non-variant equilibria or to phase transitions.

Table 1 Data from indexing of phase α-$3GeSe_2{\cdot}SnTe$

D_{exp}/Å	$(I/I_0)100$/%	$Q=1/d^2$	$h\,k\,l$	D_{calc}/Å
7.9647	4	0.0158	1 0 0	7.955
6.7230	4	0.0221	0 1 0	6.711
5.8369	100	0.0294	0 0 1	5.831
3.4314	11	0.0849	2 1 0	3.422
3.3532	13	0.0889	0 2 0	3.355
3.2665	7	0.0937	2 0 1, $\bar{2}$ 0 1	3.286
3.0874	26	0.1042	1 2 0, 1 $\bar{2}$ 0	3.092
2.9250	43	0.1169	0 0 2	2.916
2.8860	34	0.1201	0 2 1	2.877
2.7799	91	0.1294	1 2 $\bar{1}$	2.759
2.5873	5	0.1494	2 2 0	2.565
2.3328	12	0.1838	2 2 1	2.331
2.2005	9	0.2065	$\bar{2}$ 1 2, 2 1 2	2.205
2.1741	14	0.2116	0 2 2	2.173
2.1082	5	0.2250	0 3 $\bar{1}$	2.107
1.9625	19	0.2597	3 0 2, $\bar{3}$ 0 2	1.962
1.9110	7	0.2738	$\bar{2}$ 2 2, 2 2 2	1.907
1.7997	11	0.3087	0 3 $\bar{2}$	1.797
1.7559	5	0.3244	0 3 2	1.753
1.7251	8	0.3360	1 3 2	1.712
1.6505	7	0.3671	4 0 $\bar{2}$	1.643
1.6153	12	0.3833	0 4 $\bar{1}$	1.623
1.5623	6	0.4097	2 $\bar{2}$ 3	1.564
1.5199	5	0.4329	3 1 3	1.520
1.4750	7	0.4596	0 4 $\bar{2}$	1.471
1.4188	9	0.4967	0 1 4	1.417
1.4097	9	0.5032	3 2 3	1.409

The high-temperature effects, corresponding to the liquidus line (col. 7), are well pronounced (sharp peaks) and of large area.

The results obtained at measuring the microhardness, *HV* and the density, *d*, are depicted in Figs 2 and 3 (*HV* is measured with accuracy ±3% and $d-\pm2\%$).

In each of the concentration ranges 0–25, 25.0–66.7 and 90–100 mol% SnTe two different values of *HV* are measured that is characteristic for two-phase samples with compositions within the mentioned ranges and is suggesting the existence of two intermediate phases, dividing the phase diagram into three two-phase regions. Two of the

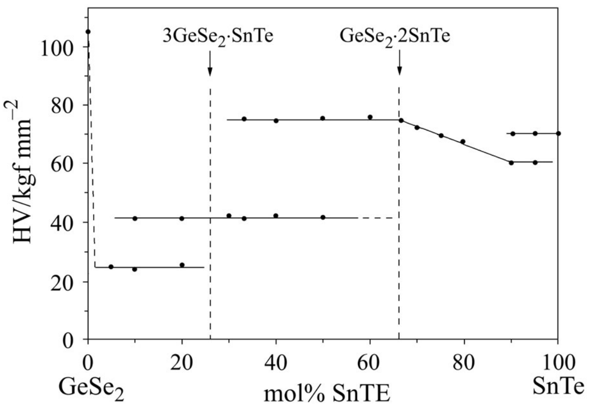

Fig. 2 Dependence HV(x) for samples of the system $GeSe_2$–SnTe

values of *HV* have to be related to the start-up components $GeSe_2$ and SnTe, that is in agreement with communications in [16, 17]. The other two correspond to intermediate phases – $3GeSe_2 \cdot SnTe$ and $GeSe_2 \cdot 2SnTe$. The microhardness of the phases $3GeSe_2 \cdot SnTe$ and $GeSe_2 \cdot 2SnTe$ is 40 and 60–75 kgf mm^{-2}, respectively (Fig. 2).

The density (d) of the samples from the $GeSe_2$–SnTe system varies in the limits 4.2–6.5 g cm^{-3} – Fig. 3. Within the concentration limits 0–100 mol% SnTe the additive law is not followed suggesting that complex physico-chemical processes take place. Probably, the intermediate phases $3GeSe_2 \cdot SnTe$ and $GeSe_2 \cdot 2SnTe$ are obtained as a result of these processes.

Table 2 Data from indexing of low-temperature phase $GeSe_2 \cdot 2SnTe$

d_{exp}/Å	$(I/I_0)100$/%	$Q=1/d^2$	$h\ k\ l$	D_{calc}/Å
6.063	5	0.2720	1 0 0	6.063
4.287	4	0.0544	1 1 0	4.288
3.510	4	0.0812	1 1 1	3.501
3.033	100	0.1087	2 0 0	3.032
2.710	5	0.1362	2 1 0	2.712
2.472	3	0.1636	2 1 1	2.475
2.146	73	0.2171	2 2 0	2.144
2.020	3	0.2451	3 1 0	2.021
1.830	3	0.2986	3 1 1	1.828
1.752	20	0.5707	2 2 2	1.750
1.515	13	0.4357	4 0 0	1.516
1.426	4	0.4918	4 1 1	1.429
1.357	24	0.5431	4 2 0	1.356

Table 3 Endothermal effects of the studied system $GeSe_2$–SnTe

SnTe/mol%	Temperatures/°C						
0							710
5	275					493	685
10	395					495	660
20				398		495	600
25				400		495	555
30				400	475		
33.3				402	475	501	501
40				398	475		475
5				400	475		592
60			388				628
66.7			385				660
70			390				682
75			386				705
80		585					732
90	192	698					
95	125	752					793
100							810

Discussion

In the concentration ranges 66.7–90.0 mol% SnTe a shift of the lines is observed in direction toward increased inter-plane distance *d*. This is a proof for the existence of a field of solid solutions based on $GeSe_2 \cdot 2SnTe$ (Fig. 1). The intermediate phase $3GeSe_2 \cdot SnTe$ and the start-up components $GeSe_2$ and SnTe do not possess fields of homogeneity or if such exist they are in very narrow concentration ranges.

In each of the ranges 0–25, 25.0–66.7 and 90–100 mol% SnTe lines of two phases exist simultaneously as follows: $GeSe_2+3GeSe_2 \cdot SnTe$, $3GeSe_2 \cdot SnTe+GeSe_2 \cdot 2SnTe$ and $GeSe_2 \cdot 2SnTe+SnTe$, respectively. Thus, these concentration ranges correspond to two-phase fields in the phase diagram of the system $GeSe_2$–SnTe.

The gradual variation of the dependence $HV(x)$ in the ranges $0.0 \leq x < 5$ and $66.7 \leq x < 100.0$ mol% SnTe suggests the presence of solid solutions based on $GeSe_2$ and $GeSe_2 \cdot 2SnTe$ (Fig. 2).

The observed specific variation of the dependence $d(x)$ at $x=25$ and $x=66.7$ mol% SnTe is related to the existence of the intermediate phases $3GeSe_2 \cdot SnTe$ and $GeSe_2 \cdot 2SnTe$ (Fig. 3).

On the basis of the data from DTA (differential thermal analysis), X-ray diffraction analysis and from measuring the microhardness and the density the phase diagram of the system $GeSe_2$–SnTe is built-up (Fig. 4). This diagram is of a complex structure with specific features as follows:

1. Three non-variant equilibria exist: peritectic (with coordinates of the peritectic point $x \cong 33.3$ mol% SnTe and T=500°C).

$$\alpha\text{-GeSe}_2\text{+L} \xleftarrow{500\pm 10℃} 3\text{GeSe}_2\cdot\text{SnTe},$$

eutectic equilibrium (x=40 and T=475°C)

$$\text{L} \xleftarrow{475\pm 10℃} 3\text{GeSe}_2\cdot\text{SnTe+}\alpha\text{-SnTe},$$

peritectoidal equilibrium (x=75 and T=385°C)

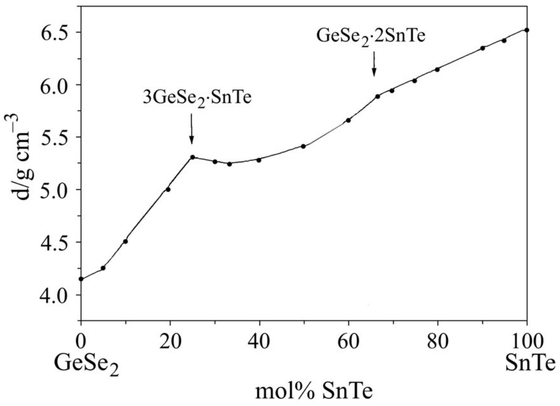

Fig. 3 Dependence d(x) for samples of the system GeSe$_2$–SnTe

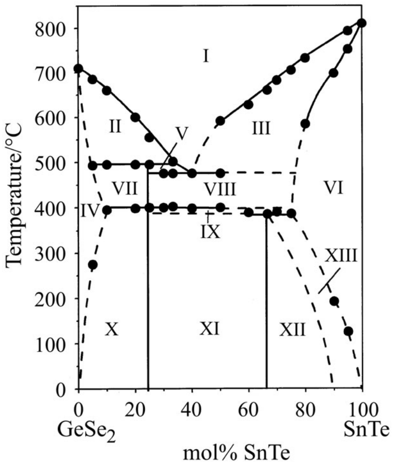

Fig. 4 Phase diagram of the system GeSe–SnTe. I – Liquid (melt-L); II – L+α-GeSe$_2$; III – L+α-SnTe; IV – α-SnTe (solid solution based on SnTe); V – β3GeSe$_2$·SnTe+L; VI – αGeSe$_2$ (solid solution based on GeSe$_2$); VII – αGeSe$_2$+α-3GeSe$_2$·SnTe; VIII – β3GeSe$_2$·SnTe+α-SnTe; IX – α3GeSe$_2$·SnTe+α-SnTe; X – αGeSe$_2$+α-3GeSe$_2$·SnTe; XI – α3GeSe$_2$·SnTe+α-GeSe$_2$·2SnTe; XII – αGeSe$_2$·2SnTe (solid solution based on α-GeSe$_2$·2SnTe); XIII – αGeSe$_2$·2SnTe+α-SnTe

$$3GeSe_2{\cdot}SnTe+\alpha\text{-}SnTe \xleftarrow{385\pm 10°C} GeSe_2{\cdot}2SnTe.$$

2. As a result of different physico-chemical interactions two intermediate phases are obtained. The one of them melts incongruently at 500°C, undergoes a polymorphic transition at 400°C and has a constant composition $3GeSe_2{\cdot}SnTe$ (A-phase). The other phase dissociates when heated through a peritectoidal reaction of the phases A+α-SnTe at 385°C and has a variable composition $GeSe_2{\cdot}(2+x)SnTe$ where x=0–7 (B-phase). Phase transition of the phase A is proved by the help of DTA and XRD methods described by Arai *et al.* [18] and Hashimoto *et al.* [19].

3. The existence of fields of limited solid solutions based on $GeSe_2$ and SnTe is observed. At elevated temperatures the solubility of SnTe in $GeSe_2$ and that of $GeSe_2$ in SnTe increase with maximum values (resp.): 400°C (10 mol% SnTe) and 385°C (appr. 25 mol% $GeSe_2$). At room temperature shift of the lines of $GeSe_2$ and SnTe is not observed i.e. at such temperature $GeSe_2$ (SnTe) does not dissolve SnTe ($GeSe_2$).

Conclusions

By means of four independent technics the phase diagram of the system $GeSe_2$–SnTe is built-up. As a result of complex physico-chemical processes in solid and liquid state two intermediate phases, respectively, peritectic and peritectoidal reactions at 500 and at 385°C: phase A with a composition $3GeSe_2{\cdot}SnTe$ and phase B with a composition $GeSe_2{\cdot}(2+x)SnTe$ (x=0–7). In the system exists 13 phasic fields. Four of the fields are mono-phasic and the rest of them two-phasic.

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