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PHASE EQUILIBRIA IN THE $GeSe_2$–SnSe SYSTEM

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The phase diagram of the system $GeSe_2$–SnSe is studied by means of X-ray diffraction, differential thermal analysis and measurements of the density and the microhardness of the material. There are no intermediate compounds in it, as well as regions of range of solid solutions at room temperature on the base of $GeSe_2$ and SnSe. There are two non-variant equilibria in the system: eutectic (where T_e=530±5ºC and x_e= 40 mol% SnSe) and metaeutectic (where T_m=550±5ºC and x_m=98 mol% SnSe).

Keywords: *eutectic and metaeutectic equilibria, phase diagram, phase equilibria*

Introduction

The system $GeSe_2$–SnSe 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 ($GeSe_2$ and SnSe) are typical semiconductors with quite opposite properties.

$GeSe_2$ is a wide gap semiconductor with an energy gap E_g=2.3 eV and specific resistivity $\rho=10^{10}$ Ω m [1].

There are two compounds in the system Ge–Se: GeSe and $GeSe_2$. The compound GeSe is obtained following a peritectic reaction at 670°C, as at 620°C a thermal effect is observed evidencing a phase transition in GeSe [2].

$GeSe_2$ melts congruently at 740°C. It is established that $GeSe_2$ forms an eutecticum with the selenium with 92 mol% Se [2]. The compounds Ge_2Se_3 and Ge_3Se_4 [3] were not observed in the system. $GeSe_2$ crystallizes in several polymorphic states: α-$GeSe_2$ – a diamond lattice with unit-cell parameters a=0.695 nm, b=1.222 nm, c=2.304 nm (coordination number z=24) [3]; β-$GeSe_2$ – in a monoclinic lattice with unit-cell parameters: a=0.703 nm, b=1.684 nm, c=1.182 nm (coordination number z=16, α=90°74') [4] and γ-$GeSe_2$ – in a tetragonal lattice with unit-cell parameters a= 0.571 nm, c=0.966 nm [5]. It is present in the composition of a number of crystalline compounds $A^{I}_{2}GeSe_{3}$, $A^{II}_{2}GeSe_{4}$, $A^{II}GeSe_3$ and $A^{III}_{2}GeSe$ and chalcogenide glasses as a glass-forming element [6]. $GeSe_2$ 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 electrografic 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 [7–9].

SnSe is a semiconductor with an energy gap E_g=1.0 eV [10] and specific resistance $\rho=10^{3}$–10^{-1} Ω m [1]. SnSe is a p-type semiconductor. When alloying SnSe with Sb a material of n-type is obtained. $SnSe_2$ is a n-type semiconductor [11].

Two compounds exist in the system Sn–Se – SnSe and $SnSe_2$. SnSe melts congruently at 870°C. Crystallizes in a diamond lattice with parameters a=0.433 nm, b=0.398 nm and c=1.118 nm [1]. It is assumed that one more rhomboid polymorphic form exists – β-SnSe (type structure TlJ) – stable over 534°C [12].

$SnSe_2$ melts congruently at 656°C. It has a CdJ_2-type lattice with parameters a=0.381 nm, b=0.614 nm and c=0.161 nm and exists in several polymorphic states [1]. The eutectic point between SnSe and $SnSe_2$ is obtained at 625°C and 61 mol% Se.

SnSe and $SnSe_2$ show interesting electrical and optical properties. P–N structures are elaborated on the basis of SnSe [6]. In the opinion of Vyas *et al.* [13], SnSe finds application as a material in optoelectronics, etc. SnSe and $SnSe_2$ can be used also in the production of semiconductor photovoltaic devices [11, 13].

In order to determine the ranges of glass formation and the stability of chalcogenide glasses in multicomponent systems of the $(GeSe_2)_x(SnSe)_yA_z$-type where A=chalcogenide, halogenide or oxide, it is necessary to know the phase diagram of the system $GeSe_2$–SnSe in the first place.

The main goal of this work is the definition of the phase equilibria in the system $GeSe_2$–SnSe by the help of differential thermal analysis (DTA [14]), X-ray phase analys (XRD [14, 15]) and data from measurements of the microhardness (HV) and the density (d) of the samples [16] and building of its phase diagram.

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Experimental

$GeSe_2$ and SnSe previously obtained by a direct monotemperature synthesis were used as initial materials for the synthesis of the investigated materials. The starting elements were with purity: Ge and Se – 5N, Sn – 3N5, respectively.

The system $(GeSe_2)_{100-x}(SnSe)_x$ was studied with 21 compositions within the concentration range 0–100 mol% SnSe. The compositions were prepared also through a direct mono-temperature synthesis [6] in evacuated and sealed quartz ampoules. During the synthesis of the compounds rich in SnSe, the internal surface of the ampoules was preliminary covered with graphite. The maximum temperature of the synthesis was 950°C with a duration of 2 h, including vibrational stirring of the melt. The synthesis ends with homogenizing temperature rise at 900°C throughout one hour with subsequent cooling of the melt in a furnace switched off regime.

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 16°C min^{-1}; reference substance (calcinated α-Al_2O_3) and the studied substain weighed 0.5 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-3 at loading 5, 10 and 20 g) and of the density of the material (hydrostatic technique with toluene as reference liquid) were carried out as well.

Results and discussion

The data obtained from the X-ray diffraction analyses are summarized in a schematic diagram (Fig. 1).

Considering the thermal curves obtained in a heating regime we determined the temperatures of the different phase transitions in the samples. The results obtained are summarized in Table 1. The typical thermal curves are shown in Fig. 2.

The results of measuring the microhardness HV and the density *d* are shown in Figs 3 and 4, respectively.

The $GeSe_2$ microhardness is 100–200 kgf mm^{-2} [17], and no information was found in literature on the HV of SnSe.

The values of *d* obtained for the system $GeSe_2$–SnSe samples fall within the values of the density corresponding to the starting components $GeSe_2$ ($d_{amorph.}$= 4.13 g cm^{-3}; $d_{cryst.}$= 4.5 g cm^{-3} [17]) and SnSe (d=6.18 g cm^{-3} [18]).

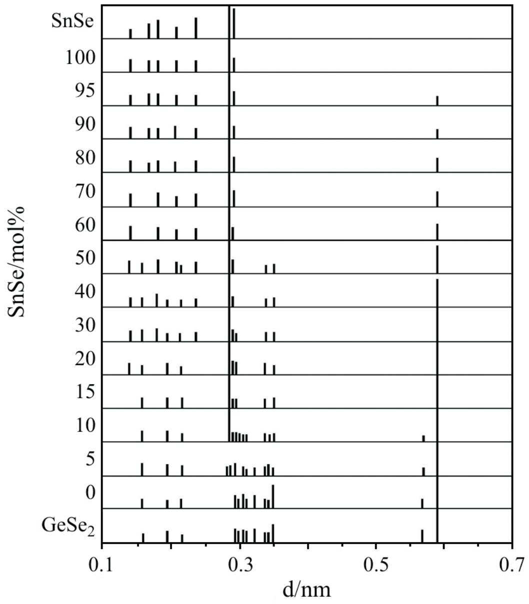

Fig. 1 Schematic diagram of the X-ray diffraction lines for the system $GeSe_2$–SnSe

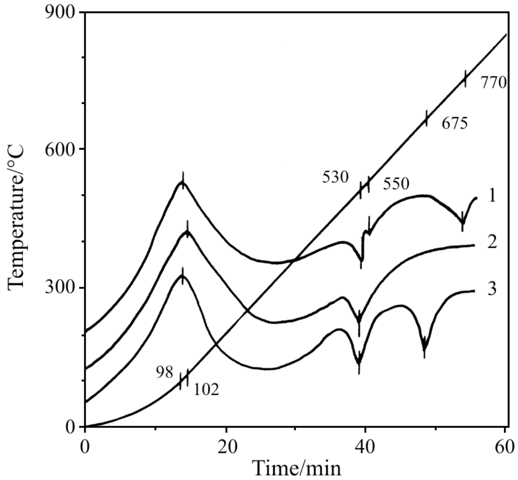

Fig. 2 Thermoeffects of samples of the system $GeSe_2$–SnSe: 1 – $(GeSe_2)_{90}(SnSe)_{10}$, 2 – $(GeSe_2)_{60}(SnSe)_{40}$ and 3 – $(GeSe_2)_{20}(SnSe)_{80}$

The schematic diagrams of X-ray diffraction lines of the starting components $GeSe_2$ and SnSe are identical to those of $GeSe_2$ [19] and SnSe [20]. No new lines, different from those of $GeSe_2$ and SnSe, are observed within the concentration region 0/100 mol% SnSe, i.e. no intermediate compounds exist in the system. The lines of $GeSe_2$ and SnSe exist simultaneously in within this concentration region, i.e. all samples located between the starting components $GeSe_2$ and SnSe, are two-phasic.

No shifting of the lines of the starting components $GeSe_2$ and SnSe is observed, i.e. there are no data that any range of solid solutions exist.

Table 1 Thermoeffects for samples of the system $GeSe_2$–SnSe

Compound/ mol%		Exo-effects/°C		Endo-effects/°C		
SnSe	$GeSe_2$	1	2	3	4	5
0	100	100				740
5	95	102	530			685
10	90	98	530			655
15	85	97	530			
20	80		530			592
25	75		532			585
30	70	102				555
33.3	66.7	98				550
40	60	102	530			
45	55	97				555
50	50					557
55	45	100	530			565
60	40	95				590
66.7	33.3	95		545		
70	30	100		550		680
75	25	95				738
80	20	98	530	550		767
90	10	98	530	550		800
95	5		532	550	642	825
98	2			550		860
100	0				555	870

For the purposes of DTA we used samples obtained immediately after the synthesis of the respective alloys. A low-temperature exo-effect is observed on the derivatograms at approximately 100ºC with maximum area where the composition corresponds to 100% $GeSe_2$ (column 1, Table 1). The area of this exo-effect lightly reduces when the content of SnSe is increased in the exo-effect is most likely connected with crystallization of the amorphous phase in the synthesized alloy. When the second compound SnSe is increased (crystalline substance), the relative share of the amorphous (glassy) phase reduces. The exo-ef-

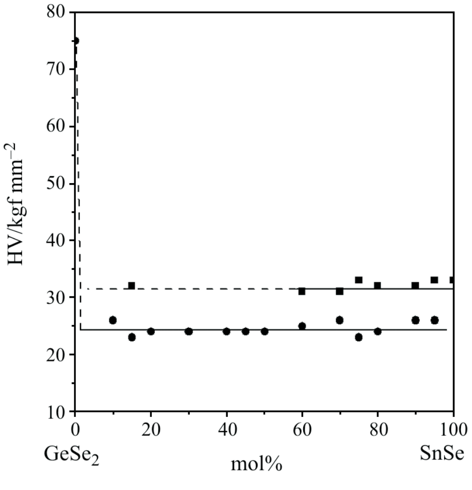

Fig. 3 Dependence of HV(x) for samples of the system $GeSe_2$–SnSe

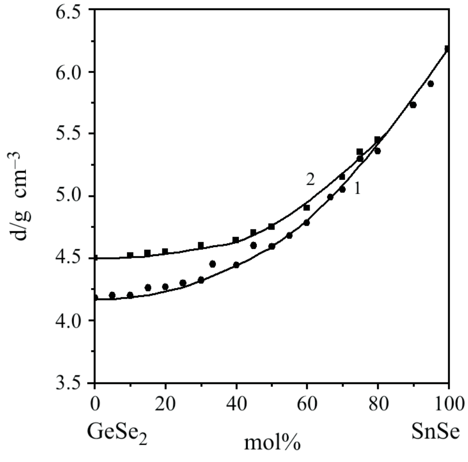

Fig. 4 Dependence between density $d(x)$ and composition of samples of the system $GeSe_2$–SnSe: 1 – amorphous phase, 2 – crystal phase (after additional anneal at T=400°C and t=2 h)

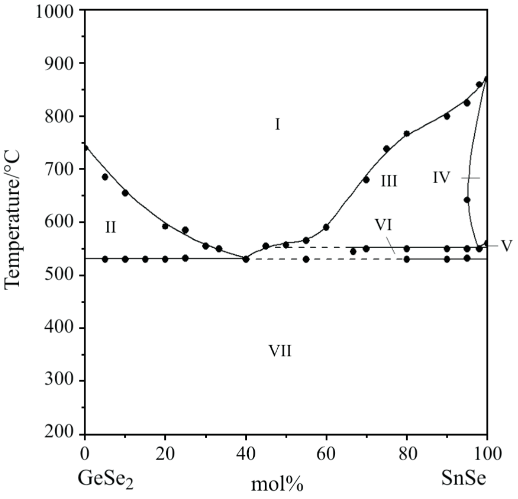

Fig. 5 Phase diagram of the system GeSe$_2$–SnSe: I – liquid (melt-L), II – GeSe$_2$+L, III – L+β-SnSe, IV – β-SnSe, V – β-SnSe+α-SnSe, VI – L+α-SnSe and VII – GeSe$_2$+α-SnSe

fects' maximums are rounded which is not typical of a classical transition amorphous→crystalline state (in the case of 'pure' crystallization the exo-effect is acute, well outlined and takes a short time interval). It is not reasonable to identify these effects with a solid-state transformation α↔β, because the literature provides no information on GeSe$_2$ and SnSe undergoing such a transformation at 100°C, on the one hand, and, on the other, this type of transformations are endothermal as a rule. Therefore, this case concerns crystallization of the amorphous component of the alloy. The composition of the amorphous component most probably is based on Se, obtained by partial decomposition of GeSe$_2$ in accordance with the following reaction GeSe$_2$=GeSe+Se. It is logical to assume that in this case an alloy rich in Se is crystallized, for example T_{cr} of GeSe$_9$ is 100°C [17]. After annealing the samples at 400°C throughout two hours quenched in a mixture H$_2$O-ice, this exo-effect practically disappears.

The thermoeffects observed (columns 2 and 3, Table 1) do not depend on the alloys' composition and are most likely connected with non-variant equilibria.

The thermoeffects (column 5, Fig. 2) are well outlined and depend on the composition, i.e. they can be referred to the liquidus line of this system.

The area of the endo-effects (column 2, Fig. 2) decreases on the left and on the right of the point with composition 40 mol% SnSe, which point should be interpreted as non-variant, and most probably eutectic.

Two HV values were measured within the concentration region from 0 to 100 mol% SnSe of most of the studied compositions, which is typical of two-phasic samples – Fig. 3.

We measured the density immediately after the synthesis of the alloys (curve 1, Fig. 4) and after crystallization (curve 2, Fig. 4). The dependencies $d_{\text{amorph.}}$ (x) and $d_{\text{cryst.}}$ (x) coincide with the concentration region 60–100 mol% and within the frames of preciseness they could be interpreted as a straight line. When increasing the content of GeSe$_2$ in the alloys (from 0 to 60 mol% SnSe) the two dependencies differ from one another. This is related to the increase of probability of obtaining amorphous (glassy) phase.

The dependency $d_{\text{cryst.}}$ (x) is not linear which evidences that in solid-state there is certain interaction between the two starting compounds, i.e. the character of the two-phasic samples is not one of a mechanical mix.

Based on the results of the DTA, the X-ray diffraction analysis and the microhardness and density measurements, the phase diagram of the system GeSe$_2$–SnSe (Fig. 5) was constructed.

The phase diagram has the following characteristics:

There are two non-variant equilibria:

- eutectic: $L\xrightarrow{530\pm5^\circ C}GeSe_2+\alpha\text{-SnSe}$ (T_e=530±5ºC; x_e=40 mol% SnSe);
- metaeutectic: $\beta\text{-SnSe}\xrightarrow{550\pm5^\circ C}\alpha\text{-SnSe}+L$ (T_m=550±5ºC; x_m=98 mol% SnSe).

No intermediate compound is observed on the macrodiagram, as well as regions of range of solid solutions on the base of GeSe$_2$ and SnSe.

Phase transition $T_{\alpha\leftrightarrow\beta}$=555°C of the compound SnSe is proved by the help of DTA method described by Abdel-Aziz [15].

Conclusions

This is the first time that the phase diagram of the system GeSe$_2$–SnSe was constructed, with the following characteristics: *i*) two non-variant equilibria are effected: eutectic (T_e=530±5°C) and metaeutectic (T_m=550±5°C); *ii*) there is not any intermediate compounds and regions of border solid solutions; *iii*) as a result of the complex physico-chemical processes in solid and liquid state 7-phasic fields are formed, two of which are mono-phasic (I and IV), and the rest are two-phasic.

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