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Phase equilibria in the $\mathrm{GeSe_2}$–PbTe system

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Abstract

The phase diagram of the $\mathrm{GeSe_2}$–PbTe system is studied by means of X-ray diffraction, differential thermal analysis and measurements of the microhardness and the density of the material. The unit-cell parameters of the intermediate phase $\alpha\text{-}\mathrm{GeSe_2}\cdot(2-x)\mathrm{PbTe}$, ($x = 0/1$) were determined: $a = 6.200$ Å, $b = 3.807$ Å, and $c = 3.645$ Å, $\alpha = 106.47°$, $\beta = 99.85°$, and $\gamma = 87.22°$. The intermediate phase $\alpha\text{-}\mathrm{GeSe_2}\cdot\mathrm{PbTe}$ receives a peritectic reaction at 425 °C. This phase has variable composition $\mathrm{GeSe_2}\cdot(2-x)\mathrm{PbTe}$ ($x = 0/1$), it melts congruently at 425 °C and stands polymorphic transition at $T_{\alpha\leftrightarrow\beta} = 325$ °C, which dependents of the composition (x).

The existence of a narrow regions of solid solutions based on PbTe is supposed.

Keywords: Phase equilibria; Phase diagram; Unit-cell parameters

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1. Introduction

The system $\mathrm{GeSe_2}$–PbTe is interest in scientific and practical attitude, because its building compounds are typical semiconductors with quite opposite properties. In interaction of $\mathrm{GeSe_2}$ with PbTe new phases with interesting properties could be received, which are applicable in the solid-state electronics. The binary system $\mathrm{GeSe_2}$–PbTe may serve as a base for ternary system of the $\mathrm{GeSe_2}$–PbTe–$\mathrm{Me}_m\mathrm{Ch}_n$ (Me = Ag, Sb, As, Bi and all.; Ch = S, Se and Te) kind. In the last mentioned exists an area of new multicomponent glasses based on $\mathrm{GeSe_2}$.

Some data exist in the literature, according to which the phase diagram $\mathrm{GeSe_2}$–PbTe is of eutectic type with narrow area of solubility on the bases of the initial components [1]. In our opinion, in the system $\mathrm{GeSe_2}$–PbTe might exist intermediate phases, since there are such in the binary systems of the $\mathrm{GeSe_2}\cdot(3-x)\mathrm{As_2Se_3}$ ($0 \le x \le 2/3$) [2], $3\mathrm{GeSe_2}\cdot\mathrm{SnTe}$ [3], $\mathrm{GeSe_2}\cdot(2-x)\mathrm{SnTe}$ ($0 \le x \le 7$) [3] kind and all.

$\mathrm{GeSe_2}$ is a wide gap semiconductor with an energy gap $E_\mathrm{g} = 2.2$ eV for amorphous $\mathrm{GeSe_2}$ and $E_\mathrm{g} = 2.3$ eV for crystalline $\mathrm{GeSe_2}$ [4].

There are two compounds in the system Ge–Se: GeSe and $\mathrm{GeSe_2}$. 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 [5].

$\mathrm{GeSe_2}$ melts congruently at 740 °C. It is established that $\mathrm{GeSe_2}$ forms a eutecticum with the selenium with 92 mol% Se [5]. The compounds $\mathrm{Ge_2Se_3}$ and $\mathrm{Ge_3Se_4}$ [6] were not observed in the system. $\mathrm{GeSe_2}$ crystallizes in several polymorphic states: $\alpha\text{-}\mathrm{GeSe_2}$—a rhomboid lattice with unit-cell parameters $a = 6.950$ Å, $b = 12.220$ Å, and $c = 23.040$ Å (coordination number $z = 24$) [6]; $\beta\text{-}\mathrm{GeSe_2}$—in a monoclinic lattice with unit-cell parameters: $a = 7.030$ Å, $b = 16.840$ Å, $c = 11.820$ Å, and $\alpha = 90°74'$ (coordination number $z = 16$) [6] and $\gamma\text{-}\mathrm{GeSe_2}$—in a tetragonal lattice with unit-cell parameters $a = 5.731$ Å, and $c = 9.691$ Å [7]. It is present in the composition of a number of crystalline compounds $\mathrm{A_2^{I}GeSe_3}$, $\mathrm{A_2^{II}GeSe_4}$, $\mathrm{A^{II}GeSe_3}$ and $\mathrm{A_2^{III}GeSe}$ [8] and chalcogenide glasses as a glass-forming element [9,10]. $\mathrm{GeSe_2}$ 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 [11,12].

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PbTe is a narrow-gap semiconductor with an energy gap, determined at room temperature at the end of the optical absorption, $E_g = 0.32$ eV at 300 K [8,13] and it is sensitive in the 3–5 μm spectral region (middle infrared) [14].

PbTe is the only compound in the Pb–Te system. It melts congruently at $T = 923.9$ °C and has narrow area of homogeneity at about 50 mol% Te [8]. It forms an eutectic with Te, corresponding on a composition 85.5 mol% Te, and temperature of melting of 405 °C [6]. PbTe crystallizes in a cubic mural-centred lattice, type NaCl, with parameter $a = 6.460$ Å [15,16] (coordination number $z = 4$ [17]). It obtained by a direct monotemperature synthesis. It has highest mobility of the charge carries from all lead chalcogenides – 1400 and 1100 $cm^2\ V^{-1}\ s^{-1}$ at 300 K – for the electrons and the holls, respectively [8].

PbTe is a kind of lead chalcogenide, and has found extensive usefulness in infrared (IR) optoelectronics for manufacturing IR lasers and detectors. Presently, it tends to dominate the multilayer material selection for the design of filters operating in the mid- to long-infrared wavelengths both at room and reduced temperatures. The combination of the high refractive index, together with the advantages of the PbTe semiconductor absorption edge, all assist in the production of efficient multilayer designs [15]. PbTe semiconductor is of interest due to its potential application as a thermoelectric material and a semiconductor laser in the 3–30 μm range [16].

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

The main goal of this work is the definition of the phase equilibria in the system $GeSe_2$–PbTe by the help of differential thermal analysis (DTA [18]), X-ray phase analysis (XRD [18,19]) and data from measurements of the microhardness (HV) and the density (d) of the samples [20] and building of its phase diagram.

2. Experimental

$GeSe_2$ and PbTe 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, Se and Te–5N, Pb–3N8, respectively.

The system $(GeSe_2)_{100-x}(PbTe)_x$ was studied with 22 compositions within the concentration range 0–100 mol% PbTe. The compositions were prepared also through a direct monotemperature synthesis [8] in evacuated and sealed quartz ampoules. The maximum temperature of the synthesis was 970 °C with a duration of 1.5 h, including vibrational stirring of the melt. During the synthesis of the compounds rich in PbTe, the internal surface of the ampoules was preliminary covered with graphite. The synthesis ends with homogenizing temperature rise at 300 °C throughout 1 month with subsequent cooling of the melt in a furnace switched off regime.

The phase transformation in the samples was investigated by means of several methods as follows: DTA (using equipment of the type F. Paulik–J. Paulik–L. Erdey made by MOM, Hungary, accuracy ±5 °C) at the heating rate of 16 °C min^{-1}, reference substance (calcinated α-Al_2O_3) and the studied substance 0.3 g and was placed in evacuated and sealed quartz ampoules at pressure equal to 0.1 Pa; XRD (equipment TUR-M61) with Cu Kα-radiation and Ni-filter, $\theta = 5$–$40°$; microstructure analysis (microscope MIM-7); measurements of the microhardness (instrument PMT-3 at loading of 10 g, accuracy ±4%) and of the density of the material (hydrostatic technique with toluene as reference liquid, accuracy ±2%).

3. Results and discussion

The data obtained from the X-ray diffraction analyses are summarized in a schematic diagram (Fig. 1). The schematic diagrams of X-ray diffraction lines of the starting components $GeSe_2$ and PbTe are identical to those of $GeSe_2$ [21] and PbTe [22]. For better visualization these references are plotted on the schematic diagram of the X-ray diffraction lines itself.

Within the concentration interval 0/100 mol% PbTe some new lines, not pertaining to $GeSe_2$ and PbTe, are observed. These lines are best represented with the composition correspond with 66.7 mol% PbTe. This gives us reason to assume that in this investigated system exists an intermediate phase with supposed composition $GeSe_2{\cdot}2PbTe$.

We carried out indication and determination of the unit-cell parameters of the new phase by the method of Ito [23]. The unit-cell parameters of the intermediate phase α-$GeSe_2{\cdot}2PbTe$, are $a = 6.200 \pm 0.002$ Å, $b = 3.8070 \pm 0.002$ Å, $c = 3.6450 \pm 0.002$ Å, $\alpha = 106.470 \pm 0.02°$, $\beta = 99.850 \pm 0.02°$, and $\gamma = 87.220 \pm 0.02°$. The X-ray diffraction data of the phase are shown in Table 1.

For the purposes of DTA we used samples obtained immediately after the synthesis of the respective alloys. Considering the

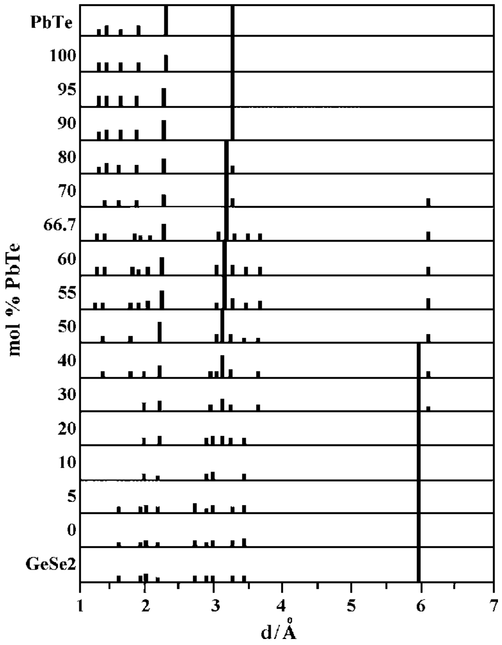

Fig. 1. Schematic diagram of the X-ray diffraction lines for the system $GeSe_2$–PbTe.

Table 1
Data from indexing of phase α-$GeSe_2 \cdot 2PbTe$

$d_{exp.}$ (Å)	(I/I_o) 100 (%)	$Q = 1/d^2$ (Å^{-2})	$h\,k\,l$	d_{calc} (Å)
6.087	23	0.0270	1 0 0	6.109
3.645	14	0.0753	0 1 0	3.651
3.450	13	0.0840	0 0 1	3.448
3.240	32	0.0953	$1\,0\,\bar{1}$	3.239
3.136	100	0.1017	$1\,1\,0$, $1\,\bar{1}\,0$	3.134
3.040	18	0.1082	2 0 0	3.054
2.955	4	0.1145	$0\,1\,\bar{1}$	2.953
2.812	6	0.1265	1 0 1	2.812
2.340	11	0.1826	$2\,\bar{1}\,0$	2.343
2.225	51	0.2020	0 1 1	2.216
1.830	14	0.2986	0 2 0	1.825
1.810	14	0.3052	$1\,2\,\bar{1}$	1.806
1.740	8	0.3303	$1\,0\,\bar{2}$	1.735
1.570	12	0.4057	2 2 0	1.567
1.410	14	0.5030	$2\,2\,\bar{2}$	1.409

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 2. The typical thermal curves are shown in Fig. 2.

Endothermal effects are observed different in size and shape, as the effects covering the larges area those of melting and the ones corresponding to the eutectic and peritectic equilibria. The effects corresponding to the solid-state transition of the intermediate phase with composition $GeSe_2 \cdot 2PbTe$ cover a considerably smaller area but have rather acute peaks.

An endothermal effect is registered with the composition $GeSe_2$ at 740 °C which corresponds to its melting temperature of 740 °C [5]. At second component (PbTe) is also registered an endoeffect at 925 °C, which also conforms well with the reference value $T_m^{PbTe} = 923.9\,°C$ [8].

Table 2
Thermoeffects for samples of the system $GeSe_2$–PbTe

Composition, mol% of PbTe	Endothermic effects on heating (*T*) (°C)			
	1	2	3	4
0	–	–	–	740
3	–	–	480	710
5	370	–	–	680
10	370	415	–	656
15	360	410	–	637
20	–	405	–	632
25	–	410	–	593
30	375	410	–	584
33.3	370	405	–	565
40	365	410	–	517
45	370	410	–	471
50	360	–	–	425
55	370	410	–	440
60	370	410	425	500
66.7	320	–	425	600
70	–	–	420	–
75	320	–	430	730
80	320	–	425	800
90	320	–	–	890
95	320	–	425	880, 910
98	–	–	–	910
100	–	–	–	925

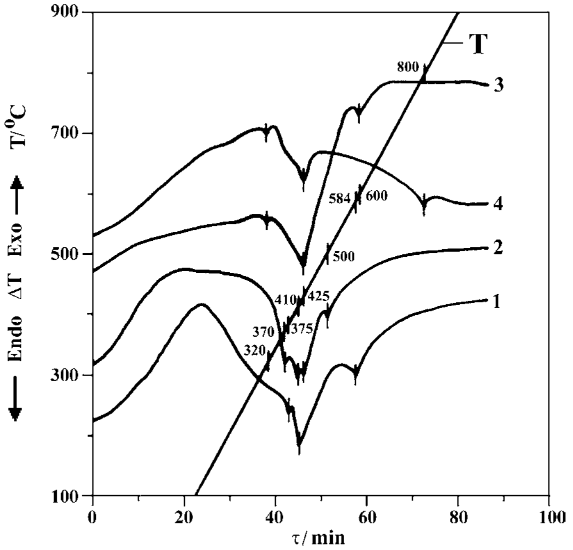

Fig. 2. DTA signal of samples of the system $GeSe_2$–PbTe: ((1) $(GeSe_2)_{70}(PbTe)_{30}$; (2) $(GeSe_2)_{40}(PbTe)_{60}$; (3) $(GeSe_2)_{33.3}(PbTe)_{66.7}$; (4) $(GeSe_2)_{20}(PbTe)_{80}$).

Very clear endothermic effects are observed on the thermograms in the concentration ranges 5/60 mol% and 60/95 mol% PbTe. Their area depends on the quantity of PbTe and has maximum value with the compositions containing ~52.5 mol% and 66.7 mol% PbTe. The temperatures of these effects are at 410 ± 5 °C and 425 ± 5 °C, respectively, and do not depend on the composition in the above-mentioned concentration ranges, i.e., they are most likely related to non-variant equilibria (eutectic and peritectic).

Many endothermal effects are registered within the concentration interval 5/95 mol% PbTe at 370 ± 5 °C and 320 ± 5 °C, as these with 60.0 mol% and 66.7 mol% PbTe cover the largest area. This can be accepted as a direct evidence of a low-temperature polymorphic transition on this temperature of the intermediate phase $GeSe_2 \cdot (2-x)PbTe$, $T_{\alpha \leftrightarrow \beta}$ depends on the composition in the interval $0.0 \le x \le 0.5$.

The results of measuring the microhardness HV are shown in Fig. 3 (the microhardness of $GeSe_2$ is 100–200 kgf mm^{-2} [24], and of PbTe is 60 kgf mm^{-2} [25]).

The samples of the investigated system are porous to a great extent which difficulties the measurement of HV. The presence of two values for HV within the concentration ranges 0/50 and 50/66.7 mol% PbTe and one value in the range of 50/66.7 mol% PbTe, independently of the poor number of values for HV, confirms the presence of two-phases in the fields IX and XI and mono-phase in field X, respectively, Fig. 5.

The values of *d* (Fig. 4) obtained for the system $GeSe_2$–PbTe samples fall within the values of the density corresponding to the starting components $GeSe_2$ ($d_{amorph.} = 4.13\ g\,cm^{-3}$; $d_{cryst.} = 4.5\ g\,cm^{-3}$ [24]) and PbTe ($d = 8.16\ g\,cm^{-3}$ [26]). The observed singular points at 50 and 66.7 mol% PbTe in the $d(x)$ dependence are connected with the presence of an intermediate phase $GeSe_2 \cdot (2-x)PbTe$. The lightly variation of d

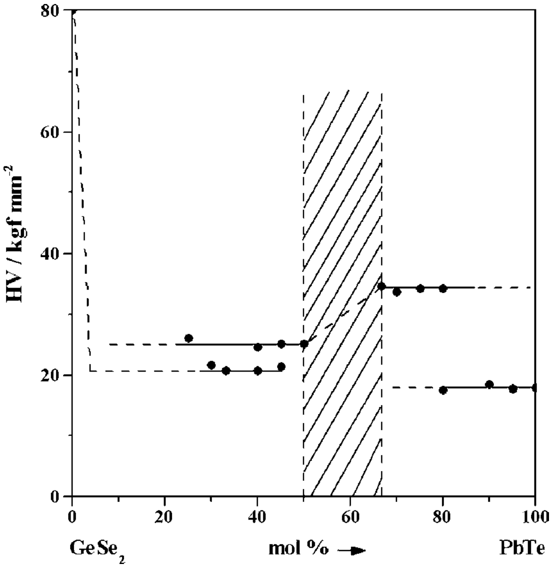

Fig. 3. Dependence of HV(x) for samples of the system $GeSe_2$–PbTe (1 kgf = 9.81 N).

within the concentration region 50/66.7 mol% PbTe is direct evidence for the existence of a region of solid solutions based on the intermediate phase $GeSe_2\cdot(2-x)PbTe$, situated on the left of the composition $GeSe_2\cdot 2PbTe$. The diversion of $d(x)$ from the linearity (dotted line) within the interval $0 < x < 50$ mol% PbTe evidences for the complexity of the physico-chemical interactions between $GeSe_2$ and PbTe, in which exists a mean component, characterized like a chemical interaction (chemical adsorption).

Based on the results of the DTA, the X-ray diffraction analysis and the microhardness and density measurements, the phase diagram of the system $GeSe_2$–PbTe (Fig. 5) was constructed.

It is characterized with two non-variant equilibria peritectic (at a temperature of 425 ± 5 °C) with the formation of an intermediate phase with composition $GeSe_2\cdot 2PbTe$ and eutectic (at a temperature of 410 ± 5 °C) with an eutectic point in case ≈53 mol% PbTe.

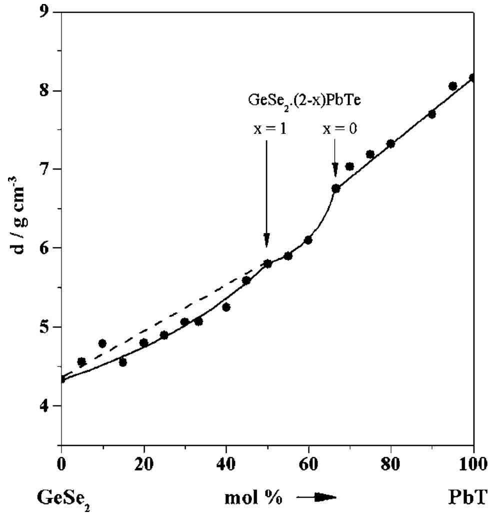

Fig. 4. Dependence between density $d(x)$ and composition of samples of the system $GeSe_2$–PbTe.

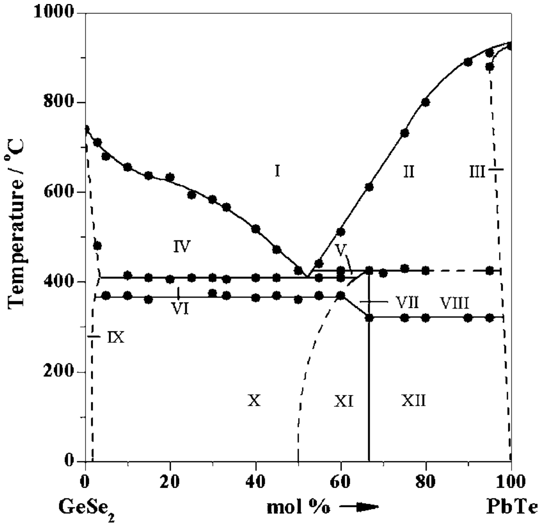

Fig. 5. Phase diagram of the system $GeSe_2$–PbTe—I: L (liquid); II: L + α-PbTe; III: α-PbTe (solid solution); IV: α-$GeSe_2$ + L; V: L + β-$GeSe_2\cdot(2-x)PbTe$; VI: α-$GeSe_2$ + β-$GeSe_2\cdot(2-x)PbTe$; VII: β-$GeSe_2\cdot(2-x)PbTe$; VIII: β-$GeSe_2\cdot(2-x)PbTe$ + α-PbTe; IX: α-$GeSe_2$ (solid solution); X: α-$GeSe_2$ + α-$GeSe_2\cdot(2-x)PbTe$; XI: α-$GeSe_2\cdot(2-x)PbTe$; XII: α-$GeSe_2\cdot(2-x)PbTe$ + α-PbTe.

The intermediate phase $GeSe_2\cdot 2PbTe$ undergoes a polymorphic transition at a temperature from 320 °C to 370 °C. It decomposes at a temperature of 425 °C:

$$GeSe_2\cdot 2PbTe \xleftrightarrow{425\,^{\circ}C} L + \alpha - PbTe$$

There are no endothermal effects present from non-variant peritectic equilibrium at 425 °C (at $x = 98$ mol% PbTe) and from horizontal line α-$GeSe_2\cdot(2-x)PbTe$ ↔ β-$GeSe_2\cdot(2-x)PbTe$ at 320 °C at the same composition. All of this is evidence that when the temperature is increased the range of homogeneity of α-PbTe expands.

The displacement of the lines at the intermediate phase $GeSe_2\cdot 2PbTe$ towards decreasement of the between-planar distance (Fig. 1) to 50 mol% PbTe and the existence of two endoeffects at 370 and 320 °C, at $x = 60$ and 66.7 mol% PbTe, respectively, evidences for the existence of a range of homogeneity based on $GeSe_2\cdot 2PbTe$. The composition of the intermediate phase can be written as $GeSe_2\cdot(2-x)PbTe$, situated on the left of this composition, where $0 \leq x \leq 1$.

In the phase diagram of the system $GeSe_2$–PbTe exist 12 phase fields, five of which are single-phase (I, III, VII, IX and XI).

4. Conclusions

By the means of four independent methods the diagram of the system $GeSe_2$–PbTe is built-up, which diagram is of eutectic type.

As a result of a peritectic reaction at 425 °C a intermediate phase with a most probable composition $GeSe_2\cdot(2-x)PbTe$, where $0 \leq x \leq 1$, is formed. This phase stands a polymorphic transition and $T_{\alpha\leftrightarrow\beta} = 370$ and 320 °C, at $x = 60$ and 66.7 mol% PbTe, respectively.

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