Polyhedration of the Pb–S–Se–Te system

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Polyhedration of the quaternary Pb–S–Se–Te system was carried out. Three new quasi-binary systems: Se–PbS, Te–PbS and Te–PbSe, and two quasi-ternary systems: PbS–PbSe–Te and PbS–Se–Te, were established. The phase equilibria in the Se–PbS, Te–PbS, and Te–PbSe quasi-binary systems were investigated by DTA, XRD and MSA. The systems belong to the eutectic type, the coordinates of the invariant eutectic points being 5 mol.% PbS, 402 K (Se–PbS), 3 mol.% PbS, 697 K (Te–PbS) and 3 mol.% PbSe, 688 K (Te–PbSe). The corresponding *T-x* phase diagrams were built. The quaternary system Pb–S–Se–Te is divided by the PbS–PbSe–PbTe, PbS–PbSe–Te, and PbS–Se–Te quasi-ternary systems into four secondary subsystems: Pb–PbS–PbSe–PbTe, Te–PbS–PbSe–PbTe, PbS–PbSe–Se–Te, and PbS–S–Se–Te.

Lead chalcogenides / Quaternary system / Polyhedration / Phase diagram

1. Introduction

Binary lead chalcogenides are important semiconductors that have attracted attention during the last sixty years. These compounds, and solid solutions based on them, are well known functional materials, which have found wide use as IR sensors (PbS, PbSe) [1-4] and in thermoelectric devices (PbTe) operating in the middle temperature range [5-9]. An active study of the functional properties of these phases began in the 50's of the 20th century [4,13] and continues to this day, as confirmed by the large number of investigations published over the last years. They are frequently used as basic materials in new directions of theoretical and applied research, such as photovoltaics, solar cells, sensor systems, detector devices, *etc*. [10-13]. This is related to the physical properties of the lead chalcogenides: narrow band gap, relatively high electrical conductivity, low thermal conductivity, photosensitivity in the IR region, *etc*. The PbS(Se,Te) compounds are characterized by a cubic crystal structure [14] (*Fm*-3*m* space group, NaCl structure type), simple composition (1:1) and congruent melting [14,15]. Recently, doped lead chalcogenides also attracted attention [16]. In this context, the investigation of the interaction in the quaternary |Pb–S–Se–Te system is of great interest.

Analysis of literature data shows that the investigations of the systems based on binary lead chalcogenides have mainly focused on the sections between the binary compounds, PbS–PbSe, PbS–PbTe and PbSe–PbTe. The PbS–PbSe, PbS–PbTe and PbSe–PbTe systems are characterized by unlimited solubility in the liquid and solid states with minimum points at 59 mol.% PbSe, 1334 K [17], 60 mol.% PbTe, 1170 K [17] and 93 mol.% PbTe, 1196 K [17], respectively. In the PbS–PbTe system the solid solution undergoes a spinodal decomposition during cooling [8,17]. The critical point has the coordinates 37 mol.% PbTe, 1075 K [17]. The quasi-ternary PbS–PbSe–PbTe system contains a single-phase region based on the solid solution $PbS_xSe_yTe_{1-x-y}$, and a two-phase region formed as a result of the spinodal decomposition of the PbS_xTe_{1-x} solid solution [18,19]. The liquidus surfaces of the Pb–PbS–PbSe, Pb–PbS–PbTe and Pb–Se–Te (concentration region 100-20 mol.% Pb) systems have also been investigated [20,21].

However, despite the practical value of phases based on PbS(Se,Te), a comprehensive study of the physico-chemical interactions in the quaternary chalcogenide system Pb–S–Se–Te has so far not been carried out. The aim of the present study was to investigate the physico-chemical interactions in the Pb–S–Se–Te system, establish the quasi-binary and

quasi-ternary sections in this system, and study the physico-chemical interactions in the established stable sections.

2. Experimental

2.1. Sample preparation

The starting compounds were high-purity (99.99 wt.%) elemental solids: lead, sulphur, selenium, and tellurium. To obtain the binary lead chalcogenides, the appropriate elemental solids in the stoichiometric molar ratio were mixed in quartz ampoules, which were then evacuated to a residual pressure of 10^{-3} Pa. After the evacuation, the quartz ampoules were heated to 1273 K (PbS, PbSe, PbTe) at a rate of 30 K per hour. After a thermal treatment for 24 h the ampoules where cooled to the homogenization temperature, 380 K, at a rate of 20 K per hour and annealed for 72 h (PbS, PbSe, PbTe).

The alloys in the ternary Pb–X^1–X^2 ($X^{1,2}$ = S, Se, Te, $X^1 \neq X^2$) systems were synthesized using the preliminarily obtained binary compounds and elemental solids by the direct single-temperature method. Heating to the highest temperature, 1250 K (treatment for 24 h), and cooling to the temperature of homogenization, 350 K (treatment for 168 h), were carried out at a rate of 30 K per hour.

2.2. Experimental techniques and methods

For the collection of X-ray diffraction (XRD) data, a DRON–4.07 X-ray powder diffractometer, equipped with a Cu tube and Ni filter, was used (angular range $5° \leq 2\theta \leq 60°$, step $\Delta 2\theta = 0.02°$). The X-ray diffraction data were processed using the PowderCell 2.4 [22] and UnitCell [23] program packages.

Differential thermal analysis (DTA) was carried out using a device including an x-y recorder PDA-1, a programmable controller Maxtermo MC-2438 and a chromel-alumel combined thermocouple.

Microstructure analysis (MSA) was conducted on a metallographic microscope Lomo Metam R1. The samples were polished using standardized Al_2O_3 and diamond pastes, followed by etching in an aqueous solution with a molar ratio of $KOH:H_2O_2 = 3:1$.

3. Results and discussion

Three congruently (PbS, PbSe, PbTe), and one incongruently (SSe_2 [24]) melting compounds are formed in the quaternary Pb–S–Se–Te system.

According to generally accepted rules [25], in the quaternary system defined above there must exist four secondary quasi-ternary systems (tetrahedrons), three quasi-ternary and six quasi-binary sections. The PbS–PbSe, PbS–PbTe and PbSe–PbTe sections do not intersect with any other section (Fig. 1) and are definitely quasi-binary, which has been confirmed by numerous experimental studies [17-19]. The location of the remaining three sections must be determined by experimental studies of the reciprocal systems PbS+Se ↔ PbSe+S, PbS+Te ↔ PbTe+S and PbSe+Te ↔ PbTe+Se. The determination of the sections was carried out by phase analysis of samples lying at the intersection of the possible quasi-binary sections (points Nos. 1-3) (see Fig. 1). The synthesized samples were two-phase and the XRD powder patterns contained sets of reflections of cubic PbS (Nos. 1, 2), PbSe (No. 3) and trigonal Te (Nos. 2, 3) (see Fig. 2, a-c). Consequently, the sections Se–PbS, Te–PbS and Te–PbSe are quasi-binary (Fig. 1).

For the study of the phase equilibria in the quasi-binary sections, samples were synthesized every 10 mol.%. The investigated quasi-binary systems Se–PbS (Fig. 3), Te–PbS (Fig. 4) and Te–PbSe (Fig. 5) belong to the eutectic type with the following coordinates of the invariant points: 5 mol.% PbS, 402 K (equilibrium process $L_1 \leftrightarrow$ Se+PbS), 3 mol.% PbS, 697 K (equilibrium process L ↔ Te+PbS) and 3 mol.% PbSe, 688 K (equilibrium process L ↔ Te+PbSe), respectively. In the Se–PbS system an immiscibility region exists in the range 5-75 mol.% PbS. A monotectic equilibrium $L_2 \leftrightarrow L_1$+PbS occurs at 957 K. The solid solution ranges based on the elemental chalcogens and binary lead chalcogenides do not exceed 5 and 10 mol.% at the annealing temperature.

The six stable sections determine the location of three quasi-ternary systems in the Pb–S–Se–Te system: PbS–PbSe–PbTe, PbS–PbSe–Te and PbS–Se–Te. The plane of the quasi-ternary PbSe–PbSe–PbTe system divides the initial tetrahedron Pb–S–Se–Te into two secondary figures: the tetrahedron Pb–PbS–PbSe–PbTe and the truncated trigonal pyramid PbS–PbSe–PbTe–S–Se–Te (see Fig. 6). The polyhedron PbS–PbSe–PbTe–S–Se–Te is further divided by the quasi-ternary systems PbS–PbSe–Te and PbS–Se–Te into three secondary tetrahedrons: PbS–PbSe–PbTe–Te, PbS–S–Se–Te and PbS–PbSe–Se–Te. According to the classification proposed in [25], the investigated system belongs to the tetrahedration type of free vertices.
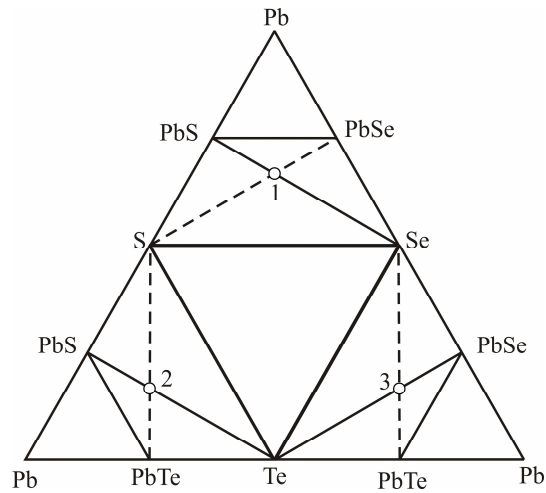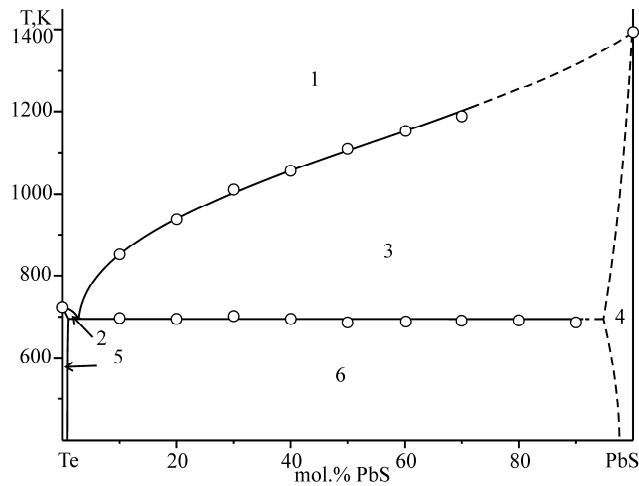
Fig. 1 Existing (solid line) and possible (dashed line) sections in the Pb–S–Se–Te system.
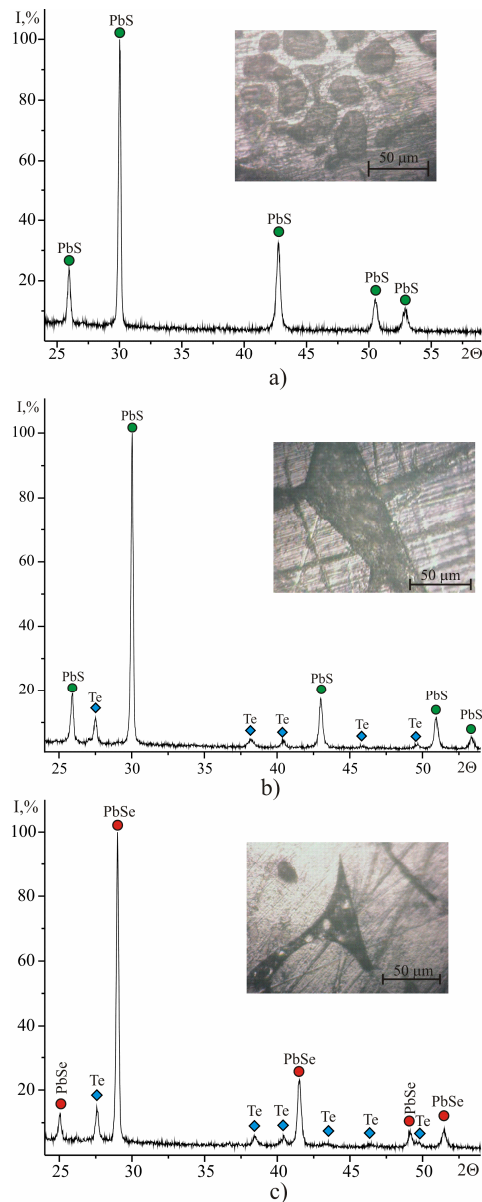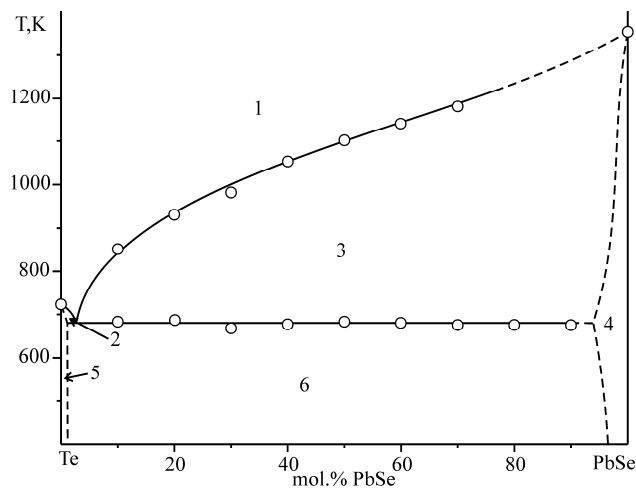

Fig. 2 XRD powder pattern and microstructure of the samples corresponding to points No. 1 (a), No. 2 (b) and No. 3 (c) in Fig. 1.
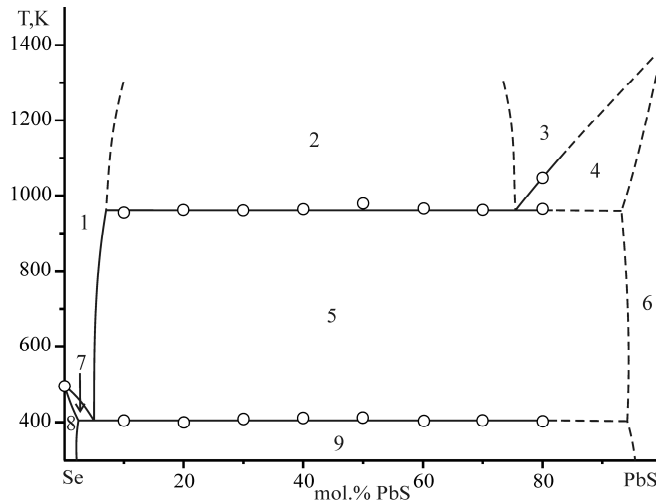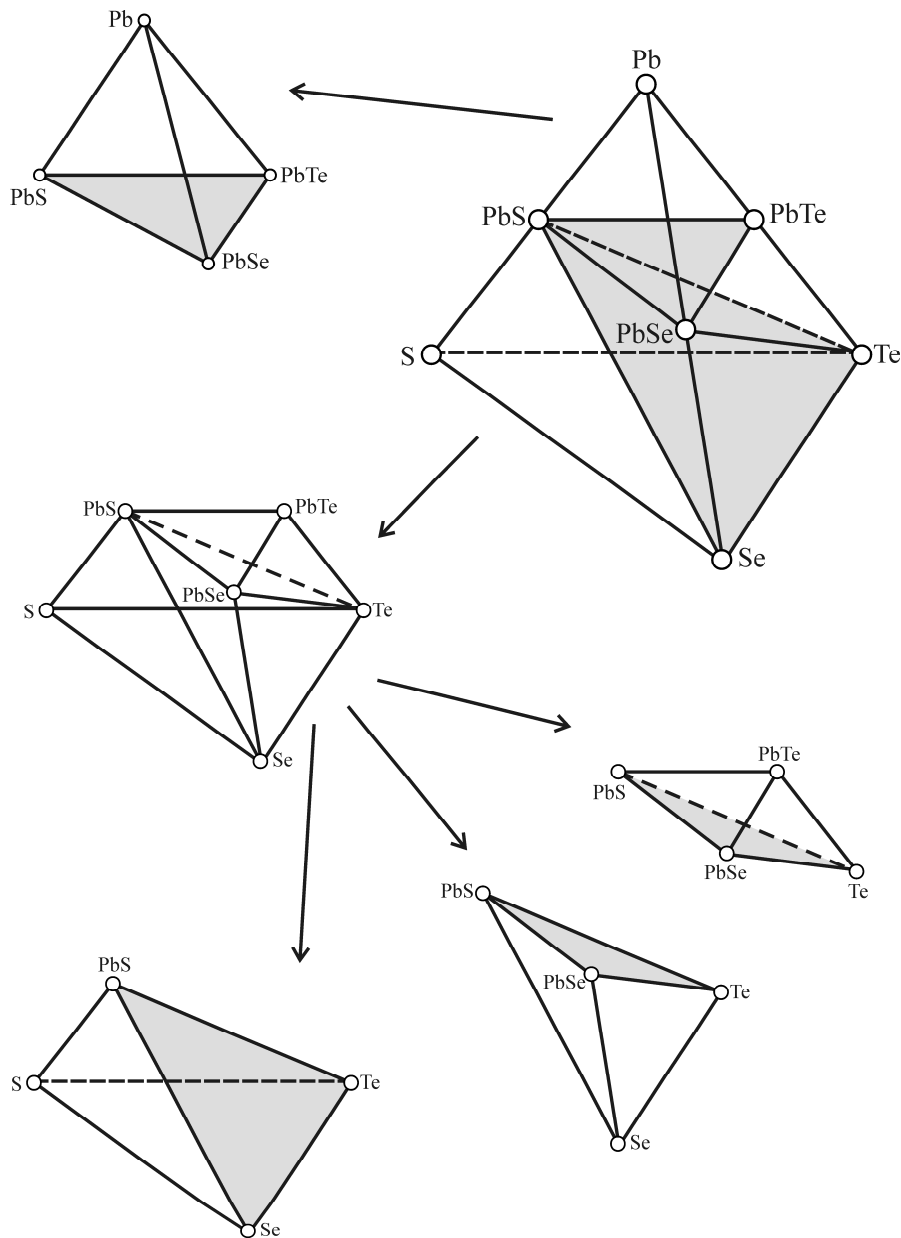
Fig. 3 *T-x* phase diagram of the Se–PbS system: 1 – L_1, 2 – L_1+L_2, 3 – L_2, 4 – L_2+PbS, 5 – L_1+PbS, 6 – PbS, 7 – L_1+Se, 8 – Se, 9 – Se+PbS.

Fig. 4 *T-x* phase diagram of the Te–PbS system: 1 – L, 2 – L+Te, 3 – L+PbS, 4 – PbS, 5 – Te, 6 – Te+PbS.

Fig. 5 *T-x* phase diagram of the Te–PbSe system: 1 – L, 2 – L+Te, 3 – L+PbSe, 4 – PbSe, 5 – Te, 6 – Te+PbSe.

Fig. 6 Quasi-ternary and secondary quaternary systems in the Pb–S–Se–Te system.

4. Conclusions

The phase equilibria in the Se–PbS, Te–PbS, Te–PbSe systems were investigated by DTA, XRD and MSA. The miscibility gaps of the initial elemental and binary phases and the coordinates of the invariant points were established. The investigated quasi-binary sections belong to the eutectic type, the eutectic points being located near the elemental components in all of the systems. The coordinates of the invariant eutectic points are: 5 mol.% PbS, 402 K (Se–PbS); 3 mol.% PbS, 697 K (Te–PbS) and 3 mol.% PbSe, 688 K (Te–PbSe). In the Se–PbS system a monotectic invariant equilibrium process $L_2 \leftrightarrow L_1 + PbS$ takes place at 957 K. The corresponding *T-x* phase diagrams were built.

Based on literature and experimental data polyhedration of the Pb–S–Se–Te system was carried out. There exist 6 quasi-binary and 3 quasi-ternary sections in the system, which divide the initial quaternary system into four quaternary subsystems.

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