# The $Cu_2Se$–$PbSe$–$As_2Se_3$ system

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Phase equilibria of the quasi-ternary system $Cu_2Se$–$PbSe$–$As_2Se_3$ were investigated by X-ray diffraction and differential thermal (DTA) analysis. The nonvariant processes in the system are located in the $As_2Se_3$-rich part of the triangle (over 70 mol.% $As_2Se_3$) in the temperature range 607-653 K.

Phase diagram / Liquidus projection / Differential thermal analysis (DTA) / X-ray diffraction (XRD)

## Introduction

No data on investigations of the quasi-ternary system $Cu_2Se$–$PbSe$–$As_2Se_3$ were found in the literature. There are conflicting reports on the quasi-binary system $PbSe$–$As_2Se_3$, concerning the formation of ternary compounds. In addition, our aim was to investigate the formation of quaternary compounds in the system $Cu_2Se$–$PbSe$–$As_2Se_3$.

The system $Cu_2Se$–$PbSe$–$As_2Se_3$ is bounded by three quasi-binary systems, $Cu_2Se$–$As_2Se_3$, $Cu_2Se$–$PbSe$ and $PbSe$–$As_2Se_3$. The $Cu_2Se$–$As_2Se_3$ system is well-studied [1-3]; it features the formation of one ternary compound, $CuAsSe_2$, by a peritectic reaction, $L_{p1}+Cu_2Se \leftrightarrow CuAsSe_2$. $CuAsSe_2$ crystallizes in space group $R3$ with the lattice parameters $a = 1.4025$ nm, $c = 0.961$ nm, structure type $Cu_7As_6Se_{13}$ [4]. The $Cu_2Se$–$PbSe$ system is of the eutectic type, with a nonvariant point having as coordinates 46 mol.% $PbSe$, $T_{e1} = 886$ K [5]. The $PbSe$–$As_2Se_3$ system was investigated in [1,6]. It is a eutectic system with a degenerate eutectic near $As_2Se_3$ and the formation of the $PbAs_2Se_4$ compound by the peritectic reaction $L_{p2}+PbSe \leftrightarrow PbAs_2Se_4$. According to [6], the compound exists in the range of 658-775 K, whereas the authors of [1] consider the compound stable at room temperature with, probably, spinel structure. For this reason our investigation started with the study of the interactions in the $PbSe$–$As_2Se_3$ system.

## Experimental

A total of 55 samples were synthesized for the investigation of the phase equilibria in the quasi-ternary system $Cu_2Se$–$PbSe$–$As_2Se_3$. They were prepared from high-purity elements (Se 99.999 wt.%, Pb 99.99 wt.%, Cu 99.99 wt.%, As 99.999 wt.%) by direct synthesis in evacuated quartz ampoules. The maximum temperature was 1370 K. For the homogenizing annealing the samples were held at 520 K for 600 h. The alloys were quenched from this temperature into cold water. All the samples were investigated by XRD and DTA.

XRD analysis as performed using a powder diffractometer DRON 4-13, Cu $K_\alpha$ radiation, in the range $10º \leq 2\theta \leq 90º$, scan step 0.05º, exposure time 2 s. The phase analysis was performed using the DRWin and Powder Cell software packages.

DTA thermograms were recorded using a Paulik-Paulik-Erdey derivatograph with a Pt/Pt-Rh thermocouple and an XY recorder. The samples were heated at a rate of 10 K/min and cooled inertially.

## Results and discussion

### The $PbSe$–$As_2Se_3$ system

The $PbSe$–$As_2Se_3$ system was investigated in the entire concentration range, using fourteen samples. XRD showed that only the samples of the system components $PbSe$ and $As_2Se_3$ were single-phase. The diffraction patterns of the other alloys contained the reflections of both the initial phases. No indication of the presence of a third phase or of solid solubility of the components was found. We additionally annealed the alloys in the range 40-60 mol.% $As_2Se_3$ at 723 K, with the aim to freeze the formation of $PbAs_2Se_4$. But
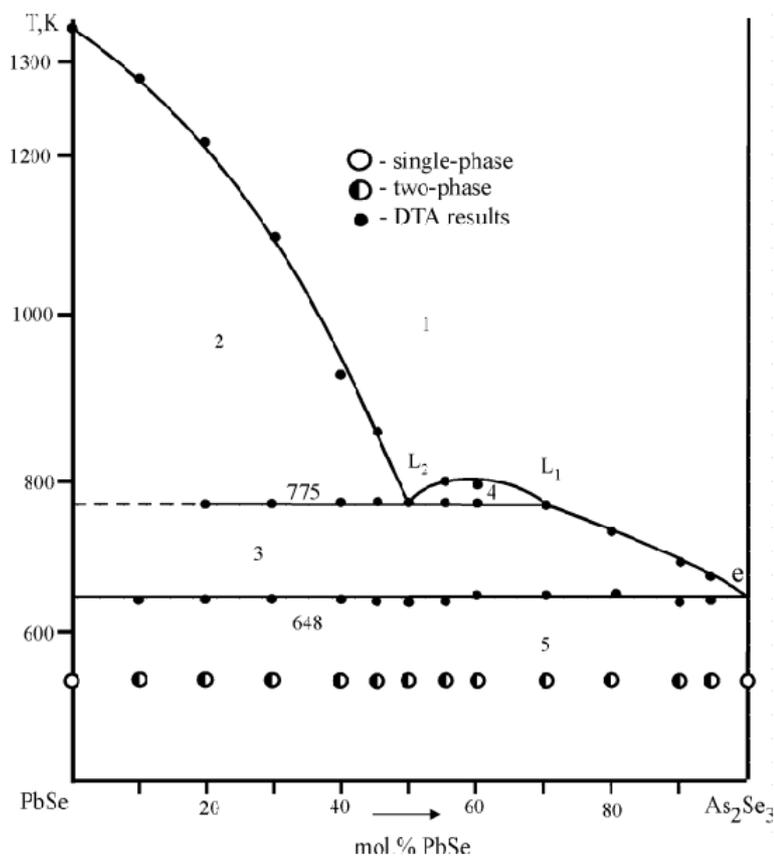
**Fig. 1** Phase diagram of the PbSe–As$_2$Se$_3$ system: 1 – L, 2 – L(L$_2$)+PbSe, 3 – L(L$_1$)+PbSe, 4 – L$_2$+L$_1$, 5 – As$_2$Se$_3$+PbSe.

the diffraction patterns of the samples quenched from this temperature only contained the reflections of PbSe and As$_2$Se$_3$ (Fig. 1). The thermograms of all of the alloys, except PbSe, showed thermal effectsthat correspond to the melting point of crystalline As$_2$Se$_3$. The monotectic process L$_2$⇔L$_1$+PbSe takes place at 775 K.

*Vertical section CuAsSe$_2$–"PbAs$_2$Se$_4$"*

The vertical section CuAsSe$_2$–"PbAs$_2$Se$_4$" was investigated on twelve samples in the entire concentration range. All the diffraction patterns, except those of the section components, contained the reflections of three phases. The diffraction pattern of CuAsSe$_2$ was single-phase; PbAs$_2$Se$_4$ turned out to be a two-phase alloy (PbSe+As$_2$Se$_3$). Using DTA and XRD, the vertical section CuAsSe$_2$–"PbAs$_2$Se$_4$" was constructed (Fig. 2). The section liquidus consists of the curves of primary crystallization of Cu$_2$Se (*ab*) and PbSe (*bc*). Field 7 contains PbSe+L$_2$+L$_1$, because the monotectic process L$_2$⇔L$_1$+PbSe takes place in the interval of temperatures from 775 K till 620 K (Table 1). This section intersects the conode L–PbSe in the point *d* (a more detailed explanation follows below). Differences between L$_2$ and L$_1$ only exist in

the region L$_2$–K–L$_1$ (Fig. 3). This explains why the fields 3 and 8 (Fig. 2) are the same. The sub-liquidus part features horizontal lines at 653 and 607 K, which result from the intersection with the planes of the transition reaction U$_1$ and the eutectic reaction E (Fig. 3, Tables 1,2).

*Vertical section CuAsSe$_2$–PbSe*

The CuAsSe$_2$–PbSe section was investigated using eleven samples spanning the entire concentration range. XRD showed that only the alloys of the compounds PbSe and CuAsSe$_2$ were single-phase. All the other samples were two-phase. Using DTA and XRD, the polythermal section CuAsSe$_2$–PbSe was constructed (Fig. 4). The section liquidus consists of the lines of primary crystallization of Cu$_2$Se (*ab*) and PbSe (*bc*). The two fields of secondary crystallization are L+CuAsSe$_2$+Cu$_2$Se (field 4) and L+Cu$_2$Se+PbSe (field 5). The horizontal line at 653 K in the sub-liquidus part results from the intersection with the plane of the transition process L$_{U1}$+Cu$_2$Se↔ CuAsSe$_2$+PbSe. On this section it ends with the disappearance of the liquid and Cu$_2$Se crystals, so that the alloys are two-phase below 653 K. This horizontal line is the section solidus.
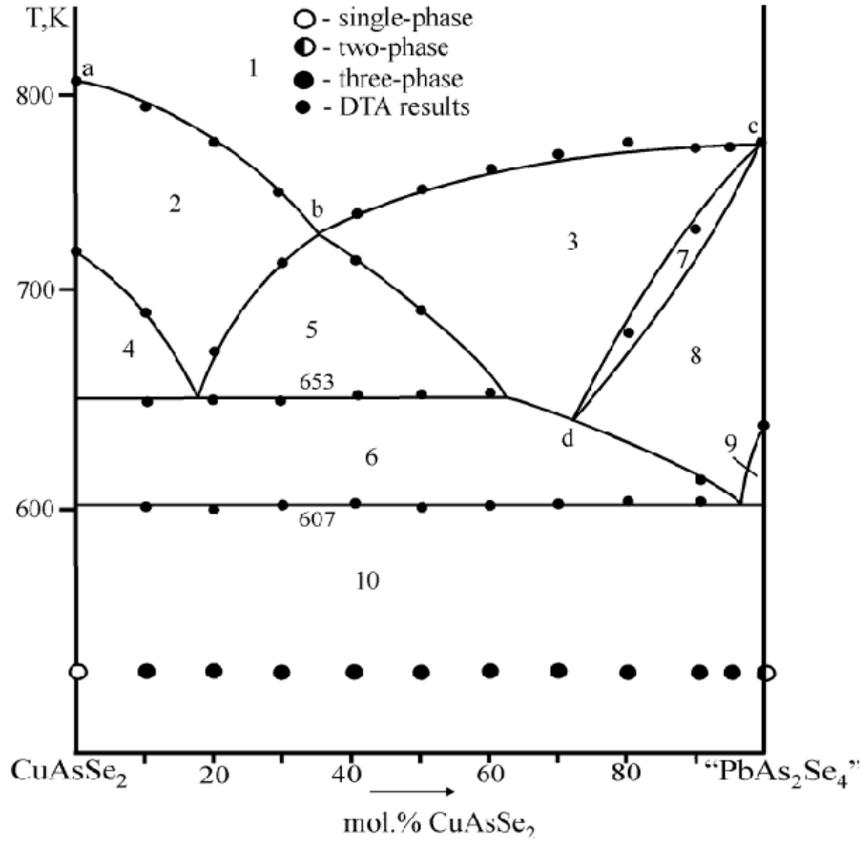
**Fig. 2** Polythermal section CuAsSe$_2$–"PbAs$_2$Se$_4$": 1 – L, 2 – L+Cu$_2$Se, 3 – L+PbSe, 4 – L+Cu$_2$Se+CuAsSe$_2$, 5 – L+PbSe+Cu$_2$Se 6 – L+CuAsSe$_2$+PbSe, 7 – L$_1$+PbSe+L$_2$, 8 – L+PbSe, 9 – L+PbSe+As$_2$Se$_3$, 10 – PbSe+CuAsSe$_2$+As$_2$Se$_3$.
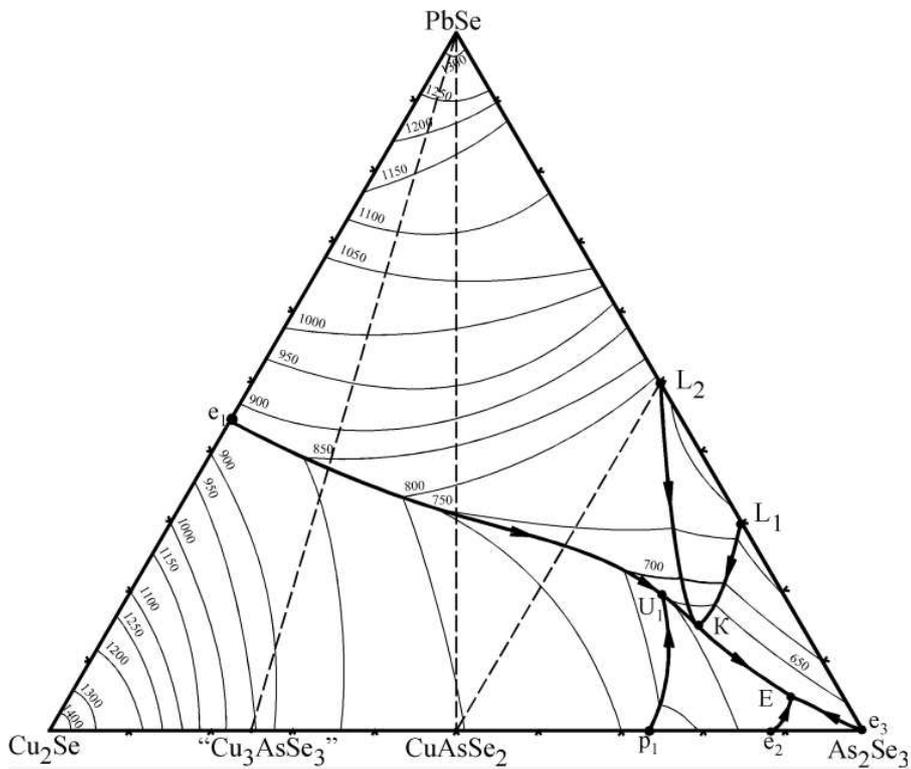


**Fig. 3** Projection of the liquidus surface of the Cu$_2$Se–SnSe$_2$–As$_2$Se$_3$ system onto the concentration triangle.

**Table 1** Nature and temperatures of the mono- and invariant processes in the quasi-ternary system Cu$_2$Se–PbSe–As$_2$Se$_3$.

| Quasi-binary system Cu$_2$Se-PbSe | Quasi-binary system Cu$_2$Se-As$_2$Se$_3$ | Quasi-ternary system Cu$_2$Se-PbSe-As$_2$Se$_3$ | Quasi-binary system PbSe-As$_2$Se$_3$ |
|---|---|---|---|
| $e_1$ : 886 K $Le_1 \rightleftarrows Cu_2Se + PbSe$ | | | |
| | $p_1$: 725 K $Lp_1 + Cu_2Se \rightleftarrows CuAsSe_2$ | | $L_2$: 775 K $L_2 \rightleftarrows L_1 + PbSe$ |
| | | $U_1$: 653 K $L_{U1} + Cu_2Se \rightleftarrows CuAsSe_2 + PbSe$ | $e_3$: 648 K $Le_3 \rightleftarrows PbSe + As_2Se_3$ |
| | $e_2$: 633 K $Le_2 \rightleftarrows CuAsSe_2 + + As_2Se_3$ | K: 620 K $L \rightleftarrows PbSe$ | |
| | | E: 607 K $L_{E1} \rightleftarrows CuAsSe_2 + + PbSe + As_2Se_3$ | |

*Vertical section PbSe–"Cu$_3$AsSe$_3$"*

Eleven samples from the entire concentration range were synthesized for the investigation of the section PbSe–"Cu$_3$AsSe$_3$". According to the XRD data, the PbSe sample was single-phase, "Cu$_3$AsSe$_3$" consisted of two phases (Cu$_2$Se+CuAsSe$_2$), and all the other alloys were three-phase.

The section liquidus, shown in Fig. 5, consists of the curves of primary crystallization of PbSe (*ab*) and Cu$_2$Se (*cb*). Point *b* is the intersection of the monovariant curve of the joint crystallization of PbSe and Cu$_2$Se. Two fields of secondary crystallization are featured in the sub-liquidus part: field *dbpq* corresponds to the joint crystallization of PbSe and Cu$_2$Se (L+PbSe+Cu$_2$Se); field *fpn* corresponds to the joint crystallization of Cu$_2$Se and CuAsSe$_2$ (L+CuAsSe$_2$+Cu$_2$Se). The horizontal line *qpn* (653 K) results from the intersection with the plane of the transition reaction $L_{U1}+Cu_2Se \leftrightarrow CuAsSe_2+PbSe$. As the section crosses the plane of the invariant transition reaction in the region with excess of the solid phase Cu$_2$Se, three phases, PbSe, Cu$_2$Se and CuAsSe$_2$, will be in equilibrium in the solid state after the completion of the process.

*Liquidus surface projection of the quasi-ternary system Cu$_2$Se–PbSe–As$_2$Se$_3$*

Based on the investigated polythermal sections and literature data on the interactions in the quasi-binary systems Cu$_2$Se–PbSe and Cu$_2$Se–As$_2$Se$_3$, the liquidus surface projection of the quasi-ternary system Cu$_2$Se–PbSe–As$_2$Se$_3$ onto the concentration triangle was constructed (Fig. 3). The coordinates of the invariant points are listed in Table 2.

The liquidus surface consists of the five fields of primary crystallization of the phases Cu$_2$Se, PbSe, As$_2$Se$_3$, and CuAsSe$_2$ (two of them belong to PbSe). A region of aliquation exists between the curves $L_2$–K–$L_1$. The critical point K, where the difference between the liquids $L_1$ and $L_2$ disappears, is located on the monovariant curve of the eutectic process $L_{U1-E} \Leftrightarrow CuAsSe_2 + PbSe$. There the conode triangle $L_1$–$L_2$–PbSe at 620 K transforms into the conode L–PbSe, which is, at the indicated temperature, part of the conode triangle of the eutectic process $L_{U1-E} \Leftrightarrow CuAsSe_2 + PbSe$ (Fig. 3). The major part of the triangle is occupied by the fields of primary crystallization of PbSe and Cu$_2$Se, which have the highest melting points. The fields of primary crystallization
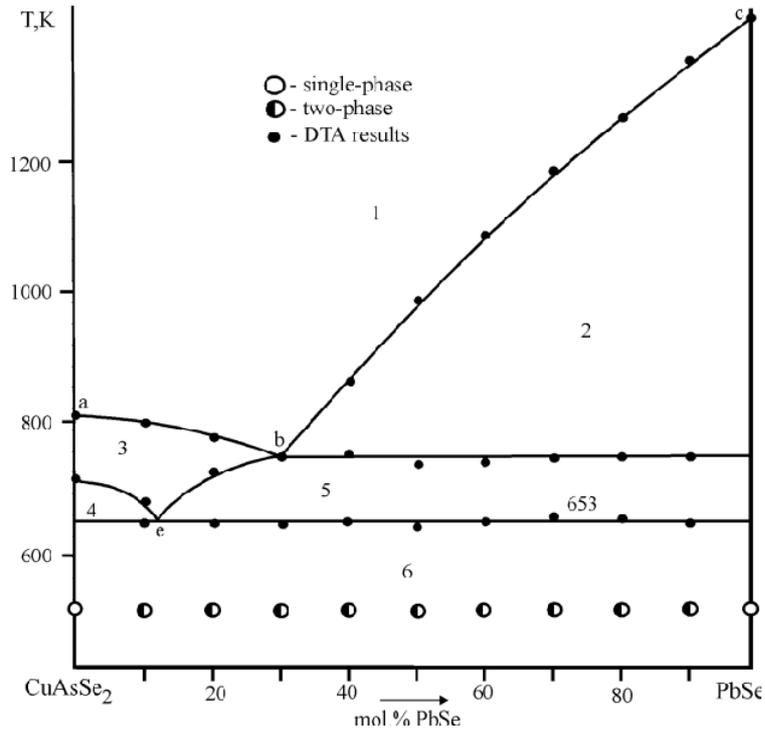
**Fig. 4** Polythermal section $CuAsSe_2-PbSe$: 1 – L, 2 – $L+PbSe$, 3 – $L+Cu_2Se$, 4 – $L+Cu_2Se+CuAsSe_2$, 5 – $L+Cu_2Se+PbSe$, 6 – $CuAsSe_2+PbSe$.
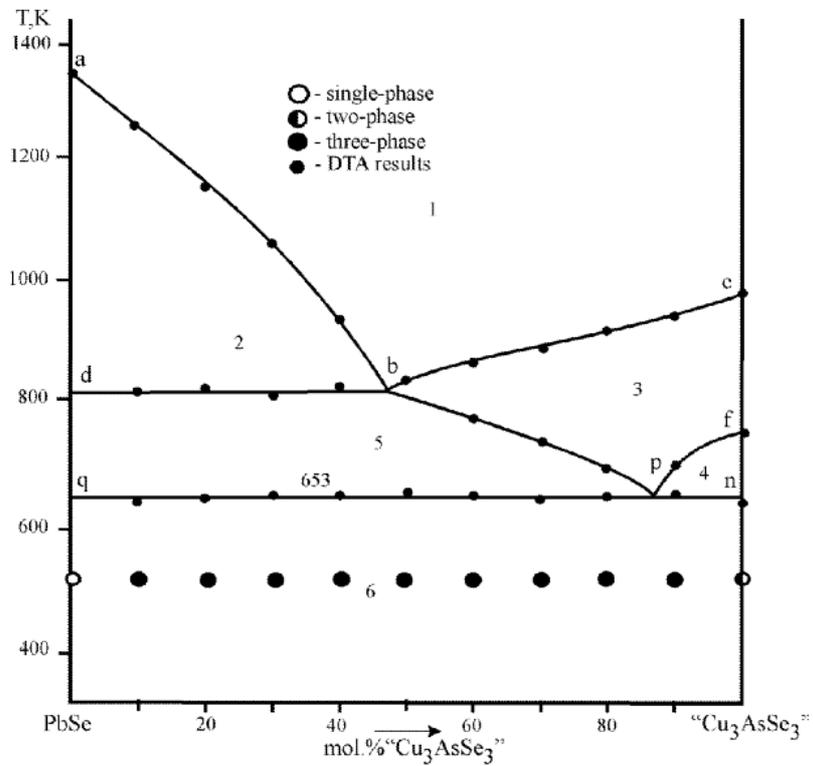


**Fig. 5** Polythermal section $PbSe-"Cu_3AsSe_3"$: 1 – L, 2 – $L+PbSe$, 3 – $L+Cu_2Se$, 4 – $L+Cu_2Se+CuAsSe_2$, 5 – $L+PbSe+Cu_2Se$, 6 – $PbSe+Cu_2Se+CuAsSe_2$.

**Table 2** Compositional coordinates of invariant points in the quasi-ternary system $Cu_2Se–PbSe–As_2Se_3$.

| Invariant point | Composition, mol.% | | |
|---|---|---|---|
| | $Cu_2Se$ | PbSe | $As_2Se_3$ |
| $U_1$ | 15 | 20 | 65 |
| E | 7 | 5 | 88 |

are separated by monovariant lines that cross in the invariant points $U_1$ and E. The crystallization isotherms are shown with thin lines; dotted lines represent the polythermal sections that were investigated in this paper.

The nature and temperatures of the monovariant and invariant processes in the quasi-ternary system $Cu_2Se–PbSe–As_2Se_3$ are summarized in Table 1.

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