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Phase equilibria in the CdI_2–Ag_2Se system

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Abstract

The phase diagram of the system CdI_2–Ag_2Se is studied by means of X-ray diffraction, differential thermal analysis and measurements of the density of the material. The unit cell parameters of the intermediate phase $2CdI_2 \cdot 3Ag_2Se$ were determined $a = 0.6387$ Å, $b = 4.311$ Å, $c = 4.044$ Å; $\alpha = 113.72°$, $\beta = 90.27°$ and $\gamma = 94.85°$. The intermediate phase $2CdI_2 \cdot 3Ag_2Se$ has a polymorphic transition at 125 °C. It melts incongruently at 660 °C.

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

1. Introduction

The system CdI_2–Ag_2Se is not studied both with respect to the phase equilibriums in it and with the possibility to form glassy phases in three-component systems of the type CdI_2–Ag_2Se–Me_nCh_m (Me_nX_n), where Ch = O, S, Se and Te; X = F, Cl, Br and I. The components of this system enter into the composition of a number of multicomponent chalcogenide [1,2], chalcochalide [3] and oxichalcochalide [4] glasses. CdI_2 considerably expands the range of glass-formation, has an effect on the permeability of glasses in the IR-range of the spectrum and improves their thermal characteristics. Ag_2Se adds some special properties to the glasses and as a result they can be used for: optical recording of information; membrane material for ionselective electrodes; material for fast switches of the Ovonic type; solid electrolytes for waveguides with low loss, etc.

The study of such a binary system has a certain scientific and practical interest because it combines components with different properties, for example, Ag_2Se is a narrow-gap semiconductor with an energy gap of 0.04–0.10 eV [5–7]. It is assumed that the different values of the energy gap are due to the presence of excess Ag-atoms. Their quantity depends on the method of obtaining [8,9]. The composition CdI_2 is a typical dielectric with a laminated structure and a wide energy gap. It is characterized with a number of polytypes of which three, depending of the method of obtaining, are the most stable [10]. For example, a hexagonal CdI_2 is obtained with unit cell parameters: $a = 4.24$ and $c = 6.835$ Å during the process of crystallization from water solutions when the pressure is $400\ N\ m^{-2}$.

This research is aimed, by means of the classical methods of physicochemical analysis (differential thermal analysis (DTA) [11], X-ray powder diffraction (XRD) [12]), the microstructure analysis and examination of the density/composition dependence, at studying the phase equilibria in the system CdI_2–Ag_2Se and at determining the limits of the solid solutions and the composition of the intermediate phases (if any) with a view to their future complex study.

2. Experimental

The phase diagram of the system CdI_2–Ag_2Se has been studied by means of 17 compositions synthesized every 5 or 10 mol% Ag_2Se in a concentration interval from 0 to 100 mol% Ag_2Se. The samples were obtained through a direct mono-temperature synthesis [13], mixing CdI_2 and Ag_2Se in a proper correlation in vacuumed quartz ampoules. It was used CdI_2 of the Fluka Company with purity purum (p.a.) and Ag_2Se, which was synthesized by the same method of Ag and Se with purity 4 and 5 N, respectively. According to CdI_2 content the maximum tempera-

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ture of synthesis was 500–1000 °C for 2 h. A vibrational stirring of the melt was used. The final step was homogenization of the solid-state phase at 250 °C for 1 h and then it was quenched in a mixture H_2O–ice.

The phase transformations in the samples were investigated by means of several methods as follows: DTA (equipment of the system F. Paulik–J. Paulik–L. Erdey made by MOM-Hungary) at heating rate of $10^\circ\,\mathrm{min}^{-1}$; 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 0.1×10^{-2} Pa; XRD (equipment TUR-M61) with Cu K_α radiation and Ni-filter, $\theta = 5$–40°, microstructural analysis (microscope MIM-7) and measurements of the density of the samples (hydrostatic technique with toluene as reference liquid [14,15]).

3. Results and discussion

The results of the X-ray diffraction analysis of the samples are summarized in the form of a schematic diagram of the X-ray diffraction lines (Fig. 1). Within the concentration interval 5–95 mol% Ag_2Se some new lines, not pertaining to CdI_2 and Ag_2Se, are observed. These lines are best represented with the composition where the CdI_2:Ag_2Se correlation is 2:3. This gives us reason to assume that with this correlation of the starting components a new phase exists having the composition $2CdI_2{\cdot}3Ag_2Se$. The schematic diagram of the X-ray diffraction lines at room temperature does not show any movement of the lines either of the starting components CdI_2 and Ag_2Se, or of the intermediate phase $2CdI_2{\cdot}3Ag_2Se$, i.e. no solid solutions are formed on their basis or if such are formed they are in a very narrow range.

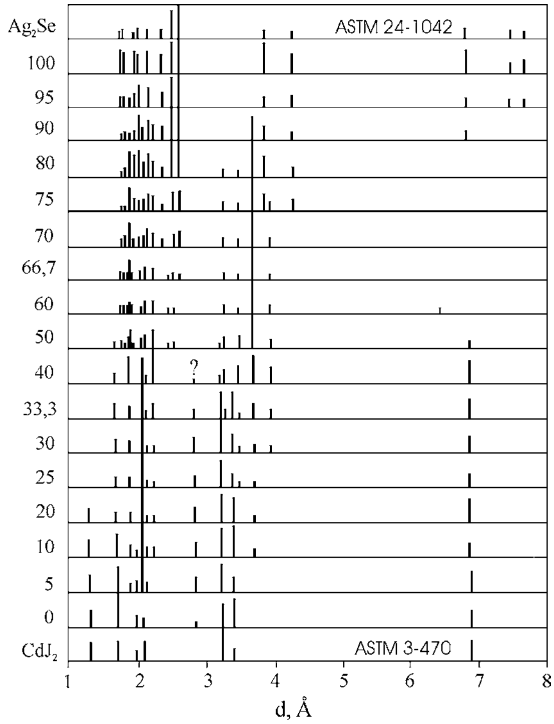

Fig. 1. Schematic diagram of the X-ray diffraction lines for the system Ag_2Se–CdI_2.

Table 1
Data from indexing of phase $2CdI_2{\cdot}3Ag_2Se$

Number	$d_{\mathrm{exp.}}$ (Å)	$(I/I_{\max}) \times 100$ (%)	$Q = 1/d^2$	$h\,k\,l$	$d_{\mathrm{calc.}}$ (Å)
1	6.362	11	0.0247	1 0 0	6.358
2	3.93	19	0.0647	0 1 0	3.929
3	3.70	100	0.0730	0 0 1	3.699
4	3.49	29	0.0821	$0\,1\,\bar{1}$	3.487
5	3.26	30	0.0941	$1\,0\,\bar{1}$	3.258
6	3.142	9	0.1013	1 0 1	3.140
7	2.54	25	0.1558	$2\,\bar{1}\,0$	2.594
8	2.46	16	0.1652	$2\,0\,\bar{1}$	2.463
9	2.27	44	0.1932	0 1 1	2.274
10	2.14	46	0.2184	$0\,2\,\bar{1}$	2.127
11	2.10	15	0.2268	1 1 1	2.088
12	1.96	31	0.2587	0 2 0	1.965
13	1.95	22	0.2630	$\bar{3}\,1\,0$	1.944
14	1.93	26	0.2684	$1\,\bar{2}\,0$	1.929
15	1.85	25	0.2922	0 0 2	1.850
16	1.83	29	0.2986	1 2 0	1.829

We carried out indication and determination of the unit cell parameters of the new phase by the method of Ito [16]. The unit cell parameters of the intermediate phase $2CdI_2{\cdot}3Ag_2Se$ are: $a = 6.387 \pm 0.002$ Å, $b = 4.311 \pm 0.002$ Å, $c = 4.044 \pm 0.002$ Å; $\alpha = 113.72 \pm 0.02^\circ$, $\beta = 90.27 \pm 0.02^\circ$, $\gamma = 94.85 \pm 0.02^\circ$. The X-ray diffraction data of this phase are shown in Table 1.

Derivatograms were also made of the samples of the studied system in a heating regime were also made. The differential thermal analysis data are summarized in Table 2.

Endothermal effects are observed different in size and shape, as the effects covering the largest area are those of melting and the ones corresponding to the eutectic and monotectic equilibrium. The effects corresponding to the solid-state transition of the intermediate phase with composition $2CdI_2{\cdot}3Ag_2Se$ cover a considerably smaller area but have rather acute peaks.

An endothermal effect is registered with the composition CdI_2 at 375 °C which corresponds to its melting temperature

Table 2
Thermoeffects during heating of the system CdI_2–Ag_2Se samples

Ag_2Se (mol%)	Temperature of endothermal effects (°C)					
0						385
5			325			365
10			330			345
20			325			340
25						390
30			325			410
33.3			335			430
40						470
50		125				550
60		125		660		710
66.7	100	125		660		755
70	105			665		770
75	100					780
80	100			660		800
90	105				730	830
95	110				830	860
100		140				890

of 378 °C [10]. Two endothermal effects are registered with the second component (Ag_2Se), at 140 and 890 °C, respectively, that also correspond well to $T_{\alpha\leftrightarrow\beta} = 145\,°C$ and $T_m^{Ag_2Se} = 897\,°C$ [9] mentioned in literature.

Very clear endothermal effects are observed on the thermograms in the concentration ranges (0.0/33.3) mol%, (60/80) mol% and (66.7/95.0) mol% Ag_2Se. Their area depends on the quantity of Ag_2Se and has maximum value with the compositions containing ≈20, 60 and 95 mol% Ag_2Se. The temperatures of these effects are at $330 \pm 5\,°C$, $660 \pm 5\,°C$ and $105 \pm 5\,°C$, 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, peritectic and eutectoidal).

Three endothermal effects are registered within the concentration interval (50.0/66.7) mol% Ag_2Se at 125 °C as the one with 60 mol% Ag_2Se covers the largest area. This can be accepted as a direct evidence of a low-temperature polymorphic transition at this temperature of the intermediate phase $2CdI_2{\cdot}3Ag_2Se$.

For the purposes of microstructure observation we prepared standard polished surfaces. For the purposes of showing the microstructure of the compositions rich in CdI_2 we used hot water ($t = 70\,°C$, $\tau = 10\,min$), and for the compositions rich in Ag_2Se–HNO_3:H_2O = 1:3 ($t = 40\,°C$, $\tau = 2\,min$).

All samples of the system CdI_2–Ag_2Se, except for CdI_2 and Ag_2Se, and the sample containing 60 mol% Ag_2Se are two-phase samples. The light phase in the concentration interval from 0 to 60 mol% Ag_2Se has a yellow colour and porous structure (CdI_2), and the dark phase is solid with characteristic metallic luster ($2CdI_2{\cdot}3Ag_2Se$). The light phase in the concentration interval from 60 to 100 mol% Ag_2Se has a silver colour, metallic luster, and unruffled surface (Ag_2Se).

The graphic correlation of the density (d) and the composition (x) is shown in Fig. 2. An break (leap) is observed in the $d(x)$ dependency which evidences the presence of the intermediate phase $2CdI_2{\cdot}3Ag_2Se$ and is a direct evidence that this phase has, though narrow, a range of homogeneity.

Based on the results of the differential thermal analysis, the X-ray diffraction analysis, the microstructure analysis and the $d(x)$ correlation we created the most probable geometrical image of the phase diagram of the system CdI_2–Ag_2Se (Fig. 3). It is characterized with three non-variant equilibria—peritectic (at a temperature of $660 \pm 5\,°C$) with the formation of an intermediate phase with a composition $2CdI_2{\cdot}3Ag_2Se$; eutectic ($325 \pm 10\,°C$) with an eutectic point in case of ≈18 mol% Ag_2Se; and eutectoidal ($105 \pm 5\,°C$) with an eutectoidal point in case of 95 mol% Ag_2Se.

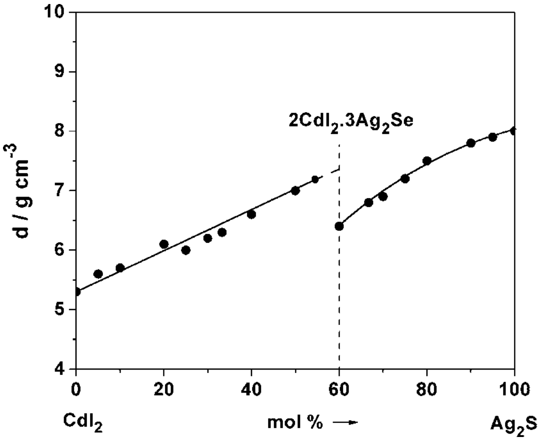

Fig. 2. Dependence $d(x)$ for samples of the system Ag_2Se–CdI_2.

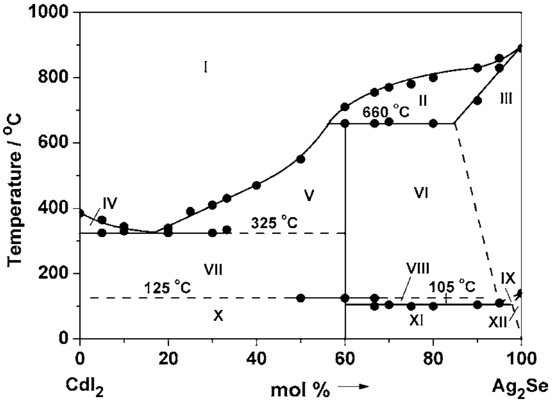

Fig. 3. Phase diagram of the system Ag_2Se–CdI_2. (I) Melt-L; (II) L + β-Ag_2Se; (III) β-Ag_2Se; (IV) CdI_2 + L; (V) L + β-$2CdI_2{\cdot}3Ag_2Se$; (VI) β-$2CdI_2{\cdot}3Ag_2Se$ + β-Ag_2Se; (VII) CdI_2 + β-$2CdI_2{\cdot}3Ag_2Se$; (VIII) α-$2CdI_2{\cdot}3Ag_2Se$ + β-Ag_2Se; (IX) β-Ag_2Se + α-Ag_2Se; (X) CdI_2 + α-$2CdI_2{\cdot}3Ag_2Se$; (XI) α-$2CdI_2{\cdot}3Ag_2Se$ + α-Ag_2Se; (XII) α-Ag_2Se.

The intermediate phase $2CdI_2{\cdot}3Ag_2Se$ undergoes a polymorphic transition at a temperature of 125 °C. It decomposes at a temperature of 660 °C:

$$2CdI_2 \cdot 3Ag_2Se \xleftrightarrow{660\,°C} L + \beta\text{-}Ag_2Se$$

No formation of solid solutions on the basis of CdI_2 is observed. There are no endothermal effects present from non-variant peritectic equilibrium at 600 °C within the range 80–100 mol% Ag_2Se and the solidus line of the concentration interval is observed as well as the effects of the non-variant eutectoidal equilibrium at 105 °C. All of this is evidence that when the temperature is increased the range of homogeneity of β-Ag_2Se expands. In the phase diagram of the system CdI_2–Ag_2Se exist 12 phase fields, three of which are single-phase (I, III and XII).

4. Conclusions

By the means of four independent methods the diagram of the system CdI_2–Ag_2Se is built-up. In the system is formed one intermediate phase with compositions $2CdI_2{\cdot}3Ag_2Se$ is formed. It with the initial compounds CdI_2 and Ag_2Se forms 12 phase fields, three of which are mono-phasic and the rest of them-two-phasic.

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