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Physico-Chemical Interaction in the Ag_2Se–Zn(Cd, Hg, Pb)Se–$SnSe_2$ Systems †

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Abstract: The quaternary compounds $A^I{}_2B^{II}C^{IV}X_4$, where A^I–Cu, Ag; B^{II}–Zn, Cd, Hg; C^{IV}–Si, Ge, Sn; and X–S, Se, Te, crystallize in non-centrosymmetric structures and may be of interest for nonlinear optics. Here, we present in detail isothermal sections and physico-chemical equilibria in the Ag_2Se–Zn(Cd, Hg, Pb)Se–$SnSe_2$ systems where some of these compounds were found. The crystal structure of $Ag_2ZnSnSe_4$ was determined for the first time as the tetragonal symmetry, S.G. $I\bar{4}2m$, lattice parameters a = 0.60434(2), c = 1.13252(5) nm. No quaternary compounds were found in the Ag_2Se–PbSe–$SnSe_2$ system. Ag_8SnSe_6–PbSe is the triangulating section in this system.

Keywords: quaternary chalcogenides; crystal structure; phase equilibria

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1. Introduction

The formation of quaternary compounds in the $A^I{}_2X$–$B^{II}X$–$C^{IV}X_2$ systems where A^I–Cu, Ag; B^{II}–Zn, Cd, Hg; C^{IV}–Si, Ge, Sn; and X–S, Se, Te is known for seven component combinations [1]. The most common are the phases with the equimolar ratio of all three binary compounds described by the $A^I{}_2B^{II}C^{IV}X_4$ formula. These quaternary compounds crystallize in non-centrosymmetric structures and may be of interest for nonlinear optics. Ag-containing compounds may be of interest due to the possible formation of compounds with high ionic conductivity [2,3].

The boundary sides of the presented systems Ag_2Se–Zn(Cd, Hg, Pb)Se–$SnSe_2$ feature only two compounds, Ag_8SnSe_6 (Ag_2Se–$SnSe_2$ system) and Hg_2SnSe_4 (HgSe–$SnSe_2$ system). High-temperature modification of Ag_8SnSe_6 crystallizes in *fcc* structure (S.G. $P4_232$); the crystal structure of the low-temperature Ag_8SnSe_6 was investigated using X-ray powder diffraction. This modification crystallizes in the orthorhombic unit cell (S.G. $Pmn2_1$) and is isostructural to β′-Ag_8GeSe_6. Hg_2SnSe_4 crystallizes in the thiogallate structure (defect chalcopyrite, S.G $I\bar{4}$).

The Ag_2Se–ZnSe–$SnSe_2$ and Ag_2Se–CdSe–$SnSe_2$ systems contain only one intermediate quaternary compound each, $Ag_2ZnSnSe_4$ and $Ag_2CdSnSe_4$ [4]. Each compound has at 670 K a minor homogeneity region stretched along the $Ag_{33.3}Sn_{16.7}Se_{50}$–Zn(Cd)Se sections. Due to the absence of a ternary compound, the sections are non-quasi-binary in the range of 0–50 mol.% Zn(Cd)Se. The crystal structure of the $Ag_2CdSnSe_4$ compound was determined in the orthorhombic symmetry, S.G. $Cmc2_1$, a = 0.42640(2), b = 0.73170(3), c = 0.69842(4) nm, R_I = 0.0782) [4]. The Ag_8SnSe_6–Zn(Cd)Se sections of these systems are quasi-binary, of the eutectic type, with large solid solution ranges of end compounds [5].

The Ag_2Se–HgSe–$SnSe_2$ system [6–8] features at 670 K three intermediate phases, $Ag_2HgSnSe_4$, $Ag_4Hg_3Sn_2Se_9$ ($Ag_{2.66}Hg_2Sn_{1.34}Se_6$) and $Ag_6HgSnSe_6$. $Ag_2HgSnSe_4$ crystallizes in the orthorhombic S.G. *Pmn2₁*, with lattice periods a = 0.8461(1), b = 0.7340(1) and c = 0.69901(6) nm [6,8]. The $Ag_4Hg_3Sn_2Se_9$ compound crystallizes in an orthorhombic unit cell (S.G. *Imm*2, a = 1.2795(2), b = 0.42631(6) and c = 0.58207(4) nm) [7]. This compound has a homogeneity region that is stretched to the ternary compound Hg_2SnSe_4 (the Ag_2Se content is 15–28 mol.%) and is negligible along the $Ag_{33.3}Sn_{16.7}Se_{50}$–HgSe section. The unit cell periods decrease within the homogeneity region to a = 1.2665(3), b = 0.4222(1) and c = 0.5739(1) nm. The structure of $Ag_6HgSnSe_6$ has not been investigated.

2. Materials and Methods

The alloys for investigation were prepared from high purity elements and the previously synthesized mercury selenide. The alloys were synthesized in evacuated quartz containers placed in a shaft-type furnace. The ampoules were heated to 1100 K at the rate of 50 K/h, kept for 6 h, then cooled at the rate of 10 K/h to 670 K. The alloys were annealed at this temperature for 500 h followed by quenching in air. Obtained ingots were compact and black.

The alloys were studied by differential thermal analysis (computer-controlled set-up of Thermodent T-04 furnace, Pt/Pt-Rh thermocouple) and powder X-ray diffraction (DRON 4-13 diffractometer, CuKα radiation).

3. Results and Discussion

3.1. Phase Equilibria in the Ag_2Se–PbSe–$SnSe_2$ System

Isothermal sections at room temperature of the title systems Ag_2Se–Zn(Cd, Hg, Pb)–$SnSe_2$ are presented in Figure 1. The systems with B^{II}–Zn, Cd and Hg were discussed in in the introduction and are shown here for visual comparison.

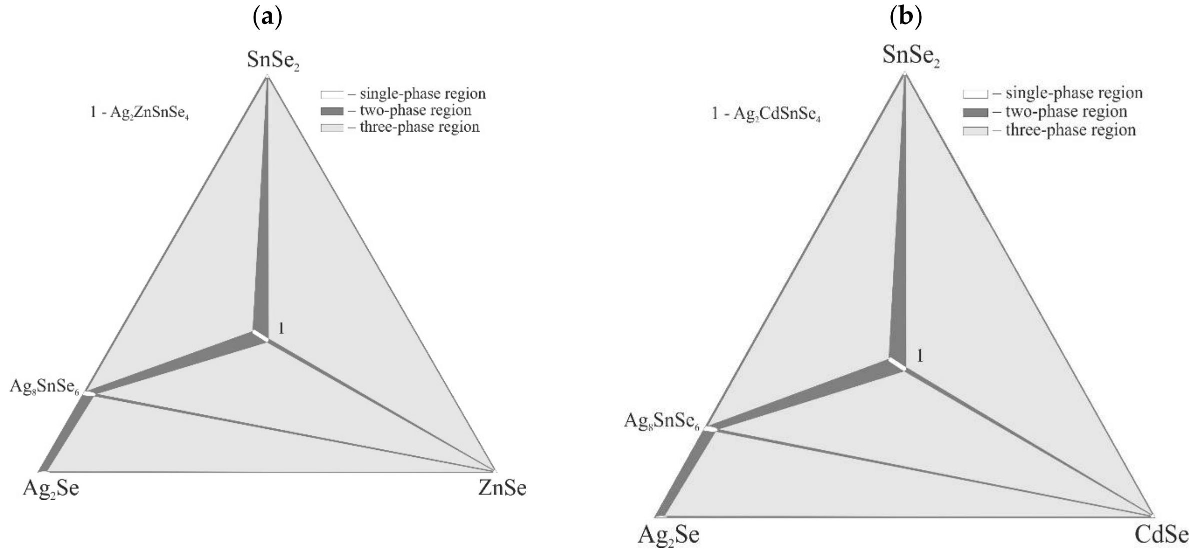

Figure 1. *Cont.*

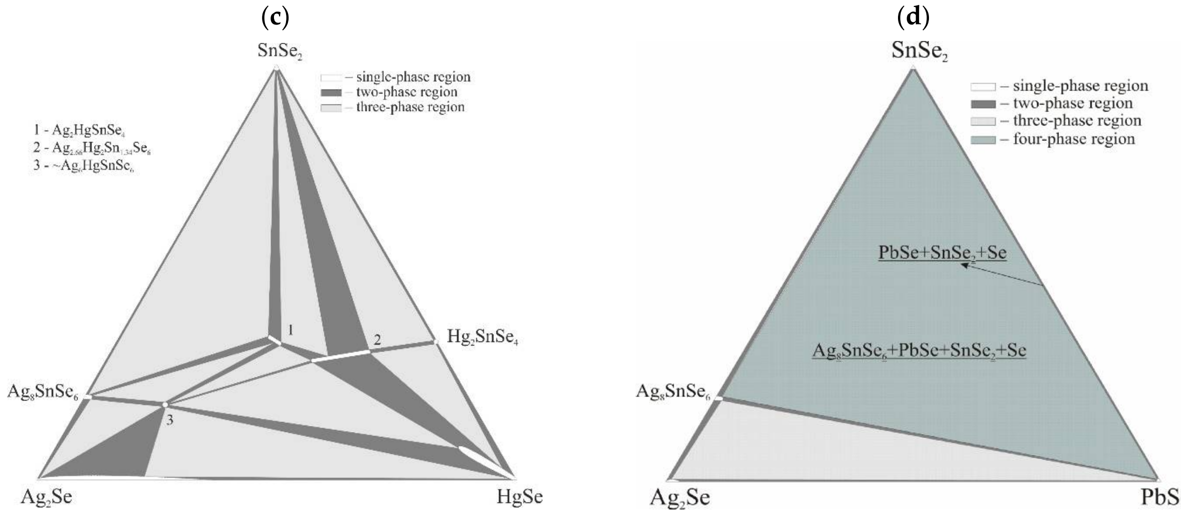

Figure 1. Isothermal sections of the Ag_2Se–Zn(Cd, Hg, Pb)Se–$SnSe_2$ systems at room temperature ((**a**)—ZnSe, (**b**)—CdSe, (**c**)—HgSe, (**d**)—PbSe).

No quaternary compounds were found in the Ag_2Se–PbSe–$SnSe_2$ system. The alloys in the Ag_8SnSe_6–PbSe–$SnSe_2$ sub-system are four-phase since the PbSe–$SnSe_2$ section is non-quasi-binary [9]. Thus, the isothermal section consists of two three-phase fields, Ag_2Se + Ag_8SnSe_6 + PbSe and PbSe + $SnSe_2$ + Se (along the PbSe–$SnSe_2$ line), one four-phase field Ag_8SnSe_6 + PbSe + $SnSe_2$ + Se and contains four two-phase equilibria.

Ag_8SnSe_6–PbSe is the only triangulating section in this system (Figure 2). The section is quasi-binary, features a eutectic at 885 K and 67 mol.% PbSe and is quite similar to the previously referenced Ag_8SnSe_6–Zn(Cd)Se sections [5].

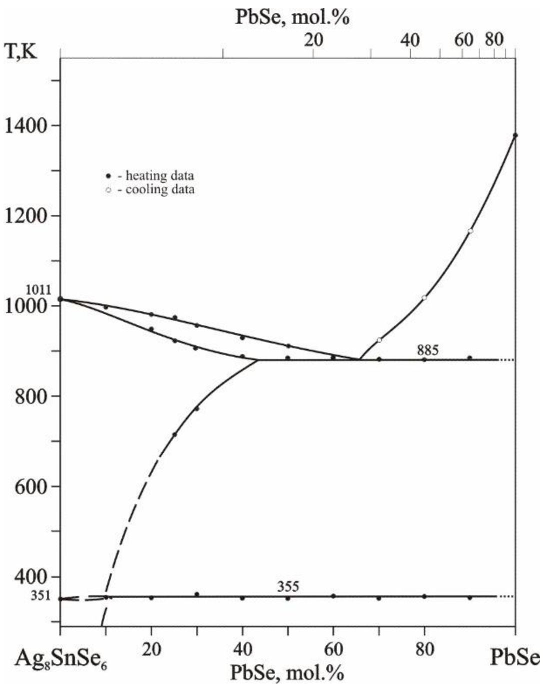

Figure 2. Phase diagram of the Ag_8SnSe_6–PbSe section (top scale is PbSe content within the Ag_2Se–PbSe–$SnSe_2$ system).

3.2. Crystal Structure of the Quaternary Compound $Ag_2ZnSnSe_4$

The crystal structure of the $Ag_2ZnSnSe_4$ compound was determined by X-ray powder method. The set of the experimental intensities of diffraction reflections was recorded in the 2Θ range 10–100° with scan step 0.05° and 20 s exposure in each point at a DRON 4-13 diffractometer (CuKα radiation). The diffraction pattern of the obtained compound was indexed well in the tetragonal structure of the Cu_2FeSnS_4 stannite type with the parameters listed in Table 1. The refinement of profile and structure parameters of $Ag_2ZnSnSe_4$ in isotropic approximation yielded in the selected model the fit factors $R_I = 0.0570$ and $R_P = 0.1277$.

Table 1. Results of the crystal structure determination of the $Ag_2ZnSnSe_4$ compound.

Compound	$Ag_2ZnSnSe_4$
Number of formula units per unit cell	2
Space group	$I\bar{4}2m$
Pearson symbol	*tI16*
a (nm)	0.60434(2)
c (nm)	1.13252(5)
c/a	1.874
Cell volume (nm^3)	0.41363(5)
Number of atoms in the cell	16.0
Calculated density (g/cm^3)	5.7454(6)
Absorption coefficient (1/cm)	884.93
Radiation and wavelength	CuKα 0.154178 nm
Diffractometer	Powder DRON 4–13
Mode of refinement	Full profile
Number of atomic sites	4
Number of free parameters	7
2Θ and sinΘ/λ (max)	99.80 and 0.496
R_I and R_P	0.0570 and 0.1277

Experimental and theoretical X-ray diffraction patterns of the $Ag_2ZnSnSe_4$ compound and their differences are plotted in Figure 3. Atomic coordinates, site occupation and isotropic parameters of temperature displacement of the atoms in the structure of this quaternary chalcogenide are listed in Table 2. According to the obtained results, the structure formula of the quaternary compound is identical to the stoichiometric $Ag_2ZnSnSe_4$.

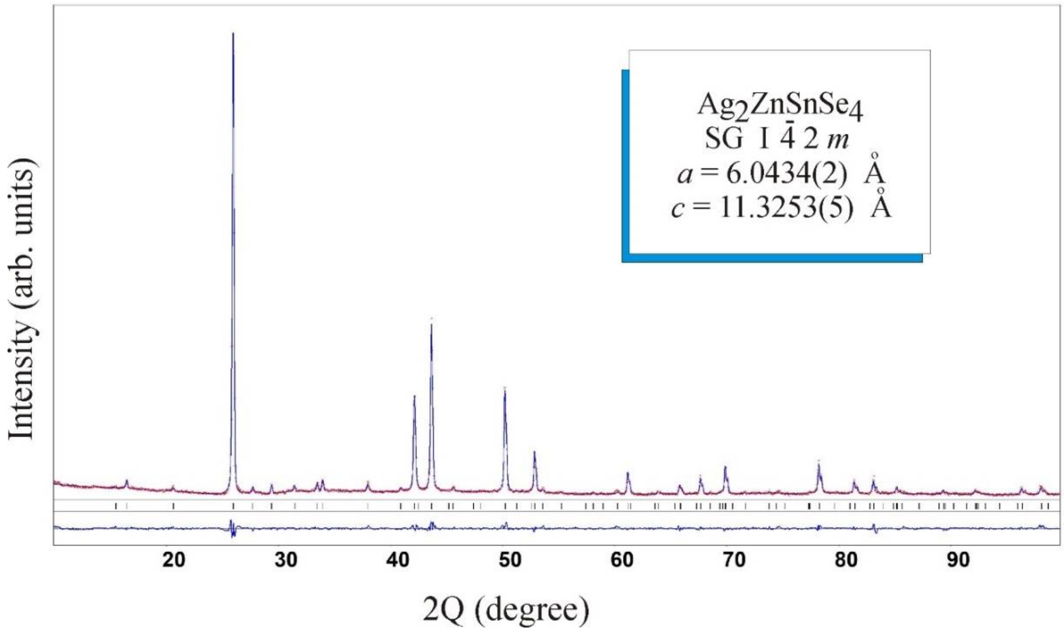

Figure 3. Experimental and theoretical X-ray diffraction patterns for $Ag_2ZnSnSe_4$ and their differences.

Table 2. Atomic coordinates and isotropic temperature displacement factors for the $Ag_2ZnSnSe_4$ structure.

Atom	**Wyckoff Site**	x/a	y/b	z/c	$B_{iso} \times 10^2$, nm^2
Ag	4(d)	0	1/2	1/4	1.21(9)
Zn	2(a)	0	0	0	3.5(3)
Sn	2(b)	0	0	1/2	0.31(9)
Se	8(i)	0.2432(4)	x	0.1129(3)	1.51(8)

The location of the atoms in the unit cell, coordination surrounding and the interatomic distances in the structure of the investigated compound are shown in Figure 4. All atoms are characterized by tetrahedral surrounding. Interatomic distances in the quaternary compound are consistent with the sum of the effective ionic radii.

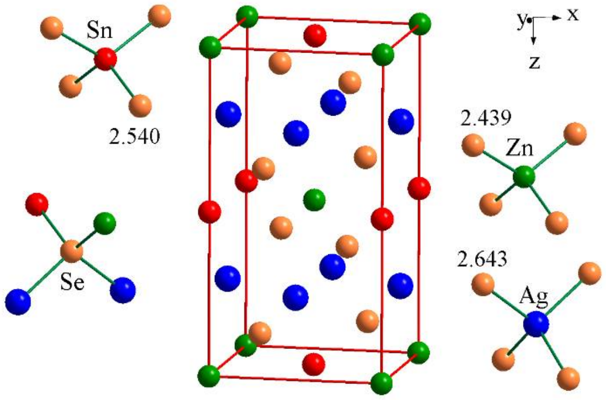

Figure 4. Location of atoms in the unit cell, coordination surrounding and interatomic distances in the $Ag_2ZnSnSe_4$ structure.

The second coordination surrounding (SCS) [10] of selenium atoms shown in Figure 5 has the shape of a cuboctahedron within which the atoms of metallic components occupy four tetrahedral cavities. Comparing the crystal structure of $Ag_2ZnSnSe_4$ and the components and compounds of the Ag_2Se–ZnSe–$SnSe_2$ system, it should be noted that in terms of SCS and its content, the $Ag_2ZnSnSe_4$ compound is related to the sphalerite structure of room-temperature ZnSe [11]. Therefore, the crystal structure of $Ag_2ZnSnSe_4$ can be derived from the cubic sphalerite structure by doubling the unit cell along the *c* axis and ordering the sites of the atoms of the metallic components. SCS of selenium atoms in the structure of $Ag_{0.67}Sn_{0.33}Se$ [12] is also of the sphalerite type where the atoms of the statistical mixture of cations occupy octahedral cavities within the SCS. Conversely, in the binary tin selenide $SnSe_2$ [13], the wurtzite-type SCS is in the form of the hexagonal analog of a cuboctahedron, where tin atoms also occupy octahedral cavities. As for the binary silver selenide Ag_2Se at room temperature [14], Ag1 atoms occupy tetrahedral voids and Ag2 atoms occupy octahedral voids within the wurtzite-type SCS.

Thus, in the quaternary compound, only zinc atoms occupy the same sites as in the binary selenide, whereas silver and tin atoms occupy atypical octahedral voids within an atypical SCS, which is abnormal for them and can produce interesting physical properties in materials based on $Ag_2ZnSnSe_4$.

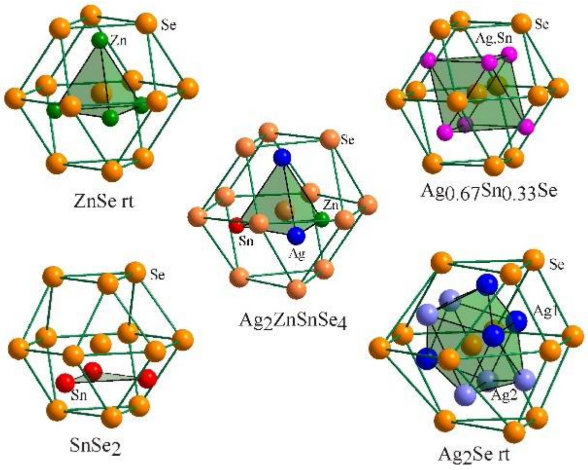

Figure 5. Second coordination surrounding of selenium atoms in the structure of $Ag_2ZnSnSe_4$ and related selenides.

Supplementary Materials: The poster presentation can be downloaded at: https://www.mdpi.com/article/10.3390/IOCC_2022-12155/s1.

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