Crystals 2022
The 3rd International Online Conference on Crystals
15–30 JANUARY 2022 | ONLINE
Chaired by PROF. DR. HELMUT CÖLFEN
crystals MDPI

Physico-chemical interaction in the Ag_2Se–Zn(Cd, Hg, Pb)–$SnSe_2$ systems

Lyudmyla Piskach[1,*], Olga Velychko[2], Anatoli Fedorchuk[3], Yuri Kogut[4], Ivan Olekseyuk[5], and Oleg Parasyuk[6]

[1, 2, 4, 5, 6] Lesya Ukrainka Volyn National University, Department of Chemistry, Ecology and Pharmacy, Lutsk, Voli Ave. 13;
[3] Lviv National University of Veterinary Medicine and Biotechnology, Department of Biological and General Chemistry, Lviv, Pekarska St. 50. ft@fm.ua

* Corresponding author: lyuda0760@ukr.net (piskach.lyudmyla@vnu.edu.ua)

Abstract: 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; X–S, Se, Te is known for seven component combinations. 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.
The boundary sides of the presented systems $Ag_2Se–Zn(Cd, Hg, Pb)–SnSe_2$ feature only two compounds, Ag_8SnSe_6 ($Ag_2Se–SnSe_2$ system) and Hg_2SnSe_4 ($HgSe–SnSe_2$ system).
The $Ag_2Se–ZnSe–SnSe_2$ and $Ag_2Se–CdSe–SnSe_2$ systems contain only one intermediate quaternary compound each, $Ag_2Zn(Cd)SnSe_4$, that form at the non-quasi-binary sections "Ag_2SnSe_3"–Zn(Cd)Se. The diffraction pattern of $Ag_2ZnSnSe_4$ was indexed in the tetragonal structure of the stannite type Cu_2FeSnS_4 (S.G. *I2m*). The structure of the $Ag_2CdSnSe_4$ compound was determined in the orthorhombic symmetry, S.G. $Cmc2_1$. The Ag_8SnSe_6–Zn(Cd)Se sections of these systems are quasi-binary, of the eutectic type, with large solid solution ranges.
The $Ag_2Se–HgSe–SnSe_2$ system features at 670 K three intermediate phases, $Ag_2HgSnSe_4$, $Ag_4Hg_3Sn_2Se_9$, and $Ag_6HgSnSe_6$. $Ag_2HgSnSe_4$ crystallizes in the orthorhombic S.G. $Pmn2_1$. The $Ag_4Hg_3Sn_2Se_9$ compound crystallizes in the orthorhombic S.G. *Imm*2. This compound has a homogeneity region that is stretched to the ternary compound Hg_2SnSe_4. The $Ag_6HgSnSe_6$ structure was not investigated.
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 equlibria.

Results and Discussion

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; 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].

1. Parasyuk O.V., Piskach L.V., Romanyuk Y.E., Olekseyuk I.D., Zaremba V.I., Pekhnyo V.I., Phase relationa in the quasi-binary Cu_2GeS_3–ZnS and quasi-ternary Cu_2S–Zn(Cd)S–GeS_2 systems abd crystal structure of Cu_2ZnGeS_4. *J. Alloys Compd*. **2005**, 397 (1-2), 85-94.
2. Parasyuk O.V., Gulay L.D., Romanyuk Ya.E., Olekseyuk I.D., The Ag_2Se–HgSe–$SiSe_2$ system in the 0-60 mol. % $SiSe_2$ region. *J. Alloys Compd*. **2003**, 348, 157-166.
3. Parasyuk O.V., Gulay L.D., Romanyuk Ya.E., Olekseyuk I.D., Piskach L.V. The Ag_2Se–HgSe–$GeSe_2$ system and crystal structures of the compounds. *J. Alloys Compd*. **2003**, 351(1-2), 135-144.

Ternary compounds

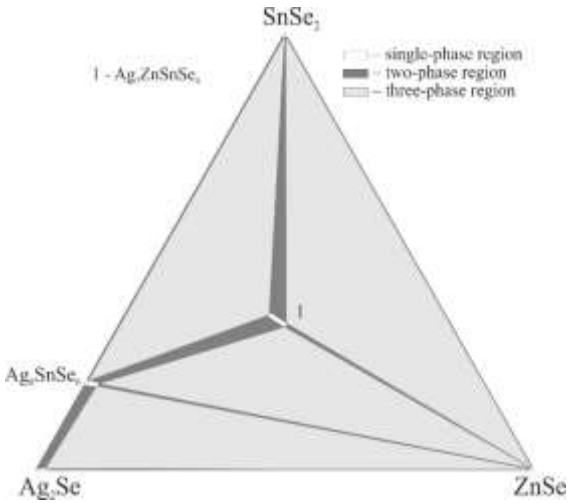
- **Ag_8SnSe_6** (Ag_2Se–$SnSe_2$ system)
- High-temperature modification of Ag_8SnSe_6 crystallizes in the cubic structure (S.G. $P4_232$).
- Low-temperature modification crystallizes in the orthorhombic unit cell (S.G. $Pmn2_1$) and is isostructural to β′-Ag_8GeSe_6.

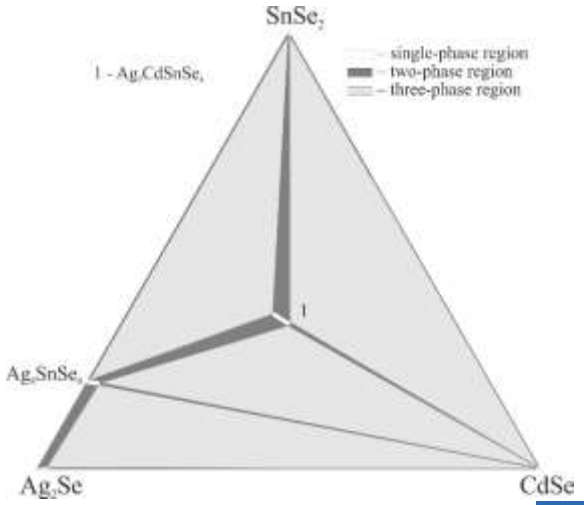
- **Hg_2SnSe_4** (HgSe–$SnSe_2$ system) crystallizes in the thiogallate structure (defect chalcopyrite, S.G $I\bar{4}$).

$Ag_2Se–ZnSe–SnSe_2$ and $Ag_2Se–CdSe–SnSe_2$ systems

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.

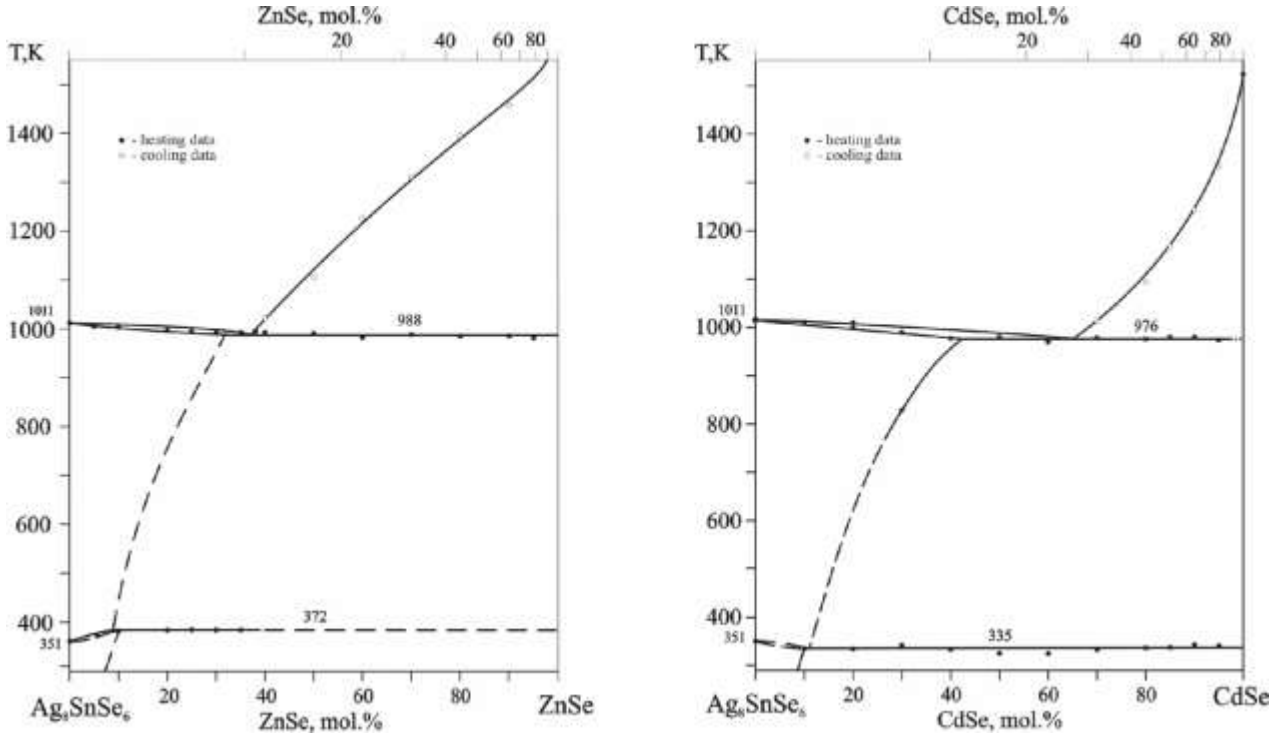
$Ag_2CdSnSe_4$ crystal structure: orthorhombic symmetry, S.G. *Cmc2₁*, *a*=0.42640(2), *b*=0.73170(3), *c*=0.69842(4) nm, R_I=0.0782) [4].





[4] Parasyuk O.V., Gulay L.D., Piskach L.V., Olekseyuk I.D., The Ag2Se–CdSe–SnSe2 system at 670 K and the crystal structure of the Ag2CdSnSe4 compound. *J. Alloys Compd*., 2002, 335(1):176-180.

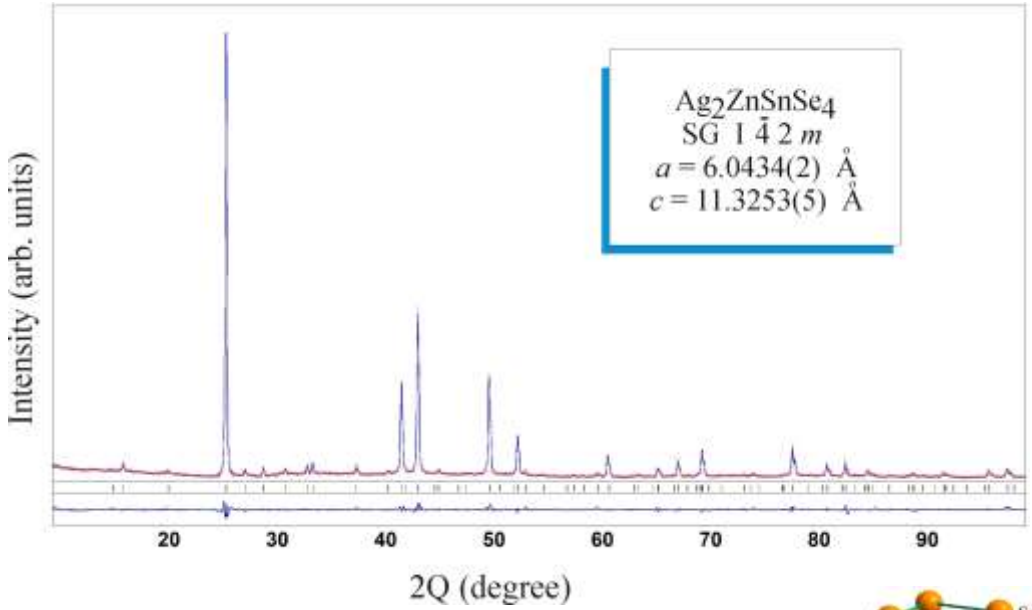
Ag_8SnSe_6–Zn(Cd)Se sections



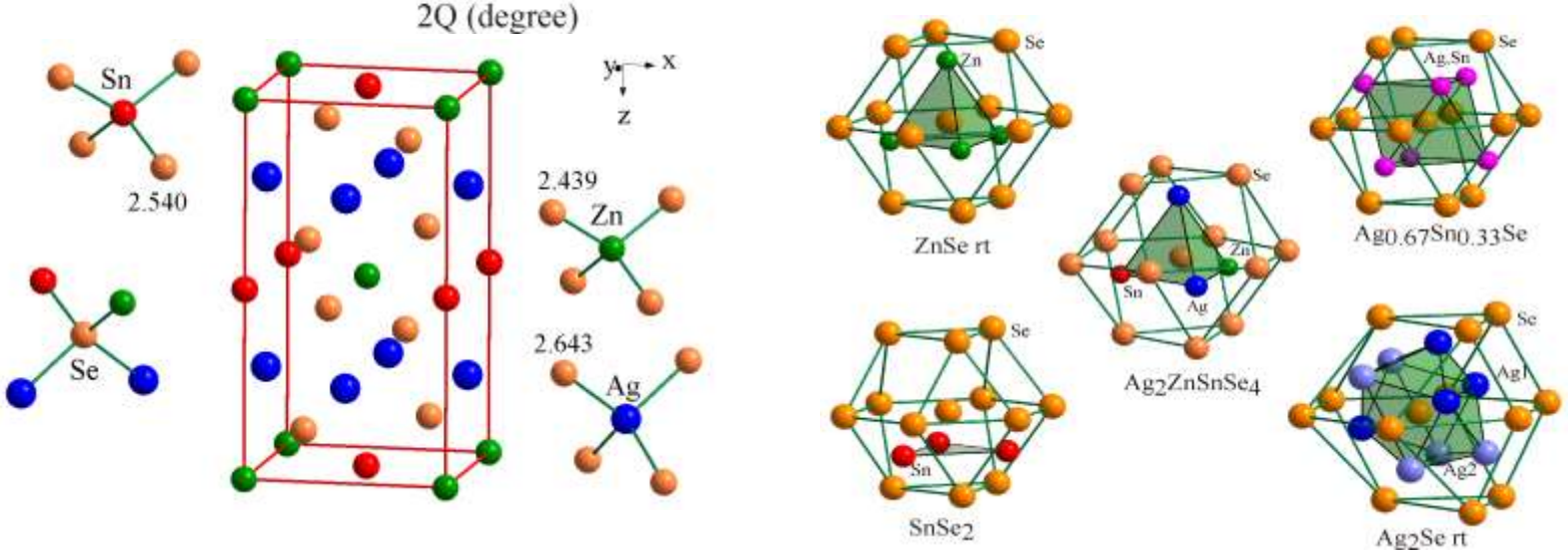
The Ag8SnSe6–Zn(Cd)Se sections of these systems are quasi-binary, of the eutectic type, with large solid solution ranges of end compounds [5].

[5] Piskach L.V., Parasyuk O.V., Olekseyuk I.D., Romanyuk Ya.E., Volkov S.V., Pekhnyo V.I. Interaction of argyrodite family compounds with the chalcogenides of II-b elements. *J. Alloys Compd*., **2006**, 421/1-2, 98-104.

Crystal structure of $Ag_2ZnSnSe_4$

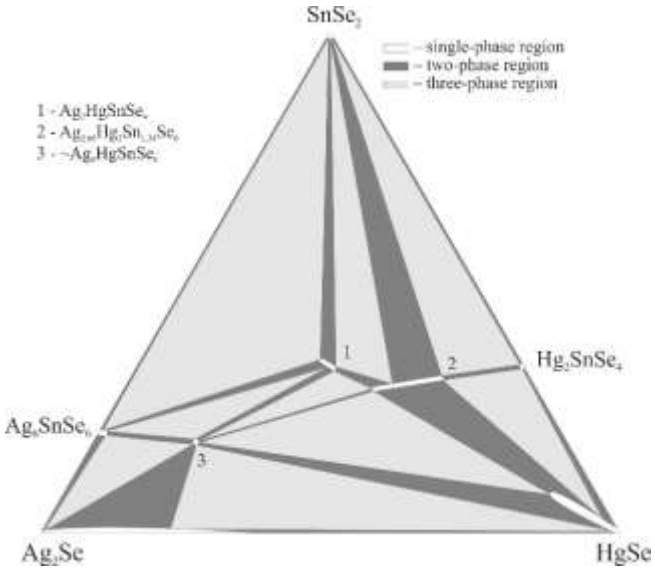


- Experimental and theoretical X-ray diffraction patterns of the $Ag_2ZnSnSe_4$ compound and their difference (top)
- Location of atoms in the unit cell, coordination surrounding, and interatomic distances (bottom left)
- Second coordination surrounding of selenium atoms in $Ag_2ZnSnSe_4$ and related selenides (bottom right)



Crystals 2022

$Ag_2Se–HgSe–SnSe_2$ system



- The Ag2Se–HgSe–SnSe2 system [6-8] features at 670 K three intermediate phases, Ag2HgSnSe4, Ag4Hg3Sn2Se9 (Ag2.66Hg2Sn1.34Se6), and Ag6HgSnSe6.
- Ag2HgSnSe4 crystallizes in the orthorhombic S.G. *Pmn21*, with lattice periods *a*=0.8461(1), *b*=0.7340(1), *c*=0.69901(6) nm [6, 7].
- The Ag4Hg3Sn2Se9 compound crystallizes in an orthorhombic unit cell (S.G. *Imm*2, *a*=1.2795(2), *b*=0.42631(6), *c*=0.58207(4) nm) [8].
- The structure of AgHgSnSe6 has not been investigated.

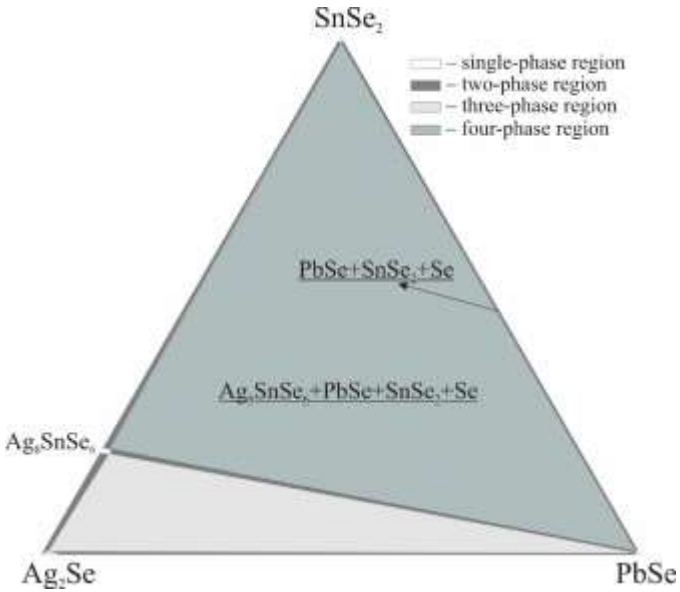
[6]. Parasyuk O.V., Phase relations of the Ag2SnS3–HgS and Ag33.3Sn16.7Se/Te/50–HgSe/Te/ section in Ag–Hg–Sn–S/Se,Te/ systems. *J. Alloys Compd*. **1999**, 291/1-2 () 215-219.

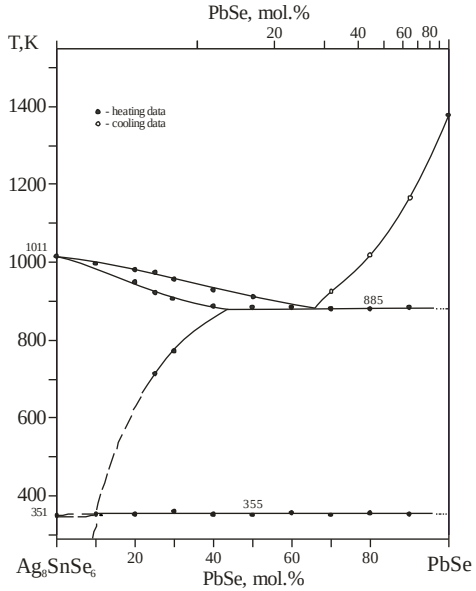
[7]. Parasyuk O.V., Gulay L.D., Piskach L.V., Kumanska Yu. O. The Ag2Se—HgSe—SnSe2 System and the Crystal Structure of the Ag2HgSnSe4 Compound. *J. Alloys Compd*. **2002**, 339/1-2, 140-143.

[8]. Parasyuk O.V., Gulay L.D., Crystal structure of the Ag2.66Hg2Sn1.34Se6 and Hg2SnSe4 compounds. *J. Alloys Compd*. **2002**, 337/1-2, 94-98.

Crystals 2022

Ag_2Se–PbSe–$SnSe_2$ system





- No quaternary compounds were found in the Ag_2Se–PbSe–$SnSe_2$ system. Ag_8SnSe_6–PbSe is the only triangulating section in this 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 equlibria.

[9]. Dal Corso S., Liautard B., Tedenac J.C. The Pb–Sn–Se System: Phase Equilibria and Reactions in the PbSe–SnSe–Se SubTernary *J. Phase Equilibria*. **1995**, 16, 4, 308-314.

Crystal structure of the quaternary compound $Ag_2ZnSnSe_4$

Table 1. $Ag_2ZnSnSe_4$ crystal structure determination

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 $\sin\Theta/\lambda$ (max)	99.80 and 0.496
R_I and R_P	0.0570 and 0.1277

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)

Conclusions

Acknowledgments

Insert here, logos of sponsors

Crystals 2022