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journal homepage: <http://www.journals.elsevier.com/opto-electronics-review>Ag₈SnSe₆ argyrodite synthesis and optical propertiesIhor Semkiv^{a,*}, Hryhoriy Ilchuk^a, Marek Pawlowski^b, Viktor Kusnezh^a^a Lviv Polytechnic National University, Physics Department, S. Bandera 12, 79013 Lviv, Ukraine^b Warsaw University of Technology, Faculty of Physics, Semiconductor Division, Koszykowa 75, 00-662 Warszawa, Poland

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ABSTRACT

The Ag₈SnSe₆ argyrodite compound was synthesized by the direct melting of the elementary Ag, Sn and Se high purity grade stoichiometric mixture in a sealed silica ampoule. The prepared polycrystalline material was characterized by the X-ray diffraction (XRD), visible (VIS) and near-infrared (NIR) reflection and photoluminescence (PL) spectroscopy. XRD showed that the Ag₈SnSe₆ crystallizes in orthorhombic structure, *Pmn*2₁ space group with lattice parameters: *a* = 7.89052(6) Å, *b* = 7.78976(6) Å, *c* = 11.02717(8) Å. Photoluminescence spectra of the Ag₈SnSe₆ polycrystalline wafer show two bands at 1675 nm and 1460 nm. Absorption edge position estimated from optical reflectance spectra is located in the 1413–1540 nm wavelength range.

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1. Introduction

The recent years are characterized by the extension of Moore's law which describes the doubling of transistor density in an integrated circuit every two years [1]. However, a traditional charge based flash memories now have significant challenges as the transistor size decreases further into the nanosize [2]. One of the promising candidates for non-volatile memories is the resistive random access memory (RRAM) with simple sandwiched structure exhibits an attractive performance metrics including excellent scaling potential, low power consumption and high speed [3,4]. The resistive memory cell materials are phase-change chalcogenides [5] including the Ag₈SnSe₆ argyrodite. With ultralow lattice thermal conductivity, Ag₈SnSe₆ with properly tuned carrier density may be a promising candidate of thermoelectric materials [6,7]. Ag₈SnSe₆ is the material with the lowest sound velocity in known thermoelectric semiconductors [8].

In scopes of its practical application it is crucial to know basic structural, optical and electric parameters of the Ag₈SnSe₆ semiconductor compound. The intensive study of argyrodite family started with the publication [9]. After two decades the interest to these materials decreased, but in recent years the number of papers reviewed multinary chalcogenides which illustrate the continuing interest to the old-new multinary chalcogenides materials [10–13]. The compounds with a common formula A₈^IB^{IV}X₆ (A^I = Cu,

Ag; B^{IV} = Si, Ge, Sn; X = S, Se, Te) which belong to the argyrodite family are superionic semiconductors [9,12]. These compounds were reported by several authors and arouse particular interest because of their photosensitivity [14], high ionic conductivity [15] and low-temperature phase transition [16]. Argyrodites display a wide spectrum of electrical conductivities, ranging from essentially electronic to almost purely ionic and can be used as ion-selective electrodes, solid-state electrolytes in the different kind of electric batteries, sensors, displays [17,18], RRAM memory, etc.

The Ag₈SnSe₆ argyrodite can exist only in two phases: low-temperature β'- and high-temperature γ-phase with phase transition (β' → γ) at 356 K. The β'-Ag₈SnSe₆ modification [19] belongs to orthorhombic structure (*Pmn*2₁ space group), with lattice parameters at the room temperature *a* = 7.9168(6) Å, *b* = 7.8219(6) Å, *c* = 11.04538(3) Å. High-temperature γ-phase Ag₈SnSe₆ crystallizes in the primitive cubic cell (*F*-43*m* space group), lattice parameter *a* = 11.1230(9) Å [5] with disordered Ag⁺ cation sublattice. Optical properties of the Ag₈SnSe₆ crystals were investigated only in part. The 0.83 eV optical band gap value was determined from absorption edge and band gap dependence on external pressure was studied [20]. The exciton band was observed at low temperatures in the spectral range of direct optical transitions [20,21]. The band structure calculation [22,23] and symmetrical analysis of the phonon spectra [24] suggest as well that Ag₈SnSe₆ has a direct band gap.

In this paper, we report the time and the energy saving synthesis procedure of the Ag₈SnSe₆ argyrodite compound polycrystalline material for subsequent thin film deposition and further use in resistive switching cells.

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Table 1
X-ray powder diffraction peaks position and Miller indices.

2θ	hkl	2θ	hkl
24.1	112	42.25	321
26.65	103	44.45	232
27.85	022	46.3	224
30.0	122	48.55	402
35.25	331	54.45	141
39.75	132		

2. Experimental

2.1. Synthesis of Ag_8SnSe_6

The Ag_8SnSe_6 compound was synthesized by the direct melting of the stoichiometric mixture of the Ag, Sn and Se of high purity grade (not less than 99.999%) in a sealed (1.5×10^{-3} Pa) silica ampoule. Synthesis was performed in a one-zone furnace equipped with rotation and vibration facility, a description can be found in [22]. The ampoule was placed in thermal integrator, and heated to 1050 K with the $90^\circ/\text{h}$ rate, and held for 3–3.5 h at this temperature to promote sample homogeneity. Heating procedure was performed with intermediate constant 500, 550, 720 K temperature 1 h exposures, and in overall lasted for 15 h. Finally, sample was cooled down to the room temperature. The mass of melted ingot after reaction was found to match the value of initial elements measured before the reaction. This suggests the possibility of stoichiometric materials formation. Confirmation of the argyrodite stoichiometry conducted using XRD (shown below). Therefore, the Ag_8SnSe_6 compound ingot 27–30 h synthesizes was conducted. The proposed method is much less time and energy consuming in comparison to the 500 h of similar synthesis approaches [25] for complex silver chalcogenides. For optical properties investigation the homogenous polycrystalline wafers with acetone cleaned surfaces were used. The powder of milled material with an average grain size not exceeding $10 \mu\text{m}$ was used for structural investigation.

2.2. Characterization and analysis

X-ray powder diffraction patterns were recorded with a DRON-3M powder diffractometer with monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The samples were placed on a glass substrate for XRD characterization, and the 2θ range used in the measurement was $10^\circ \leq 2\theta \leq 60^\circ$. The 0.05° step size with 4 s per data point was used to scan. The crystal structure was determined using the FullProf Suite (3.0) program [26].

Optical reflection spectra $R(\lambda)$ of the wafers were studied at room temperature using a Bentham PVE300 setup.

For the photoluminescence studies the sample was put in the cryostat. The 514 nm laser light was used as the excitation source. The detailed PL setup description can be found in Ref. [27].

3. Results and discussion

3.1. Crystal structure of the Ag_8SnSe_6

Fig. 1 shows the XRD patterns of the synthesized argyrodite. The diffraction peaks appearing in XRD spectra can be assigned to planes presented in Table 1. The standard β -phase Ag_8SnSe_6 diffraction peaks, referred from the Inorganic Crystal Structure Database number of No.95093 for the orthorhombic structure with the $Pmn2_1$ space group. The calculated $a = 7.89052(6) \text{ \AA}$, $b = 7.78976(6) \text{ \AA}$, $c = 11.02717(8) \text{ \AA}$ lattice parameters compare favorably with measurements made by previous investigators [19,28]. From Fig. 1 one can note the absence of peaks related to

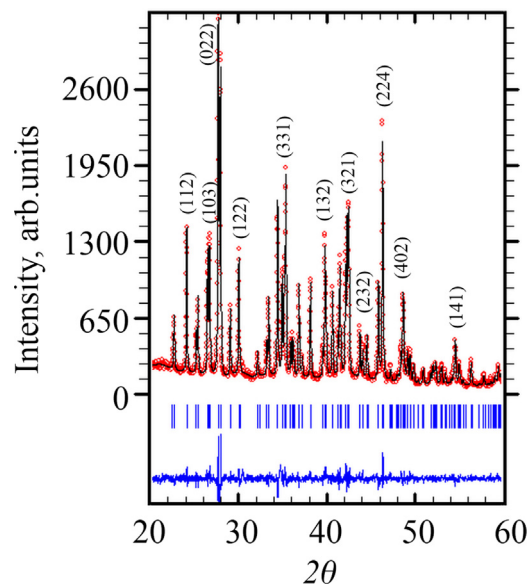


Fig. 1. X-ray diffraction pattern of the β -phase Ag_8SnSe_6 argyrodite at the room temperature. Experimental data (circles), theoretical profile (solid line) are presented with the calculated Bragg positions (vertical lines) and difference curve (bottom solid line).

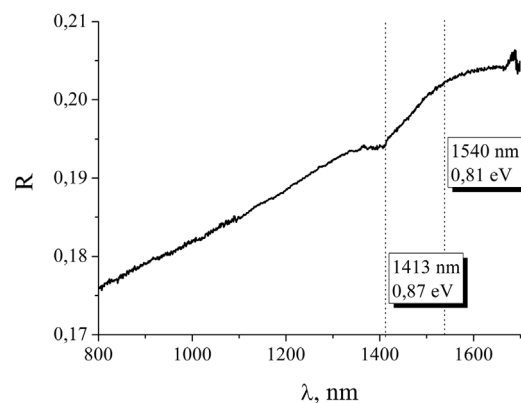


Fig. 2. Reflectance spectral dependence of the Ag_8SnSe_6 polycrystalline wafer.

impurity phases such as the SnSe_2 , Ag_2Se , and Ag, which confirm the reaction of the Ag–Sn–Se ternary compound synthesis. The composition of synthesized samples is the same with Ag, Sn, Se precursors.

3.2. Optical reflectance spectra

For Ag_8SnSe_6 polycrystalline wafers, the reflectance (R) spectra were measured in a 800–1750 nm wavelengths (λ) range (Fig. 2). The transmittance (T) spectra (not presented) were measured, but samples have absorbed practically all the light in the investigated region. Hence, we could not calculate absorption coefficient (α) to determine optical band gap (E_g) using $(\alpha \cdot h\nu) = A(h\nu - E_g)^n$ equation [29]. Reflection spectra allows to evaluate the position of fundamental absorption edge which is located in the 1413–1540 nm wavelength range and is in agreement with the reported value of 1495 eV [20].

3.3. Luminescence properties

The photoluminescence (PL) integrated intensity (I_{PL}) follows the power law $I_{\text{PL}} \sim P^m$ where P is the excitation power and m is the

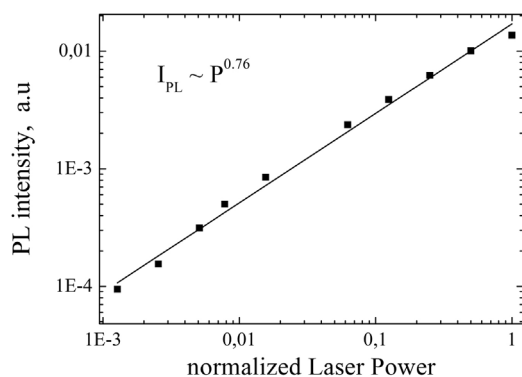


Fig. 3. Photoluminescence integrated intensity vs. normalized power of exciting laser at 17 K. In the equation in the inset I_{PL} and P denote PL integrated intensity and laser power, respectively.

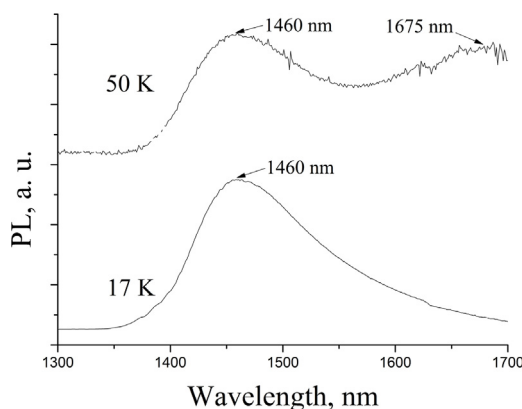


Fig. 4. Photoluminescence spectra under 17 K and 50 K. Two transitions at 1675 nm and 1460 nm are visible.

fitted parameter (Fig. 3). In our case, under 17 K, m is 0.76 which is typical for recombination involving defects [30]. In the low temperature PL spectra one broad asymmetric peak is visible (Fig. 4). Maximum of the peak is located at 1460 nm (0.85 eV) which is about 160 meV below the band gap. Under 17 K the band gap is expected to be around 1.01 eV [31] in the assumption that dE_g/dT of γ -phase is the same for β' -phase. The shape of the peak, with sharp high energy side and flatter low energy side, is typical for recombination, which occurs between the tails of conduction and/or valance band. On the other hand, peak does not shift even when excitation power is increased by three orders of magnitude (not shown here). Thus, the commonly observed effect of reducing potential fluctuations due to screening of charged defects by generated carriers is not observed [32]. The possible explanation is that band fluctuations can be a result of chemical and/or structural non-uniformity. With increasing temperature the efficient non-radiative recombination activates and above 70 K no signal can be detected. While PL quenches rapidly a new peak at 1460 nm (0.74 eV) emerges (Fig. 4). This recombination channel is likely associated with a donor–acceptor transition.

4. Conclusions

The Ag_8SnSe_6 argyrodite polycrystalline ingot was prepared by the direct melting of the high purity grade Ag, Sn and Se stoichiometric mixture for the 30 h in an evacuated quartz ampoule. The presence of crystalline peaks was revealed in the XRD patterns of the synthesized argyrodite. Another peaks absence in XRD related to impurity phase such as the SnSe_2 , Ag_2Se , and Ag, confirm the synthesis of the Ag_8SnSe_6 argyrodite polycrystalline compound. The

result of X-ray diffraction demonstrates that the Ag_8SnSe_6 argyrodite crystallizes in orthorhombic phase.

Photoluminescence spectra of the argyrodite samples have been investigated. Two optical transitions of a wavelength of 1675 nm and 1460 nm were observed. Absorption edge position of Ag_8SnSe_6 argyrodite estimated from optical reflectance spectrum is in the 1413–1540 nm range that coincides with known values.

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References

- [1] M. Lundstrom, Moore's law forever? *Science* 299 (5604) (2003) 210–211.
- [2] Nanoelectronics and Information Technology, in: R. Waser (Ed.), Wiley-VCH, Weinheim, 2003.
- [3] M.-J. Lee, C.B. Lee, D. Lee, S.R. Lee, M. Chang, J.H. Hui, Y.-B. Kim, C.-J. Kim, D.H. Seo, S. Seo, U.-I. Chung, I.-K. Yoo, K. Kim, A fast, high-endurance and scalable non-volatile memory device made from asymmetric Ta_2O_5 - x/TaO_2 - x bilayer structures, *Nat. Mater.* 10 (2011) 625–630.
- [4] R. Waser, R. Dittmann, G. Staikov, K. Szot, Redox-based resistive switching memories – nanoionic mechanisms, prospects, and challenges, *Adv. Mater.* 21 (2009) 2632–2663.
- [5] M.N. Kozicki, M. Park, M. Mitkova, Nanoscale memory elements based on solid-state electrolytes, *IEEE Trans. Nanotechnol.* 4 (2005) 331–338.
- [6] X. Zhang, C.-L. Zhang, S. Lin, H. Lu, Y. Pei, S. Jia, Thermoelectric properties of n-type Nb-doped Ag_8SnSe_6 , *J. Appl. Phys.* 119 (2016) 135101–1–135101-6.
- [7] L. Li, Y. Liu, J. Dai, A. Hong, M. Zeng, Z. Yan, J. Xu, D. Zhang, D. Shan, S. Liu, Z. Ren, J.-M. Liu, High thermoelectric performance of superionic argyrodite compound Ag_8SnSe_6 , *J. Mater. Chem. C* 4 (2016) 5806–5813.
- [8] W. Li, S. Lin, B. Ge, J. Yang, W. Zhang, Y. Pei, Low sound velocity contributing to the high thermoelectric performance of Ag_8SnSe_6 , *Adv. Sci.* 3 (11) (2016), 1600196-1–1600196-7.
- [9] W.F. Kuhs, R. Nitsche, K. Schuenemann, The argyrodites – a new family of the tetrahedrally close-packed structures, *Mater. Res. Bull.* 14 (1979) 241–248.
- [10] M.V. Chekaylo, V.O. Ukrainets, G.A. Il'chuk, Yu.P. Pavlovsky, N.A. Ukrainets, Differential thermal analysis of Ag–Ge–Se, Ge–Se charge materials in the process of their heating and Ag_8GeSe_6 , GeSe_2 compound synthesis, *J. Non-Cryst. Solids* 358 (2012) 321–327.
- [11] M.V. Moroz, M.V. Prokhorenko, Measurement of the thermodynamic properties of saturated solid solutions of compounds in the Ag–Sn–Se system by the EMF method, *Russ. J. Phys. Chem. A* 89 (2015) 1325–1329.
- [12] S.M. Bagheri, S.Z. Imamaliyeva, L.F. Mashadiyeva, M.B. Babanly, Phase equilibria in the Ag_8SnSe_6 – Ag_8SnSe_6 system, *Int. J. Adv. Sci. Tech. Res.* 4 (2) (2014) 291–296.
- [13] S.K. Kovach, A.P. Kokhan, Yu.V. Voroshilov, Electrochemical behavior and Ag_8GeSe_6 , Ag_8GeSe_6 , *Ukr. Khim. Zh.* 59 (1993) 395–398 (in Russian).
- [14] I.S. Osipishin, N.I. Bursko, B.I. Gasii, I.D. Zhezhrich, *Sov. Phys. Semicond.* 6 (1972) 974 (transl. from *Fiz. Tekh. Poluprov* 6 (1972) 1121–1123).
- [15] S.N. Starostenko, Deposited Doc, VINITI 3167 (1981) 288–291 (in Russian).
- [16] O. Gorochov, Les composes Ag_8MX_6 ($M = \text{Si, Ge, Sn}$ and $X = \text{S, Se, Te}$), *Bull. Soc. Chim. Fr.* 6 (1968) 2263–2275.
- [17] A.K. Ivanov-Shits, I.V. Murin, *Solid State Ionics*, vol. 1, Saint-Petersburg University Publ., Saint-Petersburg, 2000.
- [18] S. Hull, P. Berastegui, A. Grippa, Ag^+ diffusion within the rock-salt structured superionic conductor $\text{Ag}_4\text{Sn}_3\text{S}_8$, *J. Phys.: Condens. Matter* 17 (2005) 1067–1084.
- [19] L.D. Gulay, I.D. Oleksceyk, O.V. Parrasyuk, Crystal structure of β - Ag_8SnSe_6 , *J. Alloys Compd.* 339 (2002) 113–117.
- [20] R. Bendorius, A. Irzikevicius, A. Kindurys, E.V. Tsvetkova, The absorption spectra of $\text{Ag}_8\text{M}^{\text{IV}}\text{Se}_6$ and $\text{Ag}_8\text{GeX}^{\text{VI}}_6$ compounds, *Phys. Stat. Sol. (a)* 28 (1975) K125–K127.
- [21] A. Kindurys, A. Shileika, Investigation of the absorption edge of the compounds at phase transitions, *Inst. Phys. Conf. Ser.* 35 (1977) 67–72.
- [22] I.V. Semkiv, B.A. Lukyanets, H.A. Ilchuk, R.Yu. Petrus, A.I. Kashuba, M.V. Chekaylo, Energy structure of β -phase of Ag_8SnSe_6 crystal, *J. Nano-Electron. Phys.* 8 (1) (2016), 01011-1–01011-5.
- [23] S.V. Syrotuk, I.V. Semkiv, H.A. Ilchuk, V.M. Shved, *Condens. Matter Phys.* 19 (4) (2016), 43703-1–43703-6.
- [24] I.V. Semkiv, H.A. Ilchuk, A.I. Kashuba, R.Yu. Petrus, V.V. Kusnez, Lattice dynamic of Ag_8SnSe_6 crystal, *J. Nano-Electron. Phys.* 8 (3) (2016), 03006-1–03006-6.
- [25] Z.M. Aliyeva, S.M. Bagheri, Z.S. Aliev, I.J. Alverdiyev, Y.A. Yusibov, M.B. Babanly, The phase equilibria in the Ag_2S – Ag_8GeSe_6 – Ag_8SnSe_6 system, *J. Alloys Compd.* 611 (2014) 395–400.
- [26] <http://www.ill.eu/sites/fullprof/>.

- [27] M. Pawlowski, P. Zabierowski, R. Bacewicz, H. Marko, N. Barreau, Photoluminescence as a tool for investigations of the junction region in Cu(In,Ga)Se₂-based solar cells, *Thin Solid Films* 519 (2011) 7328–7331.
- [28] D. Carre, R. Ollitrault-Fichet, Structure de Ag₈GeSe₆β, J. Flahaut. *Acta Crystallogr. B* 36 (1980) 245–249.
- [29] J.I. Pankove, *Optical Processes in Semiconductors*, Prentice-Hall, New Jersey, 1971.
- [30] T. Schmidt, K. Lischka, W. Zulehner, Excitation-power dependence of the near-band-edge photoluminescence of semiconductors, *Phys. Rev. B* 45 (1992) 8989–8994.
- [31] O. Madelung, *Semiconductors: Data Handbook*, Springer Science & Business Media, Berlin, 2012.
- [32] Susanne Siebentritt, *Wide-gap Chalcopyrites*, vol. 1, Springer, Berlin, 2006.