



Optical constants of silver and copper indium ternary sulfides from infrared reflectivity measurements



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HIGHLIGHTS

- Infrared spectra of AgIn_5S_8 and CuIn_5S_8 are obtained in the range $50\text{--}2000\text{ cm}^{-1}$.
- Four infrared-active modes are detected in agreement with theoretical prediction.
- The observed bands are assigned to the valence and valence-deformation vibrations.
- The frequencies of transverse and longitudinal optical modes were determined.

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ABSTRACT

Infrared reflection spectra are obtained in the frequency range of $50\text{--}2000\text{ cm}^{-1}$ for AgIn_5S_8 and CuIn_5S_8 single crystals grown by Bridgman method. All four infrared-active modes are detected, which are in full agreement with the prediction of group-theoretical analysis. Spectral dependence of optical parameters; real and imaginary parts of the dielectric function, the function of energy losses, refractive index, absorption index and absorption coefficient were calculated from reflectivity experiments. The frequencies of transverse and longitudinal optical modes and oscillator strengths were also determined. The bands detected in IR spectra of studied crystals were assigned to various vibration types (valence and valence-deformation) on the basis of the symmetrized displacements of atoms obtained employing the Melvin projection operators.

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1. Introduction

I–III–VI ternary semiconductors with the general formula of AB_5C_8 (where A = Cu or Ag; B = Ga or In and C = S, Se or Te) have potentials as photo-absorbers in solar cells, optoelectronics devices, and photoelectrochemical cells. The ternary semiconducting compounds AgIn_5S_8 and CuIn_5S_8 have the same cubic spinel structure as CdIn_2S_4 [1]. These crystals can be derived from the CdIn_2S_4 , if the divalent cadmium cations are replaced by the univalent copper cations and trivalent indium cations, according to the following transformations: $\text{CdIn}_2\text{S}_4 \Rightarrow [\text{Cu}_{1/2}\text{In}_{1/2}]_t[\text{In}_2]_o \Rightarrow \text{Cu}_{1/2}\text{In}_{3/2}\text{S}_4 \Rightarrow \text{CuIn}_5\text{S}_8$. Thus, in the AgIn_5S_8 and CuIn_5S_8 crystals 1/5 of the indium cations have tetrahedral (t) and 4/5 of the indium cations have octahedral (o) coordination. AgIn_5S_8 and CuIn_5S_8 crystals are the visible-light-active materials with high-absorption coefficients, suitable band gaps, good radiation stability, and easy

conversion between n- and p-type carrier types which permits a variety of potentially low-cost homo and hetero junction [2–4]. These crystals have been confirmed as materials suitable for use in high-frequency thin films converters, infrared detectors and various types of heterojunctions [5].

The optical and electrical properties of AgIn_5S_8 and CuIn_5S_8 have been studied in Refs. [6–11]. The energy band gaps for the direct optical transitions of AgIn_5S_8 and CuIn_5S_8 are 1.78 and 1.51 eV at 300 K, and 1.88 and 1.57 eV at 96 K, respectively [12]. Earlier, photoluminescence (PL) spectra of AgIn_5S_8 crystals were investigated in the temperature range of 10–170 K [13]. The observed PL band centered at 1.65 eV was attributed to the radiative recombination of charge carriers from donor ($E_d = 0.06\text{ eV}$) to acceptor ($E_a = 0.32\text{ eV}$) states. PL spectra of CuIn_5S_8 crystals grown by Bridgman method have been studied in the wavelength region of 720–1020 nm and in the temperature range of 10–34 K [14]. A broad PL band centered at 861 nm (1.44 eV) was observed at $T = 10\text{ K}$. Radiative transitions from shallow donor level ($E_d = 17\text{ meV}$) to acceptor level ($E_a = 193\text{ meV}$) were suggested to

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be responsible for the observed PL band. Earlier, thermally stimulated current measurements were carried out on as-grown AgIn_5S_8 single crystals [15]. The investigations were performed in temperatures ranging from 10 to 70 K with heating rate of 0.2 K/s. The analysis of the data revealed the electron trap level with activation energy 5 meV.

Recently, the optical properties of AgIn_5S_8 and CuIn_5S_8 crystals were investigated by ellipsometry measurements [16,17]. Spectral dependence of optical parameters; real and imaginary parts of the pseudodielectric function, pseudorefractive index, pseudoextinction coefficient, reflectivity and absorption coefficient were obtained from the analysis of ellipsometry experiments performed in the 1.2–6.2 eV spectral region. Wemple–DiDomenico and Spitzer–Fan models were used to find the oscillator energy, dispersion energy, zero-frequency refractive index and high-frequency dielectric constant values.

Infrared reflection and Raman scattering spectra of AgIn_5S_8 and CuIn_5S_8 crystals have also been investigated and analyzed in Refs. [18–21]. In the IR spectra of CuIn_5S_8 crystals only two intensive infrared-active modes were revealed [19,20]. The model of central force constants has been proposed for the calculation of optical mode frequencies of the Brillouin zone center in spinel-type crystals in Ref. [21].

2. Experimental details

AgIn_5S_8 and CuIn_5S_8 semiconductor polycrystals were synthesized using high-purity elements taken in stoichiometric proportions. Usually, the synthesis of binary and ternary chalcogenide compounds are characterized by high pressure of the chalcogenide vapors, the endothermal reactions leading to a sharp increase in temperature and by strong interaction of the above compounds with the oxygen (especially, at high temperatures). Therefore, a special method has been developed for the synthesis of compounds with high volatile compounds. The synthesis was carried out in quartz ampoules evacuated to 10^{-5} Torr. The single crystals were grown from obtained polycrystals by the Bridgman method in silica tubes (10 mm in diameter and about 10 cm in length) with a tip at the bottom in our crystal growth laboratory. The ampoule was moved in a vertical furnace through a thermal gradient of 30°C cm^{-1} at a rate of 1.0 mm h^{-1} . The resulting ingot appeared gray in color.

In order to carry out the reflectivity measurements, the ingots were cut and the surfaces produced were ground and polished carefully according to optical techniques to have the highest optical quality. Right before the reflectivity measurements, the samples were mechanically polished with $0.5\ \mu\text{m}$ Al_2O_3 powder, followed by chemical polishing with an alkaline solution, and finally rinsed with deionized water. IR reflection spectra of AgIn_5S_8 and CuIn_5S_8 crystals were recorded in the frequency range from 50 to 2000 cm^{-1} using the long-wave diffraction IR spectrometers FIS-21 and FIS-3 with a resolution of 1 cm^{-1} .

3. Results and discussion

AgIn_5S_8 and CuIn_5S_8 compounds crystallize in the normal spinel structure with space group O_h^7 ($Fd3m$) and $Z = 4$ molecules per unit cell. The group-theoretical analysis gives the following set of vibrations at the center of Brillouin zone

$$\Gamma \equiv A_{1g} + E_g + F_{1g} + 3F_{2g} + 2A_{2u} + 2E_u + 5F_{1u} + 2F_{2u}.$$

Among them, the modes $4F_{1u}$ are infrared-active, while the $A_{1g} + E_g + 3F_{2g}$ modes are Raman-active. One F_{1u} mode is an acoustic one and $F_{1g} + 2A_{2u} + 2E_u$ modes are inactive. The symmetrized

displacements of atoms for infrared-active vibrational modes in AgIn_5S_8 and CuIn_5S_8 crystals obtained by us using Melvin projection operators [22] are presented in Fig. 1.

Fig. 2 shows the IR reflectivity spectra of AgIn_5S_8 and CuIn_5S_8 crystals in the frequency range of $50\text{--}500\text{ cm}^{-1}$. Four IR-active optical modes were revealed in the spectra.

Kramers–Kronig analysis of the spectra has been performed to get the dispersion parameters. The frequencies of transverse (ν_{TO}) and longitudinal (ν_{LO}) optical phonons were determined from the maxima of the function of the imaginary part of the dielectric constant ε_2 and the function of energy losses $\text{Im}(1/\varepsilon)$, respectively. The spectral dependencies of ε_1 , ε_2 and $\text{Im}(1/\varepsilon)$ for AgIn_5S_8 and CuIn_5S_8 are shown in Figs. 3 and 4, respectively. The determined values of ν_{TO} and ν_{LO} for AgIn_5S_8 and CuIn_5S_8 crystals are presented in Table 1.

Moreover, the dependencies of refractive index n and absorption index k on the frequency were calculated from reflectivity spectra for AgIn_5S_8 and CuIn_5S_8 (Figs. 5 and 6). The high- and low-frequency refractive indices were determined as 2.62 (2.72) ($\nu = 2000\text{ cm}^{-1}$) and 3.67 (3.70) ($\nu = 50\text{ cm}^{-1}$), respectively, with maximum values of $n = 5.12$ (8.01) corresponding to the frequencies $\nu = 197$ (209) cm^{-1} for AgIn_5S_8 (CuIn_5S_8). Knowing the values of absorption index it is possible to calculate the absorption coefficient (α) employing the relationship $\alpha = 4\pi k/\lambda$, where λ is the wavelength. The computed spectral dependencies of absorption coefficients of AgIn_5S_8 and CuIn_5S_8 crystals are presented in the insets of Figs. 5 and 6. Maximum magnitudes of α , 9980 and 19180 cm^{-1} for AgIn_5S_8 and CuIn_5S_8 , respectively, are occurred at the same frequency of 216 cm^{-1} .

The oscillator strength was determined as

$$S = \frac{\gamma}{\nu_{\text{TO}}} \varepsilon_2(\text{max}),$$

where $\varepsilon_2(\text{max})$ is the value of the imaginary part of the dielectric constant in the reflection band maximum and γ is the full-width at half maximum of ε_2 peak (the damping constant) (see Table 1). Using the obtained values of $\varepsilon_2(\text{max})$ and γ (see Figs. 2 and 3, Table 1), the magnitudes of oscillator strength for all infrared-active modes were found and presented in Table 1. The high-frequency dielectric constant $\varepsilon_\infty = 6.85$ (7.40) for AgIn_5S_8 (CuIn_5S_8) were established from the high-frequency reflection coefficients R_∞ ($\nu = 2000\text{ cm}^{-1}$) in accordance with formula

$$\varepsilon_\infty = \left(\frac{1 + \sqrt{R_\infty}}{1 - \sqrt{R_\infty}} \right)^2.$$

The low-frequency dielectric constants ε_0 , determined from relation $\varepsilon_0 = \varepsilon_\infty + \sum_1^4 S$ were found to be 12.91 (13.34) for AgIn_5S_8 (CuIn_5S_8) crystals.

It is known that at substitution of tetrahedrally coordinated Me atoms (Ag, Cu) in AgIn_5S_8 and CuIn_5S_8 crystals, the lattice constants and the distances between the nearest atoms are changed slightly ($a = 1.082$ (1.070) nm, Me–S = 0.261 (0.259) nm, In–S = 0.255 (0.251) nm, S–S = 0.465 (0.460) nm for AgIn_5S_8 (CuIn_5S_8)). Since the force constants of atomic interaction are mainly determined by the bond lengths, one can suppose that the modes frequencies caused by the antiphase vibrations along the coordinate axes (valence vibrations) of sulfur atoms and octahedrally coordinated indium atoms (F_{1u}^2 and F_{1u}^4 Fig. 1) must have near values in the crystals studied [23]. Indeed, the close frequencies of the two most intensive modes in the IR spectra of AgIn_5S_8 ($F_{1u}^2 = 207$ and $F_{1u}^4 = 313\text{ cm}^{-1}$) and CuIn_5S_8 ($F_{1u}^2 = 213$ and $F_{1u}^4 = 306\text{ cm}^{-1}$) attract attention (Table 1). The influence of the tetrahedral cations (Ag, Cu) on the frequencies of these modes is relatively small.

Moreover, the spectra of AgIn_5S_8 and CuIn_5S_8 crystals exhibit two modes with small LO–TO splitting:

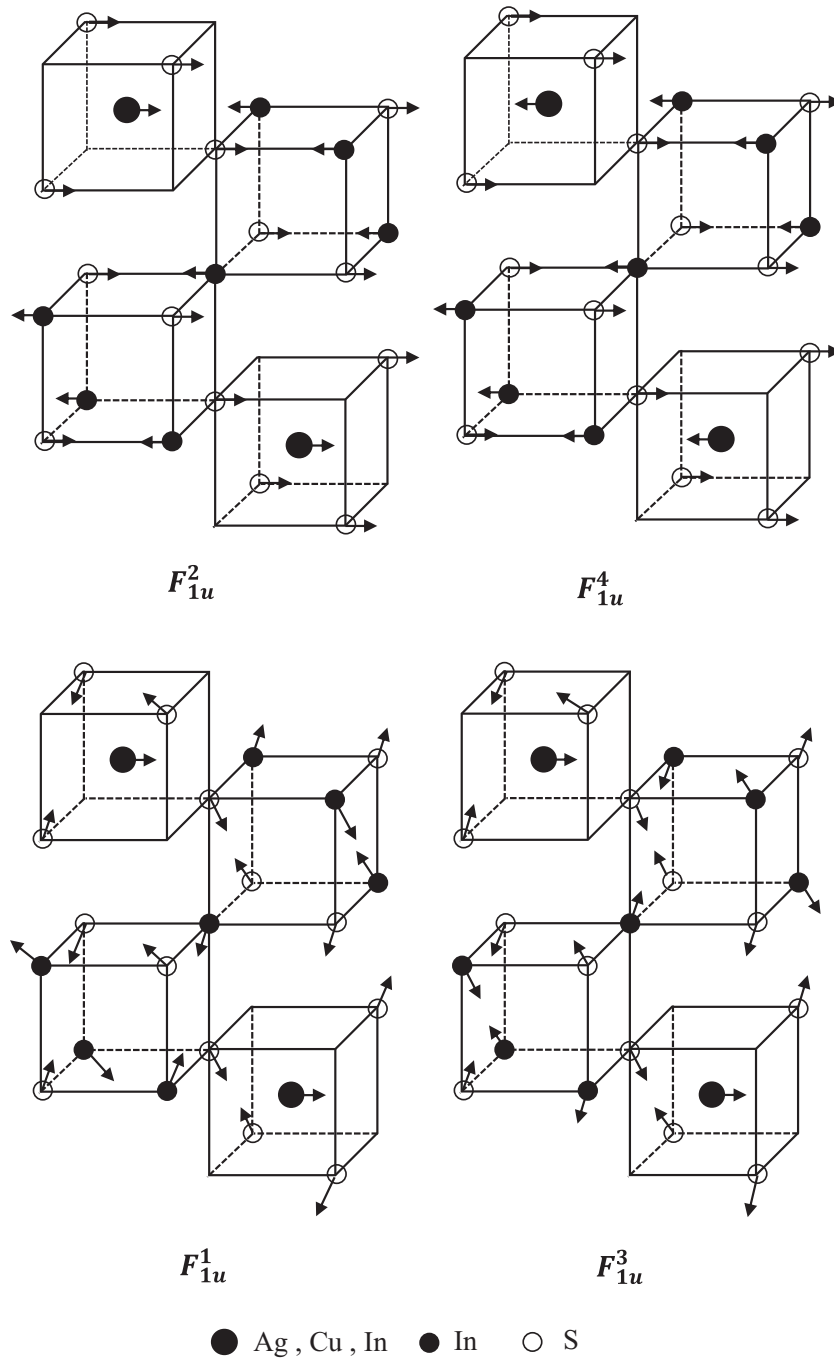


Fig. 1. The symmetrized displacements of atoms for infrared-active vibrational modes F_{1u} in AgIn_5S_8 and CuIn_5S_8 crystals.

- (a) The mode with frequencies $284\text{--}278\text{ cm}^{-1}$ (AgIn_5S_8) and $282\text{--}280\text{ cm}^{-1}$ (CuIn_5S_8).
- (b) The most low-frequency modes $87\text{--}83\text{ cm}^{-1}$ (AgIn_5S_8) and $95\text{--}93\text{ cm}^{-1}$ (CuIn_5S_8).

These modes correspond to IR-active modes F_{1u}^3 and F_{1u}^1 , respectively, in which only the tetrahedral coordinated Ag, Cu and In atoms are displaced strictly along the coordinate axes, whereas the octahedral coordinated In and S atoms accomplish deformation vibrations (Fig. 1). Thus, the observed in the IR spectra of AgIn_5S_8 and CuIn_5S_8 crystals low-intensity modes are the mixed valence-deformation modes.

In Table 1 we presented also the zone center phonon frequencies of AgIn_5S_8 and CuIn_5S_8 crystals determined by means of analytically solving the dynamical matrix of order 42×42 , proposed earlier in Ref. [21]. It should be noted that the obtained frequencies of three high-frequency transverse optical modes for both compounds showed satisfactory agreement with experimental ones (the discrepancy about 2–7%). However, for the lowest-frequency modes of crystals under study the significant difference in the frequency was observed (about 25%).

At this point, it is worthwhile comparing the refractive indices presented above with those previously reported for AgIn_5S_8 and CuIn_5S_8 crystals from ellipsometric measurements in the

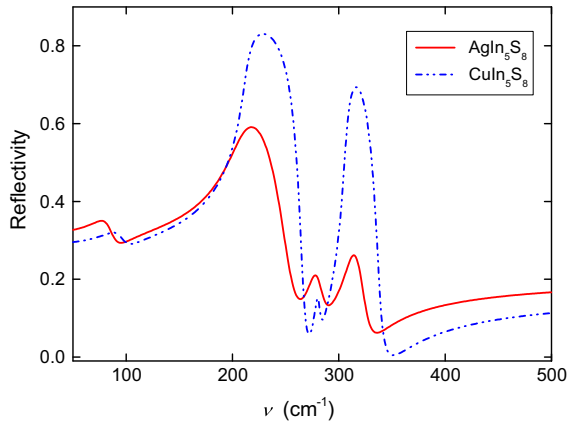


Fig. 2. Reflectivity spectra of AgIn₅S₈ and CuIn₅S₈ crystals.

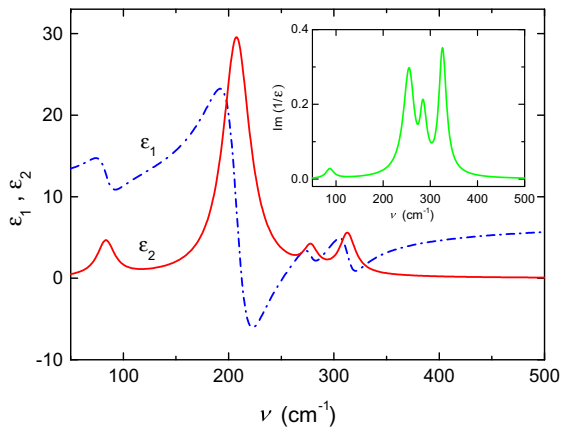


Fig. 3. The spectral dependencies of ϵ_1 , ϵ_2 and $\text{Im}(1/\epsilon)$ for AgIn₅S₈ crystal.

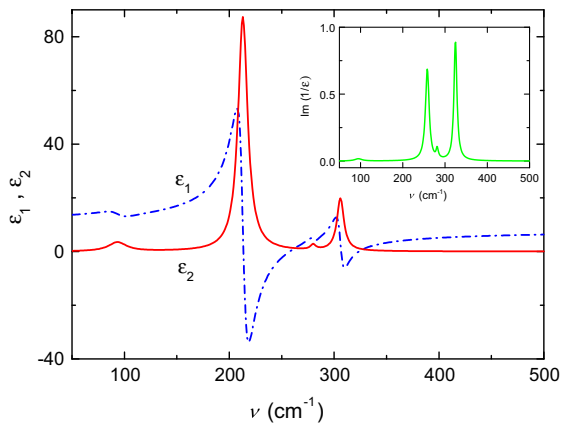


Fig. 4. The spectral dependencies of ϵ_1 , ϵ_2 and $\text{Im}(1/\epsilon)$ for CuIn₅S₈ crystal.

1.2–6.2 eV spectral range [16,17]. In the present study, the values of the refractive indices determined from IR reflection spectra, corresponding to $(\nu = 2000 \text{ cm}^{-1})$, were found to be 2.62 (AgIn₅S₈) and 2.72 (CuIn₅S₈). The magnitudes of the refractive indices reported for AgIn₅S₈ and CuIn₅S₈ crystals from ellipsometric experiments, corresponding to photon energy $E = 1.2 \text{ eV}$ ($\nu \approx 9700 \text{ cm}^{-1}$), were equal to 2.59 (AgIn₅S₈) [16] and 2.63 (CuIn₅S₈) [17]. It is evident, that the obtained results are close to each other for both crystals under study.

Table 1

Transverse (ν_{TO}) and longitudinal (ν_{LO}) optical mode frequencies, damping constants (γ) and oscillator strengths (S) of AgIn₅S₈ and CuIn₅S₈ single crystals.

Crystal	Mode	ν_{TO} (cm ⁻¹)	ν_{TO} (cm ⁻¹) theory [21]	ν_{LO} (cm ⁻¹)	γ (cm ⁻¹)	S
AgIn ₅ S ₈	F_{1u}^1	83	67	87	21	1.19
	F_{1u}^2	207	198	255	30	4.35
	F_{1u}^3	278	293	284	12	0.19
	F_{1u}^4	313	307	325	18	0.33
CuIn ₅ S ₈	F_{1u}^1	93	73	95	21	0.87
	F_{1u}^2	213	199	258	11	4.49
	F_{1u}^3	280	293	282	6	0.06
	F_{1u}^4	306	311	325	8	0.52

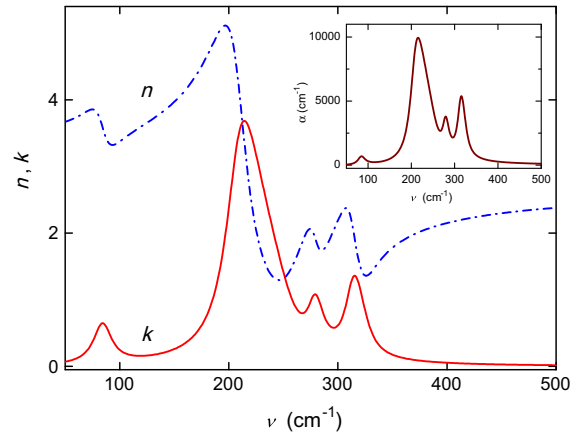


Fig. 5. The spectral dependencies of n , k and α for AgIn₅S₈ crystal.

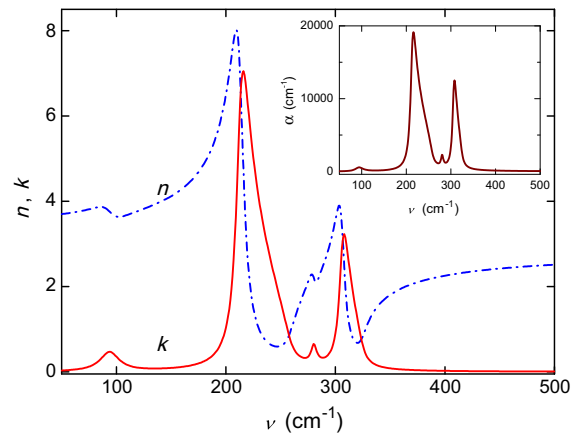


Fig. 6. The spectral dependencies of n , k and α for CuIn₅S₈ crystal.

4. Conclusions

Infrared reflection spectra are studied in AgIn₅S₈ and CuIn₅S₈ single crystals grown by Bridgman method. Four IR-active modes F_{1u} are revealed in the frequency range 50–2000 cm^{-1} . Spectral dependencies of optical constants: refractive index, absorption index and absorption coefficient were calculated from measured reflectivity. The frequencies of transverse (ν_{TO}) and longitudinal (ν_{LO}) optical modes, oscillator strength (S) and damping constant (γ) were also determined. The bands observed in IR spectra of crystals under study were attributed to various vibration types (valence and valence-deformation) on the basis of the symmetrized

displacements of atoms obtained by us using the Melvin projection operators.

Conflict of interest

There is no conflict of interest.

References

- [1] L. Gastaldi, L. Scaramuzza, On the space groups of two thiospinels, *Acta Crystallogr. B* 35 (1979) 2283–2284.
- [2] M. Gannouni, M. Kanzari, Structural, optical and electrical properties of CuIn_5S_8 thin films grown by thermal evaporation method, *J. Alloys Compd.* 509 (2011) 6004–6008.
- [3] M. Gannouni, M. Kanzari, Effects of the substrate temperature on the properties of CuIn_5S_8 thin films, *Appl. Surf. Sci.* 257 (2011) 10338–10341.
- [4] M. Gannouni, I. Ben Assaker, R. Chtourou, Experimental investigation of the effect of indium content on the CuIn_5S_8 electrodes using electrochemical impedance spectroscopy, *Mater. Res. Bull.* 61 (2015) 519–527.
- [5] I.V. Bodnar, Thermal expansion of CuIn_5S_8 single crystals and the temperature dependence of their band gap, *Semiconductors* 46 (2012) 602–605.
- [6] N. Hemiri, M. Kanzari, Investigation on dispersive optical constants and electrical properties of CuIn_5S_8 thin films, *Solid State Commun.* 160 (2013) 32–36.
- [7] M. Gannouni, I. Ben Assaker, R.J. Chtourou, Influence of electrodeposition potential on the properties of CuIn_5S_8 spinel thin films, *J. Electrochem. Soc.* 160 (2013) H446–H451.
- [8] L. Makhova, R. Szargan, I. Konovalov, Investigation of the growth process and properties of CuIn_5S_8 and AgIn_5S_8 spinel thin films, *Thin Solid Films* 472 (2005) 157–163.
- [9] L. Makhova, I. Konovalov, Alternative deposition methods of copper and silver indium ternary sulphides with spinel structure, *Thin Solid Films* 515 (2007) 5938–5942.
- [10] N. Khedmi, M. Ben Rabeh, M. Kanzari, Thickness dependent structural and optical properties of vacuum evaporated CuIn_5S_8 thin films, *Energy Proc.* 44 (2014) 61–68.
- [11] A. Sinaoui, F. Chaffar-Akkari, B. Gallas, D. Demaille, M. Kanzari, Investigation of growth and characterization of nanostructured CuIn_5S_8 thin films produced by glancing angle deposition, *Thin Solid Films* 590 (2015) 111–117.
- [12] N.S. Orlova, I.V. Bodnar, E.A. Kudritskaya, Crystal growth and properties of the AgIn_5S_8 and CuIn_5S_8 compound, *Cryst. Res. Technol.* 33 (1998) 37–42.
- [13] N.M. Gasanly, A. Serpenguzel, A. Aydinli, O. Gurlu, I. Yilmaz, Donor–acceptor pair recombination in AgIn_5S_8 single crystals, *J. Appl. Phys.* 85 (1999) 3198–3201.
- [14] N.M. Gasanly, Low-temperature photoluminescence in CuIn_5S_8 single crystals, *Pramana* 86 (2016).
- [15] T. Yildirim, N.M. Gasanly, Shallow trapping center parameters in as-grown AgIn_5S_8 crystals by thermally stimulated current measurements, *Cryst. Res. Technol.* 44 (2009) 1267–1271.
- [16] M. Isik, N.M. Gasanly, Ellipsometry study of optical parameters of AgIn_5S_8 crystals, *Physica B* 478 (2015) 127–130.
- [17] M. Isik, N.M. Gasanly, Optical characterization of CuIn_5S_8 crystals by ellipsometry measurements, *J. Phys. Chem. Solids* 91 (2016) 13–17.
- [18] N.M. Gasanly, A.Z. Magomedov, N.N. Melnik, B.G. Salamov, Raman and infrared studies of AgIn_5S_8 and CuIn_5S_8 single crystals, *Phys. Status Solidi (B)* 117 (1993) K31–K35.
- [19] H. Neumann, H. Sobotta, V. Riede, V.E. Tezlevan, N.N. Syrbu, Infrared lattice vibration study of CuIn_5S_8 , *Cryst. Res. Technol.* 25 (1990) 579–586.
- [20] K. Wakamura, S. Endo, T. Irie, Effect of annealing on phonon and free carrier spectra of CuIn_5S_8 , *Cryst. Res. Technol.* 31 (1996) 923–926.
- [21] M.M. Sinha, P. Ashidhir, H.C. Gupta, B.B. Tripathi, Vibrational analysis of zone centre phonons in sulfospinels AgIn_5S_8 and CuIn_5S_8 , *Phys. Status Solidi (B)* 187 (1995) K33–K36.
- [22] M.A. Melvin, Simplification in finding symmetry-adapted eigenfunctions, *Rev. Mod. Phys.* 28 (1956) 18–44.
- [23] H.D. Lutz, M. Feher, Die absorptionspektren von chalcogenospinellen in langwelligen infrarot, *Spectrochim. Acta* 27 A (1971) 357–365.