



Original research article

# Far-infrared lattice vibration spectra of copper gallium (indium) ternary selenides (tellurides): A consequence of trivalent cation and anion interrelation

N.M. Gasanly<sup>a,b,\*</sup><sup>a</sup> Department of Physics, Middle East Technical University, 06800 Ankara, Turkey<sup>b</sup> Virtual International Scientific Research Centre, Baku State University, 1148 Baku, Azerbaijan

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## ABSTRACT

Experimental spectra for copper gallium (indium) ternary selenides (tellurides) crystals, measured in the 50–500 cm<sup>-1</sup> frequency range, revealed four infrared-active modes. Spectral dependencies of refractive index and absorption coefficient were computed from reflectivity experiments. The frequencies of optical modes, damping constants and oscillator strengths were also evaluated. The bands observed in IR spectra were provisionally attributed to various vibration types (valence and valence-deformation). Crystal structure and atomic composition ratio of the constituent elements in Cu<sub>3</sub>Ga<sub>5</sub>Se<sub>9</sub>, Cu<sub>3</sub>In<sub>5</sub>Se<sub>9</sub> and Cu<sub>3</sub>In<sub>5</sub>Te<sub>9</sub> crystals were revealed from structural characterization techniques of X-ray diffraction and energy dispersive spectroscopy.

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## 1. Introduction

Cu<sub>3</sub>B<sub>5</sub>C<sub>9</sub> ternary semiconductors, where B = Ga or In and C = Se or Te, have potentials as photo-absorbers in solar cells, optoelectronics devices, and photoelectrochemical cells. They are visible-light-active crystals with high-absorption coefficients, suitable band gaps, and easy conversion between *n*- and *p*-type carrier types which permits a variety of potentially low-cost homo- and hetero-junction [1,2]. Optical and photoelectrical properties of these crystals have been studied previously [3–6].

Cu<sub>3</sub>Ga<sub>5</sub>Se<sub>9</sub> (CGS), Cu<sub>3</sub>In<sub>5</sub>Se<sub>9</sub> (CIS) and Cu<sub>3</sub>In<sub>5</sub>Te<sub>9</sub> (CIT) compounds are the representatives of above-mentioned materials. The minute state diagrams of the CuGaSe<sub>2</sub>–Ga<sub>2</sub>Se<sub>3</sub>, CuInSe<sub>2</sub>–In<sub>2</sub>Se<sub>3</sub> and CuInTe<sub>2</sub>–In<sub>2</sub>Te<sub>3</sub> systems have been investigated in Refs. [7,8]. It has been found that at 25 mol% Ga<sub>2</sub>Se<sub>3</sub>, In<sub>2</sub>Se<sub>3</sub> and In<sub>2</sub>Te<sub>3</sub>, the CGS, CIS and CIT compounds, melting congruently at 1088, 1025 and 750 °C, respectively, are formed. The electrical resistivity and Hall mobility of CIS crystals were investigated in the temperature range 35–475 K [8]. The room temperature values of resistivity, mobility and carrier concentration in CIS were found to be 3.0 × 10<sup>3</sup> Ωcm, 140 cm<sup>2</sup>/Vs and 1.3 × 10<sup>13</sup> cm<sup>-3</sup>, respectively. The energy gap *E<sub>g</sub>* = 0.99 eV was obtained from temperature dependence of resistivity. The cathode- and photo-luminescence spectra of CGS crystals have been measured at different excitation intensities and temperatures [9]. The results indicate that the radiative recombination of non-equilibrium charge carriers occurs primarily through impurity levels due to anion and cation vacancies. The band

\* Corresponding author at: Department of Physics, Middle East Technical University, Ankara, 06800, Turkey.  
E-mail address: [nizami@metu.edu.tr](mailto:nizami@metu.edu.tr)

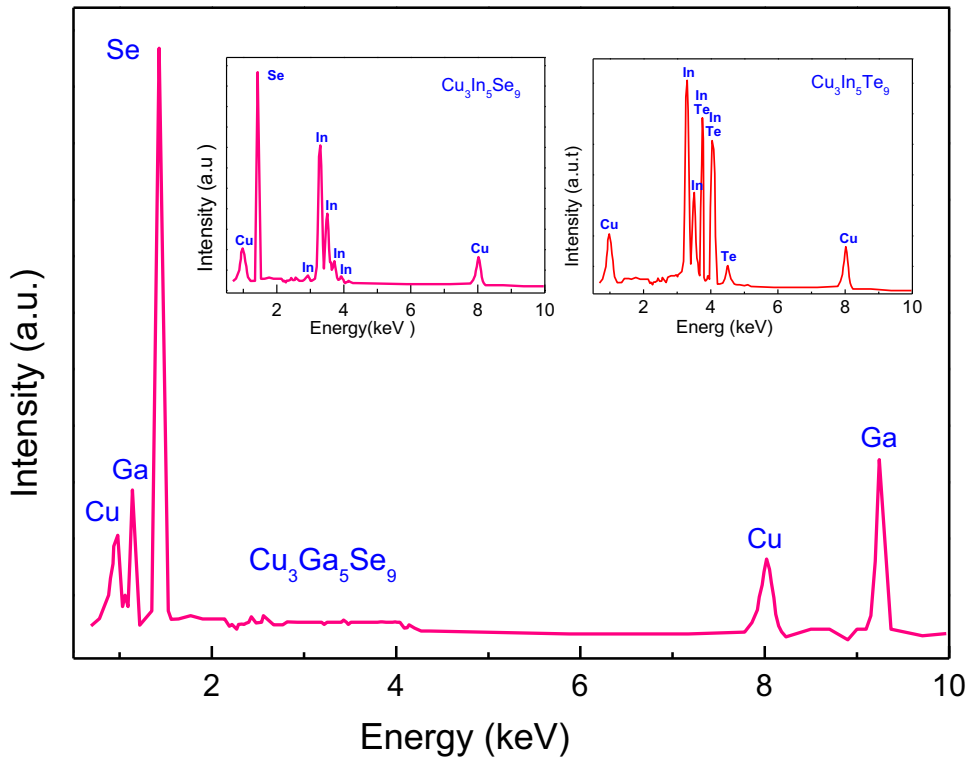


Fig. 1. Energy dispersive spectroscopic analysis of CGS, CIS and CIT crystals.

gap for optical transitions was found to be 1.74 eV at room temperature. The fabrication of detectors based on CGS single crystals for high-intensity radiation was suggested.

The electrical resistivity and Hall mobility of CIT crystals were investigated in the temperature range of 35–475 K [8]. The values of resistivity, mobility and carrier concentration at room temperature were identified as  $8.5 \times 10^{-3} \Omega \text{ cm}$ ,  $120 \text{ cm}^2/\text{Vs}$  and  $6.0 \times 10^{18} \text{ cm}^{-3}$ , respectively. The temperature dependence of mobility indicated the presence of lattice and ionized impurity scattering mechanisms above and below 160 K, respectively. The electrical and optical properties of CIT crystals have been also studied in Ref. [10]. The energy band gap for the direct optical transitions was established as 0.78 eV at room temperature, with the rate of direct band gap variation with temperature of  $-2.0 \times 10^{-4} \text{ eV/K}$ . Infrared reflectivity, studied in the frequency range of  $50\text{--}500 \text{ cm}^{-1}$  for isostructural crystals  $\text{Ag}_3\text{Ga}_5\text{S}_9$  and  $\text{Ag}_3\text{In}_5\text{S}_9$  [11] and  $\text{Ag}_3\text{In}_5\text{Se}_9$  and  $\text{Ag}_3\text{In}_5\text{Te}_9$  [12] were reported previously. The inversion of LO- and TO-mode frequencies was observed for latter crystals.

The present paper reports the results of the study of optical constants, essential in the fabrication of optoelectronic devices, in copper gallium (indium) ternary selenides (tellurides) by infrared reflection method in the  $50\text{--}500 \text{ cm}^{-1}$  frequency range.

## 2. Experimental details

CGS, CIS and CIT polycrystals were synthesized in evacuated ( $10^{-5}$  Torr) quartz tubes using individual elements taken in stoichiometric proportions. The single crystals were grown by the Bridgman method in evacuated ampoules in our crystal growth laboratory. The ampoule was lowered in a vertical furnace having a thermal gradient of  $30^\circ\text{C/cm}$  at a rate of 1.0 mm/h.

The chemical compositions of CGS, CIS and CIT crystals were determined by energy dispersive spectroscopic analysis using JSM-6400 electron microscope in the 0–10 keV energy range (Fig. 1). Since every element has unique energy levels, each element produces characteristic X-rays that make it possible to determine the elemental composition of the sample by analyzing the spectra. The atomic compositions of the studied samples (Cu: Ga: Se), (Cu: In: Se) and (Cu: In: Te) were found to be 17.9: 29.6: 52.5; 18.0: 29.8: 52.2 and 18.1: 29.6: 52.3, respectively. The atomic weight ratios of the constituent elements in the crystals show slight changes from that of initial ratios (17.7: 29.4: 52.9) in the growth process. In the grown crystal, some deficiency occurs in the compositions of chalcogenes. The slight deficiency of these elements in the grown crystals can be explained with the higher volatility of them as compared to the copper, gallium and indium.

The crystal structure properties were identified using x-ray diffraction (XRD) experiments. Measurements were performed using “Rigaku miniflex” diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda = 0.154049 \text{ nm}$ ). The scanning speed of the diffractometer was  $0.02^\circ/\text{s}$ . Experiments were accomplished in the diffraction angle ( $2\theta$ ) range of  $10\text{--}80^\circ$ .

To carry out the reflectivity measurements, the obtained ingots were cut and the surfaces produced were ground precisely. Before the reflectivity measurements, the samples were mechanically polished with  $0.5 \mu\text{m}$   $\text{Al}_2\text{O}_3$  powder. IR reflection

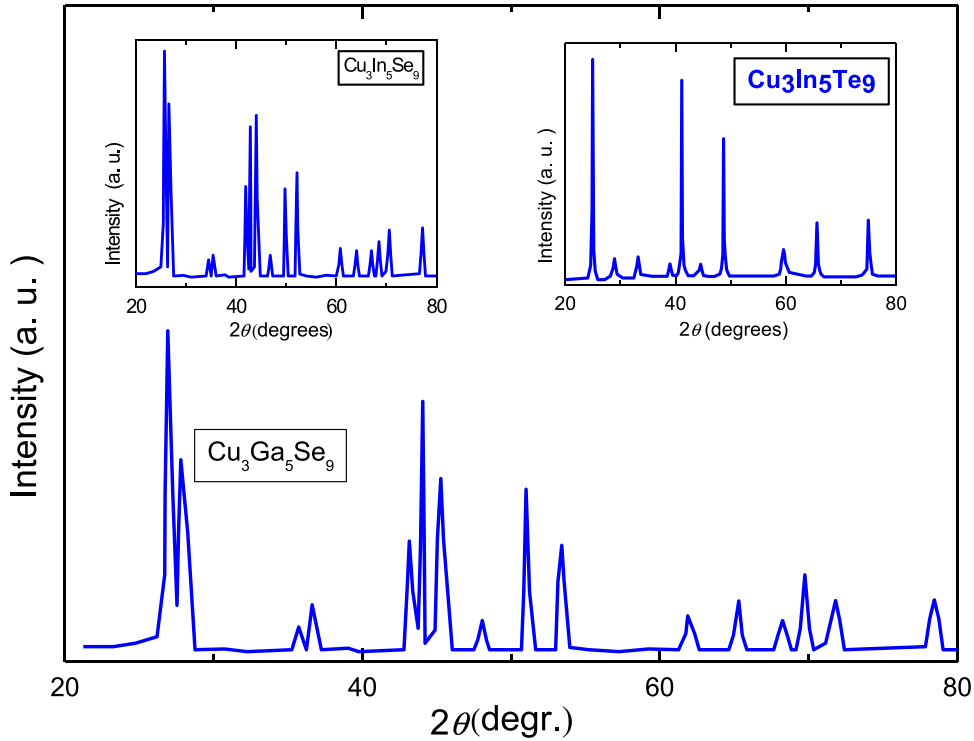


Fig. 2. X-ray diffraction patterns of CGS, CIS and CIT crystals.

spectra of CGS, CIS and CIT crystals were registered in the frequency range between 50 and 500  $\text{cm}^{-1}$  handling the diffraction IR spectrometers FIS-21 with a resolution of 1  $\text{cm}^{-1}$ .

### 3. Results and discussion

XRD technique was used to obtain the structural parameters of the CGS, CIS and CIT crystals. The crystal system and lattice parameters were evaluated using a least-squares computer program "DICVOL 04". Fig. 2 presents the X-ray diffractograms of CGS, CIS and CIT crystals. The sharp diffraction peaks are the indication of the well crystallinity of the samples. The lattice parameters of the orthorhombic unit cells were found to be  $a=0.9767$ , continue the line

$b=0.9225$ ,  $c=0.5257$  nm;  $a=0.9613$ ,  $b=0.9078$ ,  $c=0.5183$  nm and  $a=1.2364$ ,  $b=1.1118$ ,  $c=0.4374$  nm for CGS, CIS and CIT crystals, respectively.

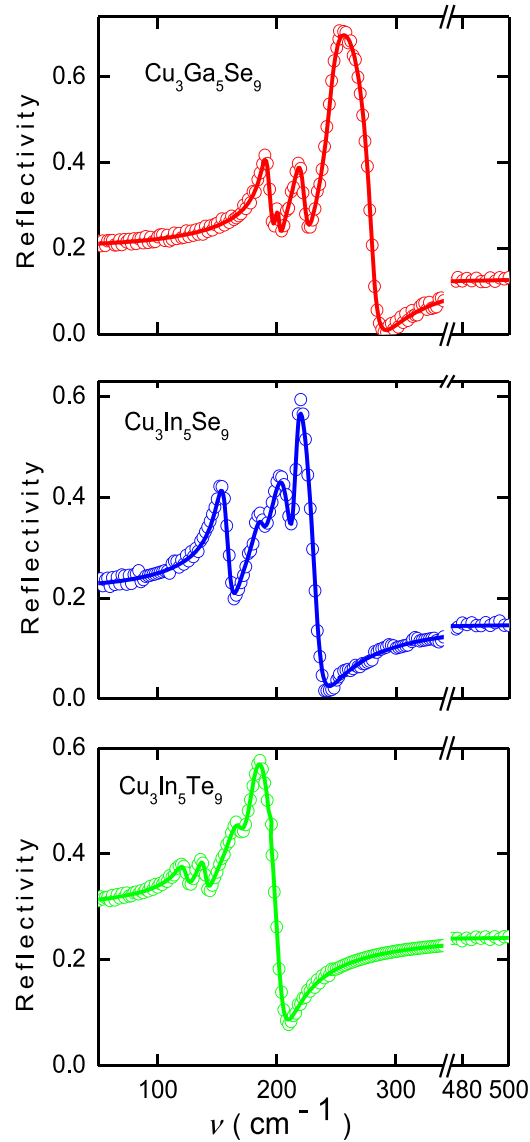
Fig. 3 shows the infrared reflectivity spectra of CGS, CIS and CIT crystals in the frequency range of 50–500  $\text{cm}^{-1}$ . Four IR-active optical modes were observed in the spectra. By replacing light gallium cations by heavier indium ones in CGS crystal, all the bands of CIS crystal shift towards low frequencies compared with CGS crystal. Accordingly, substitution of light selenium anions by heavier tellurium ones in CIS crystal also results in shifting the bands of CIT crystal to low frequencies relatively to CIS crystal.

The analysis of reflectivity ( $R$ ) was carried out employing the coming next dispersion relations [13]:

$$\varepsilon_1 = \varepsilon_\infty + \sum_{i=1}^4 \frac{S_i v_{Ti}^2 (v_{Ti}^2 - v^2)}{(v_{Ti}^2 - v^2)^2 + \gamma_i^2 v^2},$$

$$\varepsilon_2 = \sum_{i=1}^4 \frac{S_i v_{Ti}^2 v \gamma_i}{(v_{Ti}^2 - v^2)^2 + \gamma_i^2 v^2},$$

$$R = \frac{(\varepsilon_1^2 + \varepsilon_2^2)^{\frac{1}{2}} - \left(2 \left((\varepsilon_1^2 + \varepsilon_2^2)^{\frac{1}{2}} + \varepsilon_1\right)\right)^{\frac{1}{2}} + 1}{(\varepsilon_1^2 + \varepsilon_2^2)^{\frac{1}{2}} + \left(2 \left((\varepsilon_1^2 + \varepsilon_2^2)^{\frac{1}{2}} + \varepsilon_1\right)\right)^{\frac{1}{2}} + 1}.$$



**Fig. 3.** Reflectivity spectra of CGS, CIS and CIT crystals. Open circles are experimental data; Solid curves are calculated data. (Note the break in the range of 350–475  $\text{cm}^{-1}$ ).

Here,  $\varepsilon_1$  and  $\varepsilon_2$  are the real and imaginary parts of dielectric constant, respectively,  $\varepsilon_\infty$  is the high-frequency dielectric constant,  $\nu_T$  is the transverse mode frequency,  $\gamma$  is the damping constant and  $S$  is the oscillator strength.

The parameters of the IR-active modes in studied crystals, established by best agreement between the calculated reflectivity spectra with those measured experimentally, are presented in Table 1. The spectral dependencies of  $\varepsilon_2$  and  $\text{Im}(1/\varepsilon)$  for CGS, CIS and CIT are displayed in Fig. 4. The longitudinal mode frequencies  $\nu_L$  were determined from the maxima of the function of energy losses  $\text{Im}(1/\varepsilon) = \varepsilon_2/(\varepsilon_1^2 + \varepsilon_2^2)$  (Table 1). The high-frequency dielectric constant  $\varepsilon_\infty = 5.0 \pm 0.2$ ,  $5.4 \pm 0.2$  and  $9.1 \pm 0.4$  for CGS, CIS and CIT, respectively, were established from the high-frequency reflection coefficients

$R_\infty (\nu = 500 \text{ cm}^{-1})$ . The low-frequency dielectric constants  $\varepsilon_0$ , determined from relation  $\varepsilon_0 = \varepsilon_\infty + \sum_1^4 S$ , were found to be

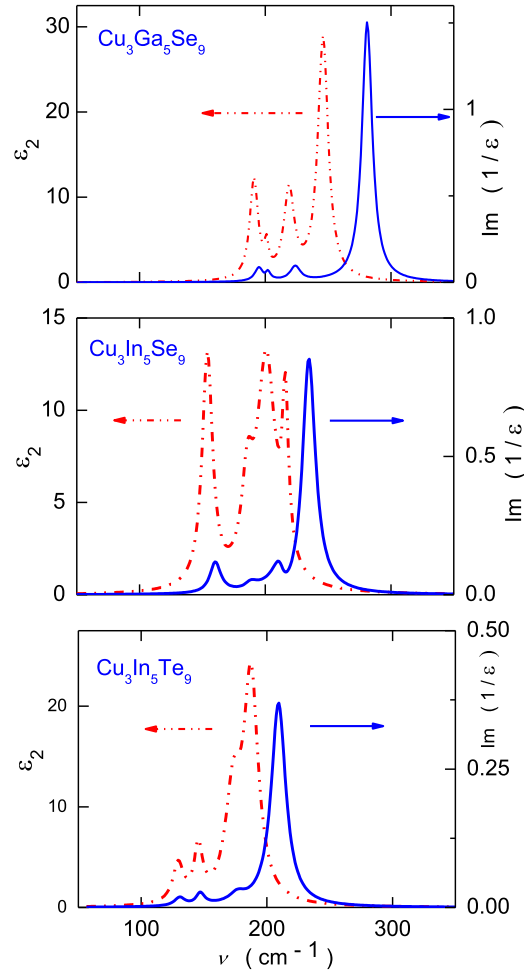
$7.3 \pm 0.3$ ,  $8.3 \pm 0.3$  and  $13.1 \pm 1.0$  for CGS, CIS and CIT crystals, respectively.

The first three modes of CGS, CIS and CIT crystals (see Table 1) may be attributed to IR-active modes, in which only the tetrahedral coordinated Cu and Ga(In) atoms are displaced strictly along the coordinate axes, whereas the octahedral coordinated Ga(In) and Se(Te) atoms accomplish deformation vibrations [14]. Hence, the detected in the IR spectra of copper gallium (indium) ternary selenides (tellurides) modes, having small LO – TO splitting, are the mixed valence-deformation

**Table 1**

Transverse ( $\nu_T$ ) and longitudinal ( $\nu_L$ ) optical mode frequencies, damping constants ( $\gamma$ ) and oscillator strengths ( $S$ ) of  $\text{Cu}_3\text{Ga}_5\text{Se}_9$ ,  $\text{Cu}_3\text{In}_5\text{Se}_9$  and  $\text{Cu}_3\text{In}_5\text{Te}_9$  single crystals.

Crystal	Mode	$\nu_T$ ( $\text{cm}^{-1}$ )	$\nu_L$ ( $\text{cm}^{-1}$ )	$\gamma$ ( $\text{cm}^{-1}$ )	$S$
$\text{Cu}_3\text{Ga}_5\text{Se}_9$	$\nu_1$	$191 \pm 1$	$195 \pm 1$	$8 \pm 0.7$	$0.52 \pm 0.05$
	$\nu_2$	$201 \pm 1$	$203 \pm 1$	$4 \pm 0.3$	$0.11 \pm 0.01$
	$\nu_3$	$219 \pm 1$	$224 \pm 1$	$10 \pm 0.8$	$0.53 \pm 0.05$
	$\nu_4$	$246 \pm 1$	$281 \pm 1$	$10 \pm 0.8$	$1.18 \pm 0.05$
$\text{Cu}_3\text{In}_5\text{Se}_9$	$\nu_1'$	$154 \pm 1$	$159 \pm 1$	$10 \pm 0.8$	$0.86 \pm 0.08$
	$\nu_2'$	$187 \pm 1$	$190 \pm 1$	$11 \pm 0.9$	$0.51 \pm 0.05$
	$\nu_3'$	$201 \pm 1$	$210 \pm 1$	$18 \pm 1.4$	$1.19 \pm 0.11$
	$\nu_4'$	$216 \pm 1$	$235 \pm 1$	$6 \pm 0.5$	$0.34 \pm 0.03$
$\text{Cu}_3\text{In}_5\text{Te}_9$	$\nu_1''$	$123 \pm 1$	$125 \pm 1$	$10 \pm 0.8$	$0.38 \pm 0.03$
	$\nu_2''$	$139 \pm 1$	$141 \pm 1$	$8 \pm 0.7$	$0.39 \pm 0.03$
	$\nu_3''$	$169 \pm 1$	$172 \pm 1$	$15 \pm 1.2$	$1.34 \pm 0.12$
	$\nu_4''$	$191 \pm 1$	$203 \pm 1$	$14 \pm 1.1$	$1.88 \pm 0.17$

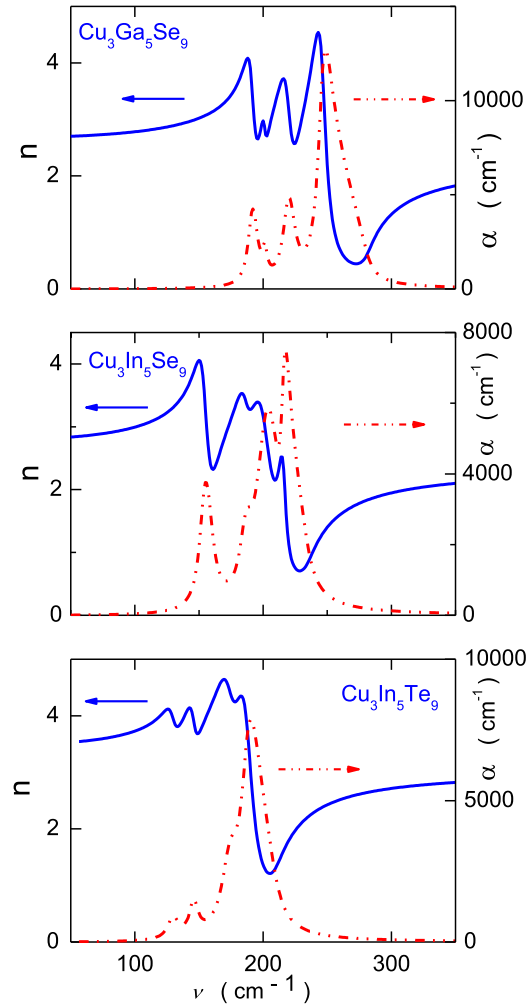


**Fig. 4.** The spectral dependencies of the imaginary part of the dielectric constant  $\epsilon_2$  and the function of energy losses  $\text{Im}(1/\epsilon)$  for CGS, CIS and CIT crystals.

modes. The high-intensity modes with frequencies  $\nu_4 = 246 \text{ cm}^{-1}$  ( $\text{Cu}_3\text{Ga}_5\text{Se}_9$ ),  $\nu_4' = 216 \text{ cm}^{-1}$  ( $\text{Cu}_3\text{In}_5\text{Se}_9$ ) and  $\nu_4'' = 191 \text{ cm}^{-1}$  ( $\text{Cu}_3\text{In}_5\text{Te}_9$ ) are associated with antiphase vibration of cation and anion sublattices [15,16].

Moreover, the dependencies of refractive index  $n$  and absorption index  $k$  on the frequency were calculated from reflectivity spectra for CGS, CIS and CIT using the following relations [13]:

$$n = \left[ \left( \epsilon_1 + (\epsilon_1^2 + \epsilon_2^2)^{1/2} \right) / 2 \right]^{1/2}, \tag{1}$$



**Fig. 5.** The spectral dependencies of refractive indices  $n$  and absorption coefficients  $\alpha$  for CGS, CIS and CIT crystals.

$$k = \left[ \left( -\varepsilon_1 + (\varepsilon_1^2 + \varepsilon_2^2)^{1/2} \right) / 2 \right]^{1/2}. \quad (2)$$

The spectral dependencies of refractive index  $n$  for CGS, CIS and CIT are shown in Fig. 5. The high- and low-frequency refractive indices were determined as  $2.24 \pm 0.03$ ,  $2.32 \pm 0.03$  and  $3.02 \pm 0.04$  ( $\nu = 500 \text{ cm}^{-1}$ ) and  $2.70 \pm 0.03$ ,  $2.84 \pm 0.03$  and  $3.62 \pm 0.04$  ( $\nu = 50 \text{ cm}^{-1}$ ), respectively, with maximum values of  $n = 4.54$ ,  $4.06$  and  $4.65$  corresponding to the frequencies  $\nu = 243$ ,  $150$  and  $169 \text{ cm}^{-1}$  for CGS, CIS and CIT, respectively. Knowing the values of absorption index  $k$ , it was possible to calculate the absorption coefficient ( $\alpha$ ) employing the relationship  $\alpha = 4\pi k/\lambda$ , where  $\lambda$  is the wavelength [13]. The computed spectral dependencies of absorption coefficients of CGS, CIS and CIT crystals are presented in Fig. 5. Maximum magnitudes of  $\alpha$ ,  $12710$ ,  $7500$  and  $7870 \text{ cm}^{-1}$ , are occurred at the frequencies of  $249$ ,  $217$  and  $191 \text{ cm}^{-1}$  for CGS, CIS and CIT, respectively.

#### 4. Conclusions

Copper gallium (indium) ternary selenides (tellurides) single crystals grown by Bridgman method were characterized by X-ray powder diffraction and energy dispersive spectroscopy analysis. The parameters of the orthorhombic unit cells were determined as  $a = 0.9767$ ,  $b = 0.9225$ ,  $c = 0.5257 \text{ nm}$ ;  $a = 0.9613$ ,  $b = 0.9078$ ,  $c = 0.5183 \text{ nm}$  and  $a = 1.2364$ ,  $b = 1.1118$ ,  $c = 0.4374 \text{ nm}$  for CGS, CIS and CIT crystals, respectively. The atomic compositions of the studied samples (Cu: Ga: Se), (Cu: In: Se) and (Cu: In: Te) were found to be 17.9: 29.6: 52.5; 18.0: 29.8: 52.2 and 18.1: 29.6: 52.3, respectively. IR spectra, registered in the frequency range of  $50 - 500 \text{ cm}^{-1}$ , revealed four modes for all studied crystals. Spectral dependencies of optical constants: refractive index, absorption index and absorption coefficient were computed from measured reflectivity. The frequencies of transverse ( $\nu_T$ ) and longitudinal ( $\nu_L$ ) optical modes, oscillator strengths ( $S$ ) and damping constants

( $\gamma$ ) were also determined. The bands observed in infrared spectra of studied crystals were tentatively assigned to various vibration types (valence and valence-deformation).

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