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ORIGINAL PAPER

Study of vibrational modes in $Cu_xAg_{1-x}In_5S_8$ mixed crystals by infrared reflection measurements

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Abstract: Infrared reflection spectra of $Cu_xAg_{1-x}In_5S_8$ mixed crystals, grown by Bridgman method, were studied in the wide frequency range of 50–2000 cm^{-1}. All four infrared-active modes were detected, which are in full agreement with the prediction of group-theoretical analysis. Real and imaginary parts of the dielectric function, refractive index and the energy losses function were evaluated from reflectivity measurements. The frequencies of TO and LO 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. The linear dependencies of optical mode frequencies on the composition of $Cu_xAg_{1-x}In_5S_8$ mixed crystals were obtained. These dependencies display one-mode behavior.

Keywords: Semiconductors; Crystal growth; Phonons; Optical spectroscopy

PACS Nos.: 78.40.Fy; 78.20.Ci; 78.30.-j

1. Introduction

I–III–VI ternary semiconductors with the general formula of AB_5C_8 have potential as photo absorbers in solar cells, optoelectronics devices, and photoelectrochemical cells. $AgIn_5S_8$ and $CuIn_5S_8$ crystals are visible-light-active materials with high-absorption coefficients, suitable band gaps and good radiation stability [1, 2]. These compounds have been confirmed as materials applicable for employment in high-frequency thin films convertors and infrared detectors [3]. Moreover, such crystals due to their crystallochemistry structure may be of particular interest for the photovoltaics and IR laser operated devices [4].

The optical properties of $AgIn_5S_8$ and $CuIn_5S_8$ have been reported in Refs. [5–8]. 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 [9]. Infrared reflection and Raman scattering spectra of $AgIn_5S_8$ and $CuIn_5S_8$ crystals were reported in Refs. [10–12]. In $Cu_xAg_{1-x}In_5S_8$, the existence of continuous mixed crystals ($0 \leq x \leq 1$), when substituting copper for silver within the spinel crystal structure, offers the possibility for creating absorber layers with tailored compositional gradients and therefore achieving the desired band gap profile [13, 14]. Their band gap energy varies from 1.51 to 1.78 eV within the wide continuous series of mixed crystals. The density, lattice parameters, microhardness [13], mobility and charge concentrations [14] in $Cu_xAg_{1-x}In_5S_8$ ($0 \leq x \leq 1$) crystals were also reported. Moreover, the reflectance spectra of $Cu_xAg_{1-x}In_5S_8$ solid solutions were previously studied in the restricted frequency range of 150–400 cm^{-1} [14]. Lately, photoluminescence (PL) and thermally stimulated current (TSC) in $Cu_xAg_{1-x}In_5S_8$ ($x = 0.5$) crystals have been studied in the energy region of 1.46–1.60 eV and in the temperature range of 10–42 K (PL) and in the temperature range of 10–100 K (TSC) [15].

In the present paper, infrared reflectivity spectra of $Cu_xAg_{1-x}In_5S_8$ mixed crystals ($0 \leq x \leq 1$) were investigated in the wide frequency range of 50–2000 cm^{-1}. The predicted four vibrational modes were determined together with the phonon parameters. In addition, linear

dependencies of optical mode frequencies on the composition of $Cu_xAg_{1-x}In_5S_8$ mixed crystals were observed.

2. Experimental details

$Cu_xAg_{1-x}In_5S_8$ $(0 \leq x \leq 1)$ semiconductor polycrystals were synthesized using high-purity elements which were taken in stoichiometric proportions. Generally, the synthesis of ternary chalcogenide compounds is accompanied by high pressure of the chalcogenide vapors. That is why, a special method has been developed for the synthesis of compounds with high volatile components. The single crystals were grown by Bridgman method from resultant polycrystalline ingots in evacuated $(10^{-5}$ Torr) silica tubes (10 mm in diameter and about 55 cm in length) with a tip at the bottom. No seed crystal was used. The final ingot exhibited monocrystalline nature.

To carry out the reflectivity experiments, the grown ingots were cut and the surfaces were ground and polished carefully. Directly before the reflectivity measurements, the samples were mechanically polished with 0.5 μm Al_2O_3 powder. IR reflection spectra of $Cu_xAg_{1-x}In_5S_8$ mixed crystals were registered in the frequency range of 50 and 2000 cm^{-1} using IR spectrometers FIS-21 and Hitachi-225 with a resolution of 1 cm^{-1}.

3. Results and discussion

$Cu_xAg_{1-x}In_5S_8$ mixed crystals have the spinel structure with space group O_h^7 and four molecules per Bravais cell [14]. The group-theoretical analysis provides the subsequent set of modes at Brillouin zone center: $A_{1g} + E_g + F_{1g} + 3F_{2g} + 2A_{2u} + 2E_u + 5F_{1u} + 2F_{2u}$. Four out of these five F_{1u} modes are infrared-active and the remaining one is acoustic. The $A_{1g} + E_g + 3F_{2g}$ modes are Raman-active and $F_{1g} + 2A_{2u} + 2E_u$ modes are inactive in the infrared and Raman scattering. The symmetrized displacements of atoms for infrared-active vibrational modes in $Cu_xAg_{1-x}In_5S_8$ mixed crystals obtained by us employing Melvin projection operators [16] are demonstrated in Fig. 1.

Four IR-active optical modes were revealed in the experimental spectra of $Cu_xAg_{1-x}In_5S_8$ mixed crystals. Figure 2 presents the infrared reflectivity spectrum for one representative of $Cu_xAg_{1-x}In_5S_8$ mixed crystals $(x = 0.5)$ in the frequency range of 50–500 cm^{-1}. Due to the absence of infrared bands in region between 500 and 2000 cm^{-1}, the figures related to IR measurements in this study were demonstrated in 50–500 cm^{-1} range. The analysis of reflectivity (R) was accomplished using the known dispersion relations [17]:

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

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

$$R = \frac{\left(\varepsilon_1^2 + \varepsilon_2^2\right)^{1/2} - \left(2\left(\left(\varepsilon_1^2 + \varepsilon_2^2\right)^{1/2} + \varepsilon_1\right)\right)^{1/2} + 1}{\left(\varepsilon_1^2 + \varepsilon_2^2\right)^{1/2} + \left(2\left(\left(\varepsilon_1^2 + \varepsilon_2^2\right)^{\frac{1}{2}} + \varepsilon_1\right)\right)^{1/2} + 1}. \tag{3}$$

Here, ε_1 and ε_2 are the real and imginary parts of dielectric constant, respectively, ε_∞ is the high-frequency dielectric constant, v_T is the frequency of transverse mode, γ is damping constant and S is oscillator strength.

The frequencies of the longitudinal modes (v_L) were determined from the maxima of the function $Im(1/\varepsilon) = \varepsilon_2/\left(\varepsilon_1^2 + \varepsilon_2^2\right)$. The frequency dependencies of refractive index n were calculated from fitted reflectivity spectra of $Cu_xAg_{1-x}In_5S_8$ mixed crystals using the relation [16]:

$$n = \left[\left(\varepsilon_1 + (\varepsilon_1^2 + \varepsilon_2^2)^{1/2}\right)/2\right]^{1/2}. \tag{4}$$

The spectral dependencies of refractive index n and Im $(1/\varepsilon)$ for $Cu_xAg_{1-x}In_5S_8$ $(x = 0.5)$ crystals are displayed in Fig. 3. The high-frequency dielectric constants (ε_∞) of $Cu_xAg_{1-x}In_5S_8$ mixed crystals, ranging from 6.85 $(x = 0)$ to 7.40 $(x = 1)$, were computed employing the high-frequency reflectivity coefficients R_∞ ($v = 2000$ cm^{-1}). The low-frequency dielectric constants (ε_0), estimated from relation $\varepsilon_0 = \varepsilon_\infty + \sum_{i=1}^{4} S_i$, were found to be changing between 12.90 $(x = 0)$ and 13.34 $(x = 1)$. The determined low- and high-frequency refractive indices n for $Cu_xAg_{1-x}In_5S_8$ mixed crystals vary from 3.67 $(x = 0)$ to 3.70 $(x = 1)$ and from 2.62 $(x = 0)$ to 2.72 $(x = 1)$, respectively.

Compositional dependencies of IR-active mode parameters (i.e. frequencies of active modes, oscillator strengths, refractive index and damping constants) of $Cu_xAg_{1-x}In_5S_8$ mixed crystals determined by the analyses of the experimental spectra are presented in Figs. 4 and 5. As seen from the figures, these parameters demonstrate almost linear dependence on the composition of mixed crystals studied.

It is worth mentioning here that the modes F_{1u}^2 and F_{1u}^4 are caused in the main by antiphase vibrations along the coordinate axes (valence vibrations) of sulfur atoms and octahedral coordinated indium atoms (Fig. 1) [18]. The effect of the tetrahedral coordinated cations (Ag, Cu) on the frequencies of these modes is relatively small. In addition, the spectra of $Cu_xAg_{1-x}In_5S_8$ mixed crystals display two modes with slight LO-TO splitting (Fig. 4):

Fig. 1 The symmetrized displacements of atoms for infrared-active vibrational modes F_{1u} in $Cu_xAg_{1-x}In_5S_8$ mixed crystals

$$F_{1u}^2 \qquad F_{1u}^4$$

$$F_{1u}^1 \qquad F_{1u}^3$$

⬤ Ag , Cu , In   ⬤ In   ○ S
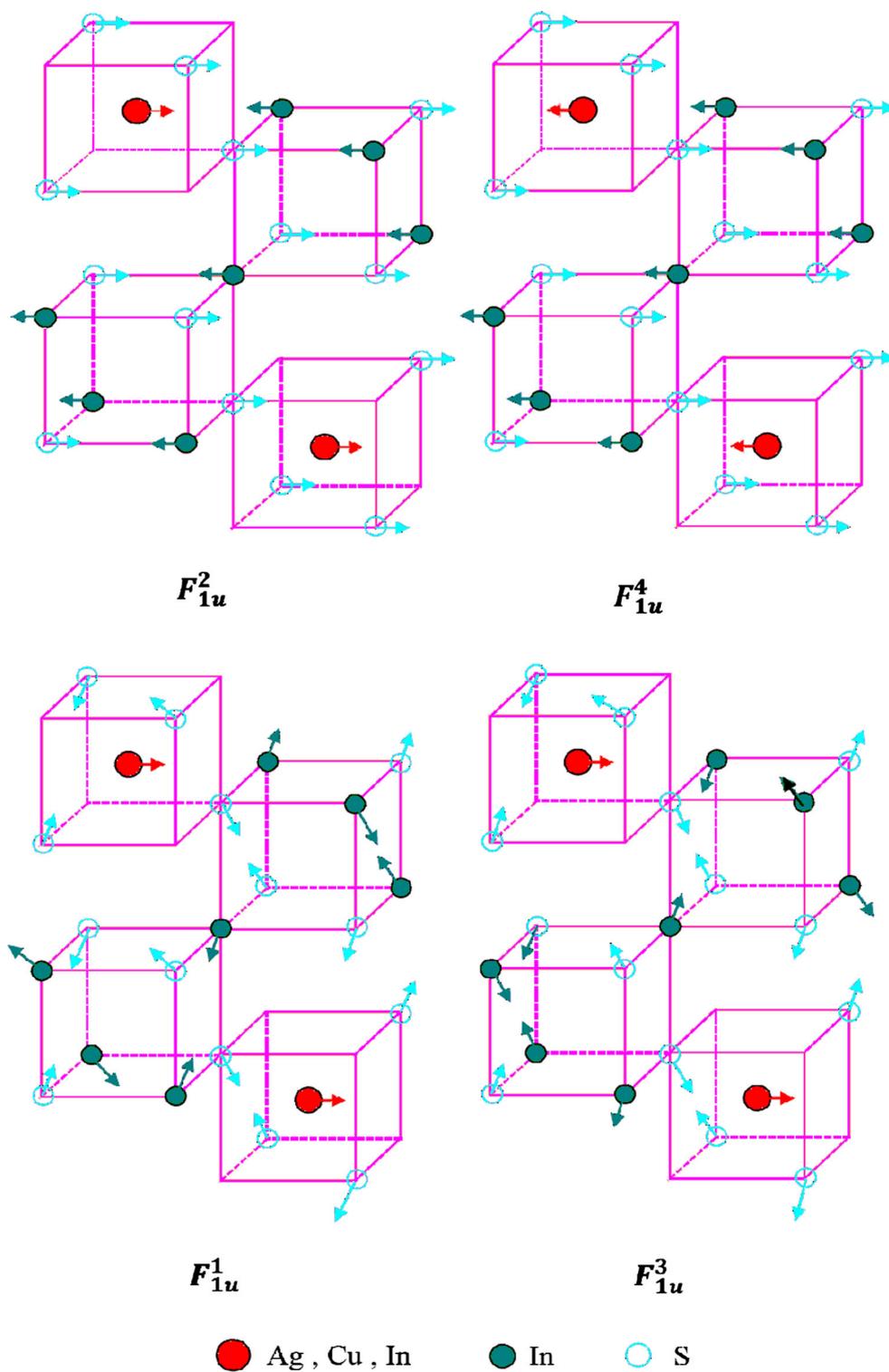
1. The low-intensity modes with frequencies around 280 cm^{-1}.
2. The relatively low-frequency modes.

The above mentioned modes relate 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 exactly along the coordinate axes, whereas the octahedral coordinated In and S atoms accomplish deformation vibrations (Fig. 1). Hence, the observed in IR spectra of $Cu_xAg_{1-x}In_5S_8$ mixed crystals low-intensity modes present the mixed valence-deformation modes.
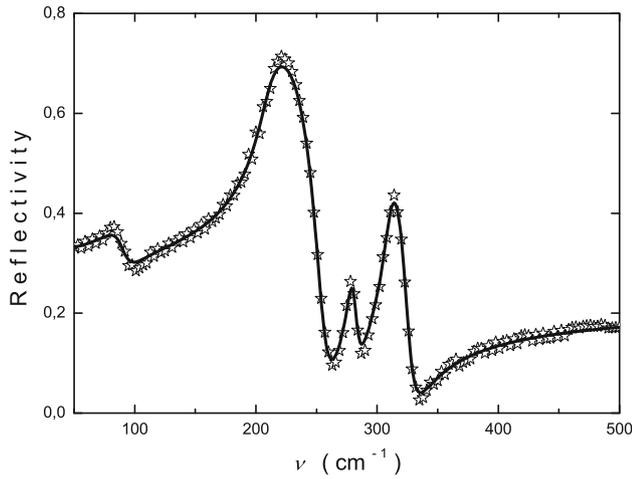
Fig. 2 Reflectivity spectra of $Cu_xAg_{1-x}In_5S_8$ $(x = 0.5)$ crystals. Stars are experimental data; Solid line is fitted curve
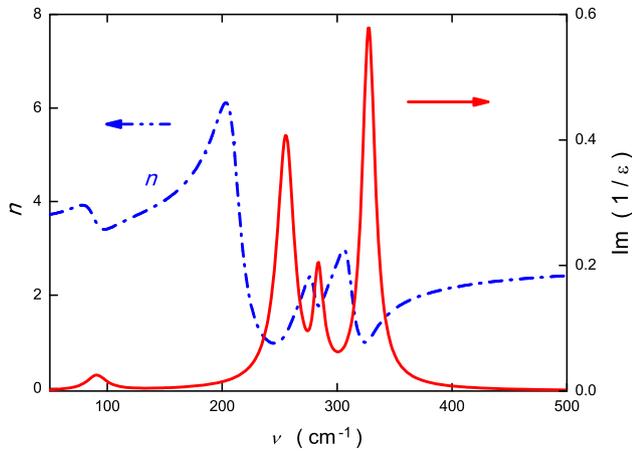
Fig. 3 The spectral dependencies of refractive index n and Im $(1/\varepsilon)$ for $Cu_xAg_{1-x}In_5S_8$ $(x = 0.5)$ crystals

Fig. 4 Frequencies of IR-active optical modes versus composition of $Cu_xAg_{1-x}In_5S_8$ mixed crystals. The data for $AgIn_5S_8$ and $CuIn_5S_8$ crystals are taken from Ref. [12]. The dashed-dotted lines are only guides for the eyes
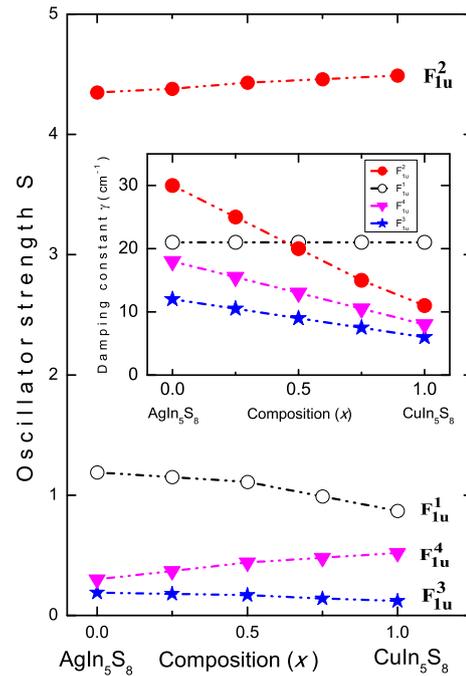
Fig. 5 Compositional dependencies of oscillator strengths (S) and damping constants (γ) in $Cu_xAg_{1-x}In_5S_8$ mixed crystals. The data for $AgIn_5S_8$ and $CuIn_5S_8$ crystals are taken from Ref. [12]. The dashed-dotted lines are only guides for the eyes

It is well-known that at substitution of tetrahedral coordinated Me atoms (Ag, Cu) in $AgIn_5S_8$ and $CuIn_5S_8$ crystals, the distances between the nearest atoms are changed slightly [Me-S = 0.261 (0.259) nm, In-S = 0.255 (0.251) nm, S − S = 0.465 (0.460) nm for $AgIn_5S_8$ ($CuIn_5S_8$)] [10]. Since the force constants of atomic interactions are mainly effected by the bond lengths, it was supposed that the modes frequencies should have near values in the crystals under study [18]. Indeed, the closeness of frequencies of the transverse (TO) and longitudinal (LO) optical phonon frequencies in the IR spectra of $AgIn_5S_8$ and $CuIn_5S_8$ were reported previously [11]. The compositional dependencies of TO- and LO-mode frequencies of $Cu_xAg_{1-x}In_5S_8$ mixed crystals, displaced in Fig. 4, revealed that the mode frequencies rise linearly with the increase of copper atoms content in the mixed crystals. It is noticeable, that all infrared-active optical phonons in $Cu_xAg_{1-x}In_5S_8$ mixed crystals show one-mode

behavior. As seen from Fig. 4, the phonon frequencies of $Cu_xAg_{1-x}In_5S_8$ increase at the substitution of large silver atoms by small copper ones. It should be noted here, that the covalent radii of the silver and copper atoms are equal to 0.153 and 0.138 nm, respectively. As it was reported previously, through the similar replacement of atoms

(larger atoms by smaller ones) in the $Cu_xAg_{1-x}In_5S_8$ mixed crystals the density, lattice parameters and unit cell volumes showed the quite reverse behavior [14].

4. Conclusions

Vibrational spectra are studied in $Cu_xAg_{1-x}In_5S_8$ mixed crystals ($0 \leq x \leq 1$) grown by Bridgman method. Four IR-active modes F_{1u} are revealed in the frequency range of 50–2000 cm^{-1}. The frequencies of transverse and longitudinal optical modes, refractive index, oscillator strengths and damping constants were also determined. The bands observed in infrared spectra of crystals under study were assigned to different vibration types (valence and valence-deformation) on the basis of the symmetrized displacements of atoms obtained by us using the Melvin projection operators. The almost linear dependencies of optical mode frequencies on the composition of $Cu_xAg_{1-x}In_5S_8$ mixed crystals were established.

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