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Infrared-active modes in $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ single crystals: An influence of trivalent cation substitution

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ABSTRACT

Infrared reflection spectra are registered in the frequency range of 50–2000 cm^{-1} for $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ single crystals grown by Bridgman method. Four infrared-active modes are detected in spectra. By replacing the gallium atoms by indium ones in $Ag_3Ga_5S_9$ crystal, the observed bands shift to low frequencies. 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 strength were also determined. The highest frequency bands observed in an infrared spectra of studied crystals were tentatively assigned to the antiphase vibration of the trivalent cation and anion sublattices.

1. Introduction

$Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ belong to the species of compounds with general formula $A_3B_5C_9$, where A = Cu, Ag, Au; B = Ga, In; C = S, Se, Te. The production probability of $A_3B_5C_9$-type semiconductors has been established based on the state diagram of ABC_2–B_2C_3 systems [1]. Optical and photoelectrical properties of these crystals have been studied previously [2–9]. The detailed state diagrams of the $AgGaS_2$–Ga_2S_3 and $AgInS_2$–In_2S_3 systems have been investigated in Ref. [10]. It has been reported that at 25 mol% Ga_2S_3 and In_2S_3, the $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ compounds are formed having melting points of 910 and 925 °C, respectively. $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ crystals are crystallized in tetragonal and monoclinic structures with the parameters $a = 0.5759$ and $c = 1.0314$ nm, and $a = 0.4362$, $b = 0.7661$ and $c = 1.0813$ nm, respectively. The optical and electrical properties of $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ crystals have been studied in Ref. [11]. The room temperature energy band gaps for the direct optical transitions were established as 1.98 and 1.52 eV, respectively. Preliminary study of long-wavelength infrared lattice vibration of $Ag_3In_5S_9$ crystals was carried out in Ref. [12].

2. Experimental details

$Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ semiconductor polycrystals were synthesized using high-purity elements. Usually, the synthesis of binary and ternary chalcogenide compounds are characterized by high pressure of the chalcogenide vapors, the endother-

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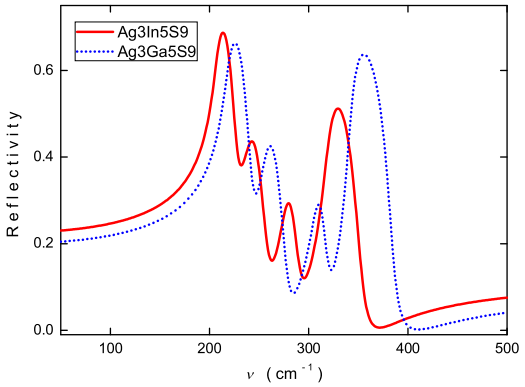

Fig. 1. Reflectivity spectra of $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ crystals.

mal reactions leading to a sharp increase in temperature and by strong interaction of the above compounds with the oxygen. Therefore, a special method has been developed for the synthesis of compounds with high volatile compounds. The single crystals were grown in our crystal growth laboratory 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. 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 chemical compositions of $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ crystals were determined by energy dispersive spectroscopic analysis using JSM-6400 electron microscope. The atomic compositions of the studied samples (Ag: Ga: S) and (Ag: In: S) were found to be 18.4: 29.8: 51.8 and 18.2: 30.0: 51.8, respectively.

In order to carry out the reflectivity measurements, the ingots were cut and the surfaces produced were ground and polished carefully to have the highest optical quality. Right before the reflectivity measurements, the samples were mechanically polished with 0.5 μm Al_2O_3 powder, followed by chemical polishing with an alkaline solution. IR reflection spectra of $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ crystals were recorded in the frequency range from 50 to 2000 cm^{-1} using the long-wave diffraction IR spectrometers FIS-21 and Hitachi-225 with a resolution of 1 cm^{-1}.

3. Results and discussion

Fig. 1 shows the infrared reflectivity spectra of $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ crystals in the frequency range of 50–500 cm^{-1}. Four IR-active optical modes were revealed in the spectra. Due to the lack of IR bands in the frequency range detected between 500 and 2000 cm^{-1}, the figures related to IR measurements in this study were plotted in the 50–500 cm^{-1} range. By replacing in $Ag_3Ga_5S_9$ crystal the gallium atoms by indium ones, the observed bands shift to low frequencies. Kramers–Kronig analysis of the spectra has been performed to get the dispersion parameters. The phase angle θ, the refractive index n, the absorption index k, the real and imaginary parts of dielectric constant ε_1 and ε_2, and the function of energy losses Im $(1/\varepsilon)$ were calculated from reflectivity measurements employing the following relations [13]:

$$\theta(a) = \frac{1}{2\pi}\int_{50}^{2000} ln\left|\frac{\omega - a}{\omega + a}\right| \frac{d}{d\omega}(\ln R)d\omega,$$

$$n = \frac{1-R}{1+R+2\sqrt{R}\cos\theta}, k = \frac{2\sqrt{R}\sin\theta}{1+R+2\sqrt{R}\cos\theta},$$

$$\varepsilon 2 = 2nk, \mathrm{Im}\left(1/\varepsilon\right) = \varepsilon_2/(\varepsilon 12 + \varepsilon 22).$$

The frequencies of transverse (ν_T) and longitudinal (ν_L) optical phonons were determined from the maxima of the function of imaginary part of dielectric constant ε_2 and the function of energy losses Im $(1/\varepsilon)$, respectively. The spectral dependencies of ε_2 and Im $(1/\varepsilon)$ for $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ are shown in Fig. 2. The determined values of ν_T and ν_L for $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ crystals are presented in Table 1.

The calculated spectral dependencies of refractive index for $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ are demonstrated in Fig. 3. The high- and low-frequency refractive indices were determined as 1.87 (2.05) (ν = 2000 cm^{-1}) and 2.65 (2.85) (ν = 50 cm^{-1}), respectively, with maximum values of n = 5.45 (5.98) corresponding to the frequencies ν = 215 (204) cm^{-1} for $Ag_3Ga_5S_9$ ($Ag_3In_5S_9$). Knowing the values of absorption index, one can calculate the absorption coefficient (α) employing the relationship $\alpha = 4\pi k/\lambda$, where λ is the wavelength [13]. The computed spectral dependencies of absorption coefficients of $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ crystals are presented in the inset of Fig. 3. Maximum magnitudes of α, 12290 and 12860 cm^{-1}, are occurred at the frequencies of 222 and 211 cm^{-1} for $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$, respectively.

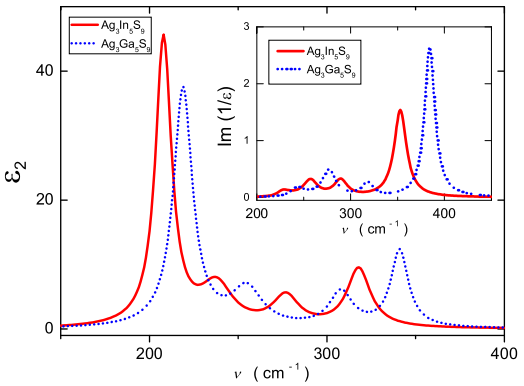

Fig. 2. The spectral dependencies of ε_2 and Im $(1/\varepsilon)$ for $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ crystals.

Table 1
Transverse (ν_T) and longitudinal (ν_L) optical mode frequencies, damping constants (γ) and oscillator strengths (S) of $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ single crystals.

Crystal	Mode	ν_T (cm^{-1})	ν_L (cm^{-1})	γ (cm^{-1})	S
$Ag_3Ga_5S_9$	ν_1	219	243	13	2.23
	ν_2	254	277	21	0.59
	ν_3	308	318	16	0.32
	ν_4	341	384	12	0.44
$Ag_3In_5S_9$	ν'_1	208	229	11	2.42
	ν'_2	237	257	22	0.75
	ν'_3	277	289	18	0.37
	ν'_4	318	353	16	0.48

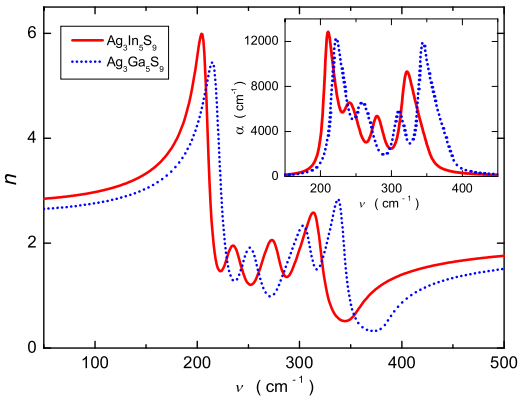

Fig. 3. The spectral dependencies of refractive indices (n)and absorption coefficients (α) for $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ crystals.

The oscillator strength was determined as

$$S = \frac{\gamma}{\nu_T}\varepsilon_2(\max),$$

where ε_2 (max) is the value of 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 ε_2 (max) and γ (see Fig. 2 and Table 1), the magnitudes of oscillator strength for all infrared-active modes were found and presented in Table 1. The high-frequency dielectric constant $\varepsilon_\infty = 3.50$ (4.20) for $Ag_3Ga_5S_9$ ($Ag_3In_5S_9$) 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 $\varepsilon_0 = \varepsilon_\infty + \sum_{i=1}^{4} S_i$, were found to be 7.08 (8.22) for $Ag_3Ga_5S_9$ ($Ag_3In_5S_9$) crystals.

It is interesting to point out that the frequency of the highest-energy mode, the antiphase vibration of the cation and anion sublattices, is determined primarily by the III–VI bond [14]. Supposing that the force constants between gallium and sulfur atoms are close to those between indium and sulfur atoms, the simpler expression $\nu^2 = f/\mu$ may be employed, where f is some effective force constant and μ is the reduced mass given by

$$\mu = \frac{m_{III} \times m_{VI}}{m_{III} + m_{VI}}.$$

Let compare the frequencies of transverse highest-energy modes in the spectra of $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ crystals, $\nu_4 = 341\,cm^{-1}$ and $\nu_4' = 318\,cm^{-1}$, respectively. Taking into account the mass $m_{Ga} = 69.72$, $m_{In} = 114.82$ and $m_S = 32.06$, the effective reduced masses of trivalent cations and anions were calculated as μ_1 (Ga – S) = 21.96 and μ_2 (In – S) = 25.06. As a result, the ratio of the square of mode frequencies $\nu_4^2/\nu_4'^2 = 1.15$ and the ratio of reduced masses $\mu_2/\mu_1 = 1.14$ are in satisfactory agreement with each other. With regard to the predominant influence of the III–VI bond on the highest mode frequencies [15], it is worth mentioning that a similar situation seems to be present also in Tl-based compounds. Earlier published value for the highest transverse optical mode frequency for $TlGaS_2$ crystal [16] ($\nu_T = 364\,cm^{-1}$) is near to that for $Ag_3Ga_5S_9$ crystal ($341\,cm^{-1}$). It should be noted that the frequencies of this mode for $AgGaS_2$ and $CuGaS_2$ crystals, 367 and $365\,cm^{-1}$ respectively, are also close to each other [14,15]. As for In-based compound ($Ag_3In_5S_9$), it is worth comparing the frequency of the highest optical mode ($318\,cm^{-1}$) with those of $AgInS_2$, $CuInS_2$ and $TlInS_2$ crystals, 329, 321 and $326\,cm^{-1}$, respectively [16,17]. It is evident, that there are little differences in the frequencies observed for these compounds.

4. Conclusions

Infrared reflectivity spectra are studied in $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ single crystals grown by Bridgman method. Four IR-active modes 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 using Kramers-Kronig method. The frequencies of transverse (ν_T) and longitudinal (ν_L) optical modes, oscillator strength (S) and damping constant (γ) were also determined. The highest frequency bands observed in infrared spectra of studied crystals were tentatively attributed to the antiphase vibration of the trivalent cation and anion sublattices.

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