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Long-wavelength lattice vibrations of $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ single crystals: An inversion of LO- and TO-mode frequencies

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Infrared (IR) reflectivities are registered in the frequency range of 50–2000 cm^{-1} for $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ single crystals grown by Bridgman method. Three infrared-active modes are detected in spectra. The 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 (TO and LO modes) and oscillator strength were also determined. The bands detected in infrared spectra were tentatively attributed to various vibration types (valence and valence-deformation). The inversion of LO- and TO-mode frequencies of the sandwiched pair was observed for studied crystals.

Keywords: Semiconductors; chalcogenides; optical properties; infrared reflection.

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1. Introduction

$Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ belong to the class of compounds with formula $A_3B_5C_9$, where A = Cu, Ag, Au; B = Ga, In; and C = S, Se, Te. The possibility of formation of $A_3B_5C_9$-type semiconductors has been revealed based on the state diagram of ABC_2–B_2C_3 systems.[1] Optical and photoelectrical properties of these crystals have been studied previously.[2–7] The detailed state diagrams of the AgInSe$_2$–In$_2$Se$_3$ and AgInTe$_2$–In$_2$Te$_3$ systems have been investigated in Refs. 8 and 9. It has been found that at 25 mol.% of In$_2$Se$_3$ and In$_2$Te$_3$, the $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ compounds, melting congruently at 825°C and 710°C, respectively, are formed. $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ are crystallized in tetragonal structures with the parameters $a = 0.671$ nm and $c = 1.043$ nm and $a = 0.721$ nm and $c = 1.457$ nm,[8] respectively.

The results of investigation of current–voltage characteristics, Hall coefficient and saturation of the current in $Ag_3In_5Se_9$ were reported in Ref. 10. Gakhramanov *et al.*[11] studied the low-frequency oscillations of the current in $Ag_3In_5Se_9$ crystals stimulated by infrared (IR) radiation and electric field. Four deep levels with activation energies of 0.12, 0.43, 0.73 and 1.09 eV were revealed from thermally stimulated current experiments. The electrical resistivity and Hall mobility of $Ag_3In_5Se_9$ crystals were investigated in the temperature range of 65–480 K.[9] The room temperature values of conductivity and mobility in $Ag_3In_5Se_9$ were found to be 7.2×10^{-5} $(\Omega \cdot cm)^{-1}$ and 20 $cm^2/V \cdot s$, respectively. The activation energies of impurity states of 0.02, 0.07 and 0.76 eV were obtained from temperature dependence of conductivity. The band gap of $Ag_3In_5Se_9$ crystals at room temperature deduced from the spectral dependence of photoconductivity was found to be 1.22 eV. The optical and electrical properties of $Ag_3In_5Te_9$ crystals have been studied in Ref. 12. The energy band gaps for the direct optical transitions were established as 0.96 eV and 1.01 eV at 300 K and 77 K, respectively. Preliminary study of infrared reflection spectra of $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ crystals were carried out in Ref. 13.

2. Experimental Details

$Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ 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 components. 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 $30°C \cdot cm^{-1}$ at a rate of 1.0 mm $\cdot h^{-1}$.

The chemical compositions of the $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ crystals were determined using the energy dispersive spectroscopy (EDS) experiments which were performed by a JSM-6400 scanning electron microscope having two pieces of equipment called as "Noran System 6 X-ray Microanalysis System" and "Semafore Digitizer" which take part in the analysis of experimental data. Figure 1 shows the EDS results used to determine the chemical composition of the crystal. Since every element has distinctly unique energy levels, each element produces characteristic X-rays which get an opportunity to determine the elemental composition of the sample by analyzing the spectra.[14] The atomic composition ratio of constituent elements in the mixed crystal was determined from the relative counts of the detected X-rays. The emission energies for Ag, In, Se and Te elements are equal to (2.984, 3.150, 3.350, 3.519, 3.522 keV), (3.286, 3.487, 3.920, 3.729 and 3.937 keV), (1.379, 1.419, 1.434 and 1.475 keV) and (3.769, 4.029, 4.301, 4.342, 4.570 and 4.612 keV), respectively.[15]
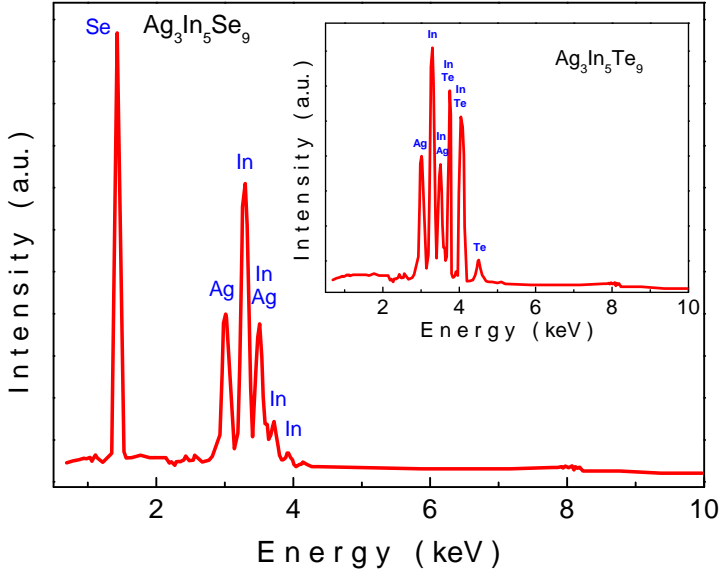
Fig. 1.   Energy dispersive spectroscopic analysis of $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ crystals.

The atomic compositions of the studied samples (Ag:In:Se) and (Ag:In:Te) were found to be 17.9:29.6:52.5 and 17.7:29.5:52.8, respectively.

In order to carry out the reflectivity measurements, the ingots were cut and the surfaces produced were ground and polished carefully. 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 $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ crystals were recorded in the frequency range between 50 cm^{-1} and 2000 cm^{-1} employing the long-wave diffraction IR spectrometers FIS-21 and Hitachi-225 with a resolution of 1 cm^{-1}.

3. Results and Discussion

Figure 2 shows the infrared reflectivity spectra of $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ crystals in the frequency range of 50–500 cm^{-1}. Three IR-active optical modes were revealed in the spectra. By replacing selenium atoms by tellurium ones in $Ag_3In_5Se_9$ crystal, the observed bands shift towards low frequencies. Kramers–Kronig analysis of the spectra has been performed to get the dispersion parameters. The frequencies of transverse optical (ν_{TO}) and longitudinal optical (ν_{LO}) 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 $Im(1/\varepsilon)$, respectively. The spectral dependencies of ε_2 and $Im(1/\varepsilon)$ for $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ are shown in Fig. 3. The determined values of ν_{TO} and ν_{LO} for $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ crystals are presented in Table 1.
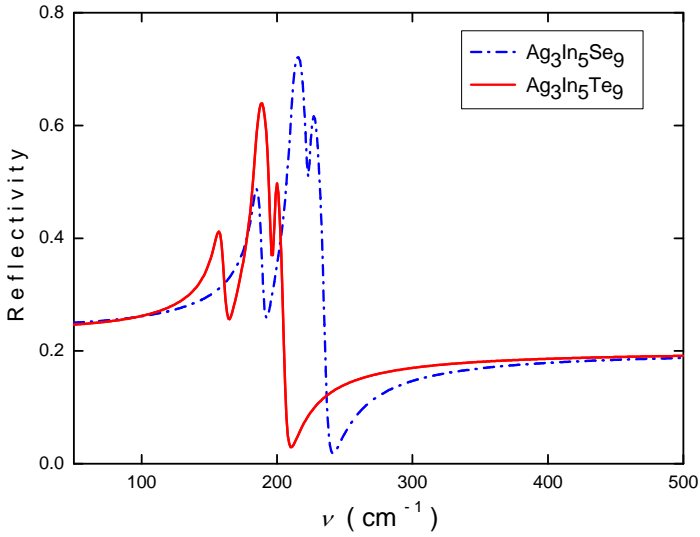
Fig. 2. Reflectivity spectra of Ag₃In₅Se₉ and Ag₃In₅Te₉ crystals.
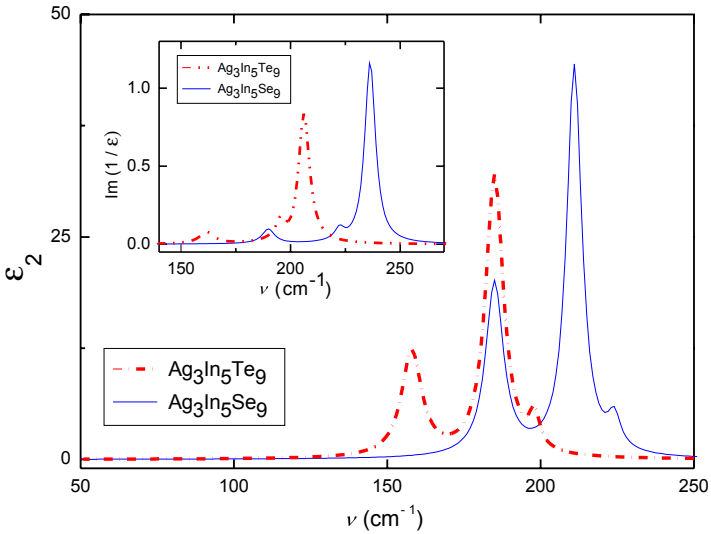
Fig. 3. The spectral dependencies of ε_2 and $\mathrm{Im}(1/\varepsilon)$ for Ag₃In₅Se₉ and Ag₃In₅Te₉ crystals.

Moreover, the dependencies of refractive index n and absorption index k on the frequency were calculated from reflectivity spectra for Ag₃In₅Se₉ and Ag₃In₅Te₉ using the following relations[16]:

$$n = \left[\frac{\left(\varepsilon_1 + (\varepsilon_1^2 + \varepsilon_2^2)^{1/2} \right)}{2} \right]^{1/2}, \qquad (1)$$

Table 1.   Transverse optical mode (ν_{TO}) and longitudinal optical mode (ν_{LO}) frequencies, damping constants (γ) and oscillator strengths (S) of Ag$_3$In$_5$Se$_9$ and Ag$_3$In$_5$Te$_9$ single crystals.

Crystal	Mode	ν_{TO} (cm^{-1})	ν_{LO} (cm^{-1})	γ(cm^{-1})	S
Ag$_3$In$_5$Se$_9$	ν_1	185 ± 1	190 ± 1	5 ± 0.4	0.54 ± 0.05
	ν_2	224 ± 1	221 ± 1	6 ± 0.5	0.16 ± 0.02
	ν_3	211 ± 1	236 ± 1	7 ± 0.6	1.47 ± 0.13
Ag$_3$In$_5$Te$_9$	ν_1'	158 ± 1	162 ± 1	6 ± 0.5	0.47 ± 0.04
	ν_2'	198 ± 1	195 ± 1	7 ± 0.6	0.22 ± 0.02
	ν_3'	185 ± 1	206 ± 1	8 ± 0.7	1.21 ± 0.10

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

The spectral dependencies of n and k for Ag$_3$In$_5$Se$_9$ and Ag$_3$In$_5$Te$_9$ are shown in Figs. 4 and 5, respectively. The high- and low-frequency refractive indices were determined as 2.61 (2.85) ($\nu = 2000$ cm^{-1}) and 3.00 (3.19) ($\nu = 50$ cm^{-1}), respectively, with maximum value of $n = 5.72$ (5.26) corresponding to the frequency $\nu = 209$ (183) cm^{-1} for Ag$_3$In$_5$Se$_9$ (Ag$_3$In$_5$Te$_9$). Knowing the values of absorption index, it was possible to calculate the absorption coefficient (α) by employing the relationship $\alpha = 4\pi k/\lambda$, where λ is the wavelength.[16] The computed spectral dependencies of absorption coefficients of Ag$_3$In$_5$Se$_9$ and Ag$_3$In$_5$Te$_9$ crystals are presented in the insets of Figs. 4 and 5, respectively. Maximum magnitudes of α, 13,200 cm^{-1} and 9480 cm^{-1}, have occurred at the frequencies of 213 cm^{-1} and 187 cm^{-1} for Ag$_3$In$_5$Se$_9$ and Ag$_3$In$_5$Te$_9$, respectively.

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 Fig. 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 $\varepsilon_\infty = 6.80$ (8.12) for Ag$_3$In$_5$Se$_9$ (Ag$_3$In$_5$Te$_9$) was calculated by employing the high-frequency reflection coefficient R_∞ ($\nu = 2000$ cm^{-1}). The low-frequency dielectric constant ε_0, determined from the relation $\varepsilon_0 = \varepsilon_\infty + \sum_1^3 S$, was found to be 8.97 (10.02) for Ag$_3$In$_5$Se$_9$ (Ag$_3$In$_5$Te$_9$) crystal.

We would like to point out that the frequency of the highest intensity mode, the antiphase vibration of the cation and anion sublattices, is determined primarily by the III–VI bond.[17] Let us compare the frequencies of transverse high-intensity modes in the spectra of Ag$_3$In$_5$Se$_9$ and Ag$_3$In$_5$Te$_9$ crystals, $\nu_{\text{T3}} = 211$ cm^{-1} and $\nu_{\text{T3}}' = 185$ cm^{-1}, respectively (Table 1). Supposing that the force constants between
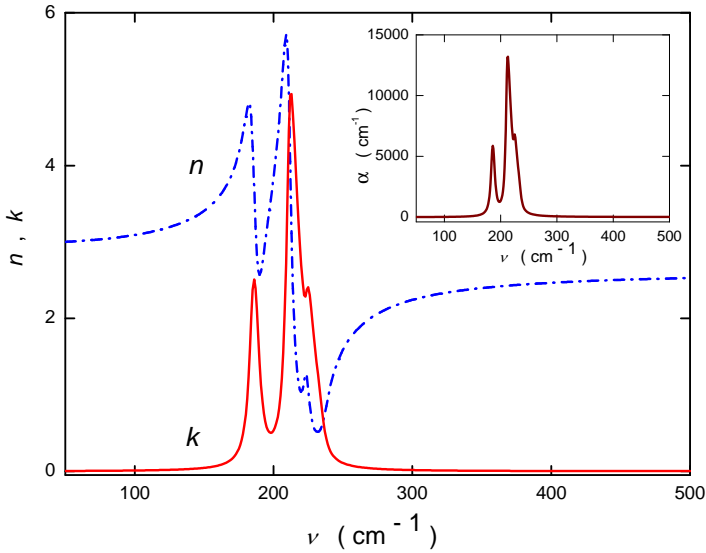
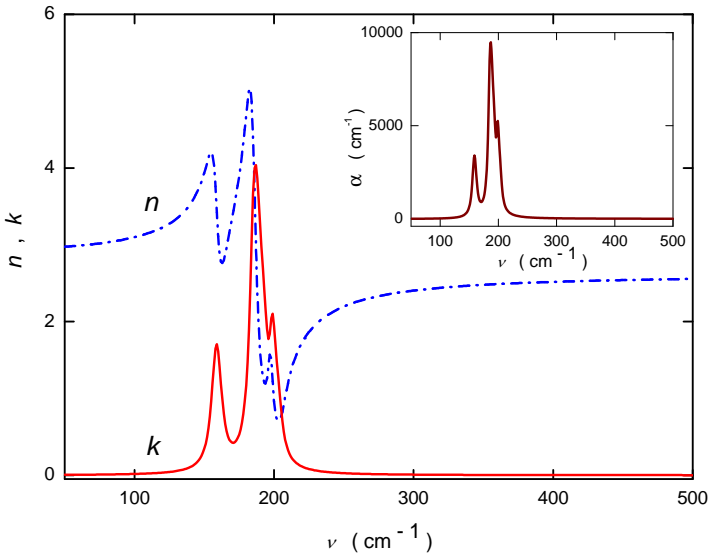Fig. 4.   The spectral dependencies of n, k and α for $Ag_3In_5Se_9$ crystal.

Fig. 5.   The spectral dependencies of n, k and α for $Ag_3In_5Te_9$ crystal.

indium and selenium atoms are close to those between indium and tellurium 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 $\mu = (m_{III} \times m_{VI})/(m_{III} + m_{VI})$. Taking into account the mass of atoms $m_{In} = 114.82$, $m_{Se} = 78.96$ and $m_{Te} = 127.60$, the effective reduced masses of trivalent cation and anions were estimated as

μ_1(In–Se) $= 46.79$ and μ_2(In–Te) $= 60.44$. As a result of calculation, the ratio of the square of mode frequencies $\nu_{T3}^2/\nu'^2_{T3} = 1.30$ and the ratio of reduced masses $\mu_2/\mu_1 = 1.29$ were found to be in satisfactory agreement with each other. With regard to the predominant influence of the III–VI bond on the highest mode frequencies,[18] it is worth to compare the frequency of the highest optical mode of $Ag_3In_5Se_9$ compound ($\nu_{T3} = 211$ cm^{-1}) with those of $AgInSe_2$ and $CuInSe_2$ crystals, 215 cm^{-1} and 212 cm^{-1}, respectively.[19,20] There is little difference in the frequencies observed for these compounds. As for tellurium-based compound $Ag_3In_5Te_9$, it is worthy of comparison the frequency of the highest optical mode ($\nu'_{T3} = 185$ cm^{-1}) with those of $AgInTe_2$ and $CuInTe_2$ crystals, 173 cm^{-1} and 172 cm^{-1}, respectively, which are close to each other.[17,19]

Moreover, the spectra of $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ crystals exhibited modes with small LO–TO splitting (Table 1): The most low-frequency modes $190(\nu_{L1})$–$185(\nu_{T1})$ cm^{-1} ($Ag_3In_5Se_9$) and $162(\nu'_{L1})$–$158(\nu'_{T1})$ cm^{-1} ($Ag_3In_5Te_9$). These modes may be attributed to IR-active modes, in which only the tetrahedral coordinated Ag and In atoms are displaced strictly along the coordinate axes, whereas the octahedral coordinated In and Se(Te) atoms accomplish deformation vibrations.[21] Thus, the observed low-frequency modes in the infrared spectra of $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ crystals are the mixed valence-deformation modes.

As seen from Table 1, the inversions of optical mode frequencies take place for $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ crystals, i.e. the frequencies of longitudinal optical modes ($\nu_{L2} = 221$ cm^{-1} ($Ag_3In_5Se_9$) and $\nu'_{L2} = 195$ cm^{-1} ($Ag_3In_5Te_9$)) were found to be less as compared to frequencies of the corresponding transverse optical modes ($\nu_{T2} = 224$ cm^{-1} and $\nu'_{T2} = 198$ cm^{-1}). According to Kirk,[22] for multi-oscillator system an LO-mode frequency is always interspersed between any two successive TO-mode frequencies and vice versa. In case of $Ag_3In_5Se_9$ crystal, for the ν_{L2}–ν_{T2} (221–224 cm^{-1}) pair — lying sandwiched between the frequencies of another pair ($236(\nu_{L3})$–$211(\nu_{T3})$ cm^{-1}) — interspersion is accommodated by the inversion of frequencies of the ν_{L2}–ν_{T2} sandwiched pair. As a result, we have the following sequence of the mode frequencies: $\nu_{L3} > \nu_{T2} > \nu_{L2} > \nu_{T3}$. For the $Ag_3In_5Te_9$ crystal, the frequencies of the ν'_{L2}–ν'_{T2} (195–198 cm^{-1}) pair lie between the frequencies of another pair ($206(\nu'_{L3})$–$185(\nu'_{T3})$ cm^{-1}). In a similar manner, a following sequence of optical mode frequencies $\nu'_{L3} > \nu'_{T2} > \nu'_{L2} > \nu'_{T3}$ was obtained.

4. Conclusions

Infrared reflection spectra are studied in $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ single crystals grown by Bridgman method. Three 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. The frequencies of transverse namely (ν_{TO}) and longitudinal optical (ν_{LO}) modes, oscillator strength (S) and damping constant (γ) were also determined. The

bands observed in infrared spectra of crystals under study were tentatively assigned to various vibration types (valence and valence-deformation). The inversion of LO- and TO-mode frequencies was observed for $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ crystals.

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