Compositional Dependence of Optical Modes Frequencies in $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ Layered Mixed Crystals ($0 \leq x \leq 1$)

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The infrared transmittance and Raman scattering spectra in $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ ($0 \leq x \leq 1$) layered mixed crystals grown by the Bridgman method were studied in the frequency ranges of 400–2000 and 250–400 cm^{-1} , respectively. The bands observed at room temperature in IR transmittance spectra of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ were interpreted in terms of multiphonon absorption processes. The dependences of the frequencies of IR- and Raman-active modes on the composition of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals were also established. The structural characterization of the mixed crystals was investigated by means of X-ray diffraction measurements and compositional dependence of lattice parameters was revealed.

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1. Introduction

The family of crystals designated with the chemical formula TlBX_2 (where B = In or Ga, X = S, Se or Te) are known as thallium dichalcogenides. Members of this family have both layered (TlGaS_2 , TlGaSe_2 , TlInS_2) and chain (TlInSe_2 , TlInTe_2 , TlGaTe_2) structures [1, 2]. The possible applications of TlInS_2 and TlGaS_2 in the optoelectronic device area have forced the researchers to get detailed information about the properties of these crystals. Optical and photoelectrical properties of TlInS_2 and TlGaS_2 crystals were studied in Refs. [3–6]. A high photosensitivity in the visible range of spectra, high birefringence in conjunction with a wide transparency range of 0.5–14 μm make this crystal useful for optoelectronic applications [7].

Previously, the compounds TlInS_2 and TlGaS_2 have been characterized in point of phonon spectra deduced from infrared and Raman scattering measurements [8–10]. The low frequency translational modes and high-frequency “intramolecular” modes have been reported by means of obtained spectra. TlInS_2 and TlGaS_2 form a continuous series of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ ($0 \leq x \leq 1$) mixed crystals. The optical properties of the $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ crystals have been studied by means of transmission and reflection measurements in the wavelength range of 400–1100 nm [11, 12]. The optical indirect band gap energies were determined through the analysis of the absorption data. It was found that the energy band gaps increase with increase of gallium atoms content in the $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ crystals. These measurements allowed also the determination of the spectral dependence of refractive index for all compositions of the mixed crystals studied.

The aim of the present work was to study the phonon spectra of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ layered mixed crystals using infrared transmittance and Raman spectroscopy at room temperature. The experimentally revealed bands in IR transmittance spectra were assigned to multiphonon absorption by means of the combination of Raman-active mode frequencies.

2. Experimental details

Single crystals of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ ($x = 0, 0.25, 0.5, 0.75, 1$) were grown by Bridgman method from a stoichiometric melt of starting materials sealed in the evacuated and carbon coated silica tubes with a tip at the bottom in our crystal growth laboratory. The chemical composition of the $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals were determined by the energy dispersive spectroscopic analysis using JSM-6400 electron microscope. The samples for the measurements were taken from the middle part of the ingots.

The atomic composition ratios of the studied samples are presented in Table I. X-ray powder diffractometer Philips PW1740 ($\text{Cu } K_\alpha$ radiation) was used for structural characterization. X-ray diffractograms of studied crystals were indexed by using the computer program “Treor 90”.

Inset of Fig. 1 presents the X-ray pattern of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals ($x = 0.5$). The calculated Miller indices (hkl) are displayed in this figure. Figure 1 shows the compositional variations of the lattice parameters (a , b and c) of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals. Presently evaluated lattice parameters $a = 1.0312$; $b = 1.0431$; $c = 1.5072$ nm (TlGaS_2) and $a = 1.0942$; $b = 1.0484$; $c = 1.5606$ nm (TlInS_2) agree well with the corresponding data of Ref. [13]. As seen from Fig. 1, the lattice parameters a , b and c of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals decrease with the substitution of indium atoms

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by gallium. This observation may be accounted for considering the covalent radius of replacing atoms, which are equal to 0.144 and 0.126 nm for indium and gallium, respectively. The smaller atoms replacing the larger ones in the mixed crystals cause the observed lattice reduction in the mixed crystals studied.

TABLE I
The atomic composition ratios (%) of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals.

Composition	Tl	Ga	In	S
$x = 1$	25.4	25.6	—	49.0
$x = 0.75$	26.1	19.0	6.1	48.8
$x = 0.50$	25.9	13.0	13.1	48.0
$x = 0.25$	25.8	6.6	19.2	48.4
$x = 0$	25.6	—	25.2	49.2

Fig. 1. The compositional variations of the lattice parameters (a , b and c) of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals. The dashed-dotted lines are only the guides for the eye. Inset: X-ray diffraction pattern of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals ($x = 0.5$).

Crystals suitable for measurements were obtained by easy cleavage perpendicular to optical c -axis. The freshly cleaved surfaces are mirror-like. IR transmittance spectra were registered at room temperature in the frequency range 400–2000 cm^{-1} using a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific Inc., USA). 128 scan were co-added and zero filled for a spectral resolution of 2 cm^{-1} . The electrical vector of incident light was in the layer plane. The Raman scattering experiments in $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ crystals were performed at room temperature in the backscattering geometry in the frequency

range 250–400 cm^{-1} . A 632.8 nm line of He–Ne laser was used as the exciting light source. The scattered light was analyzed using a double grating spectrometer with a focal length of 1 meter and a cooled GaAs photomultiplier supplied with the usual photon counting electronics.

3. Results and discussion

The IR transmittance spectra of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals were studied as a function of composition x in the frequency range 400–2000 cm^{-1} . Figure 2 shows the infrared spectrum of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ ($x = 0.5$). As seen from the figure, three minima at frequencies approximately 648, 925 and 1083 cm^{-1} were observed in the spectrum. The frequencies of the minima in the IR spectra for the studied compositions of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals ($0 \leq x \leq 1$) are displayed in Table II. Figure 3 shows the extended low-frequency parts (400–850 cm^{-1}) of IR spectra for various compositions ($0 \leq x \leq 1$) of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ crystals. The frequencies of the observed minima in these spectra range from 604 to 660 cm^{-1} with increase of x from 0 to 1.

Fig. 2. IR transmittance spectrum of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals ($x = 0.5$) at room temperature. Inset: High-frequency Raman spectra of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals at room temperature.

The Raman scattering spectra of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals were studied as a function of composition x in the high-frequency range 250–400 cm^{-1} . Unpolarized excitation and detection, allowing all the lines to be visible, have been used for these spectra. The measurements have been performed on the same samples used for the IR experiments. The frequencies of observed lines for TlInS_2 and TlGaS_2 crystals are fairly well correlated with previously reported ones [8–10]. Inset of Fig. 2 shows the Raman spectra of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals ($0 \leq x \leq 1$). In the analysis, we deconvoluted the complex contour of the Raman-active modes with Lorentzian peaks using least squares approach. As a result of this procedure, we obtained information about the position for each peaks.

Fig. 3. Extended low-frequency parts of IR transmittance spectra for various compositions of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals.

Fig. 4. Frequency dependences of IR transmittance minima and Raman-active modes on composition of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals.

TABLE II

The frequencies of Raman and IR modes (cm^{-1}) of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals, and assignments of IR transmittance minima due to multiphonon absorption processes in the crystals.

Comp.	Raman	IR transm.	Proposed assignment
$x = 1$	315	660	$326 \times 2 = 652$
	323		$326 \times 3 = 978$
	326	968	
	390	1110	$390 \times 2 + 326 = 1106$
$x = 0.75$	309	645	$323 \times 2 = 646$
	316		$316 \times 3 = 948$
	323	943	
	388	1115	$388 \times 2 + 323 = 1094$
$x = 0.50$	301	635	$315 \times 2 = 630$
	309		$309 \times 3 = 927$
	315	925	
	374	1121	$374 \times 3 = 1122$
$x = 0.25$	290	622	$309 \times 2 = 618$
	301		$301 \times 3 = 903$
	309	911	
	370	1125	$370 \times 3 = 1110$
$x = 0$	283	604	$304 \times 2 = 608$
	294		$294 \times 3 = 882$
	304	883	
	347	1130	$283 \times 4 = 1132$

The dependences of the frequencies of IR- and Raman-active modes on the composition of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ crystals are depicted in Fig. 4. We analyzed in detail the compositional dependence of four high-frequency “intramolecular” Raman-active modes in $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ crystals, which exhibit one-mode behavior. Their frequencies vary from 347, 304, 294 and 283 cm^{-1} ($x = 0$) to 390, 326, 323 and 315 cm^{-1} ($x = 1$). The highest-frequency mode in the Raman spectra of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals, which is due to only the motions of chalcogen atoms, shows the significant increase in frequency (43 cm^{-1}) with the substitution of the heavy indium atoms by lighter gallium ones.

By analogy to the situation in A^3B^6 layered crystals [14, 15], it can be expected that the phonon combination modes are due to zone-centered phonons. The bands observed in the transmittance spectra of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals fit closely with the possible combinations among the frequencies found from the Raman spectra. The proposed assignments of these bands are presented in Table II. In our recent study, the low-frequency bands in IR transmittance spectra near 604 cm^{-1} ($x = 0$, TlInS_2) and 660 cm^{-1} ($x = 1$, TlGaS_2) were attributed to the first overtones of modes with frequencies of 304 and 326 cm^{-1} observed in the Raman spectra of TlInS_2 and TlGaS_2 crystals, respectively [16]. The mid-frequency bands in IR transmittance spectra with frequencies 883 cm^{-1} (TlInS_2) and 968 cm^{-1} (TlGaS_2) were assigned to the second overtones of modes with

frequencies of 294 and 326 cm^{-1} observed in the Raman spectra of TlInS_2 and TlGaS_2 crystals, respectively. The high-frequency minimum in the IR spectrum of TlGaS_2 crystals with frequency 1110 cm^{-1} is due to three-phonon absorption processes. As for high-frequency band 1130 cm^{-1} (TlInS_2), it may be regarded as third overtones of mode with frequency of 283 cm^{-1} observed in the Raman spectrum of TlInS_2 crystals.

Based on the above consideration, we would like to focus on the assignment of the bands observed in the IR transmittance spectra of $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals with compositions $x = 0.75, 0.5$ and 0.25 (Table I). Similar assignments can be made for the low-frequency bands (645, 635 and 622 cm^{-1}) of modes as the first overtones of corresponding Raman-active modes (323, 315 and 309 cm^{-1}) like in the case of pure compounds TlInS_2 and TlGaS_2 . Further, the attribution to the second overtones of Raman-active modes 316, 309 and 301 cm^{-1} can also be argued for the mid-frequency bands 943, 925 and 911 cm^{-1} observed in the IR transmittance spectra of intermediate compositions $x = 0.25, 0.5$ and 0.75 , respectively. As for the high-frequency bands (at 1121 and 1125 cm^{-1}) observed in the spectra for $x = 0.5$ and 0.25 , they can be assigned to the second overtones of modes with frequencies 374 and 370 cm^{-1} , respectively. Finally, we may attribute the band with frequency 1115 cm^{-1} , belonging to the composition $x = 0.75$, to the three-phonon absorption process, as in the case of pure compound TlGaS_2 .

4. Conclusions

The infrared and Raman scattering spectra for $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ layered mixed crystals were investigated for a wide range of composition ($0 \leq x \leq 1$) in the frequency region of 400–2000 and 250–400 cm^{-1} , respectively. The frequencies of modes in the Raman spectra of mixed crystals increase as high as 43 cm^{-1} with the substitution of the heavy indium atoms by lighter gallium ones. An attempt was made to interpret the observed bands in IR transmittance spectra in terms of two-, three- and four-phonon absorption processes. As a result, the satisfactory assignments were established. Structural characterization of the studied mixed crystals was accomplished using X-ray diffraction measurements. Analysis of the measurements showed that lattice parameters of the $\text{TlGa}_x\text{In}_{1-x}\text{S}_2$ mixed crystals decrease with increase of the content of gallium atoms.

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