



Vibrational modes in $(\text{TlGaS}_2)_x-(\text{TlGaSe}_2)_{1-x}$ mixed crystals by Raman measurements: compositional dependence of the mode frequencies and line-shapes

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Abstract

TlGaS_2 and TlGaSe_2 ternary semiconducting compounds have been of scientific interest due to their large ultrafast optical nonlinearity characteristics. These remarkable properties make them promising semiconducting materials in photonic applications. A series of $(\text{TlGaS}_2)_x-(\text{TlGaSe}_2)_{1-x}$ layered mixed crystals grown by Bridgman method were investigated from the standpoint of their Raman spectroscopy characteristics. Experimental Raman scattering study of crystals were reported in the frequency range of $80\text{--}400\text{ cm}^{-1}$ for compositions of $x=0, 0.25, 0.50, 0.75$ and 1.0 . The effects of crystal disorder on the line-width broadening of Raman-active modes were studied in detail. The asymmetry in the Raman line-shape was analyzed for two highest-frequency intralayer mode presenting two-mode behavior. It was shown that mixed crystal disorder effect is the major source for change of Raman line-shape with composition.

1 Introduction

Layered semiconducting compounds have been investigated for years due to their various favorable structural and optical characteristics. The weak van der Waals bonding structure within the layers provides these compounds a potential to exist as quasi-two dimensional. Two-dimensional layered semiconductors have been one of the most attractive research interests in recent years and investigated due to their optoelectronic device applications like transistors [1], solar cells [2], electro-optical devices [3], biomedical sensors and power devices [4].

TlGaS_2 and TlGaSe_2 anisotropic single crystals which are the interest of present study belongs to layered semiconductor family and have been the subject of remarkable number

of research papers [5–9]. The lattice of compounds is formed by properly periodic two-dimensional layers whose arrangement takes place parallel to (001) plane. A layer within the lattice is positioned perpendicularly to the previous one. The indirect and direct gap energies of layered semiconductors were revealed as 2.45 and 2.63 eV for TlGaS_2 and 1.97 and 2.26 eV for TlGaSe_2 [10]. The studies on device characterization of compounds showed that they carry the potential to be used in ultrafast nonlinear optical material devices [11], acousto-optical, ultrathin phototransistor and optoelectronic devices [2], ultraviolet detection visible applications [12], and infrared detectors [13].

TlGaS_2 and TlGaSe_2 layered semiconductors form $(\text{TlGaS}_2)_x-(\text{TlGaSe}_2)_{1-x}$ mixed crystals without any concentration restriction ($0 \leq x \leq 1$). Our research group focused on investigation of various characteristics of these mixed crystals [14–16]. The advantage of these mixed compounds is seen as a point of that a compound having some desired optical and electrical properties may be grown by adjusting the composition x . For instance, direct band gap energies of $(\text{TlGaS}_2)_x-(\text{TlGaSe}_2)_{1-x}$ mixed crystals were obtained as increasing from 2.19 to 2.67 eV almost linearly [14]. Taking into consideration the attractiveness of TlGaS_2 and TlGaSe_2 layered semiconductors and some of the adjustable characteristics of mixed compounds, it would be worthwhile for research interest to introduce characteristics of these mixed compounds. Previously, high-performance visible light

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photo-detector based on TlGaS_2 ($x=0.5$) single crystal was fabricated and investigated in Ref. [17]. The p–n junction fabricated by p-type TlGaS_2 and n-type boron nitride were investigated and characterized for optoelectronic applications of the compound [18]. Raman spectroscopy is a well-known, practical and valuable tool to investigate lattice vibration characteristics of compounds. The room temperature phonon spectra of interest mixed crystals were reported previously using Raman, infrared reflection and Brillouin scattering experiments. The frequency dependencies of Raman-active modes of $(\text{TlGaS}_2)_x-(\text{TlGaSe}_2)_{1-x}$ crystals were revealed in Ref. [19]. The present paper aims at studying the line-shape (line-width and asymmetry) of optical modes in $(\text{TlGaS}_2)_x-(\text{TlGaSe}_2)_{1-x}$ by Raman spectroscopy. The comparison of experimental data and its analyses indicated that anharmonicity and compositional disorder in mixed crystals have remarkable relation. We discuss in detail the effect of crystal disorder on the line-width (full-width at half-maximum) and the asymmetry in the Raman line-shape of two highest-frequency intralayer modes exhibiting two-mode behavior.

2 Experimental details

The interest $(\text{TlGaS}_2)_x-(\text{TlGaSe}_2)_{1-x}$ mixed semiconducting crystals with compositions $x=0, 0.25, 0.50, 0.75$ and 1.0 were grown by Bridgman method applied as follows: The constituent elements with high-purity in stoichiometric proportions were firstly used to synthesize semiconducting polycrystals. Then these polycrystals were placed into evacuated ($\approx 10^{-5}$ Torr) silica tubes (diameter: 1 cm, length: 55 cm) having a tip at the bottom to grow single crystals. The growth of single crystals from polycrystals was accomplished by moving the ampoule in a vertical furnace at a rate of 0.55 mm/h. The used furnace employs with thermal gradient of 30 °C/cm between 900 and 650 °C. It was observed that the color of the crystals turns to dark red (TlGaSe_2) from yellow (TlGaS_2) as selenium concentration was increased in the mixed crystals. The layered structure of studied compounds let us easily cleave crystals perpendicular to the optical c -axis. Raman spectra recorded in the back-scattering geometry in the region of 80–400 cm^{-1} with Horiba Yvon RMS-550 Raman spectrometer were achieved by 532 nm line of YAG: Nd^{3+} laser. The Raman line positions were determined within an accuracy of $\pm 0.1 \text{ cm}^{-1}$.

3 Results and discussion

The X-ray diffraction data indicated that grown samples are monocrystalline with monoclinic unit cell [20]. According to analyses of X-ray diffraction measurements, the crystalline

structure of both compounds was reported as monoclinic with lattice constants of $a=1.031, b=1.043, c=1.507 \text{ nm}$, $\beta=99.6^\circ$ for TlGaS_2 [21] and $a=1.0772, b=1.0771, c=1.564 \text{ nm}$, $\beta=100.06^\circ$ for TlGaSe_2 [10]. The unit cell volumes of TlGaS_2 and TlGaSe_2 were calculated as 1.59783 and 1.78412 nm^3 , respectively. As seen, replacement of larger element (Se) with smaller one (S) results in decrease in the unit cell volume of the structure as expected according to theory. The atomic composition ratios of the studied samples ($\text{Tl}:\text{Ga}:\text{S}:\text{Se}$) were found to be 25.4:25.2:49.4 ($x=0$), 25.8:26.0:12.2:36.0 ($x=0.25$), 25.7:25.9:24.1:24.3 ($x=0.50$), 26.0:25.8:35.9:12.3 ($x=0.75$) and 25.4:25.6:49.0 ($x=1$) [14].

Raman spectra observed experimentally in the 80–400 cm^{-1} range at room temperature for all studied $(\text{TlGaS}_2)_x-(\text{TlGaSe}_2)_{1-x}$ mixed crystals are indicated in Fig. 1. Raman spectra of end-members, TlGaS_2 and TlGaSe_2 , present six and five distinct peaks, respectively. These modes agree well with previously reported ones in Refs. [22, 23]. The phonon spectra belonging to TlGaS_2 and TlGaSe_2 crystals display typical behavior of vibrational spectra of molecular crystals. That means low-frequency translational modes of the system consisting of Ga_4S_6 (Ga_4Se_6) units and Tl atoms [interlayer vibrations, vibrations of Tl atoms, vibrations of Tl atoms and Ga_4S_6

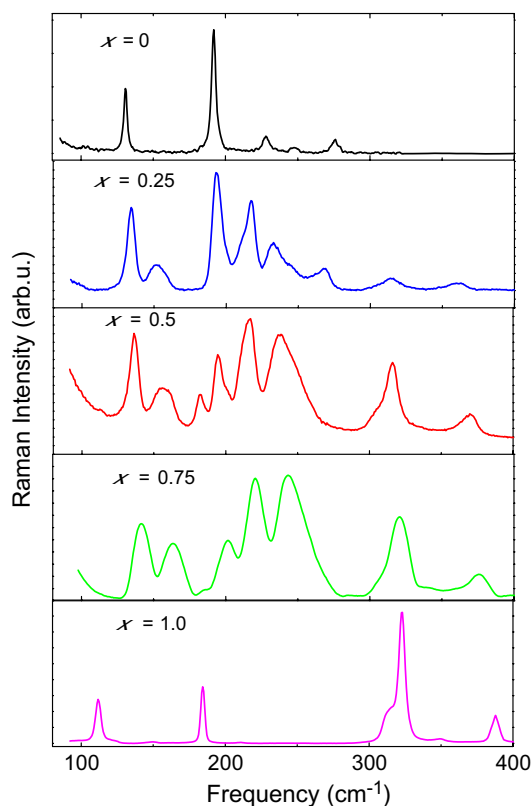


Fig. 1 Raman spectra of $(\text{TlGaS}_2)_x-(\text{TlGaSe}_2)_{1-x}$ mixed crystals

(Ga₄Se₆) units] and high-frequency “intramolecular” modes of the Ga₄S₆ (Ga₄Se₆) units were presented in the spectra. (TlGaS₂)_x–(TlGaSe₂)_{1–x} mixed crystals come into existence by substitution of sulfur atoms with selenium atoms which take part in the same group (VI-group). In the mixed crystals, compositional disorder appears due to random distribution of constituent binary compounds. This distribution leads to fluctuations in the masses and force constants in the neighborhood. Vibrational characteristics of mixed compounds may be affected due to this compositional disorder and also layer-stacking faults and various type of defects. Broadening and existence of asymmetry of phonon modes in a Raman peak are two possible observed changing vibrational characteristics for mixed crystals.

The compositional dependencies of frequencies and line-widths of the phonons belonging to (TlGaS₂)_x–(TlGaSe₂)_{1–x} compounds were investigated taking into consideration the peaks observed in Fig. 1. As seen from the figure, Raman peaks shift to higher frequencies with increase of sulfur content. Figure 2 clearly shows the compositional dependencies of each Raman-active mode frequencies. In mixed crystals, two types of behavior of the phonon bands (one- and two-mode behavior) have been reported in the past. One-mode behavior describes the situation in which $q=0$ optical mode frequencies of the mixed crystals vary continuously with concentration from a frequency characteristic of that of one

end-member crystal to that of the other end-member crystal, i.e., in each composition for every allowed mode only one common mode is observed. In two-mode behavior, for each allowed optical mode two bands are observed in the vicinity of those of the pure compounds. Two-mode behavior of optical modes was revealed in the Brillouin zone center of mixed crystals above $\nu = 100 \text{ cm}^{-1}$. Furthermore, new bands appeared around 150 and 220 cm^{-1} for the compositions of $x=0.25, 0.5$ and 0.75 . It is noteworthy that the frequencies of these bands are almost independent of the compositions of the mixed crystals. Since these modes exist only for mixed crystals in which both of sulfur and selenium are presented, they are assigned to sulfur–selenium vibrations. Moreover, the studies on Raman spectroscopy characteristics of Mo_xW_(1–x)S₂ mixed crystal compositions indicated similar behavior in which low wavenumber modes are independent of disorder effect [24, 25].

Figure 3a, b represents the expanded two highest-frequency peaks observed in Raman spectra of (TlGaS₂)_x–(TlGaSe₂)_{1–x} crystals. In Fig. 3a, the convolutions of the complex contour of the Raman-active modes with Lorentzian peaks for two representatives ($x=0.75$ and 1.0) of the mixed crystals were shown. The dash-dotted lines represent the convoluted peaks. When the spectra were looked through and compared, a remarkable point related with phonon line shapes is observed. As seen from the spectra of mixed crystals, a tail in the ascending part of peaks appears. This feature is assigned to the fact that anharmonicity existing due to compositional disorder deforms peak shapes. The anharmonicity is mainly because of compositional disorder-induced anharmonicity.

It is generally difficult for mixed compounds to possess ideal, perfect periodic lattice. The increase of sulfur concentration in (TlGaS₂)_x–(TlGaSe₂)_{1–x} results in increase of disorder effect and correspondingly, TlGaSe₂ (TlGaS₂) region decreases (increases). The finite periodicity in mixed compound crystalline structure leads to relaxation of $q=0$ Raman selection rule and correspondingly there exist broadening and asymmetry in Raman line-shape. Detailed analyses were accomplished about the compositional dependence of two representatives of the Raman-active modes in (TlGaS₂)_x–(TlGaSe₂)_{1–x}, which exhibit a two-mode behavior: highest-frequency intralayer mode with frequency increasing from 361.3 cm^{-1} ($x=0.25$) to 388.0 cm^{-1} ($x=1.0$) and high-frequency mode with frequency varying between 314.1 and 323 cm^{-1} . These peaks show significant increases in frequency (26.7 cm^{-1} and 8.9 cm^{-1}) with substitution of the heavy selenium atoms by the lighter sulfur ones. Figure 4 indicates compositional dependencies of the line-widths belonging to these modes. It is well-known fact that increase in compositional disorder results in decrease of lifetime of phonons. Therefore, strongly interacting optical phonons decay into weakly interacting acoustic ones. As

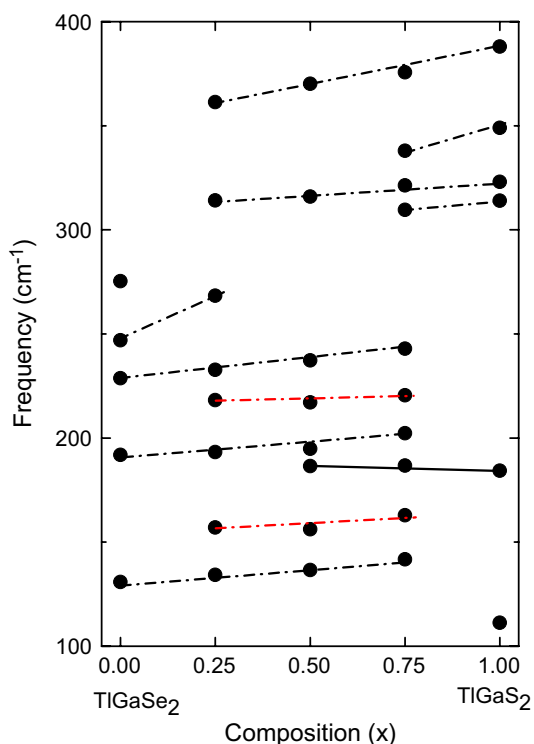
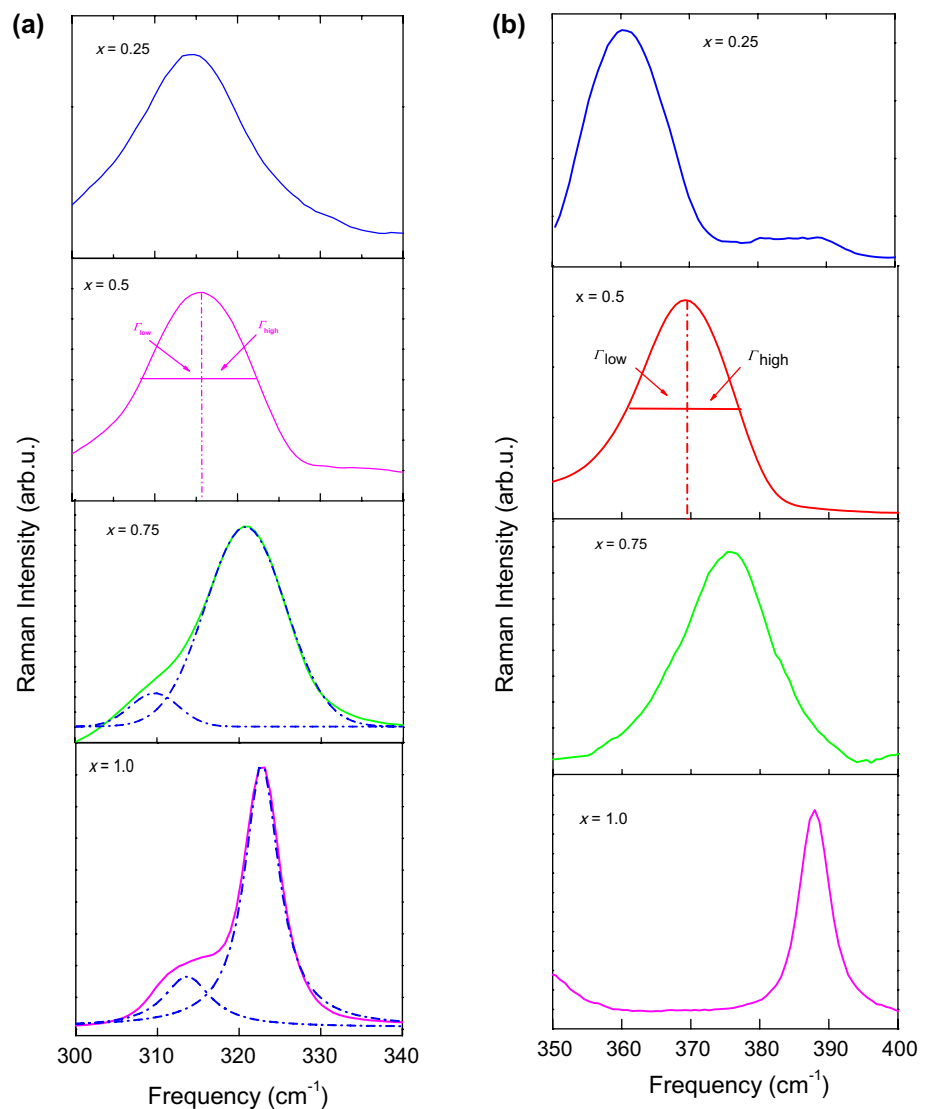


Fig. 2 Frequency dependencies of Raman-active modes on the composition of (TlGaS₂)_x–(TlGaSe₂)_{1–x} mixed crystals

Fig. 3 Extended low-frequency (300–340 cm^{-1}) (a) and high-frequency (350–400 cm^{-1}) (b) parts of Raman spectra of $(\text{TlGaS}_2)_x-(\text{TlGaSe}_2)_{1-x}$ mixed crystals. In Fig. 3a, the convolutions of the complex contour for two representatives ($x=0.75$ and 1.0) of the mixed crystals are shown. The dash-dotted lines represent the convoluted peaks



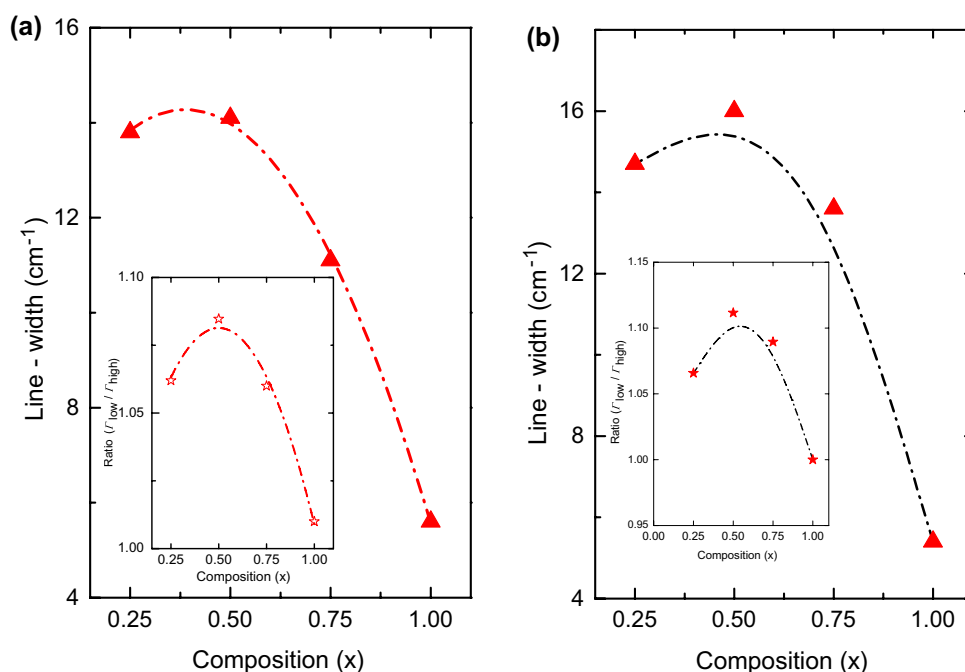
expected, composition vs. line-width plot related to these modes exhibits maximum line-width for composition of $x=0.5$ which have the maximum substitutional disorder among the $(\text{TlGaS}_2)_x-(\text{TlGaSe}_2)_{1-x}$ mixed crystals. Raman spectra of $\text{Mo}_x\text{W}_{(1-x)}\text{S}_2$ layered mixed crystals exhibited the similar Raman line-shape [25]. The maximum of the line-width was also reported for $x=0.5$ composition in the reference.

Symmetric phonon lines of ternary TlGaS_2 and TlGaSe_2 turned out to be asymmetric for $(\text{TlGaS}_2)_x-(\text{TlGaSe}_2)_{1-x}$ quaternary compounds (Figs. 1 and 3). The lower-frequency region half-width (Γ_{low}) became larger than high-frequency region one (Γ_{high}). The inset of Fig. 4 presents compositional dependency of the asymmetry ratios $\Gamma_{\text{low}}/\Gamma_{\text{high}}$ for two highest-frequency intralayer modes of $(\text{TlGaS}_2)_x-(\text{TlGaSe}_2)_{1-x}$ compounds, exhibiting the two-mode feature. The ratios ($\Gamma_{\text{low}}/\Gamma_{\text{high}}$) for these modes has their maximums for composition of $x=0.5$. This points out that the change

of Raman line-shape with composition is a result of mixed crystal disorder effect.

It is worth nothing here that these Raman line-shape change characteristics were also observed previously for various mixed crystals like $\text{TlInS}_{2x}\text{Se}_{2(1-x)}$ [26], $\text{GaAs}_{1-x}\text{P}_x$ and $\text{In}_x\text{Ga}_{1-x}\text{As}$ [27], $\text{ZnS}_{1-x}\text{Te}_x$ [28]. In these references, this behavior was explained under the light of one-dimensional linear chain model and following the spatial correlation model. Since the necessary parameters are not reported for TlGaS_2 and TlGaSe_2 , it is not possible to apply this model at the present time to explain broadening and asymmetric behavior of phonon lines in $(\text{TlGaS}_2)_x-(\text{TlGaSe}_2)_{1-x}$. Moreover, the line-widths of corresponding modes observed in spectrum of TlGaSe_2 were noticed as higher than those of TlGaS_2 (see Fig. 4). This point may be explained by considering atomic radii of covalently bonded selenium and sulfur elements. The mentioned radii are 0.116 and 0.102 nm for selenium and sulfur, respectively [29]. Due to a larger radius, higher

Fig. 4 Dependencies of line-widths for low-frequency (300–340 cm^{-1}) (a) and high-frequency (350–400 cm^{-1}) (b) modes of Raman spectra of $(\text{TlGaS}_2)_x-(\text{TlGaSe}_2)_{1-x}$ mixed crystals. The dash-dotted lines show guides for the eye. Insets: composition dependencies of the ratios $\Gamma_{\text{low}}/\Gamma_{\text{high}}$. The dash-dotted lines show guides for the eye



probability of defect formation is expected for selenium-containing crystals.

4 Conclusions

The detailed investigation of Raman spectra of $(\text{TlGaS}_2)_x-(\text{TlGaSe}_2)_{1-x}$ crystals was accomplished for five different compositions in the range of $0 \leq x \leq 1$. The Raman spectrum of TlGaS_2 exhibited six peaks at 111.3, 184.3, 314, 323, 349 and 388 cm^{-1} while that of TlGaSe_2 presented five peaks around 130.8, 191.9, 228.7, 247 and 275.3 cm^{-1} . Moreover, new bands appeared around 150 and 220 cm^{-1} for the compositions of $x=0.25, 0.5$ and 0.75 . It was observed that Raman peaks shift to higher frequencies and all observed optical modes broaden with increase of sulfur concentration in the mixed crystals. The compositional dependencies of line-widths and asymmetries of revealed phonon lines associated with crystal disorder were established in the present study. The maximum line-width and asymmetry parameters were found to possess maximum for $x=0.5$ composition as expected. It was observed that asymmetric broadening of phonon line-shapes for constituent binary compounds in $(\text{TlGaS}_2)_x-(\text{TlGaSe}_2)_{1-x}$ crystals is larger for high-frequency modes as compared with low-frequency ones.

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