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TEMPERATURE DEPENDENCE OF RAMAN-ACTIVE MODES OF $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ SINGLE CRYSTALS

The unpolarized Raman spectra of $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystals in the frequency interval 16–340 cm^{-1} are studied in the temperature interval $30 \leq T \leq 293$ K. The Raman spectra are analyzed by a multipeak simulation using Lorentzian contours. The temperature behavior of the vibrational band parameters (half-width, intensity, and frequency) is studied with the emphasis on the temperature range, where changes related to phase transformations are revealed.

Keywords: Raman scattering, layered crystal, phase transition.

1. Introduction

The physical properties of layered ferroelectrics are determined by their quasi-two-dimensionality and a strong structural anisotropy, which make them interesting objects for investigation [1–4]. One of the materials of this class is TlInS_2 , which is characterized by a complex sequence of phase transitions (PTs) in the temperature interval 190–216 K [1, 2] and poly-critical phenomena in the (p, T) -phase diagram in the pressure interval $580 \leq p \leq 660$ MPa [5–8]. In the row of $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ crystalline solid solutions, the crystal structure changes from C_{2h}^6 to D_{4h}^{18} symmetry at a Se content x near 0.7–0.75 [9–12]. It was shown [12–14] that the isovalent S \rightarrow Se anionic substitution results in a downward shift of the structural phase transition temperatures with a simultaneous shrinking of the temperature interval of the incommensurate phase existence. It was concluded that, in the (x, T) phase diagram of $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ crystals, a Lifshitz type point can exist at $x = 0.05$ [12, 13]. Several works were devoted to Raman spectroscopic studies of $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ solid solutions

($0 < x < 1$), where the compositional transformation of Raman spectra was investigated mostly at room temperature [15–19], as well as at lower temperatures [19]. With regard to the studies of vibrational spectra in a broad temperature range, including the phase transition range, such data were obtained for TlInS_2 crystals by several research teams [20–29]. A detailed analysis of the polarized Raman spectra of TlInS_2 was performed in a broad temperature range, including the temperature dependences of spectral positions and half-widths of low-frequency modes, and a conclusion was made on the existence of soft modes [24, 25]. Recently, several studies were published including the temperature-dependent analysis of the spectral positions and half-widths of other Raman modes in the TlInS_2 crystal spectra [26–29]. A detailed analysis of the spectral interval 120–400 cm^{-1} in the temperature interval 77–300 K is presented in Ref. [27], the spectral interval 35–150 cm^{-1} was analyzed in Ref. [28], polarized spectra in the 35–180 cm^{-1} interval at temperatures from 77 to 320 K are presented in Ref. [29]. With regard to infrared reflection spectroscopy of the $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ single crystal system, a detailed study of vibration band parameters (half-width, intensity, and frequency) down

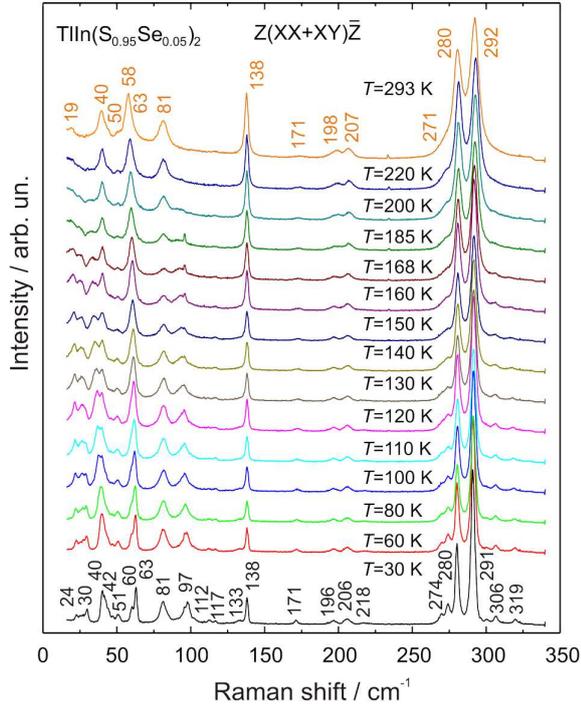


Fig. 1. Raman spectra of a $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystal in the $Z(\text{XX}+\text{XY})\bar{Z}$ configuration at different temperatures

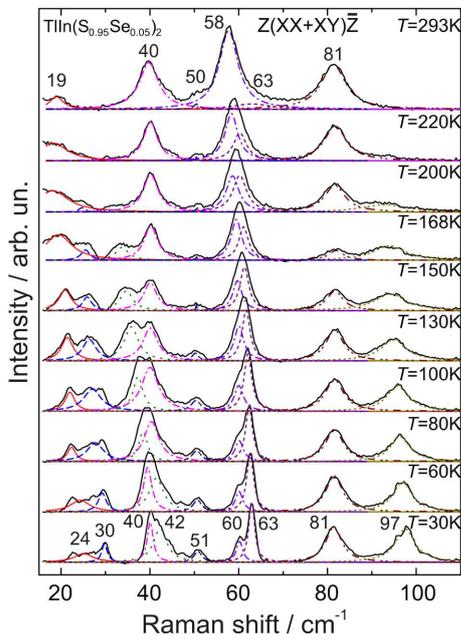


Fig. 2. Raman spectra of a $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystal in the $Z(\text{XX}+\text{XY})\bar{Z}$ configuration in the interval 16–110 cm^{-1} at 30–293 K and their multipeak Lorentzian simulation

to the liquid nitrogen temperature was carried out only for crystals with $x = 0.2$ [30]. This motivates the interest toward the investigation of sulfur-rich $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ mixed crystals by vibrational spectroscopy. Here, we present the results of Raman studies of $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystals in the temperature interval $30 \leq T \leq 293$ K.

2. Materials and Methods

$\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystals were grown by the Bridgman technique [16]. The crystal quality and chemical composition were checked by methods described in Ref. [16]. The results of X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy obtained for the samples under investigation agree well with the data for the C_{2h}^6 space group typical of TlInS_2 -type crystals at room temperature and atmospheric pressure [1, 2]. Raman measurements were performed using a Dilor XY 800 spectrometer equipped with a CCD camera. The instrumental resolution was in all cases better than 2 cm^{-1} . A Kr^+ laser operating at 647.1 nm was used for the excitation. Raman spectra were measured in the backscattering configuration from the (001) plane using the $Z(\text{XX}+\text{XY})\bar{Z}$ (unpolarized) geometry. The samples were placed in a cryostat coupled to a temperature control system that is capable of stabilizing the sample temperature with an accuracy of ± 0.01 K.

3. Results and Discussion

It is worth noting that the analysis of compositional dependences of frequencies, half-widths, and integrated intensities of Raman bands in $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ ($0 \leq x \leq 0.25$) single crystal spectra measured at 30 K in the $Z(\text{XX} + \text{XY})\bar{Z}$ configuration was performed in our earlier paper [19]. Below, we present the experimental data and analysis of the temperature behavior of frequencies, half-widths, and intensities of first-order Raman-active optical phonons of $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ crystals. This can be helpful for acquiring the additional information about the character of forces and bonds in the crystal lattice and their transformation under structural phase transitions in the $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ mixed crystal system.

The Raman spectra of $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystals were studied in the interval 16–350 cm^{-1} at temperatures $30 \leq T \leq 293$ K (Figs. 1 and 2). The number of Raman bands and their spectral positions

at $T = 30$ K and $T = 293$ K agree with the data available from the literature for TlInS_2 crystals [20–29] in view of the known features of a compositional transformation of the Raman spectra for $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ single crystals [19]. The experimental Raman spectra of $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystals were analyzed by multippeak simulation using Lorentzian contours, and the band parameters (frequencies, half-widths, and integrated intensities) were determined. An example of such simulation is shown in Fig. 2.

One should note that the temperature variation of the $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystal Raman spectra includes the typical temperature dependence of phonon band characteristics in crystals (a slight frequency decrease, increasing half-widths and integrated intensities with temperature), as well as a phase transition-related transformation of phonon spectra. The latter can be revealed in different frequency ranges as an essential frequency decrease, a considerable increase of half-widths, and a redistribution of intensities of several modes, as well as a possible drastic spectral transformation with temperature manifested as a change of the number of first-order Raman active optical phonon modes. As can be seen from Fig. 1, the transformation of the Raman spectra is observed in the low-frequency interval $16\text{--}100$ cm^{-1} and in higher-frequency intervals $190\text{--}220$ cm^{-1} and $270\text{--}320$ cm^{-1} .

In the low-frequency interval $16\text{--}50$ cm^{-1} , a complicated transformation of the spectra with temperature is observed (Figs. 1 and 2). The band centered at 24 cm^{-1} ($T = 30$ K) shifts down to 19 cm^{-1} ($T = 293$ K), while the band centered at 30 cm^{-1} ($T = 30$ K) vanishes with increasing temperature at 293 K. Note that a detailed analysis of the band half-widths and intensities in this lowest-frequency spectral range in the temperature interval $180\text{--}220$ K is encumbered by the Rayleigh wing, the intensity of which increases, while approaching this temperature interval. The transformation of the 40 cm^{-1} and 42 cm^{-1} bands is of complicated character. As can be seen from Figs. 1 and 2, at $T = 30$ K, two bands at 40 cm^{-1} and 42 cm^{-1} are registered. Their intensities increase with the temperature and are nearly equal at $T = 100$ K.

One should note the importance of a comparison of spectra measured at $T = 60$ K and $T = 80$ K. The comparison of the intensities shows that, apparently, the spectral position of the band at

40 cm^{-1} ($T = 30$ K) remains practically unchanged, while the other band centered at 42 cm^{-1} at 30 K decreases. With a further increase in the temperature, the intensity of the latter band decreases, and its half-width increases (Fig. 3). At $T = 220$ K, this band is no longer observed in the spectrum. Considering the other band (40 cm^{-1} at $T = 30$ K), its spectral position remains stable up to room temperature. Such “crossing” of the temperature dependences of Raman modes near $40\text{--}42$ cm^{-1} in the temperature interval $60\text{--}80$ K is a clear evidence of their different symmetry, similarly to the case of a PbTiO_3 single crystal [31]. With regard to the temperature behavior of TlInS_2 single crystals, there are two points of view concerning the Raman bands in the $38\text{--}50$ cm^{-1} interval [24, 25, 29]. According to Ref. [29], the higher-frequency band position (48.7 cm^{-1} at 77 K) does not vary with temperature and is no longer registered at 218 K, while the lower-frequency band position (38.8 cm^{-1} at 77 K) increases at a rate $\partial\nu/\partial T = 6.4 \times 10^{-3}$ cm^{-1}/K , and the intermediate band frequency (45.2 cm^{-1} at 77 K) decreases to 41.5 cm^{-1} . In earlier publications [24, 25], a somewhat different behavior of a transformation of the vibrational bands was reported. The authors of Ref. [25] claim that the behavior of the band at 42 cm^{-1} ($T = 12$ K) is characteristic of a soft mode. This conclusion was made from the temperature behavior of the band frequency and half-width. At least, its frequency is the most strongly temperature-dependent in comparison with other low-frequency modes. A detailed analysis of the temperature dependences of TlInS_2 crystal vibrational modes [24] revealed, in particular, two bands at 24 cm^{-1} and 42 cm^{-1} ($T = 22$ K) in the $Z(\text{YX})\text{Y}$ scattering configuration, which are claimed to possess a soft mode character, interacting with rigid modes [24]. One should note that, according to these authors, the modes at 39 cm^{-1} and 42 cm^{-1} ($T = 10$ K) interact at temperatures below $T = 100$ K [24]. Temperature changes can also be observed for other spectral intervals of the $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystal Raman spectra (Figs. 1 and 4). In particular, the band at 97 cm^{-1} vanishes at 200 K. The band at 218 cm^{-1} is no longer observed above 160 K, while the bands at 133 cm^{-1} , 306 cm^{-1} , and 319 cm^{-1} vanish above 168 K, which can be also related to their weak intensities. For other (not discussed above) translational and “intermolecular” modes of $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ sin-

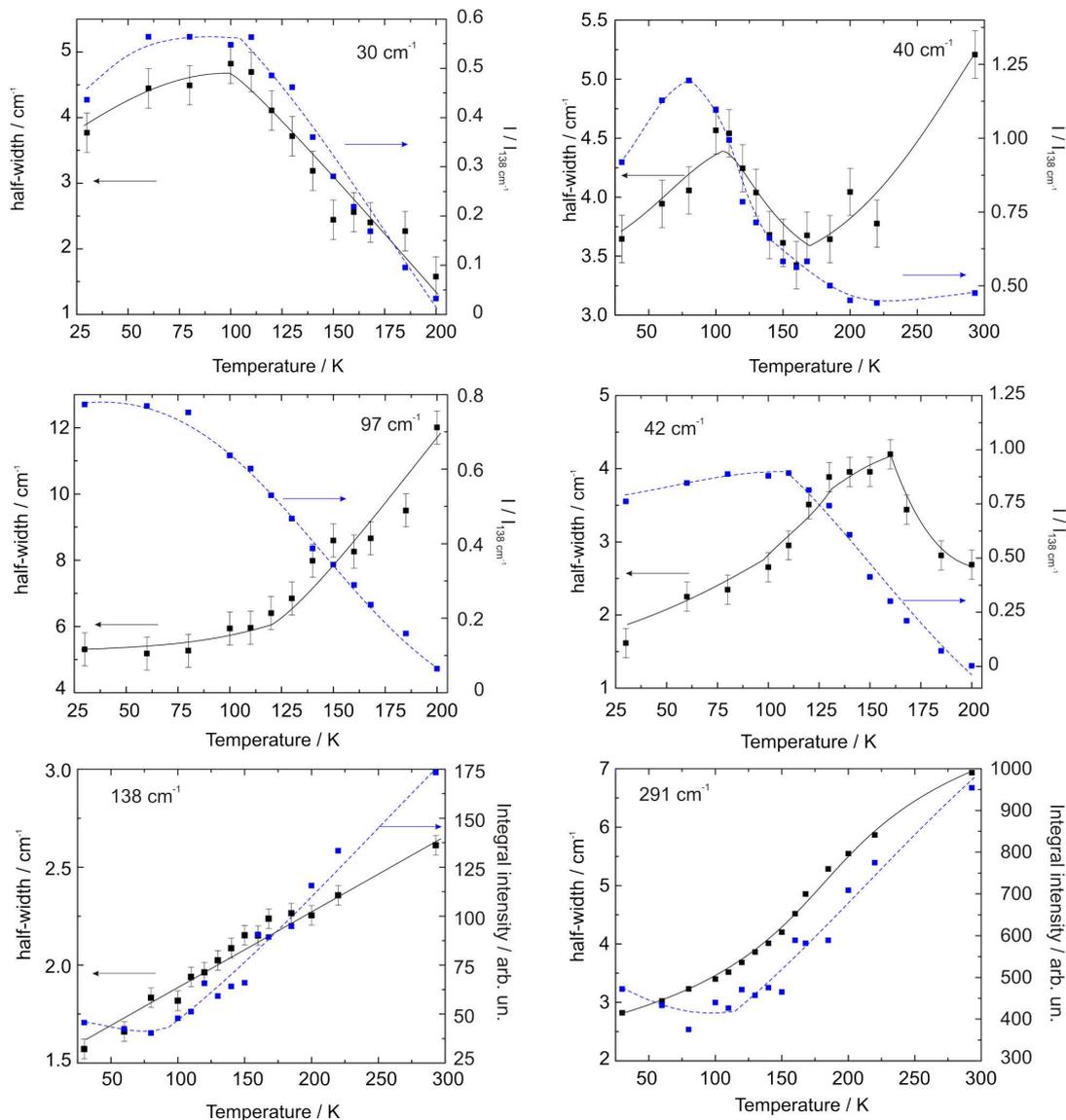


Fig. 3. Temperature dependences of half-widths, normalized intensities of Raman peaks centered at 30 cm^{-1} , 40 cm^{-1} , 42 cm^{-1} , and 97 cm^{-1} ($T = 30 \text{ K}$), and integral intensities at 138 cm^{-1} , 291 cm^{-1} ($T = 30 \text{ K}$) for a $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystal

gle crystals, the temperature-related broadening and integrated intensity increase (see, e.g., Fig. 3) and the slight frequency decrease (Figs. 1 and 4) are due to the anharmonicity of lattice vibrations and the thermal expansion, similarly to InS [32] and TlInS_2 [26] layered crystals. Unpolarized Raman studies of TlInS_2 crystals in the temperature range 10–300 K showed that, for all modes except for those at 280.9 and 292.3 cm^{-1} , the frequencies decrease with tem-

perature [26]. Note that our earlier spectroscopic ellipsometry studies and dielectric constant measurements by an ac bridge of $\text{TlIn}(\text{S}_{1-x}\text{Se}_x)_2$ single crystals [33] enabled us to conclude on the existence of phase transitions in a $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ crystal in the interval 170–220 K. As can be seen from Figs. 1 and 3 and the above analysis, it is this temperature interval where the transformations of the $\text{TlIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ Raman spectra occur. Thus, the temperature stud-

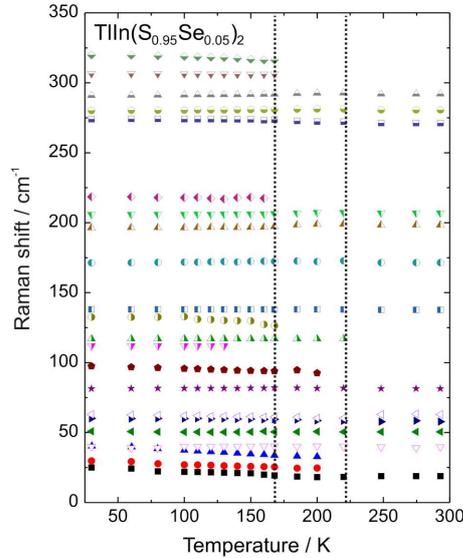


Fig. 4. Dependence of the Raman line frequencies for a $\text{TIIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystal on the temperature

ies of the $\text{TIIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ Raman line frequencies, half-widths, and integrated intensities show that the changes in the phase transition range are similar to those observed by different research groups for TIInS_2 crystals [24–26, 29]. Hence, in our opinion, $\text{TIIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystals can be characterized by a phase transition sequence similar to TIInS_2 rather than by a Lifshitz-type point in the (x, T) phase diagram of $\text{TIIn}(\text{S}_{1-x}\text{Se}_x)_2$ crystals at $x = 0.05$, as claimed in Ref. [12]. Note that, in order to build the (x, T) phase diagram and to judge on a possibility of the existence of the Lifshitz point at $x = 0.05$, one should perform all-round detailed studies of sulfur-rich $\text{TIIn}(\text{S}_{1-x}\text{Se}_x)_2$ crystals using various techniques.

4. Conclusions

The Raman spectra of $\text{TIIn}(\text{S}_{0.95}\text{Se}_{0.05})_2$ single crystals in the frequency range of $16\text{--}340\text{ cm}^{-1}$ are studied experimentally in the temperature interval $30\text{ K} \leq T \leq 293\text{ K}$ in the $Z(\text{XX}+\text{XY})\bar{Z}$ configuration. The Raman spectra are analyzed by a multipeak simulation using Lorentzian contours. The temperature behavior of the vibration band parameters (half-width, intensity, and frequency) was studied. A complicated transformation of the low-frequency spectral interval $16\text{--}50\text{ cm}^{-1}$ with temperature is observed. Two modes at 24 cm^{-1} and 42 cm^{-1} (at $T = 30\text{ K}$) exhibit the most pronounced temperature dependence

in the temperature range $30 \leq T \leq 200\text{ K}$ in comparison with other low-frequency bands. Note that a “crossing” behavior of the temperature dependences of two Raman modes near $40\text{--}42\text{ cm}^{-1}$ in the temperature interval $60\text{--}80\text{ K}$ is a clear evidence of the different symmetries of the relevant vibrations. At temperatures above 168 K , the number of modes in the spectra is reduced. This is related to the existence of phase transitions: the bands at 30 cm^{-1} , 42 cm^{-1} , and 97 cm^{-1} vanish at $T > 200\text{ K}$, while the bands at 132 cm^{-1} , 218 cm^{-1} , 306 cm^{-1} , and 319 cm^{-1} are no longer observed above 160 K , which may, however, be related to their low intensities.

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1. K.R. Allakhverdiev, T.G. Mamedov, B. Akmoglu, S.S. Elialtioglu. Phase transitions in ternary layered $A^3B^3C_2^6$ group ferroelectric semiconductors. *Tr. J. Phys.* **18**, 1 (1994).
2. A.M. Panich. Electronic properties and phase transitions in low-dimensional semiconductors (Topical Review). *J. Phys.: Condens. Matter* **28**, 293202/1 (2008).
3. I. Martynyuk-Lototska, I. Trach, O. Kokhan, R. Vlokh. Efficient acousto-optic crystal, TIInS_2 : Acoustic and elastic anisotropy. *Appl. Opt.* **56**, 3179 (2017).
4. A. Say, I. Martynyuk-Lototska, D. Adamenko, A. Pogodin, O. Kokhan, R. Vlokh. Thermal expansion anisotropy of β - TIInS_2 crystals in the course of phase transitions. *Phase Transitions* **91**, 1 (2017).
5. K.R. Allakhverdiev, T.G. Mamedov, G.I. Peresada, E.G. Ponatovski, Ya.N. Sharifov. Phase diagrams of layered semiconductors TIInS_2 , TlGaS_2 , and TlGaSe_2 under hydrostatic pressures up to 1.2 GPa . *Sov. Phys. Solid State* **27**, 568 (1985).
6. O.O. Gomonnai, P.P. Guranich, M.Y. Rigan, I.Y. Roman, A.G. Slivka. Effect of hydrostatic pressure on phase transitions in ferroelectric TIInS_2 . *High Press. Research.* **28**, 615 (2008).
7. O.O. Gomonnai, R.R. Rosul, P.P. Guranich, A.G. Slivka, I.Y. Roman, M.Y. Rigan. Optical properties of TIInS_2 layered crystal under pressure. *High Press. Research.* **32**, 39 (2012).
8. P.P. Guranich, R.R. Rosul, O.O. Gomonnai, A.G. Slivka, I.Y. Roman, A.V. Gomonnai. Ferroelasticity of TIInS_2 crystal. *Solid State Commun.* **184**, 21 (2014).
9. N.M. Gasanly, H. Ozkan, S.A. Culfaz. Composition variations of lattice parameters of $\text{TIIn}(\text{Se}_{1-x}\text{Te}_x)_2$,

- TlIn(S_{1-x}S_x)₂, and TlIn_{1-x}Ga_xSe₂ mixed crystals. *Cryst. Res. Technol.* **30**, 109 (1995).
10. A.U. Sheleg, V.G. Hurtavy, V.V. Shautsova, V.A. Aliev. X-ray diffraction study of the crystallographic characteristics of TlInS_xSe_{2-x} solid solutions. *Crystall. Rep.* **59**, 186 (2014).
 11. N.M. Gasanly. Composition dependence of lattice parameters and band gap energies of thallium based layered mixed crystals. *Indian J. Phys.* **89**, 657 (2015).
 12. M.Yu. Seyidov, R.A. Suleymanov, F. Salehli. Origin of structural instability in TlInS_{2(1-x)}Se_{2x} solid solutions. *Phys. Scripta* **84**, 015601 (2011).
 13. A.U. Sheleg, V.G. Hurtavy, V.V. Shautsova, V.A. Aliev. Dielectric properties and phase transitions in crystals of TlInS_xSe_{2-x} solid solutions. *Phys. Solid State* **54**, 622 (2012).
 14. R.R. Rosul, P.P. Guranich, O.O. Gomonnai, A.G. Slivka, M.Yu. Rigan, V.M. Rubish, O.G. Guranich, A.V. Gomonnai. Dielectric properties of TlIn(S_{1-x}Se_x)₂ polycrystals near phase transitions. *Semicond. Phys., Quant. Electr. and Optoelectr.* **15**, 35 (2012).
 15. N.A. Bakhyshov, N.M. Gasanly, B.M. Yavadov, V.I. Tagirov, Sh.M. Efendiev. Mixed one- and two-mode behaviour of optical phonons in TlGaS_{2x}Se_{2(1-x)} and TlInS_{2x}Se_{2(1-x)} layer solid solutions. *Phys. Status Solidi B* **91**, K1 (1979).
 16. A.V. Gomonnai, I. Petryshynets, Yu.M. Azhniuk, O.O. Gomonnai, I.Yu. Roman, I.I. Turok, A.M. Solomon, R.R. Rosul, D.R.T. Zahn. Growth and characterisation of sulphur-rich TlIn(S_{1-x}Se_x)₂ single crystals. *J. Cryst. Growth* **367**, 35 (2013).
 17. I. Guler, N.M. Gasanly. Raman scattering in TlInS_{2x}Se_{2(1-x)} layered mixed crystals (0.25 ≤ x ≤ 1): Compositional dependence of the mode frequencies and line widths. *Physica B: Condensed Matter* **406**, 3374 (2011).
 18. I. Guler, N.M. Gasanly. Compositional dependence of Raman-active mode frequencies and line widths in TlInS_{2x}Se_{2(1-x)} mixed crystals. *Appl. Surf. Science* **318**, 113 (2014).
 19. O.O. Gomonnai, M. Ludemann, A.V. Gomonnai, I.Yu. Roman, A.G. Slivka, D.R.T. Zahn. Low-temperature Raman studies of sulfur-rich TlIn(S_{1-x}Se_x)₂ single crystals. *Vibrational Spectroscopy* **97**, 114 (2018).
 20. N.M. Gasanly, B.N. Mavrin, K.E. Sterin, V.I. Tagirov, Z.D. Khalafov. Raman study of layer TlGaS₂, β-TlInS₂ and TlGaSe₂ single crystals. *Phys. Status Solidi B* **86**, K49 (1978).
 21. W. Henkel, H.D. Hochheimer, C. Carlone, A. Werner, V. Ves, H.V. Schnering. High-pressure Raman study of the ternary chalcogenides TlGaS₂, TlGaSe₂, TlInS₂, and TlInSe₂. *Phys. Rev. B* **26**, 3211 (1982).
 22. N.M. Gasanly, A.F. Goncharov, N.N. Melnik, A.S. Ragimov, V.I. Tagirov. Optical phonons and structure of TlGaS₂, TlGaSe₂, and TlInS₂ layer single crystals. *Phys. Status Solidi B* **116**, 427 (1983).
 23. M. Isik, N.M. Gasanly, F. Korkmaz. Multiphonon absorption processes in layered structured TlGaS₂, TlInS₂ and TlGaSe₂ single crystals. *Phys. B: Cond. Matter* **421**, 50 (2013).
 24. V.M. Burlakov, A.P. Ryabov, M.P. Yakheev, E.A. Vinogradov, N.N. Melnik, N.M. Gasanly. Raman spectroscopy of soft and rigid modes in ferroelectric TlInS₂. *Phys. Status Solidi B* **153**, 727 (1989).
 25. K.R. Allakhverdiev, S.S. Babaev, M.M. Tagiev, M.M. Shirinov. Low temperature IR and Raman scattering of TlInS₂ layered crystal. *Phys. Status Solidi B* **152**, 317 (1989).
 26. N.S. Yuksek, N.M. Gasanly, A. Aydinli. Anharmonic line shift of the optical Raman modes in TlInS₂ layered crystals. *J. Raman Spectrosc.* **35**, 55 (2004).
 27. R. Paucar, K. Harada, R. Matsumoto, K. Wakita, Y.G. Shim, O. Alekperov, N. Mamedov. Phase transition and Raman-active modes in TlInS₂. *Phys. Status Solidi C* **10**, 1132 (2013).
 28. R. Paucar, Y.G. Shim, K. Wakita, O. Alekperov, N. Mamedov. Temperature dependence of low-frequency optical phonons in TlInS₂. *Phys. Status Solidi C* **12**, 826 (2015).
 29. R. Paucar, Y.G. Shim, K.O. Mimura, K. Wakita, O. Alekperov, N. Mamedov. Temperature dependence of low-frequency polarized Raman scattering spectra in TlInS₂. *Phys. Status Solidi C* **14**, 1600214 (2017).
 30. Sh. Nurov, V.M. Burlakov, E.A. Vinogradov, N.M. Gasanly, B.M. Dzhavadov. Vibrational spectra of TlInS₂, TlIn_{0.95}Ga_{0.05}S₂, TlIn(S_{0.8}Se_{0.2})₂ crystals in the vicinity of phase transitions. *Phys. Status Solidi B* **137**, 21 (1986).
 31. S.M. Cho, H.M. Jang. Softening and mode crossing of the lowest-frequency A₁ (transverse-optical) phonon in single-crystal PbTiO₃. *Appl. Phys. Lett.* **76**, 314 (2000).
 32. N.M. Gasanly, H. Ozkan, A. Aydinli, I. Yilmaz. Temperature dependence of the Raman active phonon frequencies in indium sulfide. *Sol. State Commun.* **110**, 231 (1999).
 33. O.O. Gomonnai, O. Gordan, P.P. Guranich, A.G. Slivka, A.V. Gomonnai, D.R.T. Zahn. Temperature-dependent dielectric functions and interband critical points of sulfur-rich TlIn(S_{1-x}Se_x)₂ layered solid solution crystals. *Appl. Surf. Science* **424**, 383 (2017).

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ТЕМПЕРАТУРНА ЗАЛЕЖНІСТЬ
РАМАНІВСЬКИХ АКТИВНИХ МОД
КРИСТАЛІВ TlIn(S_{0,95}Se_{0,05})₂

Резюме

Досліджено неполяризовані спектри раманівського розсіювання світла монокристалів TlIn(S_{0,95}Se_{0,05})₂ в діапазоні частот 16–340 см⁻¹ в температурному інтервалі 30 К ≤ T ≤ 293 К. Проведено апроксимацію експериментальних спектрів суперпозицією лоренцових контурів і визначено температурні залежності напівширин, інтенсивностей та частот оптичних мод. Показано, що деякі особливості температурних залежностей пов'язані з існуванням фазових переходів у досліджуваних об'єктах.