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MATERIALS

OF INTERNATIONAL SCIENTIFIC AND TECHNICAL CONFERENCE

LASER TECHNOLOGIES. LASERS AND THEIR APPLICATION LTLA-2019

June 11–13, 2019
Truskavets, Ukraine

TEMPERATURE-DEPENDENT RAMAN STUDIES OF LAYERED $TlIn(S_{1-x}Se_x)_2$ ($0 \le x \le 0.25$) SINGLE CRYSTALS

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Raman spectroscopy is an efficient tool to study crystal lattice dynamics, in particular, with regard to phase transitions. $TlMX_2$-type crystals (M = Ga, In, X = Se, S) were the first low-dimensional semiconductors, for which a series of phase transitions with modulated structures was discovered [1]. At room temperature $TlInS_2$ and $TlInSe_2$ crystals are characterized by layered and chain-like structure, respectively [1]. For mixed $TlIn(S_{1-x}Se_x)_2$ crystals at $x \approx 0.7$–0.75 the crystal structure changes with x from C_{2h}^6 to D_{4h}^{18} [1]. S→Se isovalent substitution results in a decrease of the structural phase transition temperatures. In the (x, T) phase diagram of $TlIn(S_{1-x}Se_x)_2$ a Lifshitz type point at $x = 0.05$ was reported [2]. Raman scattering studies at 30 K in the $Z(XX+XY)\bar{Z}$ configuration were performed for $TlIn(S_{1-x}Se_x)_2$ ($0 \le x \le 0.25$) single crystals in our earlier paper [3]. The present study is devoted to the analysis of the temperature behaviour of frequencies, halfwidths, and intensities of first-order Raman-active optical phonons in sulfur-rich $TlIn(S_{1-x}Se_x)_2$ single crystals in the temperature interval 30 K $\le T \le$ 293 K.

$TlIn(S_{1-x}Se_x)_2$ ($0 \le x \le 0.25$) single crystals were grown by the Bridgman technique. Raman spectra were measured 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^+ (647.1 nm) laser was used for excitation. The measurements were performed in the frequency range 16–340 cm^{-1} in $Z(XX+XY)\bar{Z}$ scattering configuration in the temperature range of 30 $K \le T \le 293$ K. The samples were placed in a cryostat coupled to a temperature control system capable of setting the sample temperature with an accuracy of ± 0.01 K.

Raman spectra of $TlIn(S_{0.99}Se_{0.01})_2$, $TlIn(S_{0.90}Se_{0.10})_2$, $TlIn(S_{0.85}Se_{0.15})_2$, and $TlIn(S_{0.75}Se_{0.25})_2$ single crystals at different temperatures are shown in Fig. 1. The number of Raman bands for the mixed crystals and their spectral positions at T= 30 K and T= 293 K are in good agreement with the data available from literature for $TlInS_2$ with the account of the known compositional behaviour of

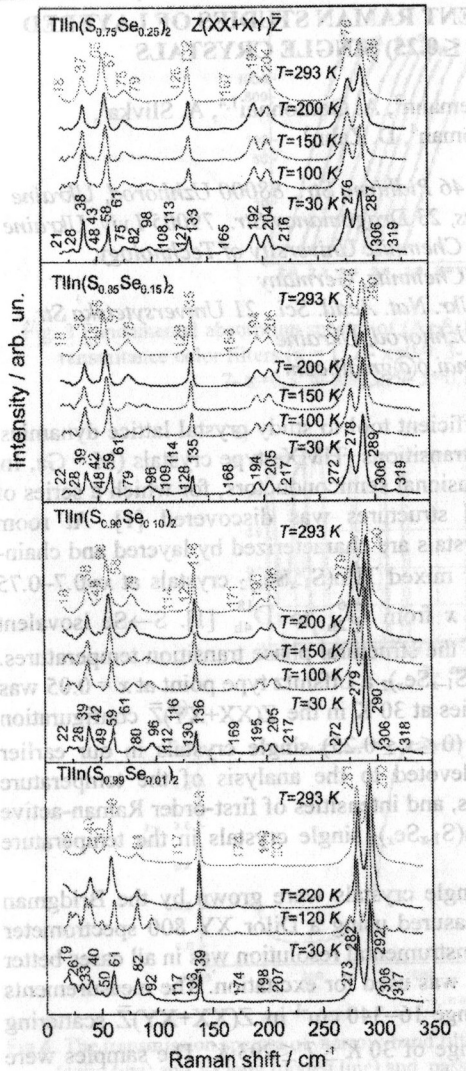

Fig.1. Raman spectra of a $TlIn(S_{1-x}Se_x)_2$ single crystals in the $Z(XX+XY)\bar{Z}$ configuration at different temperatures.

the $TlIn(S_{1-x}Se_x)_2$ phonon spectra [3, 4]. An example of multi-peak simulation of the experimental $TlIn(S_{1-x}Se_x)_2$ Raman spectra by Lorentzian contours is shown in Fig. 2.

Two groups of features can be distinguished in the temperature behaviour of the $TlIn(S_{1-x}Se_x)_2$ Raman spectra: (i) typical temperature dependence of phonon band characteristics in crystals (a slight frequency downshift, increasing halfwidths and integrated intensities with increasing T) and (ii) phase transition-related transformation of the phonon spectra.

In the low-frequency spectral range of 16–50 cm^{-1} the Raman features undergo a complicated transformation with temperature. Among them two modes (at 28 cm^{-1} and 43 cm^{-1} at 30 K for $TlIn(S_{0.75}Se_{0.25})_2$ and similar vibrations at corresponding frequencies for other compositions) reveal the most pronounced temperature dependence in the temperature range $30\ K \le T \le 220\ K$. For other translational and "intermolecular" modes of $TlIn(S_{1-x}Se_x)_2$ crystals, the temperature-related broadening and integrated intensity increase as well as slight frequency decrease are due to the anharmonicity of the lattice vibrations and consequent thermal expansion. A similar temperature behaviour is observed for the modes in the

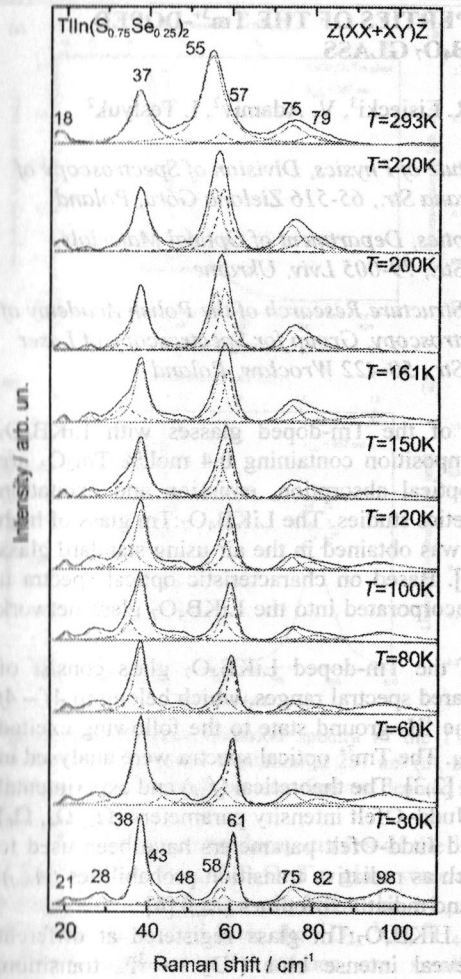

Fig. 2 Raman spectra of $TlIn(S_{0.75}Se_{0.25})_2$ single crystal in the $Z(XX+XY)\bar{Z}$ configuration in the range of 16–110 cm^{-1} at 30–293 K and their multi-peak Lorentzian simulation.

high-frequency groups at 190–220 cm^{-1} and 250–350 cm^{-1}.

At temperatures above 120 K (for x=0.25 crystal) the number of modes in the spectra decreases. Similar effects are revealed for other crystals of the family, for which the temperatures of the observed changes differ. This can be related to phase transitions which occur at relevant temperatures. For instance, for x=0.25 crystal the bands at 28 cm^{-1} and 43 cm^{-1} vanish at $T > 220$ K, modes 48 cm^{-1}, 98 cm^{-1}, 108 cm^{-1}, and 113 cm^{-1} vanish at $T = 180$ K, while the bands at 306 cm^{-1}, and 319 cm^{-1} are no longer observed above 120 K which may, however, be also related to their low intensities.

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