Optical absorption edge and Urbach tails for Tl\textsubscript{0.999}GaPr\textsubscript{0.001}Se\textsubscript{2}, Tl\textsubscript{0.995}GaPr\textsubscript{0.005}Se\textsubscript{2} and TlGaSe\textsubscript{2}

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Two-layer crystals of TlGaSe\textsubscript{2}, Tl\textsubscript{1-x}GaPr\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} and Tl\textsubscript{1-x}GaPr\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} single crystals were grown by the Stockbarger method. The absorption measurements were carried out in these samples in temperature range 10-320 K with a step of 10 K. The phonon energies calculated in TlGaSe\textsubscript{2}, Tl\textsubscript{1-x}GaPr\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} and Tl\textsubscript{1-x}GaPr\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} are 60.0±5, 55.0±5 and 130.0±5 meV respectively. The first defect levels (n=1) have been found as 2.259, 2.235, 2.200 and 2.149 eV for Tl\textsubscript{1-x}GaPr\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} and 2.254, 2.225, 2.189 and 2.149 eV for Tl\textsubscript{1-x}GaPr\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} at 10, 100, 200 and 300 K. At 300 K direct band gap of TlGaSe\textsubscript{2} is 2.156 eV, and indirect band gap is 2.075 eV. There are abrupt changes in the Urbach energy peaks for Tl\textsubscript{1-x}GaPr\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} at 100 and 200 K, and Tl\textsubscript{1-x}GaPr\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} at 200 and 260 K. There is an abrupt change in the σ\textsubscript{0} values for Tl\textsubscript{1-x}GaPr\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} and Tl\textsubscript{1-x}GaPr\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} in the temperature range 140-180 K and 220-260 K. These temperatures obtained from the changing of Urbach energy and σ\textsubscript{0} values may be phase transition temperatures.

1 Introduction

The ternary semiconducting chalcogenides with the formula ABX\textsubscript{2} (A, B represent metal atoms and X represents chalcogen atoms) have been studied intensively for years[1,3]. The ternary compounds TlGaS\textsubscript{2}, and TlGaSe\textsubscript{2}, crystallize in two layers and contain 64 atoms[4]. Layer crystals consist of separate layers with strong (covalent) bonding between atoms within the layers. The bonding between them is weak, predominantly of Van der Waals type. Such crystal structure causes the specific shape of phonon branches in layer crystals[5]. The p-type TlGaSe\textsubscript{2} crystals were prepared by the Bridgman-Stockbarger method[6]. Large crystals of TlGaSe\textsubscript{2} were grown by using the Bridgman method[8].

Optical absorption spectra of CuInSe\textsubscript{2} single crystals were measured for the samples with −0.150 ≤ x ≤ 0.053, where x represents a degree of non-stoichiometry in formula Cu\textsubscript{1−x}In\textsubscript{x}Se\textsubscript{2}. The Urbach tail was observed for all samples between 90 K and room temperature. The Urbach’s energy which represents an arbitrary intensity of exciton-phonon interaction, was almost constant for Cu-rich samples (x < 0), while it increasing In composition for the In-rich[9] ones (x > 0). The Steepness constant in Urbach rule for the absorption spectra[10] of EuSe has been determined for the first time to be 0.79.

The energy gap structure and the lattice dynamics of ternary layer A\textsuperscript{III}B\textsuperscript{III}C\textsuperscript{VI} semiconductor, particularly that of TlGaSe\textsubscript{2} known to exhibit a strong anisotropy of the electronic and vibrational spectra have been attracting considerable attention[6]. The present report gives results obtained while studying the photoelectrical properties of TlGaSe\textsubscript{2} crystals non-doped and doped with rare-earth impurities.

The long-wavelength tail of the optical absorption in TlGaSe\textsubscript{2} at α = 30-150 cm\textsuperscript{-1} is shown to obey the Urbach rule[11-12] in the temperature range 4.2-293 K. The anomalous behaviour of the parameters of this rule suggests the presence of two phase transitions in TlGaSe\textsubscript{2} at 246 K and 101 K besides the known phase transitions at 120 and 107 K. The presence of phase transitions in TlGaSe\textsubscript{2} at 246 K and 101 K is
also conformed by means of the heat capacity measurement\textsuperscript{14-15}. It has been shown from transition measurement that TlInS\textsubscript{2} has incommensurate phase at 220 K. It has been suggested that TiGaSe\textsubscript{2} transforms to a commensurate phase at 120 K.

The behaviour of several dopants such as Pr in TiGaSe\textsubscript{2} and other III-III-VI compounds is interesting because of their Pr effect on crystal anisotropy.

2 Experimental Details

TiGaSe\textsubscript{2}, Tl\textsubscript{0.995}GaPr\textsubscript{0.005}Se\textsubscript{2} and Tl\textsubscript{0.995}GaPr\textsubscript{0.005}Se\textsubscript{2}
single crystals were grown by the Stockbarger method. TiGaSe\textsubscript{2} compound has a melting point\textsuperscript{16} of 820±5 °C. Sealed quartz ampoule was annealed at 1050 °C for 10 hr in the outgassing furnace. The temperature of quartz ampoule was decreased to room temperature in 9 hr. The mixture of stoichiometric Se-Ti-Ga-Pr-Se was put into quartz ampoule which subsequently was sealed under a vacuum of 10\textsuperscript{-6} mbar. A quartz crucible (13 mm in diameter and about 250 mm in length) with carbon coating was used. The crucible was suspended in the middle of a vertical two zone furnace. The temperature of furnace was increased heated to 920 °C and waited for 34 hr. The temperature of low zone of furnace was lowered to 560 °C at a rate of 5 °C/hr. Both of the furnace zones cooled to 350 °C in 68 hr. The solidified ingot was cooled to room temperature in 52 hr. The prepared TiGaSe\textsubscript{2}, Tl\textsubscript{0.995}GaPr\textsubscript{0.005}Se\textsubscript{2} and Tl\textsubscript{0.995}GaPr\textsubscript{0.005}Se\textsubscript{2} single crystal ingots were 12 mm in diameter and about 60 mm in length. Ingots did not have cracks and voids on the surface. Absorption spectra were measured on freshly cleaved (001) surfaces. The TiGaSe\textsubscript{2}, Tl\textsubscript{0.995}GaPr\textsubscript{0.005}Se\textsubscript{2} and Tl\textsubscript{0.995}GaPr\textsubscript{0.005}Se\textsubscript{2} samples used in this study were prepared in 2.0x1.50, 1.8x2.1 and 1.75x1.95 mm\textsuperscript{2} in size respectively.

The absorption coefficients were obtained from the transmission data using the relationship\textsuperscript{13}

\[
T = (1-R)^2 \exp(-\alpha d) = (1-R)^2 \exp(-\alpha d)
\]

where \(R\) is the reflectivity, \(A\) the absorbance, \(\alpha\) the optical absorption coefficient (cm\textsuperscript{-1}) and \(d\) is the sample thickness. The optical absorption coefficients determined for all temperatures using the values of \(R\) at room temperature by assuming that the temperature changes from 10 to 320 K produces a small change in \(R\). The multiple reflection and the interference fringes the samples were put with a small angle with respect to the incident beam.

The fundamental absorption edge in most semiconductors follows the exponential law. Above the exponential tail, the absorption coefficient of a semiconductor has been observed to obey the equation:

\[
\alpha \nu W = B(\nu W - E_a)^n
\]

where \(\alpha \nu W\) is the absorption coefficient of an angular frequency of \(\nu = 2\pi \nu\), \(B\) is a constant and \(n\) is an index which can be assumed to have values of 1/2, 3/2, 2 and 3, depending on the nature of electronic transition responsible for the absorption. \(n=1/2\) for the direct allowed transition (high energy part of the spectra), \(n=3/2\) for forbidden direct transition, \(n=2\) for the indirect allowed transition (low energy part of the spectra) and \(n=3\) for forbidden indirect transition\textsuperscript{14}.

An exponentially increasing absorption edge in a number of insulators including ionic crystals, semiconductors, and organic crystals follows the empirical expression\textsuperscript{15}:

\[
\alpha = \alpha_\infty \exp \left[ \frac{\sigma(h\nu - E_a)}{kT} \right]
\]

where \(\alpha_\infty\) and \(E_a\) are the characteristic parameters of the material, \(\sigma\) is the steepness parameter, \(k\) the Boltzmann constant and \(T\) is the temperature.

The steepness parameter \(\sigma\) characterizes the steepness of the straight line near the absorption edge is expressed empirically as a function of temperature\textsuperscript{16}:

\[
\sigma = \sigma_\infty \left( \frac{2kT}{\nu W} \right) \tanh \left( \frac{\nu W}{2kT} \right)
\]

where \(\sigma_\infty\) is temperature-independent but material dependent parameter. Some researcher have stated that \(h\nu_a\) corresponded to the energy of phonons
associated with Urbach tail. The absorption coefficients obtained for a 1 s-exciton considering only the quadratic term of the exciton-phonon interaction operator are very similar to those expressed by Eq. (3), and the parameter \( \alpha/kT \) for the interaction between exciton and longitudinal-optical (LO) phonons coincides with Eq. (4) with a constant factor\(^{16} \).

The following empirical expression is often used to describe the temperature dependence of the energy gap\(^{17} \):

\[
E_g(T) = E_g(0) - \delta \frac{T^2}{T + \beta}
\]

where \( E_g(T) \) is the energy gap at the sample temperature, \( E_g(0) \) is the energy gap at 0 K and \( \delta \) and \( \beta \) are constants depending on the material. The constant \( \beta \) is approximately equal to the Debye temperature \( \theta_D \).

The optical measurements as a function of temperature were made in a closed-cycle He cryostat. For optical measurements the Perkin Elmer UV/VIS Lambda 2S Spectrometer was used which works in the wavelength range of 190-1100 nm. Wavelength resolution of the spectrometer is approximately better than \( \pm 0.3 \) nm. Therefore \( E_g \) can be calculated with an accuracy of approximately better than \( \pm 0.003 \) eV considering the wavelength accuracy of our spectrometer.

3 Results and Discussion

This paper presents the results of the absorption experiments and Urbach tails in TiGaSe₂, \( \text{Ti}_{0.999}\text{GaPr}_{0.001}\text{Se}_2 \) and \( \text{Ti}_{0.995}\text{GaPr}_{0.005}\text{Se}_2 \) crystals over the temperature range of 10 K to room temperature.

The absorption spectra were measured on freshly cleaved surfaces with thickness 140, 142 and 140 \( \mu \)m. The freshly cleaved crystals had a mirror-like surface and there was no need of mechanical treatment. \( \text{TiGaSe}_2 \), \( \text{Ti}_{0.999}\text{GaPr}_{0.001}\text{Se}_2 \) and \( \text{Ti}_{0.995}\text{GaPr}_{0.005}\text{Se}_2 \) samples were found to be of p-type that by using hot probe techniques. The absorption coefficient spectra have been obtained from the experimental absorbance values at different sample temperatures using Eq. 1.

The typical absorption spectra of TiGaSe₂, \( \text{Ti}_{0.999}\text{GaPr}_{0.001}\text{Se}_2 \) and \( \text{Ti}_{0.995}\text{GaPr}_{0.005}\text{Se}_2 \) samples versus temperatures at 10 K and 300 K are shown in Fig. 1. The direct absorption edges of the investigated compounds shifted considerably when the temperature was changed from 10 to 320 K. As seen in Fig. 1, the absorption spectra of \( \text{Ti}_{0.999}\text{GaPr}_{0.001}\text{Se}_2 \) and \( \text{Ti}_{0.995}\text{GaPr}_{0.005}\text{Se}_2 \) single crystals, defect and exciton levels appear at low temperatures (10-120 K). When added praseodymium to TiGaSe₂, these levels appear. These levels for \( \text{Ti}_{0.999}\text{GaPr}_{0.001}\text{Se}_2 \) and \( \text{Ti}_{0.995}\text{GaPr}_{0.005}\text{Se}_2 \) were found to be 2.166 ± 0.003 and 2.181 ± 0.003 eV at 10 K respectively. This result agrees with investigation by Abdullaeva et al.\(^{19} \) and Ibragimov and Mamedov\(^{20} \) who have shown the exciton levels at 2.160, 2.181 and 2.154 eV (10 K). On the other hand, the phonon energies calculated in TiGaSe₂, \( \text{Ti}_{0.999}\text{GaPr}_{0.001}\text{Se}_2 \) and \( \text{Ti}_{0.995}\text{GaPr}_{0.005}\text{Se}_2 \) are 60.0 ± 5, 55.0 ± 5 and 130 ± 5 meV, respectively. Pr doping in the TiGaSe₂ changes the absorption coefficient peak in the lower energy region. This effect causes a change in the phonon energy.

The energy gaps of the indirect and direct optical absorptions for TiGaSe₂ are obtained from the upper and lower parts of Fig. 1 using the dependencies \( (\alpha)^{1/2} \) versus \( \hbar \omega \) and \( (\alpha^2) \) versus \( \hbar \omega \) by extrapo-
lation of the straight lines down to $a^{1/2} = 0$ and $a^2 = 0$ (Eq. 2), respectively. The direct band gaps of TlGaSe$_2$ are 2.269, 2.244, 2.204 and 2.156 eV at 10, 100, 200 and 300 K, respectively. The indirect band gaps of TlGaSe$_2$ are 2.204, 2.175, 2.124 and 2.075 eV at 10, 100, 200 and 300 K respectively. These results are in agreement with our previous investigation of Dy doped and undoped$^{21}$ p-type TlGaSe$_2$. These results are in agreement with literature. The temperature dependence of the experimental and theoretical (obtained from Eq. 5) indirect and direct band gap have been shown in Fig. 2. This curve represents the values of $E_g(T)$ found by Eq. (5). In addition, the temperature dependence of the indirect and direct band gap for TlGaSe$_2$ is presented in Fig. 2.

The Urbach tail is observed for all samples between 10-320 K. Typical Urbach tails for various temperature are shown in Figs. 3(a), (b) and (c). It is found that all extrapolations of the Urbach tails converge at $(E_0, a_0) = 2.343$ eV, 4014.63 cm$^{-1}$; 2.234 eV, 1327.01 cm$^{-1}$ and 2.178 eV, 164.64 cm$^{-1}$ as shown in Figs. 3(a), (b) and (c) respectively. These results show that absorption spectra of all samples obey Urbach rule. All of the points intersect the same $(E_0, a_0)$ point at the temperature range 10-320 K (see Figs. 3(a,b,c)).
Fig. 4 shows the Urbach energy $kT/\sigma$ which corresponds to the inverse of a slope of the Urbach tail of the Pr-rich sample. $(x = 0.001$ and $x = 0.005)$ as a function of temperature. Urbach energy decreases with increasing $x$ ratio. Figs. 5 and 6 show steepness parameters ($\sigma$) and $\sigma_0$ values of the Pr-rich sample. $(x = 0.001$ and $x = 0.005)$ as a function of temperature, respectively. Steepness parameter ($\sigma$) and $\sigma_0$ values decrease with increasing $x$ ratio. There is abrupt change in the Urbach energy peak for $Tl_{0.999}GaPr_{0.001}Se_2$ at 100 and 200 K, and $Tl_{0.999}GaPr_{0.001}Se_2$ at 200 and 260 K. However, there are abrupt change in the $\sigma_0$ values for $Tl_{0.999}GaPr_{0.001}Se_2$ and $Tl_{0.999}GaPr_{0.001}Se_2$ in the temperature ranges 140-180 K and 220-260 K. The values obtained from the Urbach energy and $\sigma_0$ values change may be phase transition temperatures. The maximum values obtained from heat-capacity measurements are 340, 253, 117.2, 108.9, 106 and 101 K. The phase transition found in at 250 K was blurred, whereas in this study a sharp heat-capacity peak has been obtained for a TiGaSe$_2$ single crystal. The values obtained from the energy peak change may be phase transition temperature. The Urbach energy of TiGaSe$_2$ is increased by Pr (Fig. 4). The Urbach energy increases with increasing temperature.

Fig. 7(a and b) and Fig. 8(a and b) show some typical absorption spectra containing the sample temperatures 10, 100, 200 and 300 K. Fig. 7(b) and Fig. 8(b) obtained from the difference between absorption constants in TiGaSe$_2$, $Tl_{0.999}GaPr_{0.001}Se_2$ and TiGaSe$_2$-$Tl_{0.999}GaPr_{0.001}Se_2$ at the same temperature. Fig. 7(b) and Fig. 8(b), the first defect levels ($n = 1$) have been found as 2.259, 2.235, 2.200 and 2.149 eV for $Tl_{0.999}GaPr_{0.001}Se_2$ and 2.254, 2.225, 2.189 and
The optical absorption spectra versus photon energy (a) TlGaSe$_2$-Tl$_{0.999}$GaPr$_{0.001}$Se$_2$ samples, (b) Pr spectrum for $x=0.001$.

2.149 eV for Tl$_{0.999}$GaPr$_{0.001}$Se$_2$ at the 10, 100, 200 and 300 K. The second defect levels ($n=2$) have been found as 2.159 and 2.157 eV for Tl$_{0.999}$GaPr$_{0.001}$Se$_2$ at the 10, 100 K and 2.180, 2.157 and 2.178 eV for Tl$_{0.999}$GaPr$_{0.001}$Se$_2$ at the 10, 100 and 200 K. The defect levels which exist in TlGaSe$_2$:Pr but not exist in pure TlGaSe$_2$ can be observed with adding Pr in the range 10-320 K.

The temperature coefficients (β) were calculated for direct and indirect band gaps as 5.143x10$^{-4}$ eV/K and 5.40x10$^{-4}$ eV/K for TlGaSe$_2$ from a satisfactory fitting of the experimental curve using the above Eq.(5) and these results agree with results of Guseinov et al.$^{23}$ However, for TlGaSe$_2$ sample, β were calculated at 125 K and 105 K respectively. TlGaSe$_2$ and Tl$_{0.999}$GaPr$_{0.001}$Se$_2$.

The direct and indirect energy gaps for TlGaSe$_2$ decrease towards lower values as the increasing temperature and the temperature coefficient has a negative sign (Fig. 2). As seen from Fig. 1, the indirect band gap of TlGaSe$_2$ and Tl$_{0.999}$GaPr$_{0.001}$Se$_2$ is smaller than that of TlGaSe$_2$. That is, the region that was calculated the indirect band gap of TlGaSe$_2$ single crystal is sub-region of absorption spectrum. This sub-region may be called the region that defects (exciton defects) exist commonly as well. In these samples, praseodymium creates the defects in this region and ideal absorption spectrum will change in to the non-ideal. The reason of this change may be from the increase of Pr ratio.

The other important results are that 1- the defect levels and defect absorption peaks which results from Pr has been observed (Fig. 7(b) and 8(b). The defect levels which exist in TlGaSe$_2$ but not exist in pure TlGaSe$_2$ can be observed with adding Pr in the range 10-320 K. The rare earth (RE) elements cause the new appearance and changing of the absorption peak intensity, Tl$_{0.999}$GaPr$_{0.001}$Se$_2$ and Tl$_{0.999}$GaPr$_{0.001}$Se$_2$. As seen in Fig.1, the reason of this increase in the slopes is due to disappearing impurities existing in TlGaSe$_2$ crystal by adding Pr. This result shows that there are many impurities in TlGaSe$_2$ single crystal and these impurities in TlGaSe$_2$ are created by adding Pr. These are expected results because of the behaviour of the Pr atoms in the TlGaSe$_2$. 

Fig. 7 - The optical absorption spectra versus photon energy (a) TlGaSe$_2$-Tl$_{0.999}$GaPr$_{0.001}$Se$_2$ samples (b) Pr spectrum for $x=0.001$. 

Fig. 8 - The optical absorption spectra versus photon energy (a) TlGaSe$_2$-Tl$_{0.999}$GaPr$_{0.001}$Se$_2$ samples (b) Pr spectrum for $x=0.005$. 

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