Optical and electro-optical properties of Tl$_{1-x}$Cu$_x$GaSe$_2$ (0 ≤ X ≤ 0.02) crystals

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Abstract. The anisotropy of the refractive index and the electro-optical effect in Tl$_{1-x}$Cu$_x$GaSe$_2$ crystals were studied. Refractive indices were shown to rise as they approach their absorption band. The electro-optical effect in TlGaSe$_2$ crystals was studied. It was shown that the EO effect in the case where the light and external electric field are directed along the “C” axis within the studied electric fields (up to 5 kV/cm) is quadratic. The quadratic EO effect for TlGaSe$_2$ equals $1.3 \times 10^{-9}$ CGS units. It was found that when the electric field is directed perpendicular to the “C” axis and the light is directed along the “C” axis the EO effect is linear. The results of the EO measurements are consistent with the fact that the TlGaSe$_2$ compounds crystallize in a monoclinic lattice, with the space group Cc, but at the same time the TlGaSe$_2$ crystals have higher symmetry than Cc.

1. Introduction
In recent years the researchers have been paying great attention to the study of the zone structure, lattice dynamics and physical properties of semiconductor compounds of TlB$_3$C$_6$$_2$ class [1, 12-21]. This allows identifying the patterns that determine the dependence of properties on the composition, structure and nature of the chemical bond, which, in turn, makes it possible to conduct a targeted search for materials with a given combination of physical properties. Highly dispersed and thin film materials with characteristic dimensions of tens and units of nanometers are increasingly used in semiconductor opto- and quantum electronics. The TlGaSe$_2$ compound has a layered structure, therefore, it is highly likely that it has anisotropic optical properties.

In this regard, it is important to study the optical properties of crystals in a direction perpendicular to and parallel to the chipping plane. To do this, it is necessary direct the light to the mirror surface parallel and perpendicular to the chipping plane. Since it is impossible to obtain large area samples with surfaces perpendicular to the cleavage plane, the study of the anisotropy of optical properties was carried out subject to changing the angle of incidence of a flat-polarized light. The samples for
measurements having good optical qualities and uniform thickness were obtained by chipping from a single crystal ingot. By directing linearly polarized light to the chipping surface at various angles, the transparency coefficient was measured.

2. Materials and methods

The paper presents the results of experimental studies of the anisotropy of the refractive index and quadratic electro-optical effect (EO) in Tl1−xCu2xGaSe2 (0 = X ≤ 0.02) crystals earlier described in [1]. Single crystals were grown using a modified Bridgeman-Stockbarger method. The resulting crystals were p-type and had the specific resistivity of 10^8 – 10^10 Ohm·cm at 300 K. The band gap width – 2.18 eV, mobility – 65 cm^2/V·s. The measurement samples were obtained by chipping along the solder plane from Tl1−xCu2xGaSe2 massive single crystals and had dimensions of 5 x 8 x 2 mm^3. Since the samples after chipping had pronounced mirror surfaces, then the procedure described in [2, 3] was used to determine their refractive indices.

Absorption and reflection coefficients were determined by comparing transmission T1 and T2 of samples with different thicknesses d1 and d2 using a modernized spectral computational complex SDL-2 adapted for these purposes. For two samples of different thickness, the transmission will be as follows:

\[
\begin{align*}
T_1 &= \frac{(1 - R)^2 \exp(-\alpha d_1)}{1 - R^2 \exp(-2\alpha d_1)} \\
T_2 &= \frac{(1 - R)^2 \exp(-\alpha d_2)}{1 - R^2 \exp(-2\alpha d_2)}
\end{align*}
\]

(1)

The graphical solution of the system of these equations is described in [4]. The absorption and reflection coefficients were determined by solving a system of equations on a computer built into the facility.

Since the experiments used linearly polarized light, the following designations were adopted: \( R = R_\perp, \quad R_\parallel, \quad \alpha = \alpha_\perp, \quad \alpha_\parallel^* \) depending on the orientation of the electric vector \( \vec{E} \) of the incident light relative to the incidence plane. At \( \vec{V} \perp C_l, \quad (\vec{E} \parallel C_l) \) and \( \vec{V} \perp C_l, \quad (\vec{E} \perp C_l) \) the absorption coefficient will be respectively denoted as \( \alpha_\perp \) and \( \alpha_\parallel \).

To find \( \alpha_\perp \), it is necessary that the electric field vector is parallel to the cleavage plane, so it is obvious that \( \alpha_\perp = \alpha_\perp^* \). The condition \( \vec{E} \perp C_l \) must be met to determine \( \alpha_\parallel^* \). However, due to the above, \( \alpha_\parallel^* \) was determined in a roundabout way, i.e. by determining \( \alpha_\parallel^* \) and using the expression obtained in [5]:

\[
\alpha_\parallel^* = \alpha_\perp + (n_\perp \alpha_\perp - n_\parallel \alpha_\perp) \frac{\sin^2 i}{n_\parallel^2}
\]

(2)

where \( n_\perp \) and \( n_\parallel \) – refractive indices at \( \vec{E}_\perp \) and \( \vec{E}_\parallel \) of the incidence plane, respectively. Thus, it is possible to find \( \alpha_\parallel^* \) using this formula, if \( \alpha_\perp, \ n_\perp, \ n_\parallel \) and the incidence angle \( i \) are known.

When an electromagnetic wave falls on the interface of two media, the reflection coefficients for light polarized parallel and perpendicular to the incidence plane are described by the Fresnel formulas:

\[
R_\perp = \left[ \frac{\sin(i - i)}{\sin(i + i)} \right]^2
\]

\[
R_\parallel = \left[ \frac{\tan(i - i)}{\tan(i + i)} \right]^2
\]

(3)

(4)
where \( \theta \) – refractive angle.

Considering that the absorption indicator \( \chi \) is much less than the refractive index \( n \) (which is fair for this type of crystals at edge of the absorption band), let us write the snell’s law of refraction as

\[
n = \frac{\sin i}{\sin t}
\]  

(5)

Using formula (5) instead of the ratios (3) and (4), we get

\[
R_\perp = \left[ \frac{\cos i - \sqrt{n^2 - \sin^2 i}}{\cos i + \sqrt{n^2 + \sin^2 i}} \right]^2 = \left( \frac{\text{ctg} i - n \sin i}{\text{ctg} i + n \sin i} \right)^2
\]

(6)

\[
R_{II} = \left[ \frac{\cos i - \sqrt{n_{II}^2 - \sin^2 i}}{\cos i + \sqrt{n_{II}^2 - \sin^2 i}} \right]^2 = \left( \frac{\text{ctg} i - n_{II} \sin i}{\text{ctg} i + n_{II} \sin i} \right)^2
\]

(7)

where \( a = \sqrt{\sin^2 i - n_\perp^2} \), \( \sin \theta = \sqrt{\sin^2 i - n_{II}^2} \).

In this work \( n_\perp \) and \( n_{II} \) were calculated by solving equations (6) and (7) on a computer built into the facility. The error in determining the refractive index did not exceed 3%.

In the transparency area, the refractive index was determined by transmission. To determine \( n_{II} \), the polarizer and the analyzer were oriented parallel to each other, and the polarization plane was 45° with the beam incidence plane [1].

For the case of very thin samples \( n_{II} \) and \( n_\perp \) can be determined from the interference patterns obtained when the samples are illuminated with polarized light (\( n_{II} \) is found at \( \vec{E} \) parallel to the incidence plane, \( n_\perp \) at \( \vec{E} \) perpendicular to the incidence plane).

It is known that TIGaSe\(_2\) compounds crystallize in a monoclinic lattice, but have features \( a = b \) (for a monoclinic crystal system \( a \neq b \)) and \( \beta \) – slightly differs from 900. Therefore, when studying optical constants, the structure of TIGaSe\(_2\) crystals was considered pseudotetragonal. Optical constants were determined in two directions: in the light propagating in a direction perpendicular to the plane (i.e. \( \vec{E} \parallel C_{II} \)) parallel to the cleavage plane (i.e. \( \vec{E} \perp C_{II} \)).

The analytical expression of the dependence of the absorption coefficient on the photon energy at the edge of its own absorption band does not depend on the incidence angle of light, however the ratio \( \alpha_{II} / \alpha_\perp = 3 \div 5 \).

Figure 1 a, b show the dispersion refractive index curves \( n_\perp \) (\( \vec{E} \perp C_{II} \), \( \vec{V} \perp C_{II} \)) and \( n_{II} \) (\( \vec{E} \parallel C_{II} \), \( \vec{V} \parallel C_{II} \)), where \( n_\perp \) – refractive index of the beam propagating along the “"C axis. As follows from Figure 1 in the wavelength range of 0.6÷0.66 \( \mu m \) \( n_\perp < n_{II} \). Figure 1 also shows that the refractive index increases when approaching its own absorption band (\( E'_g = 2.03 \text{ eV} \)). It is known that the refractive index is associated with the wavelength of the incident light through the Zelmeyer’s ratio:

\[
n^2 - 1 = \sum f_i / \alpha_{oL}^2 - \omega^2
\]

(8)

where \( f_i \) – oscillator force; \( \alpha_{oL} \) – natural oscillation frequency of the oscillator; \( \omega \) – incident light frequency.

A rather good approximation preserving the physical meaning of the oscillator parameters (8) is the one-term Zelmeyer’s ratio:
where $\lambda_0$ – average oscillator position; $S_0$ – average oscillator force.

In general, $S_0$ and $\lambda_0$ differ from the value for any oscillator defined in equation (9). Using the dependence $(n^2 - 1)^{-1}$ on $\lambda^2$, it is also possible to define $S_0$ and $\lambda_0$ for a specific direction of light propagation. In this case, two pairs of parameters $S_{0\perp}, \lambda_{0\perp}, S_{0\parallel}, \lambda_{0\parallel}$ are defined. They refer to refractive indices in directions perpendicular ($n_\perp$) and parallel ($n_\parallel$) to the “C” axis of the crystal. The values of parameters $S_{0\perp}, \lambda_{0\perp}$ and $S_{0\parallel}, \lambda_{0\parallel}$ defined from Fig. 1 a, b are given in Table 1.

**Table 1.** Values of parameters $S_{0\perp}, \lambda_{0\perp}, S_{0\parallel}, \lambda_{0\parallel}$ defined from Fig. 1

| Material                  | $S_{0\perp} \cdot 10^8$, cm$^{-2}$ | $\lambda_{0\perp} \cdot 10^5$, cm$^{-3}$ | $S_{0\parallel} \cdot 10^8$, cm$^{-2}$ | $\lambda_{0\parallel} \cdot 10^5$, cm$^{-3}$ |
|---------------------------|-------------------------------------|------------------------------------------|----------------------------------------|------------------------------------------|
| TlGaSe$_2$                | 8.18                                | 0.711                                    | 6.00                                   | 0.713                                    |
| Tl$_{0.99}$Cu$_{0.01}$GaSe$_2$ | 9.00                                | 0.711                                    | 6.92                                   | 0.714                                    |
| Tl$_{0.98}$Cu$_{0.02}$GaSe$_2$ | 9.62                                | 0.710                                    | 7.03                                   | 0.715                                    |

The electrooptic (EO) properties of Tl$_{1-x}$Cu$_x$GaSe$_2$ ($0 \leq X \leq 0.02$) crystals were studied at room temperature using the optical procedure [2, 6, 7]. Some changes and additions were introduced into the basic flow chart of the SDL-2 facility during the transmission measurement, as shown in Fig. 2.

Let us briefly consider the polarization-optical technique. If the light passes through the polarizer, the crystal plate and the analyzer (Fig. 2), then the relative value of the intensity of the transmitted light according to [8] is as follows:

$$I = \frac{J_0}{J} = \cos^2(\alpha - \beta) \cdot \sin 2\alpha \cdot \sin^2 \beta \cdot \sin^2 \frac{\Gamma(I)}{2}$$

where $J_0$ – intensity of light incident on the crystal; $\alpha$ – angle between the direction of oscillations in the polarizer and the main optical axis of the ellipse of the indicator section perpendicular to the direction of light propagation; $\beta$ – angle between the direction of oscillations in the analyzer and the same axis of the ellipse; $\Gamma$ – phase difference between waves in the studied crystal plate. Since the phase difference
\[ \Gamma(I) = \frac{2\pi(n_i - n_j)}{\lambda} d = \frac{2\pi d}{\lambda} \Delta n \]  

(10)

where \( d \) – length of the optical path of light in a sample; \( \lambda \) – wavelength; \( \Delta n \) – change of birefringent effect.

It is easy to see that only birefringence \( \Delta n \) can be measured by the polarization-optical method and it does not allow determining the EO sign of \( r_{ijkl} \) coefficients.

The polarization-optical method can measure only absolute values \( r_{ijkl} \) and \( R_{ijkl} \) under specific conditions of the experiment. In the study of induced birefringence in Tl\(_{1-x}\)Cu\(_x\)GaSe\(_2\) crystals, the light and external electric field \( E \) were directed perpendicular to the layers. A low-frequency variable field (~ up to 10\(^4\) Hz) was used during the studies. The phase difference generated by the external electric field has the form (10).

3. Results and discussion

The relationship of induced birefringence in Tl\(_{1-x}\)Cu\(_x\)GaSe\(_2\) (0 \( \leq X \leq 0.02 \)) crystals remains quadratic at least within the studied electric fields (\( \bar{E} \sim 5 \text{ kV/cm} \)), as clearly seen in Figure 3 (curves 1, 2, 3). Using the dependence \( \Delta n \) on electric field strength at the above specified geometry of the experiment, the value \( n_{\lambda}^3 n_{\lambda 3} - n_{i j}^3 r_{\lambda} \) was calculated, where \( r_{ijkl} \) – electro-optical coefficients other than zero for the given geometry of the experiment. It turned out to be equal to \( 2 \times 10^{-9} \) CGS units.

Then we studied the dependence \( \Delta n \) on \( \lambda \). The measurements showed that with the decrease in the wavelength of the incident light and when approaching the absorption edge, \( \Delta n \) grows. In solid solutions with the growth of “X”, this dependence has a steeper (sharp change) character (Figure 3, curves 4, 5, 6).

When measuring induced birefringence it turned out that \( \Delta n \) in constant fields and in variable fields differ from each other and this difference increases with approximation to the edge of the optical absorption (this seems to be due to uneven distribution of the electric field over the crystal in case of a constant field). The presence of a photoeffect in these crystals at \( \lambda \approx 0.63 \mu\text{m} \) indicates the possibility of accumulation of volumetric charges at the boundary of the light beam.

Electron-hole pairs arising under the influence of light can create large volumetric charges on the periphery of the beam, reducing the internal field in crystals [9].

\[ I \]

\[ J \]

Figure 2. Addition to the flow chart of the SDL-2 unit to measure electrooptic properties of crystals.

1 – radiation source; 2 – modulator; 3 – polarization converter; 4 – cryostat with a sample; 5 – birefringent compensator; 6 – analyzer; 7 – FEU-100 or FEU-39; 8 – high voltage unit; 9 – photodiode; \( J_1, J_2 \) – condensers.
It should be noted that TlGaSe$_2$ crystals have a point symmetry group $Cc$ according to data [10] and $P2_1/m$ according to [11]. They have a “pseudotetragonal” monoclinic structure.

Monoclinic syngony has a linear electro-optical effect. For this class of connections (structures of TlGaS$_2$ type), $a = b$ and $\beta$ slightly differs from 90°. Therefore, it can be assumed that in a certain crystallographic direction (for example, in the direction of the “C” axis) it is more likely possible to observe the quadratic effect.

4. Conclusion

The anisotropy of the refractive index is determined at the edge of its absorption band. It was shown that for TlGaSe$_2$ crystals $n_o > n_1$. It was shown that the EO effect in the case where the light and the external electric field are directed along the “C” axis within the studied electric fields (up to 5 kV/cm) is quadratic, and when the electric field is directed perpendicular to the “C” axis and the light is directed along the “C” axis, the EO effect is linear.

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