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Frequency and temperature dependences of the physical properties of (1–*x*)$TlGaSe_2$·*x*Dy solid solutions

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Crystals with composition (1 – x)$TlGaSe_2$•xDy (x = 0, 0.01, and 0.03) were synthesized. In the crystals obtained, the dielectric properties in alternating electric fields with a frequency of f = 20–10^6 Hz were studied. The relaxation nature of the dielectric constant, the nature of the dielectric loss, and the charge transfer hopping mechanism in the samples are established. It is shown that in (1 – x)$TlGaSe_2$•xDy conductivity at alternating current, the density of localized states near the Fermi level, the average distance and time of carrier jumps increase with increasing x. The dependence of the band gap of (1 – x)$TlGaSe_2$•xDy on temperature was studied.

Keywords: *solid solutions, dielectric constant, hopping conductivity, frequency dispersion, dielectric loss, temperature coefficient of the width of forbidden gap.*

1. Introduction

$TlGaSe_2$ single crystals with a layered structure are characterized by strong anisotropy of physical properties and are promising for use as active elements in various semiconductor devices. Thus, in [1, 2], temperature dependences of the degree of anisotropy of the conductivity of isostructural $TlGaSe_2$, $TlGaS_2$ and $TlInS_2$ single crystals were studied, and it was found that $TlGaSe_2$ single crystals have the greatest degree of anisotropy. $TlGaSe_2$ single crystals are also of interest in connection with high photosensitivity, memory effect [3], and the fact that a sequence of phase transitions is observed in them [4, 5]. In [5], polytypic modifications of $TlGaSe_2$ crystals were detected by the X-ray diffraction method, and in [6] the results of low-temperature X-ray studies of $TlGaSe_2$ were reported. The dispersion of the complex dielectric constant and conductivity of $TlGaSe_2$ single crystals in the radio frequency range [7] was also studied. Different compositions of $TlGaSe_2$-based solid solutions were synthesized and their physical properties were studied [8–13]. $TlGaSe_2$ crystals containing rare earth elements are poorly studied. In materials containing Ln^{3+} various phase transformations occur. There are exchange interactions of Ln^{3+} ions and metals, whose valence electrons with the highest energy occupy the p-orbital. For example, Ln^{3+} selenides are characterized by interaction and hybridization between localized 4f and wandering 5d electrons [14]. Therefore, as in the case of thulium [13], partial cationic substitution with dysprosium (Dy) can affect the physical properties of $TlGaSe_2$ and impart new properties to (1 – x) $TlGaSe_2$ · xDy.

The purpose of this work is to study the effect of dysprosium concentration on the dielectric characteristics of (1– *x*)$TlGaSe_2$ · *x*Dy crystals, the establishment of a charge transfer mechanism in alternating electric fields of the radio frequency range and the determination of the temperature dependence of the band gap in these crystals.

2. Experiment

The following components were used as the starting components: Tl (Tl 00), Ga (Ga 5N), Se (pure-grade 15-2), Dy (99.99%). Samples (1– x) $TlGaSe_2$ · xDy (x = 0, 0.01, 0.03) were synthesized from elements taken in stoichiometric ratios by directly fusing them into quartz ampoules evacuated to 10^{-3} Pa for 5–7 h at 1000 ± 5 K. Crystals of good enough quality were obtained from the synthesized (1 – x) $TlGaSe_2$·xDy samples by the Bridgman method, similarly to that described in [13]. X-ray phase analysis of samples (1– x) $TlGaSe_2$·xDy was carried out on a D8-ADVANCE diffractometer in the range 0.5 ° <2θ <100 ° (CuK_α radiation, λ = 1.5406 Å) at 40 kV and 40 mA.

The dielectric coefficients of the samples (1 – x) $TlGaSe_2$ · xDy were measured on a 192Ø Precision LCR Meter (IET LABS. INC. USA). The frequency range of the alternating electric field was 2Ø-1Ø^6 Hz. The electric field applied to the samples was 1 V, which corresponded to the ohmic region of the current-voltage characteristics of the studied samples.

Samples from (1 – x) $TlGaSe_2$·xDy for electrical measurements were made in the form of flat capacitors. Silver paste was used as electrodes. The dielectric properties were measured in the direction perpendicular to the layers of (1 – x) $TlGaSe_2$·xDy crystals. The thickness of the studied samples obtained from (1 – x) $TlGaSe_2$·xDy ranged from 8Ø to 22Ø μm. All dielectric measurements were carried out at 298 K. The measurements of the capacity of the samples were carried out with an accuracy of ± Ø.Ø1 pF, and the error in measuring the quality factor (Q = 1 / tgδ) was Ø.ØØ1%.

3. Results and Discussion

According to DTA data, the melting point of $TlGaSe_2$ is 1143 K. On the diffractograms of samples of (1 – x)$TlGaSe_2$·xDy (x = Ø, Ø.Ø1, Ø.Ø3), all available X-ray reflections corresponded to the $TlGaSe_2$ phase and up to x = Ø.Ø3 there were no reflexes of other phases. (1– x) $TlGaSe_2$·xDy (x = Ø, Ø.Ø1, Ø.Ø3), as well as $TlGaSe_2$, correspond to a monoclinic syngony with space group C_6^{2h} ($C2/c$) at 298 K. The unit cell parameters of samples based on $TlGaSe_2$ (a = 15.623 (Ø.ØØØ2), b = 1Ø.773 (Ø.ØØØ2), c = 1Ø.744 (Ø.ØØØ2) Å) are consistent with the data for $TlGaSe_2$ [6, 13].

Here are the results of a study of the dielectric properties and electrical conductivities of the obtained (1 – x)$TlGaSe_2$·xDy solid solutions measured at alternating current.

Figure 1 shows the frequency dependences of the real component of the complex dielectric permittivity (ε') of samples of (1 – x)$TlGaSe_2$·xDy. It can be seen that in the entire frequency range studied, ε' for $TlGaSe_2$ and (1 – x)$TlGaSe_2$·xDy (x = Ø.Ø1) underwent a significant decrease with increasing frequency. In crystals (1 – x)$TlGaSe_2$·xDy (x = Ø.Ø3) ε' increased in the frequency range 2Ø–5ØØ Hz, and then its steep decline was observed up to 1 MHz. An increase in the content of dysprosium in crystals led to a marked increase in ε'. The frequency dependences of the imaginary part of the complex dielectric constant ε'' of (1 – x) $TlGaSe_2$·xDy solid solutions also indicate relaxation dispersion (Fig. 2).

Figure 3 shows the frequency dependences of the dielectric loss tangent (tgδ) in $TlGaSe_2$ (curve 1) and solid solution (1 – x)$TlGaSe_2$·xDy (curve 2) with the highest dysprosium content (x = Ø.Ø3). These

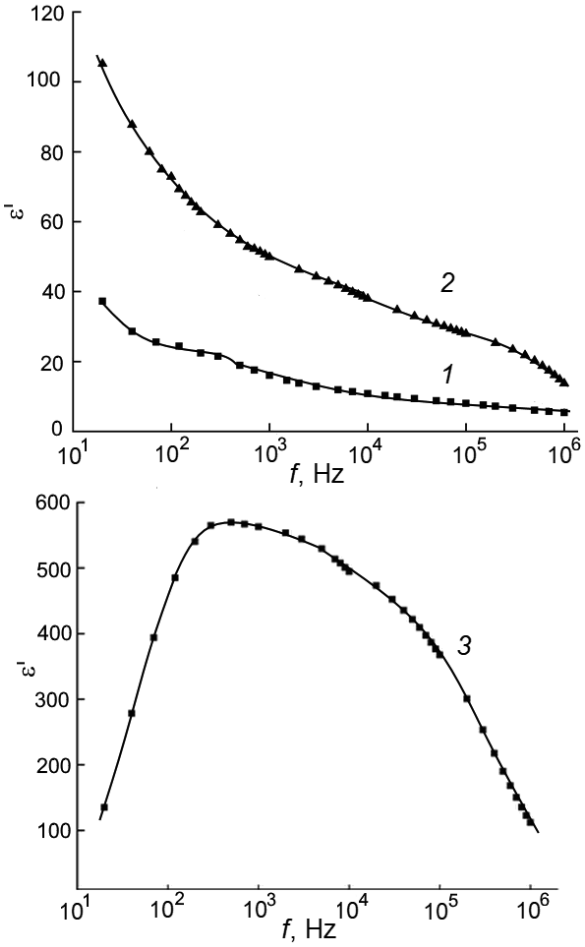

Fig. 1. Frequency dependences of the real component of the complex dielectric permittivity of crystals (1–x)$TlGaSe_2$ · xDy: x = Ø (*1*); Ø.Ø1 (*2*) and Ø.Ø3 (*3*). T = 298 K.

dependences were characterized by a hyperbolic recession, indicating the loss of through conduction. At high frequencies, there was a tendency for tgδ to increase, which indicates the onset of relaxation losses in the crystals under study. The introduction of dysprosium into $TlGaSe_2$ led to a significant increase in tgδ.

We also studied the frequency-dependent acconductivity (σ_{ac}) of (1 – x)$TlGaSe_2$·xDy solid solutions (Fig. 4). The value of σ_{ac} for solid solutions (1 – x)$TlGaSe_2$·xDy was higher than for $TlGaSe_2$. On the frequency dependence of $\sigma_{ac}(f)$ in $TlGaSe_2$, two segments were observed. First, the dependence $\sigma_{ac} \sim f^{Ø.6}$ was observed, then (at $f \geq 1Ø^4$ Hz) it passed to the law $\sigma_{ac} \sim f^{Ø.8}$. In (1 – x)$TlGaSe_2$·xDy, three regions were observed in the $\sigma_{ac}(f)$ dependence. First,

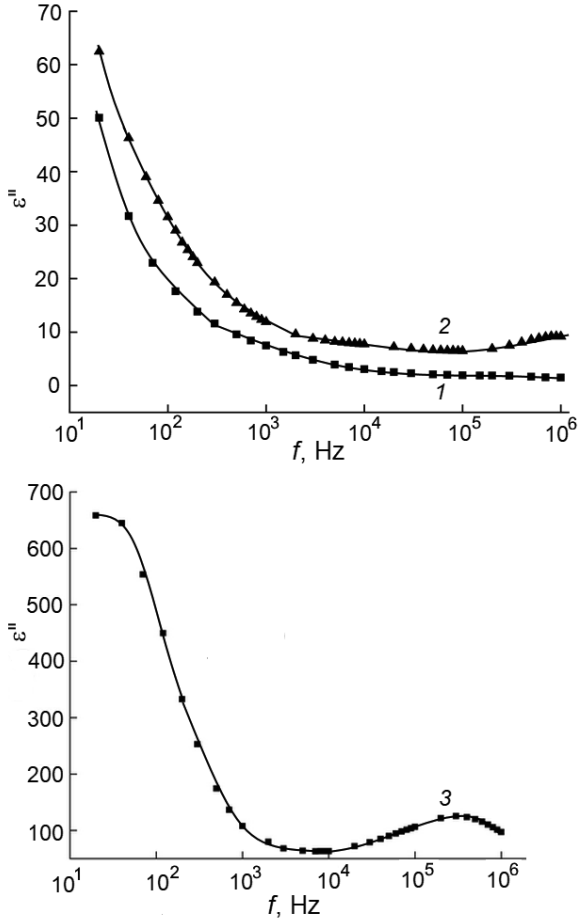

Fig. 2. Frequency dependences of the imaginary component of the complex dielectric permittivity of crystals (1–*x*)TlGaSe$_2$ · *x*Dy: *x* = 0 (*1*); 0.01 (*2*) and 0.03 (*3*). *T* = 298 K.

the dependence $\sigma_{ac} \sim f^{0.5-0.6}$ took place, then it was replaced by the dependence $\sigma_{ac} \sim f^{0.8}$, and with a further increase in frequency up to 1 MHz, the superlinear segment $\sigma_{ac} \sim f^{1.2}$ was observed.

The obtained law $\sigma_{ac} \sim f^{0.8}$ indicates a hopping mechanism of charge transfer over states localized in the vicinity of the Fermi level [15]. The first column of the table shows the frequency ranges (Δf) at which the dependences $\sigma_{ac} \sim f^{0.8}$ were observed in the crystals we studied. Using the experimentally found $\sigma_{ac}(f)$ values of (1 – x), TlGaSe$_2$·xDy samples we calculated the density of states at the Fermi level (N_F) within the framework of the Mott model using the following formula

$$\sigma_{ac}(f) = \frac{\pi^3}{96} e^2 kTN_F^2 a^5 f \left[\ln\left(\frac{\nu_{ph}}{f}\right)\right]^4, \qquad (1)$$

where *e* is the electron charge; *k* is the Boltzmann constant; N_F is the density of states near the Fermi level; $a = 1/\alpha$ is the localization radius; α is the decay constant of the wave function of the localized charge carrier $\Psi \sim e^{-\alpha r}$; ν_{ph} - phonon frequency. When calculating the N_F, the localization radius of solid solutions based on TlGaSe$_2$ was taken to be *a* = 34 Å, as in TlGaSe$_2$ [16], and the value of ν_{ph} was set to 10^{12} Hz [17]. The values obtained for N_F are shown in the table. It can be seen from the table that an increase in the concentration of dysprosium in (1 – x)TlGaSe$_2$·xDy solid solutions leads to an increase in the density of states at the Fermi level.

According to the theory of hopping conduction on alternating current, the average hopping distance (R) is determined by the following formula [15]:

$$R = \frac{1}{2\alpha} \ln\left(\frac{\nu_{ph}}{f}\right). \qquad (2)$$

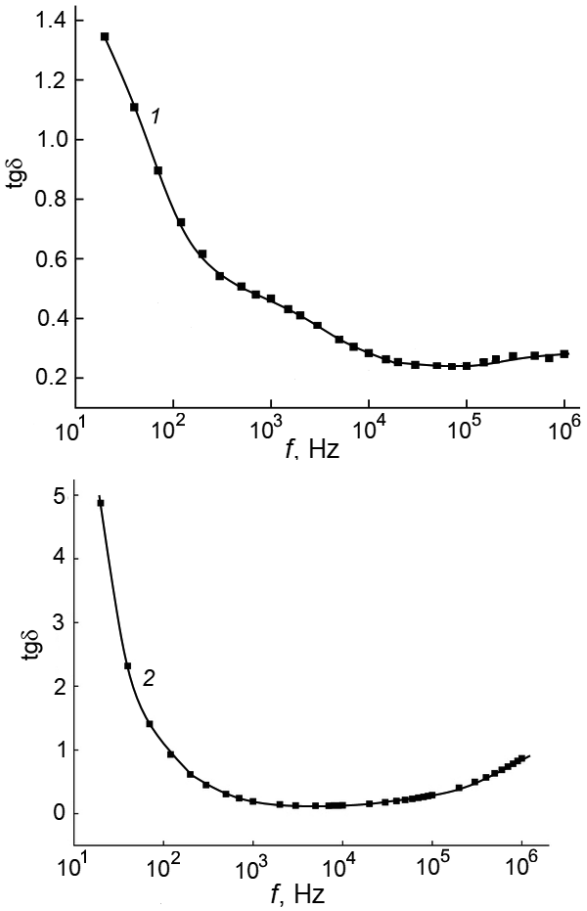

Fig. 3. Frequency dependences of dielectric loss angle tangent in (1–*x*)TlGaSe$_2$ · *x*Dy: *x* = 0 (*1*) and 0.03 (*2*). *T* = 298 K.

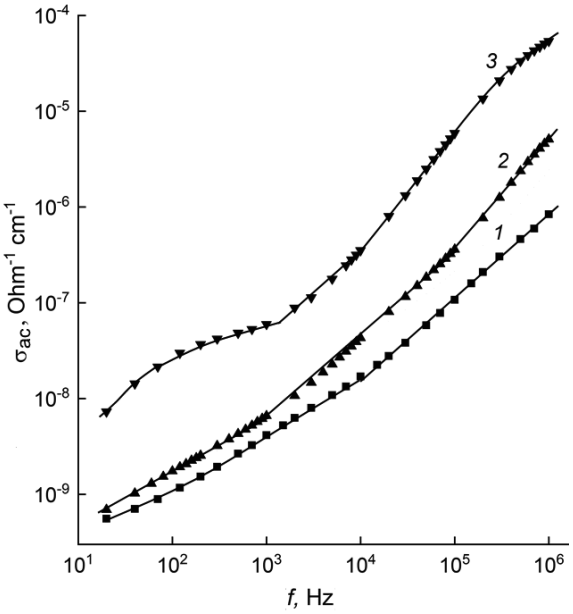

Fig. 4. Frequency dependence of the conductivity of crystals (1–*x*)TlGaSe$_2$ · *x*Dy: *x* = Ø (*1*); Ø.Ø1 (*2*) and Ø.Ø3 (*3*). *T* = 298 K.

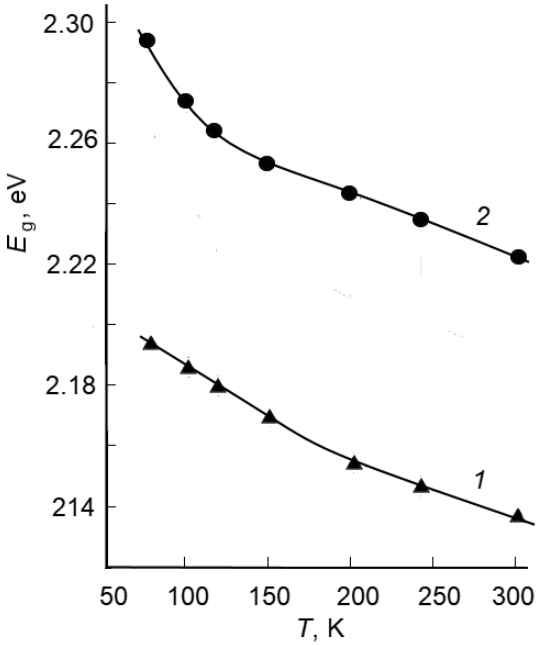

Fig. 5. Temperature dependences of the band gap for TlGaSe$_2$ (*1*) and Ø.99TlGaSe$_2$ · Ø.Ø1Dy (*2*) crystals.

In formula (2), the value of *f* corresponds to the average frequency at which $f^{0.8}$-low is observed. The values of R calculated by formula (2) for (1 – x) TlGaSe$_2$·xDy crystals are also listed in the table. These values of R are approximately 8–9 times larger than the average distance between the centers of charge carrier localization in crystals (1– x) TlGaSe$_2$·xDy.

The value of R allowed by the formula

$$\tau^{-1} = \nu_{ph} \cdot \exp(-2\alpha R) \qquad (3)$$

to determine the average jump time in (1 – x) TlGaSe$_2$·xDy crystals, the values of which are located in the fourth column of the table.

According to the formula [15]:

$$\Delta E = \frac{3}{2\pi R^3 \cdot N_F} \qquad (4)$$

in (1 – x) TlGaSe$_2$·xDy, the energy spread of the states localized near the Fermi level is estimated (the last column of the table). The table shows that

Table. The parameters of localized states in crystals of (1–*x*)TlGaSe$_2$· *x*Dy solid solutions obtained from high-frequency dielectric measurements

Crystal composition (1–*x*)TlGaSe$_2$ · *x*Dy	Δ*f* (Hz)	N_F, 10^{18} ($eV^{-1}cm^{-3}$)	τ (s)	*R* (Å)	Δ*E* (eV)
x = Ø	10^4–10^6	1.98	10^{-6}	234	1.9×10^{-2}
x = Ø.Ø1	10^3–10^5	2.97	10^{-5}	273	8×10^{-3}
x = Ø.Ø3	10^3–10^4	7.14	10^{-4}	312	2.2×10^{-3}

an increase in dysprosium concentration in solid solutions (1 – x) $TlGaSe_2$·xDy leads to a narrowing of the energy band ΔE, an increase in the density of states at the Fermi level, the average distance, and the jump time.

According to the method described in [18], the temperature dependence of the optical properties of (1 – x) $TlGaSe_2$·xDy solid solutions was studied. The absorption edges of $TlGaSe_2$ and (1 – x) $TlGaSe_2$·xDy single crystals differ from each other. The temperature coefficient of the band gap (*dEg/dT*) in the temperature range 80–120 K for $TlGaSe_2$ is $-3\cdot10^{-4}$ eV/K, and for (1 – x) $TlGaSe_2$·xDy (where x = 0.01) $dEg/dT = -7\cdot10^{-4}$ eV/K. In the temperature range of 120–300 K for both samples, $dEg/dT \approx -2.1\cdot10^{-4}$ eV/K. In (1 – x) $TlGaSe_2$·xDy (x = 0.01), as compared with $TlGaSe_2$, the band gap was shifted by ~ 90 meV to the shortwave spectral range. For example, at a temperature of 80 K for $TlGaSe_2$ *Eg* = 2.19 eV, and for (1 – x) $TlGaSe_2$·xDy (x = 0.01) *Eg* = 2.28 eV (Fig. 5). Those, the substitution of dysprosium atoms for metal atoms increases the band gap of a $TlGaSe_2$ single crystal. Thus, it was found that the introduction of dysprosium into the $TlGaSe_2$ crystal matrix modifies its physical parameters.

4. Conclusion

$(1–x)TlGaSe_2 \cdot x$Dy (x = 0, 0.01 and 0.03) solid solutions were synthesized. The dielectric properties of the obtained crystals $(1–x)TlGaSe_2 \cdot x$Dy in alternating electric fields with the frequency f = 20–10^6 Hz were studied. The regularities of changes in dielectric coefficients and conductivity of crystals $(1–x)TlGaSe_2 \cdot x$Dy depending on their composition and frequency of an alternating electric field were found. The introduction of dysprosium into the $TlGaSe_2$ crystal matrix significantly increases the real and imaginary components of the complex dielectric permittivity, the dielectric loss tangent, and alternating current conductivity. An increase in dysprosium concentration in $(1–x)TlGaSe_2 \cdot x$Dy solid solutions leads to an increase in the density of states $(1.98–7.14)\times10^{18}$ $eV^{-1}cm^{-3}$ at the Fermi level, the average distance (234–312 Å), and the jump time (10^{-6}–10^{-4} s). The band gap of $(1–x)TlGaSe_2 \cdot x$Dy single crystals increases with the replacement of metal atoms by dysprosium.

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