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Dielectric Properties and Electrical Conductivity of $(1 - x)TlGaSe_2 \cdot xTm$ Crystals

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Abstract—We have synthesized samples based on the layered compound $TlGaSe_2$ and containing thulium: $(1 - x)TlGaSe_2 \cdot xTm$ with $x = 0.001$, 0.005, 0.01, and 0.02. The polycrystalline samples have been used as charges for growing crystals with the corresponding compositions by the Bridgman method. The phase composition of the $(1 - x)TlGaSe_2 \cdot xTm$ samples has been determined by X-ray diffraction analysis. Their dielectric properties have been studied in ac electric fields at frequencies in the range $f = 5 \times 10^4$ to 3.5×10^7 Hz. We have identified the relaxation character of the dielectric permittivity, the nature of the dielectric loss, and the hopping mechanism of charge transport in the $(1 - x)TlGaSe_2 \cdot xTm$ crystals. Our results demonstrate that increasing the thulium concentration in the crystals reduces the mean hop distance and time of charge carriers and increases the ac conductivity and the density of localized states near the Fermi level in the crystals.

Keywords: crystals, dielectric permittivity, hopping conduction, frequency dispersion, dielectric loss
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INTRODUCTION

$TlGaX_2$ (X = S, Se, Te) compounds and related materials are potentially attractive for use as active elements in various semiconductor devices of modern micro- and nanoelectronics. This class of materials includes $TlGaSe_2$ crystals, which have a layered structure and highly anisotropic physical properties. As shown in studies of the temperature dependence of electrical conductivity anisotropy in single crystals of the isostructural compounds $TlGaS_2$, $TlGaSe_2$, and $TlInS_2$ [1, 2], $TlGaSe_2$ single crystals have the strongest anisotropy.

In addition, $TlGaSe_2$ single crystals are of interest because they possess high photosensitivity, exhibit a memory effect [3], and undergo a sequence of phase transitions [4]. Using X-ray diffraction, Plyushch and Sheleg [5] identified a number of polytypes of $TlGaSe_2$ crystals, and Sheleg et al. [6] reported results of a low-temperature X-ray diffraction study of $TlGaS_2$, $TlGaSe_2$, and $TlInS_2$ single crystals. Recent work was concerned with the dispersion of the complex dielectric permittivity and electrical conductivity of $TlGaSe_2$ single crystals at radio frequencies [7].

A variety of $TlGaX_2$-based solid solutions have been synthesized to date and their physical properties have been studied [8–16]. The results of that work have made it possible to understand the composition dependences of the physicochemical and physical properties of $TlGaX_2$-based materials. In this regard, rare-earth-containing $TlGaSe_2$ crystals remain poorly studied.

Semiconductor materials containing *p*- and *f*-block elements, in particular, Ln^{3+}, undergo various phase transformations, possess magnetic properties, and exhibit exchange interactions between the Ln^{3+} ions and metals whose highest energy valence electrons occupy their *p*-orbital. For example, thulium selenide is characterized by interaction and hybridization between localized 4*f* and mobile 5*d* electrons [17]. This means that partial thulium substitutions on cation sites can influence the physical properties of $TlGaSe_2$-based materials through changes in the valence state of Tm. In other words, the incorporation of thulium into $TlGaSe_2$ can impart new properties to the material.

The objectives of this work were to study the effect of composition on the dielectric properties of $(1 - x)TlGaSe_2 \cdot xTm$ ($x = 0.001$, 0.005, 0.01, 0.02) layered crystals and identify the charge transport mechanism in these materials in ac electric fields at radio frequencies.

EXPERIMENTAL

The starting chemicals used in our preparations were Tl00 thallium, Ga 5N gallium, OSCh 15-2 sul-

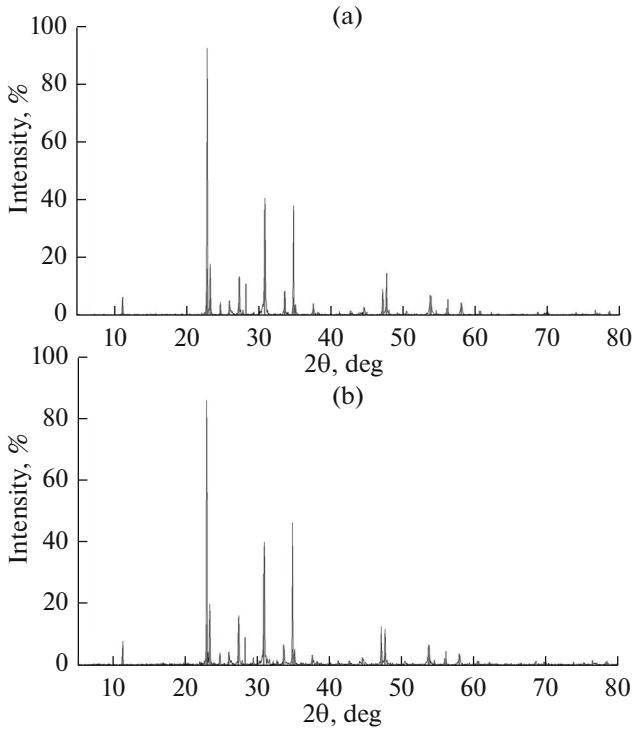

Fig. 1. X-ray diffraction patterns of the (a) $TlGaSe_2$ and (b) $(1 - x)TlGaSe_2 \cdot xTm$ ($x = 0.02$) samples ($T = 298$ K).

fur, and 99.99%-pure thulium. $TlGaSe_2\langle Tm\rangle$ (x = 0.001, 0.005, 0.01, 0.02) samples were prepared by directly melting weighed amounts of stoichiometric elemental mixtures at 1000 ± 5 K for 5–7 h in silica ampules sealed off under a vacuum of 10^{-3} Pa. High-quality crystals were grown by the Bridgman method using the synthesized $(1 - x)TlGaSe_2 \cdot xTm$ materials. During the crystal growth run, the temperature in the upper zone of the furnace was maintained at 1082 K (that is, 5 K above the melting point of $TlGaSe_2$) and that in the lower zone was maintained 50 K below the melting point of $TlGaSe_2$. The ampule translation rate in the furnace was 0.3–0.5 cm/h, and the temperature difference across the solidification front was 25 ± 5 K [13–16].

The phase composition of the $(1 - x)TlGaSe_2 \cdot xTm$ (x = 0.001, 0.005, 0.01, 0.02) samples was determined by X-ray diffraction on a D8 Advance diffractometer in the angular range $0.5° < 2\theta < 100°$ (CuK_α radiation, $\lambda = 1.5406$ Å) at 40 kV and 40 mA.

The dielectric coefficients of the $(1 - x)TlGaSe_2 \cdot xTm$ crystals were measured by a resonance technique [18]. The alternating current electric field frequency was varied from 5×10^4 to 3.5×10^7 Hz.

Samples for electrical measurements were prepared in the form of flat capacitors. Electrical contacts were made with silver paste. The dielectric properties of the samples were measured in the direction perpendicular to the layers of the $(1 - x)TlGaSe_2 \cdot xTm$ crystals. The thickness of the samples ranged from 0.03 to 0.11 cm. All of the dielectric measurements were performed at 300 K. The reproducibility in the resonance position was ±0.2 pF in terms of capacitance and ±1.0–1.5 scale divisions in terms of the quality factor (Q = 1/tanδ). The largest deviations from the average were 3–4% in ε and 7% in tan δ.

RESULTS AND DISCUSSION

All of the reflections observed in the X-ray diffraction patterns of the $(1 - x)TlGaSe_2 \cdot xTm$ (x = 0.001, 0.005, 0.01, 0.02) samples corresponded to the $TlGaSe_2$ phase, and no reflections from any other phases were detected up to $x = 0.02$ (Fig. 1). Like $TlGaSe_2$, the $(1 - x)TlGaSe_2 \cdot xTm$ samples have a monoclinic crystal structure at 298 K (space group $C_{2h}^6 = C2/c$). The unit-cell parameters of the $TlGaSe_2$-based samples studied here (a = 15.623 (0.0002), b = 10.773 (0.0002), c = 10.744 (0.0002) Å, β = 100.040°; Z = 16; V = 1780.59 Å^3; ρ = 6.446 g/cm^3) correlate with previously reported data for $TlGaSe_2$ [16].

Figure 2 shows frequency dependences of the real part of complex dielectric permittivity (ε') for the $(1 - x)TlGaSe_2 \cdot xTm$ samples with x = 0.001, 0.005, and 0.01. It is seen that, throughout the frequency range studied, ε' has the highest dispersion in the case of the $TlGaSe_2$ sample containing 0.1 mol % Tm: in this frequency range, ε' decreases by a factor of 2.4 with increasing frequency. The ε' of $TlGaSe_2$ decreases by almost a factor of 4 in this range. With increasing thulium concentration in the $(1 - x)TlGaSe_2 \cdot xTm$ samples, the frequency dispersion of ε' decreases. For example, the ε' of the $TlGaSe_2$ sample containing 1 mol % Tm decreases by a factor of 1.5. The decrease in the dielectric permittivity of $(1 - x)TlGaSe_2 \cdot xTm$ with increasing frequency observed in our experiments points to relaxation dispersion. Increasing the thulium concentration in $(1 - x)TlGaSe_2 \cdot xTm$ leads to a noticeable reduction in ε'. Whereas the ε' of $TlGaSe_2$ containing 0.1 mol % Tm is 450 at $f = 5 \times 10^4$ Hz, $TlGaSe_2$ containing 1 mol % Tm has ε' = 32 at this frequency. With increasing frequency, the difference decreases. The frequency dependences of the imaginary part of complex dielectric permittivity, ε'', of the $(1 - x)TlGaSe_2 \cdot xTm$ samples are also indicative of relaxation dispersion (Fig. 3).

The frequency dependences of the dielectric loss tangent (tan δ) for $(1 - x)TlGaSe_2 \cdot xTm$ (Fig. 4) demonstrate a hyperbolic decline, suggesting a through conduction loss. With increasing thulium concentration in the $TlGaSe_2$ crystals, their tan δ increases noticeably.

We also studied the frequency-dependent ac conductivity (σ_{ac}) of the $(1 - x)TlGaSe_2 \cdot xTm$ crystals

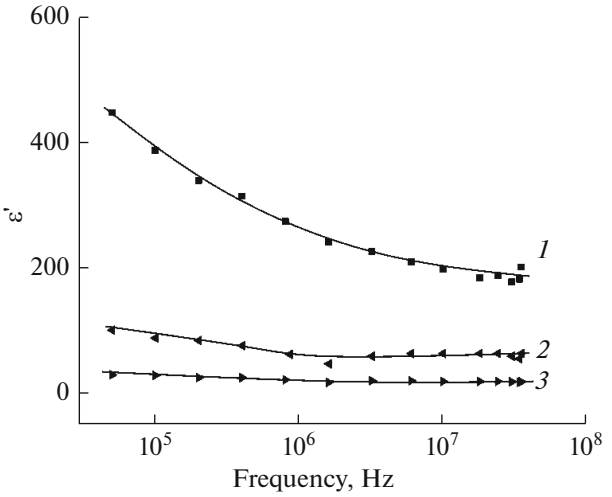

Fig. 2. Frequency dependences of the real part of complex dielectric permittivity for the $(1 - x)TlGaSe_2 \cdot xTm$ crystals with $x = (1)$ 0.001, (2) 0.005, and (3) 0.01 ($T = 298$ K).

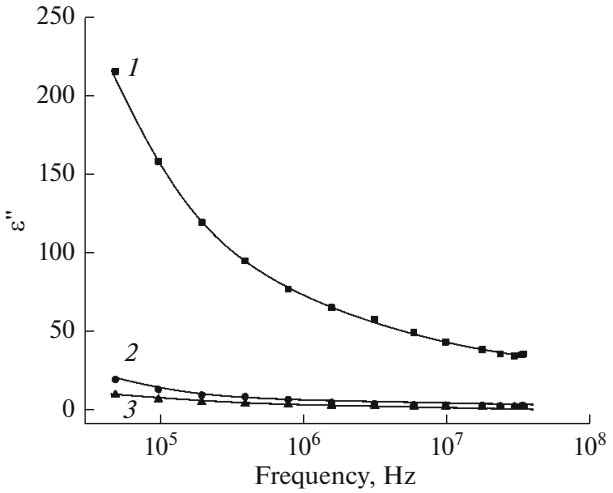

Fig. 3. Frequency dependences of the imaginary part of complex dielectric permittivity for the $(1 - x)TlGaSe_2 \cdot xTm$ crystals with $x = (1)$ 0.001, (2) 0.005, and (3) 0.01 ($T = 298$ K).

(Fig. 5). The σ_{ac} of the $(1 - x)TlGaSe_2 \cdot xTm$ samples was found to be considerably higher than that of $TlGaSe_2$. For example, at $f = 5 \times 10^4$ Hz the σ_{ac} of $TlGaSe_2$ containing 2 mol % Tm exceeds the σ_{ac} of $TlGaSe_2$ by more than two orders of magnitude. The $\sigma_{ac}(f)$ curves of all our samples can be divided into two distinct portions. The conductivity varies as $\sigma_{ac} \sim f^{0.6}$ at lower frequencies and as $\sigma_{ac} \sim f^{0.8}$ at higher frequencies. With increasing thulium concentration in the $(1 - x)TlGaSe_2 \cdot xTm$ samples, the boundary frequency (f_b) for the transition from the $\sigma_{ac} \sim f^{0.6}$ behavior to $\sigma_{ac} \sim f^{0.8}$ shifts to higher frequencies (Fig. 6).

The relation $\sigma_{ac} \sim f^{0.8}$ observed in our experiments suggests that charge transport in the crystals is due to carrier hopping between localized states near the Fermi level. From the present experimental $\sigma_{ac}(f)$ data for the $(1 - x)TlGaSe_2 \cdot xTm$ samples, using the Mott model and the formula [19]

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

where e is the electronic charge, k is Boltzmann's constant, N_F is the Fermi-level density of states, $a = 1/\alpha$ is the localization radius (α is the decay constant of the wave function of localized charge carriers, $\psi \sim e^{-\alpha r}$), and ν_{ph} is a phonon frequency, we calculated the Fermi-level density of states (N_F). In the N_F calculations, the localization radius in our samples was taken to be $a = 34$ Å, like in $TlGaSe_2$ [20], and ν_{ph} was taken to be 10^{12} Hz [21]. The N_F values thus obtained are listed in Table 1. It is seen from Table 1 that raising the thulium concentration in the $(1 - x)TlGaSe_2 \cdot xTm$ crystals leads to an increase in the Fermi-level density of states.

According to the theory of ac hopping conduction, the mean hop distance (R) of charge carriers between two localized states is given by [19]

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

In formula (2), f is the average frequency at which $f^{0.8}$ behavior is observed. The R values calculated for the $(1 - x)TlGaSe_2 \cdot xTm$ crystals using formula (2) are also presented in Table 1. These values are about a factor of 5.5 greater than the average distance between carrier localization centers in the $(1 - x)TlGaSe_2 \cdot xTm$ crystals.

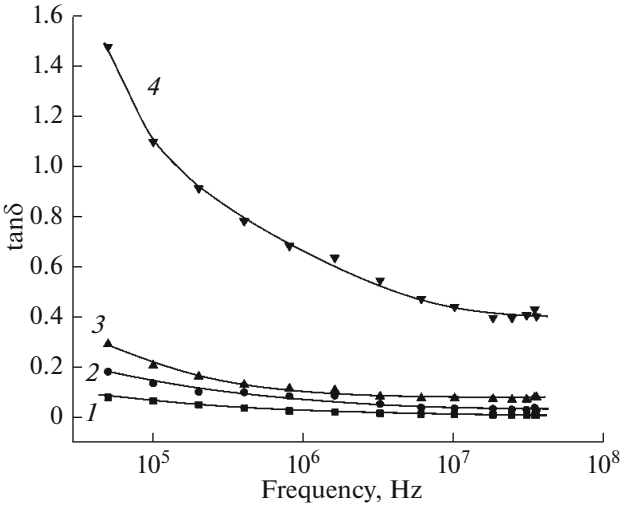

Fig. 4. Frequency dependences of the dielectric loss tangent for the $(1 - x)TlGaSe_2 \cdot xTm$ crystals with $x = (1)$ 0, (2) 0.005, (3) 0.01, and (4) 0.02 ($T = 298$ K).

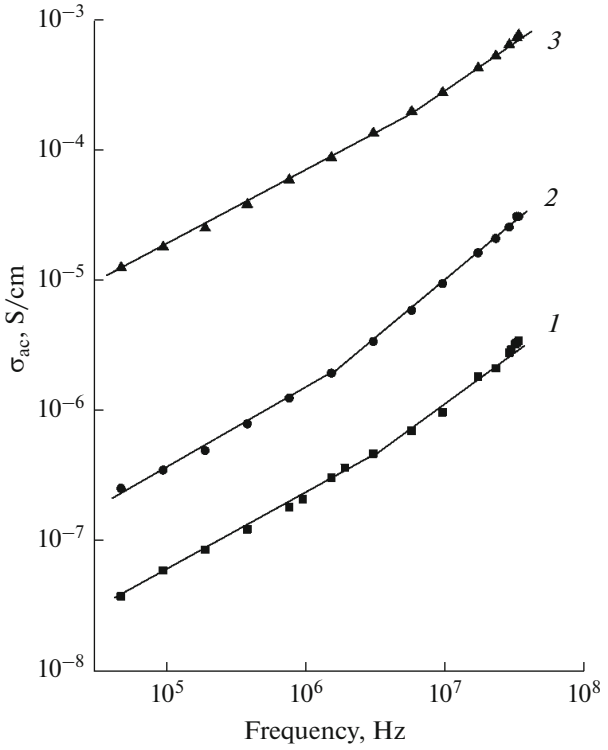

Fig. 5. Frequency dependences of ac conductivity for the $(1-x)TlGaSe_2 \cdot x$Tm crystals with x = (*1*) 0, (*2*) 0.01, and (*3*) 0.02 (T = 298 K).

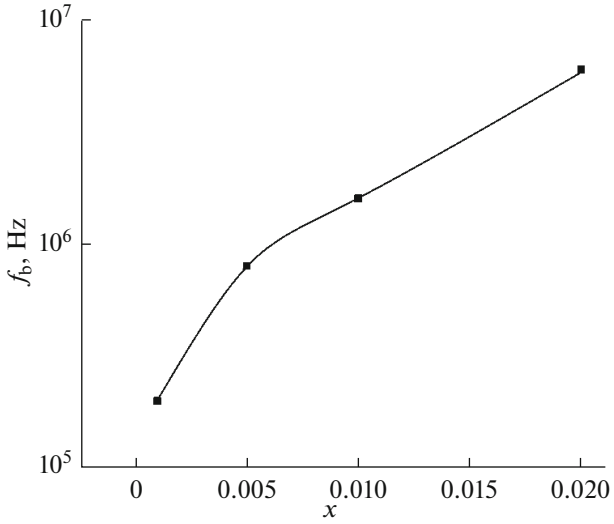

Fig. 6. Effect of Tm concentration on the boundary frequency for the onset of hopping conduction in the $(1-x)$-$TlGaSe_2 \cdot x$Tm crystals.

Using these R values and the formula [19]

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

we evaluated the mean hop time of charge carriers between two localized states in the $(1-x)TlGaSe_2 \cdot x$Tm crystals (Table 1).

Using the relation [19]

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

we evaluated the energy spread (ΔE) of the states localized near the Fermi level in the $(1-x)TlGaSe_2 \cdot x$Tm crystals. From the relation [11]

$$N_t = N_F \Delta E \quad (5)$$

we found the concentration of deep traps (N_t) responsible for ac charge transport in the crystals (Table 1). It follows from the data in Table 1 that increasing the thulium concentration in the $(1-x)TlGaSe_2 \cdot x$Tm crystals leads to an increase in the Fermi-level density of states and a decrease in the mean hop time and distance of charge carriers between two localized states.

CONCLUSIONS

The present results demonstrate that the incorporation of thulium into a crystalline $TlGaSe_2$ host allows one to modify its dielectric coefficients and ac conductivity and vary the key parameters of localized states in its band gap. We have evaluated the Fermi-level density of states in the crystals (10^{18} to 1.6×10^{19} eV^{-1} cm^{-3}), their energy spread (0.005–0.070 eV), the mean hop time (5×10^{-8} to 6×10^{-8} s) and hop distance (186–190 Å) of charge carriers between two localized states, and the concentration of deep traps responsible for ac charge trans-

Table 1. Parameters of localized states in the $(1-x)TlGaSe_2 \cdot x$Tm crystals as derived from high-frequency dielectric measurements

Composition, mol %	$N_F \times 10^{-18}$, eV^{-1} cm^{-3}	$\tau \times 10^8$, s	R, Å	ΔE, eV	$N_t \times 10^{-16}$, cm^{-3}
$TlGaSe_2$	1	6.0	190	0.070	7
99 $TlGaSe_2$ + 1 Tm	3	5.5	187	0.024	7.2
98 $TlGaSe_2$ + 2 Tm	16	5.0	186	0.005	8

port in the $(1 - x)TlGaSe_2 \cdot xTm$ (x = 0.001, 0.005, 0.01, 0.02) crystals (7×10^{16} to 8×10^{16} cm^{-3}).

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