INFLUENCE OF CHROME DOPING ON TRANSPORT PHENOMENA IN LAYERED SINGLE CRYSTALS OF THALLIUM-INDIUM SULFIDES

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The frequency dependences of the dielectric properties of the obtained samples of $TlIn_{1-x}Cr_xS_2$ single crystals (x = 0.005 and 0.01) were studied. The nature of dielectric losses, the mechanism of charge transfer has been established, and the density of states near the Fermi level, their energy spread, the average time and distance of jumps, as well as the concentration of deep traps responsible for conductivity on alternating current have been assessed. It was found that partial substitution of indium with chromium in $TlInS_2$ single crystals makes it possible to control the dielectric characteristics of the resulting crystals.

Keywords: $TlIn_{1-x}Cr_xS_2$, single crystal, frequency, dielectric permittivity, loss tangent, charge transfer, alternating field, ac-conductivity.
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1. INTRODUCTION

Modern electronic technologies stimulate interest in the production of efficient semiconductor materials characterized by highly sensitive electrical and magnetic properties, which can lead to new physical effects. In this regard, much attention is paid to promising semiconductors based on $TlBX_2$ (B = Ga, In; X = S, Se, Te), the properties of which can be varied in a wide range by substituting the cation and anion. One of the representatives of this class of materials are layered $TlInS_2$ single crystals, characterized by a wide band gap (E_g = 2.5 eV at T = 293 K) and a fairly high electrical resistance ($\rho \approx 10^{11}$ Ohm · cm at 293 K). A study of the electrical properties of $TlInS_2$ single crystals at direct [1] and alternating [2, 3] current showed that at temperatures $T < 200$ K and frequencies $f > 10^5$ Hz, they exhibit hopping conductivity of charge carriers along localized states in the vicinity of the Fermi level (dc-and ac-conductivity). To expand this class of semiconductors and vary their physical parameters, the production of solid solutions based on them opens up wide prospects.

Substitutional solid solutions obtained on the basis of $TlInS_2$ can exhibit semiconductor behavior, while also retaining, for example, ferromagnetic properties. One of the interesting and at the same time little-studied substitutional impurities is chromium Cr, which can be located in cationic positions in the $TlInS_2$ crystal structure. Our data [4] on the ability of chromium to replace In positions in $TlInS_2$ indicate the formation of $TlIn_{1-x}Cr_xS_2$ solid solutions.

The purpose of this work was to study the effect of partial substitution of indium with chromium in $TlInS_2$ on the dielectric properties and conductivity of the resulting crystals, measured at alternating current.

2. EXPERIMENTAL PART

Solid solutions were synthesized from elemental metals Tl, In, Cr of the OsCh grade and sulfur of the OsCh 16-5 grade. The samples were weighed and placed in quartz ampoules, which were evacuated to 10^{-3} Pa. The samples were synthesized in an electric furnace, where the temperature was increased stepwise. The synthesis and annealing temperatures of $TlIn_{1-x}Cr_xS_2$ were chosen based on the phase diagram of the TlS–InS system. After exposure at the $TlInS_2$ melting temperature of 1041 K, the samples were cooled to 673 K and annealed for 1 day, followed by cooling to room temperature in a furnace. The obtained samples were identified by methods (DTA and XRF).

The phase composition of the resulting polycrystalline samples was determined using XRF (DRON-2; Ni filter; CuK_α radiation; scanning speed 1 deg/min). The diffraction patterns were indexed using powder diffraction structural data known for the Tl–In–S system. The lattice parameters of the samples were refined using the least squares method by fitting. It was established that the resulting $TlIn_{1-x}Cr_xS_2$ samples (x=0; 0.005 and 0.01) were single-phase and crystallized in a monoclinic structure with the following elementary crystal lattice parameters: a = 10.9017; b = 10.9412; c = 15.1809 Å; z =16.

The replacement of an indium atom with a chromium atom in the structure of pure $TlInS_2$ does not significantly change the parameters of the crystal lattice. Single crystals of $TlIn_{1-x}Cr_xS_2$ (x = 0, 0.005 and 0.01) were grown by the Bridgman-Stockbarger method.

Dielectric measurements of $TlIn_{1-x}Cr_xS_2$ single crystals were carried out by the resonance method [5] in the frequency range of an alternating electric field $f = 5 \times 10^4$–3.5×10^7 Hz.

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Samples of $TlIn_{1-x}Cr_xS_2$ were made in the form of flat capacitors, the plane of which was perpendicular to the crystallographic C-axis of the crystal. Silver paste was used as the electrode material. The thickness of the samples made from $TlIn_{1-x}Cr_xS_2$ single crystals was $(1.5–2.0) \times 10^{-2}$ cm, and the contact area of the plates was $(1.2–1.8) \times 10^{-1}$ cm^2.

All dielectric measurements of single-crystal samples were carried out at 298 K. In dielectric measurements, the largest deviations from the average values were 3–4% for dielectric permittivity (ε) and 7% for dielectric loss tangent (tanδ). The reproducibility of the resonance position was ± 0.2 pF in terms of capacitance, and in terms of quality factor (Q = 1/tanδ) ± 1.0–1.5 scale divisions.

3. RESULTS AND ITS DISCUSSION

Figure 1 shows the frequency dependences of the dielectric permittivity of samples $TlIn_{1-x}Cr_xS_2$ (x = 0.005; 0.01) at 298 K.

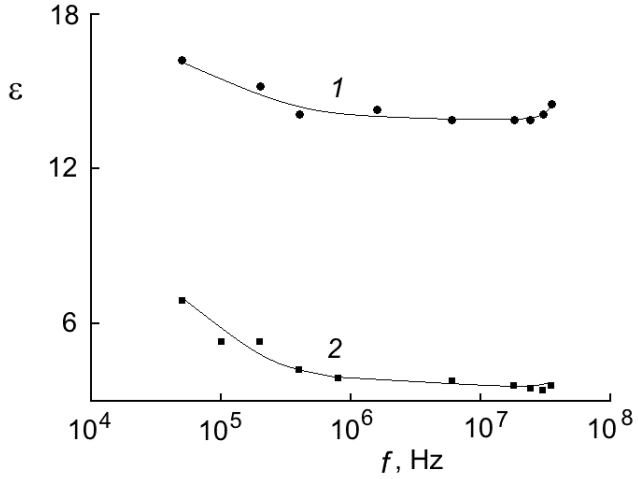

Fig. 1. Frequency dependences of dielectric permittivity for $TlIn_{0.995}Cr_{0.005}S_2$ (*1*) and $TlIn_{0.99}Cr_{0.01}S_2$ (*2*) single crystals at T = 298 K.

Comparison of curves *1* and *2* in Fig. 1 shows that if in the $TlIn_{0.995}Cr_{0.005}S_2$ sample the value of ε changes slightly with frequency (within 14.0–16.2), then in $TlIn_{0.99}Cr_{0.01}S_2$ the change in ε is noticeable (ε = 3.6–6.9 depending on the frequency). In the $TlInS_2$ single crystal over the entire frequency range studied ($f = 10^3$–3×10^7 Hz), no significant dispersion ε was observed [3]. The experimentally observed monotonic decrease in the dielectric permittivity of $TlIn_{1-x}Cr_xS_2$ single crystals with increasing frequency (Fig. 1, curves *1* and *2*) indicates relaxation dispersion.

An increase in the chromium content in $TlIn_{1-x}Cr_xS_2$ crystals from x = 0.005 to 0.01 leads to a significant decrease in the dielectric permittivity of the samples (~ 4 times in the high-frequency region).

The values of the dielectric loss tangent tanδ in $TlIn_{0.99}Cr_{0.01}S_2$ single crystals significantly exceeded the values of tanδ in $TlIn_{0.995}Cr_{0.005}S_2$ (Table).

Table

$\tan\delta$ values for $TlIn_{1-x}Cr_xS_2$ (x = 0.005; 0.01) single crystals at different frequencies at T = 298 K

Frequency, Hz	$\tan\delta \times 10^4$	
	x = 0.005	x = 0.01
5×10^4	248	1660
1×10^5	346	2477
2×10^5	284	2488
4×10^5	261	3237
8×10^5	188	3612
1.6×10^6	178	2575
3.2×10^6	265	2229
6×10^6	157	1980
1.8×10^7	179	1314
2.4×10^7	195	1253
3×10^7	211	1232
3.5×10^7	223	1069

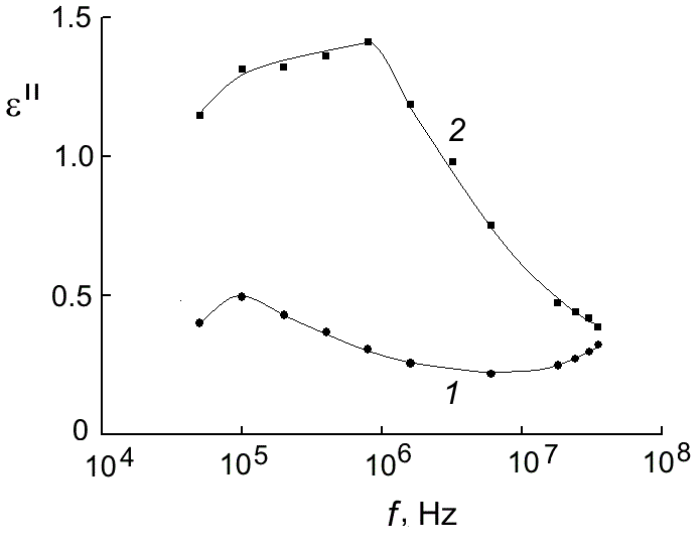

Fig. 2. Frequency dependences of the dielectric loss coefficient in $TlIn_{0.995}Cr_{0.005}S_2$ (*1*) and $TlIn_{0.99}Cr_{0.01}S_2$ (*2*) single crystals. T = 298 K

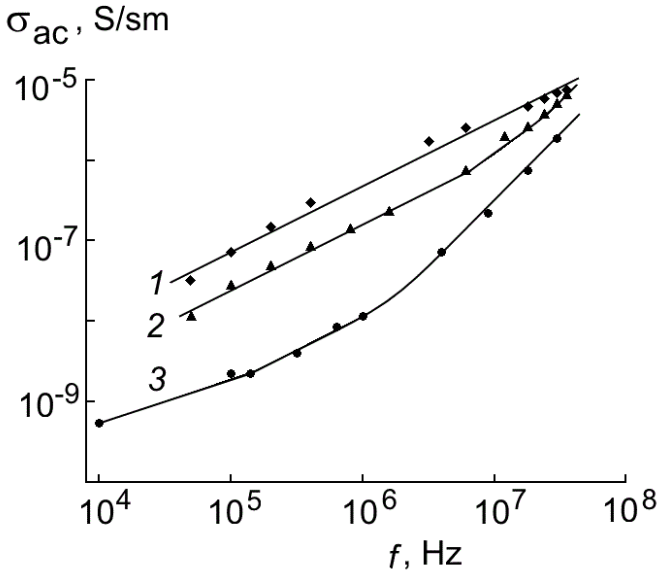

Fig. 3. Frequency dispersion of ac-conductivity of $TlIn_{0.99}Cr_{0.01}S_2$ (*1*); $TlIn_{0.995}Cr_{0.005}S_2$ (*2*) and $TlInS_2$ (*3*) single crystals. T = 298 K

In addition, in the frequency dependence of tanδ for $TlIn_{1-x}Cr_xS_2$ single crystals, in contrast to $TlInS_2$ [3], maxima were observed (Table), which confirms the presence of relaxation losses [6] in the crystals.

Figure 2 shows the frequency dependence of the dielectric loss coefficient ($\varepsilon'' = \varepsilon \cdot \tan\delta$) of $TlIn_{1-x}Cr_xS_2$ single crystals of various compositions. It can be seen that an increase in the chromium content in the crystals leads to a significant dispersion of ε″ (Fig. 2, curve *2*).

Figure 3 presents the experimental results of studying the frequency-dependent ac -conductivity of $TlIn_{1-x}Cr_xS_2$ single crystals at T = 298 K. For comparison, the same figure shows the dependence $\sigma_{ac}(f)$ for the $TlInS_2$ single crystal (Fig. 3, curve *3*).

In the frequency region $f = 10^5$–10^6 Hz, the ac-conductivity of the $TlInS_2$ varied according to the law $\sigma_{ac} \sim f^{0.8}$, and at $f \geq 10^7$ Hz the superlinear region for $\sigma_{ac}(f)$ was observed. The dispersion curve $\sigma_{ac}(f)$ of the $TlIn_{0.995}Cr_{0.005}S_2$ sample from 5×10^4 to 1.6×10^6 Hz obeyed the law $\sigma_{ac} \sim f^{0.8}$, and then the slope of the curve increased and at $f \geq 2.5 \times 10^7$ Hz it was replaced by a superlinear section. Thus. doping the $TlInS_2$ single crystal with chromium (x = 0.005) led to an elongation of the $\sigma_{ac} \sim f^{0.8}$ region and a shift of the transition point to the superlinear region towards higher frequencies. And at a higher chromium content in the crystals (x = 0.01), in the entire studied frequency range from 5×10^4 to 3.5×10^7 Hz, only the law $\sigma_{ac} \sim f^{0.8}$ was observed.

The experimental dependence $\sigma_{ac} \sim f^{0.8}$ observed by us indicates that it is caused by charge carrier jumps between states localized in the band gap. These can be

states localized near the edges of allowed bands or states localized near the Fermi level [7]. But since under experimental conditions the conductivity over states in the vicinity of the Fermi level always dominates over the conductivity over states near the edges of the allowed bands, the law we obtained $\sigma_{ac} \sim f^{0.8}$ indicates a hopping mechanism of charge transfer between states localized near the Fermi level. For such a charge transfer mechanism, the following formula was obtained:

$$\sigma_{ac}(f) = (\pi^3 / 96) \cdot e^2 \kappa T N^2_F a^5 f [\ln (\nu_{ph} / f)]^4, \quad (1)$$

where e is the electron charge, κ is the Boltzmann constant, , T is the temperature, N_F is the density of localized 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} is phonon frequency.

From formula (1) it follows that for $f << \nu_{ph}$ $\sigma_{ac}(f)$ is approximately proportional to $f^{0.8}$. Based on the experimental values of $\sigma_{ac}(f)$ and using formula (1), the density of states at the Fermi level was calculated. For $TlIn_{0.995}Cr_{0.005}S_2$ and $TlIn_{0.99}Cr_{0.01}S_2$ single crystals, the calculated N_F values were 7.9×10^{18} and 1.47×10^{19} $eV^{-1} \cdot cm^{-3}$, respectively. When calculating N_F for the localization radius of the $TlIn_{1-x}Cr_xS_2$ samples, we took the value a = 14 Å, and the ν_{ph} value for $TlInS_2$ is about 10^{12} Hz [8].

The average jumping distance (R) according to the theory of hopping conduction on alternating current can be determined by the formula [7]:

$$R = (1/2\alpha) \ln (\nu_{ph} / f_{av}) \quad (2)$$

where $1/f_{av} = \tau$ is average jumping time.

The superlinear nature of the frequency dependence of the real part of conductivity at high frequencies, according to [9], is associated with the transition from the conduction regime with a variable jump length depending on the frequency to the regime with an optimal jump length independent of the frequency.

The average hopping time in $TlIn_{0.995}Cr_{0.005}S_2$ and $TlIn_{0.99}Cr_{0.01}S_2$ single crystals was 1.2 μs and 0.057 μs, respectively. The R values calculated using formula (2) for $TlIn_{1-x}Cr_xS_2$ single crystals with compositions x = 0.005 and 0.01 were 99 and 77 Å, respectively. These R values are approximately 5.5–7 times greater than the average distance between charge carrier localization centers in single-crystal $TlIn_{1-x}Cr_xS_2$ samples.

Using the formula [7]:

$$\Delta E = 3/(2 \pi R^3 N_F) \quad (3)$$

we estimated the energy spread of states localized in the vicinity of the Fermi level. The ΔE values obtained for $TlIn_{1-x}Cr_xS_2$ were 6×10^{-2} eV at x = 0.005 and 7×10^{-2} eV at x = 0.01.

The concentration of deep traps responsible for *ac*-conductivity, determined by the formula:

$$N_t = N_F \cdot \Delta E, \quad (4)$$

was 4.8×10^{17} cm^{-3} in $TlIn_{0.995}Cr_{0.005}S_2$ and 10^{18} cm^{-3} in $TlIn_{0.99}Cr_{0.01}S_2$. Fig. 4 presents a comparison of the dependences of N_F, R, τ and ΔE on the composition of $TlIn_{1-x}Cr_xS_2$ single crystals.

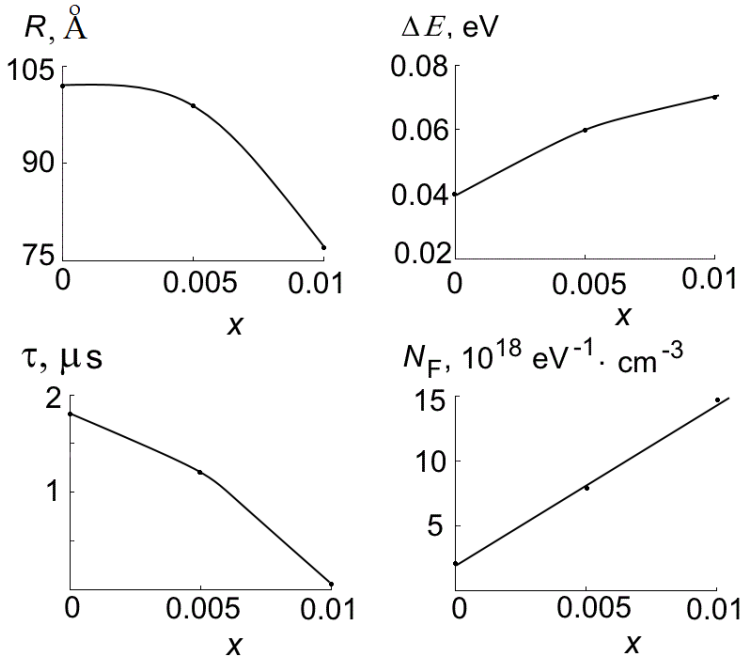

Fig. 4. Dependence of parameters N_F, R, τ and ΔE on the composition of $TlIn_{1-x}Cr_xS_2$ single crystals. T = 298 K.

From these dependences it is clear that with increasing chromium content in crystals, the density of states N_F localized near the Fermi level and their energy spread ΔE increase, and the average time and distance of jumps decrease

4. CONCLUSION

In layered single crystals $TlIn_{1-x}Cr_xS_2$ (x = 0, 0.005, 0.01), the frequency dispersion of dielectric coefficients and *ac*-conductivity (σ_{ac}) across the layers in the frequency range $f = 5 \times 10^4$–3.5×10^7 Hz was studied. It has been established that relaxation dispersion occurs in $TlIn_{0.995}Cr_{0.005}S_2$ and $TlIn_{0.99}Cr_{0.01}S_2$ single crystals. The observation of the law $\sigma_{ac} \sim f^{0.8}$ made it possible to establish the presence of a hopping mechanism of charge transfer along states localized near the Fermi level. The density ($N_F = 7.9 \times 10^{18}$ и 1.47×10^{19} $eV^{-1} \cdot cm^{-3}$) and energy spread ($\Delta E = 6 \times 10^{-2}$ and 7×10^{-2} eV) of states in the vicinity of the Fermi level, the average time (τ = 1.2 and 0.057 mks) and distance (R = 99 and 77 Å) of jumps are estimated. The influence of the composition of $TlIn_{1-x}Cr_xS_2$ crystals on their dielectric characteristics has been studied. It has been established that with increasing chromium content in $TlIn_{1-x}Cr_xS_2$ crystals, N_F and ΔE increase, and τ and R decrease.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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