FREQUENCY – DEPENDENT DIELECTRIC PROPERTIES OF $TlGa_{1-x}Co_xS_2$ SINGLE CRYSTALS

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Laylı $TlGa_{1-x}Co_xS_2$ (x = 0,005; 0,01) monokristallarda dielektrik xarakteristikaların tezlikdən asılılıqları və f = $5\cdot10^4 \div 3{,}5\cdot10^7$ Hs tezlik diapazonunda laylara perpendikulyar istiqamətdə ac-keçiriciliyi (σ_{ac}) tədqiq edilmişdir. Müəyyən edilmişdir ki, $TlGa_{1-x}Co_xS_2$ kristallarda elektrik keçiriciliyində olan itkilərlə yanaşı həmçinin relaksasiya ilə bağlı olan itkilərdə mövcuddur.
Müəyyən edilmişdir ki, $5\cdot10^4 \div 2\cdot10^7$ Hs tezlik sahəsində $TlGa_{1-x}Co_xS_2$ kristallarda yükün köçürülməsi, Fermi səviyyəsi yaxınlığında lokalizə olunmuş hallar üzrə, sıçrayış mexanizmi ilə baş verir. Bu səviyyələrin sıxlığı (N_F), energetik səpələnməsi (ΔE), sıçrayışların orta vaxtı (τ) və məsafəsi (R) qiymətləndirilmişdir. $TlGa_{1-x}Co_xS_2$ monokristalların tərkibinin onların dielektrik əmsallarına təsiri təyin edilmişdir. Müəyyən olunmuşdur ki, monokristallarda kobaltın miqdarı artdıqca N_F və ΔE yüksəlir, τ və R isə azalir.

В слоистых монокристаллах $TlGa_{1-x}Co_xS_2$ (x = 0,005; 0,01) изучены частотные зависимости диэлектрических характеристик и ac-проводимости (σ_{ac}) поперек слоёв в частотном диапазоне f = $5\cdot10^4 \div 3{,}5\cdot10^7$ Гц. Установлено, что в кристаллах $TlGa_{1-x}Co_xS_2$ наряду с потерями на электропроводность имеют место также релаксационные потери. Обнаружено, что в частотной области $5\cdot10^4 \div 2\cdot10^7$ Гц в кристаллах $TlGa_{1-x}Co_xS_2$ имеет место прыжковый механизм переноса заряда по локализованным вблизи уровня Ферми состояниям. Оценены: плотность (N_F) и энергетический разброс (ΔE) этих состояний, среднее время (τ) и расстояние (R) прыжков. Изучено влияние состава монокристаллов $TlGa_{1-x}Co_xS_2$ на их диэлектрические коэффициенты. Установлено, что с ростом содержания кобальта N_F и ΔE возрастают, а τ и R уменьшаются.

Frequency dependence of the dissipation factor tanδ, the permittivity ε, and the ac conductivity σ_{ac} across the layers in the frequency range f = $5\cdot10^4 \div 3.5\cdot10^7$ Hz were studied in layered $TlGa_{1-x}Co_xS_2$ single crystals (x = 0.005; 0.01). The results demonstrate that dielectric dispersion in the $TlGa_{1-x}Co_xS_2$ crystals has a relaxation nature. It was established that the mechanism of ac charge transport across the layers in $TlGa_{1-x}Co_xS_2$ single crystals in the frequency range from $5\cdot10^4$ to $2\cdot10^7$ Hz is hopping over localized states near the Fermi level. The Fermi level density of states (N_F), the spread of their energies (ΔE), and the mean hop distance (R) and time (τ) have been estimated. The present results demonstrate that partial substitution of cobalt for gallium offers the possibility of tuning dielectric properties of obtained crystals.

Layered $TlGaS_2$ single crystals characterized by sufficiently high density of localized states at the Fermi level (N_F). The N_F value calculated from the experimental results of dc- and ac- conductivity measurements of $TlGaS_2$ single crystals is ~ $2\cdot10^{18}$ $eV^{-1}\cdot cm^{-3}$ [1,2]. Doping of these crystals allows one to tune their physical properties. For example, in [3] it was shown that partial manganese substitution for gallium in $TlGaS_2$ leads to significant decrease of dielectric permittivity, mean hop distance and time, and also to increase of density of localized states near Fermi level.

The purpose of this work was to study the effect of partial cobalt substitution for gallium on the ac dielectric properties of $TlGaS_2$ single crystals.

Interaction in $TlGaS_2$ – $TlCoS_2$ system has been investigated by the methods of differential thermal and roentgenography analyses in our previous work [4]. Synthesis of initial $TlGaS_2$ and $TlCoS_2$ compounds produced in ampoules, evacuated to the pressure 10^{-3} Pa. Ampoules were made of melted quarts tubes. Synthesis of samples has been carried out at interactions of initial elements (Tl, Ga, Co, S) of high purity degree (> 99.999%). $TlGa_{1-x}Co_xS_2$ single crystals were growth by Bridgman method.

Measurements of the dielectric properties of $TlGa_{1-x}Co_xS_2$ (x = 0.005; 0.01) single crystals were performed at fixed frequencies in the range of $5\cdot10^4 \div 3.5\cdot10^7$ Hz by the resonant method using a TESLA BM560 Q-meter.

The single crystal $TlGa_{1-x}Co_xS_2$ samples for dielectric measurements had the form of planar capacitors normal to the C axis of the crystals, with silver-paste electrodes. The thickness of the single crystal $TlGa_{1-x}Co_xS_2$ samples was (1.0 ÷ 1.4) $\cdot10^{-2}$ cm and the area of the capacitor plates was $7.6\cdot10^{-2}$ cm^2. All dielectric measurements were performed at T = 300K. The accuracy in determining the resonance capacitance and the quality factor Q =1/tanδ of the measuring circuit was limited by errors related to the resolution of the device readings. The accuracy of the capacitor graduation was ±0.1 pF. The reproducibility of the resonance position was ±0.2 pF in capacitance and ±(1.0 ÷ 1.5) scale divisions in quality factor. The largest deviations were 3 - 4% in ε and 7% in tanδ.

Fig. 1 shows the experimental frequency dependences of the dissipation factor tanδ for $TlGa_{1-x}Co_xS_2$ (x = 0; 0.005; 0.01) single crystals at $5\cdot10^4 \div 3.5\cdot10^7$ Hz.

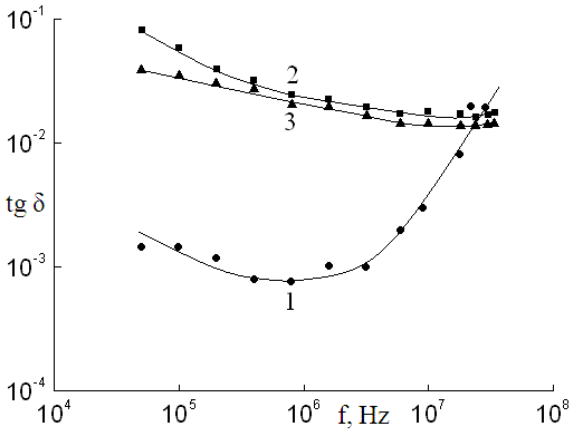

Fig. 1. Frequency dependences of the dissipation factor of $TlGa_{1-x}Co_xS_2$ single crystals: 1 – x = 0; 2 – x = 0.005; 3 – x = 0.01 (T = 300K).

The tanδ (f) curves have a steadily descending branch. This experimental result is evidence of the fact that conductivity loss becomes the main dielectric loss mechanism in studied $TlGa_{1-x}Co_xS_2$ single crystals. In $TlGaS_2$ at f >10^6 Hz significant increase of tanδ takes place up to $3\cdot10^7$ Hz. This experimental result points to relaxation losses. In $TlGa_{1-x}Co_xS_2$ (x = 0.005; 0.01) single crystals insignificant increase of tanδ takes place at f >$2\cdot10^7$ Hz.

We also measured the electric capacitance of $TlGa_{1-x}Co_xS_2$ samples in the frequency range $5\cdot10^4 \div 3.5\cdot10^7$Hz. Using the measured capacities of these samples, we calculated the permittivity ε at different frequencies ($\varepsilon = CL/\varepsilon_0 S$; L is thickness of crystal; S is contact area; ε_0 is dielectric constant).

Fig. 2 shows the frequency dependences of 300 - K dielectric permittivity for $TlGa_{1-x}Co_xS_2$ single crystals with x = 0; 0.005, and 0.01.

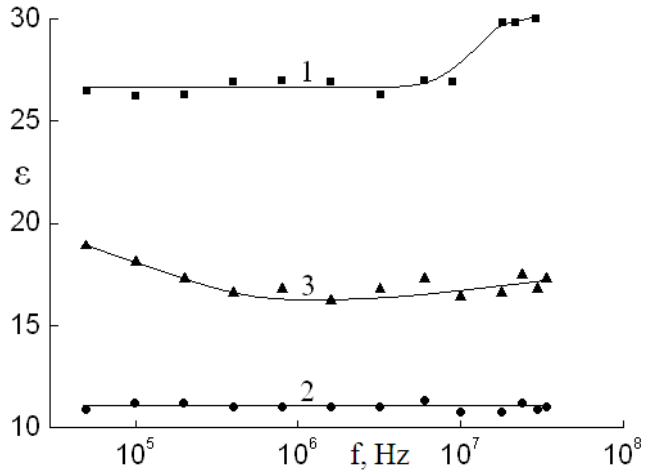

Fig. 2. Frequency dispersion of the dielectric permittivity of $TlGaS_2$ (1); $TlGa_{0.995}Co_{0.005}S_2$ (2), and $TlGa_{0.99}Co_{0.01}S_2$ (3).

Partial Ga^{3+} substitution for cobalt in $TlGaS_2$ crystals gives to considerable decreasing of ε at all frequencies. The ε values of $TlGaS_2$ and $TlGa_{0.995}Co_{0.005}S_2$ are seen to vary from 26 to 30 and from 10.7 to 11.3 respectively over the entire frequency range studied, with no significant dispersion (Fig. 2, curves 1 and 2). But in $TlGa_{0..99}Co_{0.01}S_2$ single crystal there was observed the monotonic reduction in the dielectric permittivity with increasing frequency (Fig.2, curve 3). This experimental result attests to the relaxation nature of the dispersion.

Fig. 3 shows the experimentally measured frequency dependence of the ac conductivity of $TlGa_{1-x}Co_xS_2$ single crystals at T=300K. The σ_{ac} of $TlGaS_2$ (Fig. 3, curve 1) varies as $f^{0.8}$ in the frequency range $5\cdot10^4$ to 10^6Hz and as f^2 in the range 10^6 to $3\cdot10^7$Hz. As is known [5], conductivity proportional to f^2 is due to optical transitions in semiconductors and prevails at high frequencies.

The σ_{ac} of the $TlGa_{1-x}Co_xS_2$ (x = 0.005; 0.01) samples (Fig. 3, curves 2 and 3) varies as $f^{0.8}$ at $f = 5\cdot10^4 \div 10^7$ and $5\cdot10^4 \div 2\cdot10^7$ Hz, respectively. At more high frequencies $\sigma_{ac}(f)$ – dependence of these crystals was super linear.

The $\sigma_{ac} \sim f^{0.8}$ dependence indicates that the mechanism of charge transport is hopping over localized states near Fermi level [5]. This charge transport mechanism is characterized by the following expression obtained in [6]:

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

where e is the elementary charge, k is the Boltzmann constant, N_F is the density of localized states near the Fermi level, a is the localization length, and ν_{ph} is the phonon frequency. Using expression (1), we can calculate the density of states at the Fermi level from the measured values of the conductivity. N_F was determined to be $7.9\cdot10^{18}$ and $9.1\cdot10^{18}$ $eV^{-1}\cdot cm^{-3}$ in $TlGa_{1-x}Co_xS_2$ single crystals with x = 0.005, and 0.01, respectively. As it was shown earlier, in $TlGaS_2$ N_F was determined to be $2.1\cdot10^{18}$ $eV^{-1}\cdot cm^{-3}$ [2]. In calculating N_F, the localization radius in $TlGa_{1-x}Co_xS_2$ was taken to be a = 14Å, by analogy with gallium sulfide [7], a binary analog of $TlGaS_2$. The value of ν_{ph} in $TlGaS_2$ is approximately 10^{12} Hz [8].

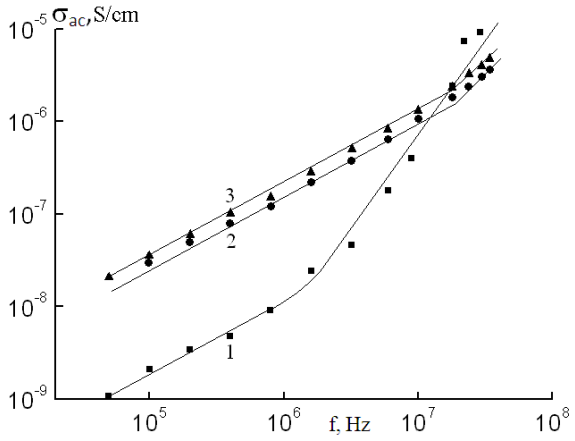

Fig. 3. Conductivity as a function of frequency for $TlGaS_2$ (1), $TlGa_{0.995}Co_{0.005}S_2$ (2), and $TlGa_{0.99}Co_{0.01}S_2$ (3).

According to the theory of hopping conduction [5], the mean hop distance in an applied ac electric field is given by

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

where $1/f = \tau$ is the mean hop time, $\alpha = 1/a$ is the decay parameter of the wave function of a localized charge carrier, $\psi \sim e^{-\alpha r}$.

The R values calculated by Eq. (2) for $TlGa_{1-x}Co_xS_2$ single crystals with x=0.005 and 0.01 are equal to 86 and 81Å, respectively. For $TlGaS_2$, R = 103Å [2]. In $TlGa_{1-x}Co_xS_2$ crystals, R is ~ 6 times greater than the average distance between localization centers (in $TlGaS_2$, R/a = 7.3 [2]). The mean hop time in $TlGa_{1-x}Co_xS_2$ crystals is 0.2μs for x = 0.005 and 0.1μs for x = 0.01 (in $TlGaS_2$, τ = 2.0μs [2]).

Using the relation [5]:

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

we evaluate the spread of the Fermi-level states in energy. We obtained for $TlGa_{1-x}Co_xS_2$ $\Delta E = 9.0\cdot10^{-2}$ eV at x = 0.005 and $9.7\cdot10^{-2}$ eV at x = 0.01.

The concentration of deep traps determining the ac conductivity of $TlGaS_2$,

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

is $7.1 \cdot 10^{17} cm^{-3}$ at x = 0.005 and $8.8 \cdot 10^{17} cm^{-3}$ at x = 0.01.

Parameters of $TlGa_{1-x}Co_xS_2$ single crystals obtained from high-frequency dielectric measurements are given in Table:

Table

Crystal composition	N_F, $eV^{-1} \cdot cm^{-3}$	R, Å	τ, s	R/a
$TlGaS_2$	$2.1 \cdot 10^{18}$	103	2.0	7.3
$TlGa_{0.995}Co_{0.005}S_2$	$7.9 \cdot 10^{18}$	86	0.2	6.1
$TlGa_{0.99}Co_{0.01}S_2$	$9.1 \cdot 10^{18}$	81	0.1	5.8

CONCLUSIONS

The dielectric properties of $TlGa_{1-x}Co_xS_2$ single crystals were studied in a broad frequency range. The nature of dielectric losses and the mechanism of charge transport in the crystals was established, and the Fermi-level density of states, the spread of their energies, the mean hop distance and time, and the concentration of deep traps determining the ac conductivity of the crystals were estimated.

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