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INFLUENCE OF Ga PARTIAL SUBSTITUTION IN $TlGaS_2$ FOR Mn ON DIELECTRIC PROPERTIES

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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 was studied in layered $TlGa_{1-x}Mn_xS_2$ single crystals (x = 0,01; 0,03). In the alternate electric fields, the ac conductivity obeyed the $f^{0,8}$ law at $f = 5\cdot10^4 \div 3{,}5\cdot10^7$ Hz. It was established that the mechanism of the ac charge transport across the layers in $TlGa_{1-x}Mn_xS_2$ single crystals is hopping over localized states near the Fermi level. Estimations yielded the following values of the parameters: the density of states at the Fermi level $N_f = 9{,}9\cdot10^{18}$ eV$^{-1}\cdot$cm^{-3} for $TlGa_{0,99}Mn_{0,01}S_2$ and $8{,}1\cdot10^{18}$ eV$^{-1}\cdot$cm^{-3} for $TlGa_{0,97}Mn_{0,03}S_2$; the average time of charge carrier hopping between localized states $\tau = 5{,}7\cdot10^{-2}$μs; average hopping distance R = 77Å for both crystals.

Introduction

$TlGaS_2$ single crystals are representatives of layered wide-band semiconductors with high electric resistivity ($\rho \approx 10^{10}$Ohm·cm at 300K) [1]. In [1] it is established by experiments that at $T \leq 200$K in $TlGaS_2$ single crystals along C-axis in dc electric field hopping conductivity with alternating length of jump in localized states near the Fermi level is taken place. In ac electric fields frequency dispersion of dielectric coefficients of $TlGaS_2$ single crystals was observed [2]. In [3] the influence of γ-radiation on dielectric permittivity and electric conductivity of $TlGaS_2$ crystals was investigated at $10^2 \div 10^6$ Hz. The influence of intercalation of $TlGaS_2$ with lithium ions on dielectric properties of obtained crystals was studied in [4].

The aim of the present paper is to study the influence of Ga partial substitution in $TlGaS_2$ for Mn on dielectric properties of obtained crystals in alternate electric fields.

Sample preparation and experimental technique

Synthesis of $TlGa_{1-x}Mn_xS_2$ (x = 0,01; 0,03) produced in quartz ampoules, evacuated to the pressure 10^{-3} Pa. Synthesis of samples has been carried out at interaction of initial elements (Tl, Ga, Mn, S) of high purity degree. Technology of growth of these single crystals has been worked out. Synthesized samples and their single crystals were exposed to roentgenphase analysis, which was carried out at diffractometer DRON-3M in $Cu_{K\alpha}$ emission (Ni filter, λ_α = 1,5418Å). Diffractogramms were recorded continuously, diffraction angles were determined by method of measurement according peak of intensity. Errors of reflection angles determination did not exceed 0,02°. X-ray analysis showed that $TlGa_{1-x}Mn_xS_2$ single crystals are crystallized in tetragonal structure with elementary cell parameters a = 7,2692Å; c = 29,8981Å; ρ_x = 5,684g/cm^3 for x = 0,01 and a = 7,2658Å; c = 29,9392Å; ρ_x = 5,676g/cm^3 for x = 0,03.

Samples from $TlGa_{1-x}Mn_xS_2$ for measurements are obtained by spalling along C-axis of the natural spall from massive crystal and have a thickness $(2.0\div 2.5)\cdot10^{-2}$ cm. $TlGa_{1-x}Mn_xS_2$ samples formed flat capacitors whose plane was perpendicular to the crystalline C-axis. The capacitor plate area was $6\cdot10^{-2} \div 8\cdot10^{-2}$ cm^2. Ohmic contacts of samples are made by Ag paste.

Measurements of the dielectric coefficients of $TlGa_{1-x}Mn_xS_2$ single crystals were performed at fixed frequencies in the range $5\cdot10^4 \div 3.5\cdot10^7$ Hz by the resonant method using a TESLA BM 560 Q-meter. For electrical measurements, the samples were placed in a specially constructed screened cell. An ac electric field was applied across the natural layers of $TlGa_{1-x}Mn_xS_2$ single crystals. The amplitude of the applied fields corresponded to the Ohmic region of the current-voltage characteristics of $TlGa_{1-x}Mn_xS_2$ samples. All measurements were performed at T = 300K. The accuracy in determining the resonance capacitance and the quality factor $Q = 1/tan\delta$ of the measuring circuit was limited by errors related to the resolution of the device readings. The accuracy of the capacitor graduation was ±0.1pF. The reproducibility of the resonance position was ± 0.2pF in capacitance and ± (1.0 – 1.5) scale divisions in quality factor.

We measured the electric capacitance of $TlGa_{1-x}Mn_xS_2$ samples in the frequency range $5\cdot10^4 – 3{,}5\cdot10^7$Hz. Using the measured capacities of samples, we calculated the permittivity ε at different frequencies.

Results and discussion

Fig.1 shows the experimental frequency dependences of the dielectric permittivity for $TlGa_{1-x}Mn_xS_2$ (x = 0; 0,01; 0,03). It is seen from Fig.1 that for $TlGaS_2$ single crystal (curve 1) significant variation of ε was not observed at studied interval of frequencies ($\varepsilon = 26 \div 30$). At Ga partial substitution in $TlGaS_2$ for Mn ε of obtained samples decreased with the rise of frequency from $5\cdot10^4$ to $3{,}5\cdot10^7$Hz. For example, ε of $TlGa_{1-x}Mn_xS_2$ single crystal decreased by 5 times for x = 0,01 and 2.5 times for x = 0,03.

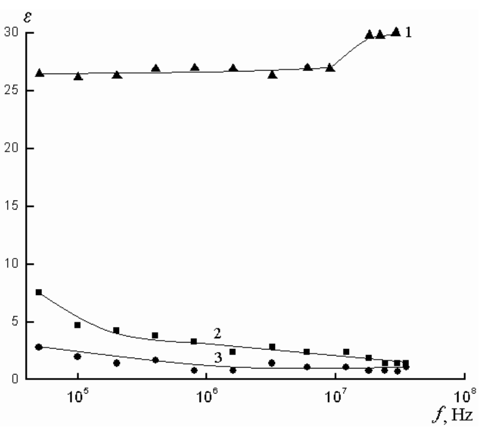

Fig.1. Frequency dispersion of the permittivity of $TlGaS_2$ (1); $TlGa_{0,99}Mn_{0,01}S_2$ (2) and $TlGa_{0,97}Mn_{0,03}S_2$ (3) at T=300K.

Observed in experiments monotonic decrease of ε with rise of frequency (Fig.1, curves 2 and 3) is evidence of relaxation dispersion.

Experimental frequency dependences of the dissipation factor tanδ for $TlGa_{1-x}Mn_xS_2$ (x = 0,01; 0,03) were characterized with presence of maximums (Table)

Table

tanδ values vs frequency for $TlGa_{1-x}Mn_xS_2$ single crystals

f, Hz	*tanδ* ·10^4	
	x = 0,01	x = 0,03
$5\cdot10^4$	1052	2449
10^5	1660	2750
$2\cdot10^5$	1602	3024
$4\cdot10^5$	1478	2130
$8\cdot10^5$	1427	3550
$1,6\cdot10^6$	1791	3058
$3,2\cdot10^6$	1252	1586
$6\cdot10^6$	1299	1695
$1,2\cdot10^7$	1150	1519
$1,8\cdot10^7$	1618	2180
$2,4\cdot10^7$	1877	1938
$3,0\cdot10^7$	1937	2335
$3,5\cdot10^7$	1917	1438

The maximums on *tanδ(f)* – dependences also confirm the fact of presence of relaxation losses.

Fig.2 shows the dependences of dielectric permittivity of $TlGa_{1-x}Mn_xS_2$ single crystals on their composition at various frequencies of alternate electric field: $5\cdot10^4$; 10^5; $3,2\cdot10^6$ and $3,0\cdot10^7$ Hz (curves 1-4). It is seen from Fig.2 that introduction of Mn to $TlGaS_2$ crystals leads to significant decrease of their dielectric permittivity at all pointed frequencies.

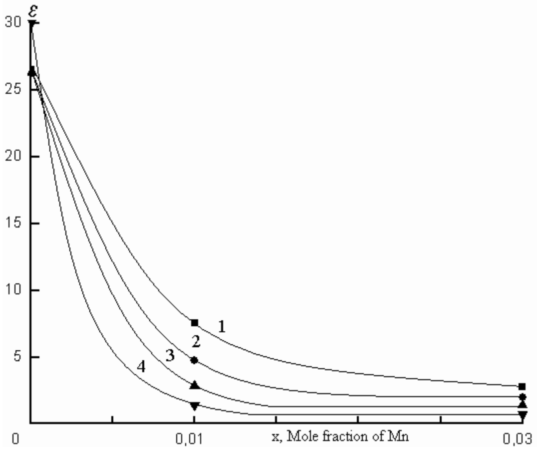

Fig.2. Dependence of the permittivity on composition of $TlGa_{1-x}Mn_xS_2$ single crystals at various frequencies of alternate electric field f, Hz: 1 - $5\cdot10^4$; 2 – 10^5; 3 – $3,2\cdot10^6$; 4 - $3\cdot10^7$.

Frequency dependence of $\varepsilon'' = \varepsilon\cdot tan\delta$ for $TlGa_{1-x}Mn_xS_2$ crystals is given in Fig.3. As it is seen from Fig.3 Ga partial substitution in $TlGaS_2$ crystals for Mn leads to modification of dispersion curves *ε″(f)*. In $TlGaS_2$ the *ε″(f)* curve has two branches: a weakly descending one at $f = 5\cdot10^4 – 10^6$Hz and a rising one at $f > 10^6$Hz. In $TlGa_{1-x}Mn_xS_2$ frequency dependences of ε″ differ from *ε″(f)* curve in $TlGaS_2$; they were characterized by significant descending up to 10^7Hz, after that ε″ values are practically independent on frequency.

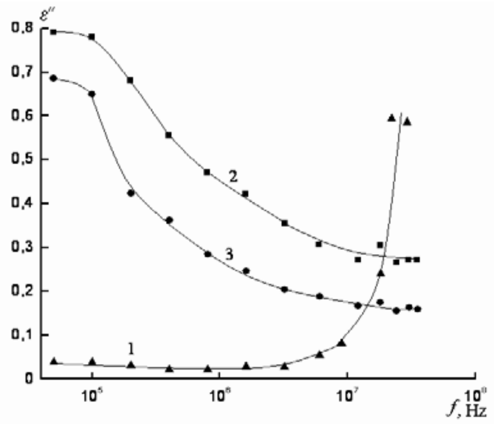

Fig.3. Frequency dependence of ε″ for $TlGaS_2$ (1); $TlGa_{0,99}Mn_{0,01}S_2$ (2) and $TlGa_{0,97}Mn_{0,03}S_2$ (3).

Fig.4 shows the experimentally measured frequency dependence of the ac conductivity of $TlGa_{1-x}Mn_xS_2$ single crystals at T = 300K. The ac conductivity σ_{ac} of $TlGaS_2$ varies as $f^{0,8}$ in the frequency range $5\cdot10^4 – 10^6$Hz (curve 1). At high frequencies ($f = 10^6 \div 3\cdot10^7$Hz) σ_{ac} of $TlGaS_2$ obeyed the f^2 – law. As it was shown in [5] the conductivity proportional to f^2 is related to optical transitions in semiconductors and is dominant at high frequencies.

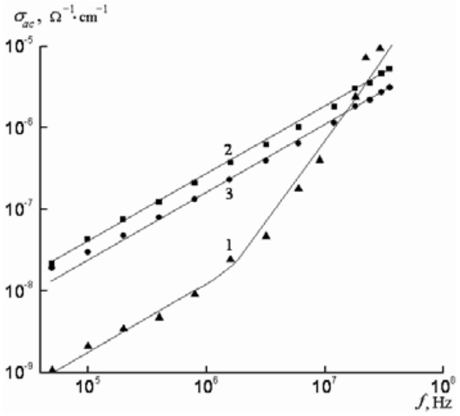

Fig.4. Frequency - dependent *ac* conductivities of $TlGa_{1-x}Mn_xS_2$ single crystals at room temperature: curve 1 – x = 0; 2 – x = 0,01; 3 – x = 0,03.

Dispersion curves $\sigma_{ac}(f)$ of $TlGa_{1-x}Mn_xS_2$ samples (Fig.4, curves 2 and 3) were characterized by $f^{0,8}$ – law at all investigated frequencies. The $\sigma_{ac} \sim f^{0,8}$ dependence indicates that the mechanism of charge transport in $TlGa_{1-x}Mn_xS_2$ single crystals in the frequency range $5\cdot10^4 – 3,5\cdot10^7$Hz is hopping over localized states near the Fermi level. This charge transport mechanism is characterized by the following expression obtained in [6]:

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

where e is the elementary charge, k is the Boltzmann constant, N_F is the density of localized states near the Fermi level, $a = 1/\alpha$ is the localization length, α is the decay parameter of the wave function of a localized charge carrier, $\psi \sim e^{-\alpha r}$, 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 $\sigma_{ac}(f)$. Calculated values of N_F for $TlGa_{1-x}Mn_xS_2$ (x = 0; 0,01; 0,03) single crystals were equal to $2{,}1\cdot10^{18}$; $9{,}9\cdot10^{18}$ and $8{,}1\cdot10^{18}$ $eV^{-1}\cdot cm^{-3}$, correspondingly (localization radius chosen as 14Å, in analogy with the GaS single crystal [7], which is a double analog of $TlGaS_2$).

The theory of ac hopping conductivity provides an opportunity to determine the average time τ of charge carrier hopping from one localized state to another using the formula [5]:

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

where R is the average hopping distance,

$$R = \frac{1}{2\alpha} \ln \frac{\nu_{ph}}{f} \qquad (3)$$

Calculated values of τ and R for both $TlGa_{1-x}Mn_xS_2$ (x = 0,01; 0,03) single crystals were equal to $5{,}7\cdot10^{-2}$µs and 77Å, correspondingly. For $TlGaS_2$ R = 103Å [2].

Knowing N_F and R from [5]:

$$\frac{4\pi}{3} R^3 N_F \cdot \frac{\Delta E}{2} = 1 \qquad (4)$$

we estimate scattering of trap states near the Fermi level: ΔE = 0,11eV for $TlGa_{0,99}Mn_{0,01}S_2$ and 0,13eV for $TlGa_{0,97}Mn_{0,03}S_2$ single crystals.

By formula:

$$N_t = N_F \cdot \Delta E \qquad (5)$$

we can determine the concentration of deep traps in $TlGa_{1-x}Mn_xS_2$: $N_t \approx 10^{17}cm^{-3}$ for both compositions x = 0,01 and 0,03.

Conclusions

Thus, the results of high-frequency dielectric measurements on $TlGa_{1-x}Mn_xS_2$ single crystals provided an opportunity to determine the mechanisms of dielectric losses and charge transport, and also to evaluate the density of states at the Fermi level; the average time of charge carrier hopping between localized states, average hopping distance, scattering of trap states near the Fermi level; concentration of deep traps.

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$TlGaS_2$-DƏ Ga-UN QİSMƏN Mn-LA ƏVƏZ EDİLMƏSİNİN DİELEKTRİK XASSƏLƏRİNƏ TƏSİRİ

$TlGa_{1-x}Mn_xS_2$ ($0 \le x \le 0{,}03$) monokristallarında $f = 5\cdot10^4 \div 3{,}5\cdot10^7$Hs tezlik intervalında dielektrik nüfuzluğunun həqiqi (ε) və xəyali (ε'') toplananları və laylara perpendikulyar istiqamətdə (σ_{ac}) keçiricilik öyrənilmişdir. $TlGa_{1-x}Mn_xS_2$ monokristalında relaksasiya dispersiyasının mövcudluğu müəyyən edilmişdir. $TlGaS_2$ monokristalında Ga ionlarının qismən Mn ionları ilə əvəz edilməsi onun dielektrik nüfuzluğunun azalmasına və dispersiya əyrilərinin $\varepsilon''(f)$ modifikasiya olunmasına səbəb olur. $TlGa_{1-x}Mn_xS_2$ monokristalı üçün ölçülən tezlik intervalında *ac*- keçiriciliyi $\sigma_{ac} \sim f^{0,8}$ qanunauyğunluğa tabe olur ki, bu da Fermi səviyyəsinə yaxın hallarda lokallaşmış yükdaşıyıcıların sıçrayışla hərəkət etməsinin xarakterik xüsusiyyətidir. Fermi səviyyəsi ətrafında yerləşən halların sıxlığı (N_F), enerjisi (ΔE), sıçrayışlar arası məsafə və orta sıçrayış vaxtı təyin edilmişdir.

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ВЛИЯНИЕ ЧАСТИЧНОГО ЗАМЕЩЕНИЯ Ga НА Mn В $TlGaS_2$ НА ДИЭЛЕКТРИЧЕСКИЕ СВОЙСТВА

В слоистых монокристаллах $TlGa_{1-x}Mn_xS_2$ ($0 \le x \le 0{,}03$) исследована частотная дисперсия тангенса угла диэлектрических потерь ($tg\delta$), действительной (ε) и мнимой (ε'') составляющих комплексной диэлектрической проницаемости, *ac* - проводимости (σ_{ac}) поперек слоев в области частот $f = 5\cdot10^4 \div 3{,}5\cdot10^7$Гц. Установлено, что в изученных монокристаллах $TlGa_{1-x}Mn_xS_2$ имеет место релаксационная дисперсия. Частичное замещение галлия в монокристаллах $TlGaS_2$ марганцем приводит к уменьшению их диэлектрической проницаемости и модифицированию дисперсионных кривых $\varepsilon''(f)$. Во всем изученном диапазоне частот *ac*-проводимость монокристаллов $TlGa_{1-x}Mn_xS_2$ подчинялась закономерности $\sigma_{ac} \sim f^{0.8}$, характерной для прыжкового механизма переноса заряда по локализованным вблизи уровня Ферми состояниям. Оценены плотность (N_F) и разброс (ΔE) состояний, лежащих в окрестности уровня Ферми, среднее время и расстояние прыжков.

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