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IMPACT OF γ-IRRADIATION ON DIELECTRIC AND ELECTRIC PROPERTIES OF $TlInS_2$<V> CRYSTALS

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The effect of γ-irradiation on the relaxor properties of the $TlInS_2$<V> compound have been studied. It is established that in this compound the Vogel-Fulcher temperature (T_f) shifts towards the low temperatures, and the Burns temperature (T_d) moves towards the high temperatures. As a result, the temperature range for the existence of a relaxor state extends by ~ 40 K. The presence of hopping conduction is established and the parameters characterizing this mechanism are determined.

INTRODUCTION

Our previous studies [1–5] showed that doping a $TlInS_2$ crystal with some impurities leads to a strong relaxation of the dielectric susceptibility in the region of the incommensurate phase. It was found that the cause of relaxation is the appearance of nanoscale polar domains, leading to the fact that the state of the dipole and ferroelectric glass precedes the ordered phase. Doping atoms, which lead to the appearance of a relaxor state, in turn, form attachment levels in the band gap of the $TlInS_2$ semiconductor ferroelectric. The charge carriers, occupied these levels, turn out to be spatially limited, and as a result, the conductivity in this case is carried out by tunneling through potential barriers. This was observed when studying the charge transfer process in $TlInS_2$ crystals doped with Fe, Mn, Cr, B, V atoms, i. e. in these crystals, in the region of the incommensurate phase, without-activated, temperature–independent hopping conductivity was established. This paper presents the results of studies of the effect of γ-irradiation on the electrical and dielectric properties of the $TlInS_2$<V> compound, where V is 0.3%.

The purpose of this work was to establish the temperature range of existence of a relaxor state in $TlInS_2$ crystals doped with vanadium and the impact of γ-irradiation on the range of existence of the relaxor $TlInS_2$<V>, as well as to establish the mechanism of conduction in the temperature range of the relaxor state of the system under study.

EXPERIMENTAL METHODS

$TlInS_2$<V> single crystals were grown using the modified Bridgman-Stockberger method. The measurements were carried out on faces cut perpendicular to the polar axis. The edges were polished and covered with silver paste. The dielectric constant (ε) was measured using E7-8 alternating current bridges (1 kHz), E7-12 (1 MHz), P 5058 (10 kHz), and Tesla BM 560 (100 kHz) Mobility meter in the temperature range 150…250 K. The temperature scan rate was 0.1 K/min. The irradiation of the samples (^{60}Co) was carried out at room temperature. The radiation dose was accumulated by successive exposures in the same sample and was 4 MGy. Measurements of ε(T) were carried out after each irradiation.

Fig. 1 shows the temperature dependences of the dielectric constant ε(T) of the $TlInS_2$<V> crystal. The study of frequency dispersion was carried out at four frequencies of the measuring field. Offset of diffuse maximums of ε(T) in a $TlInS_2$<V> crystal with an increase in the frequency from 1 kHz to 1 MHz was ~ 5 K (see Fig. 1, curves 1–4). We suppose that the condition for the appearance of relaxor behavior in a $TlInS_2$<V> crystal is the coincidence of the phase transition temperature with the temperature range of thermal filling of local centers. The properties of relaxors can be significantly changed by introducing even an insignificant amount of impurities that affect the charge state of compounds [1–5]. In this case, the temperature shift of the maximum dielectric constant can reach several degrees.

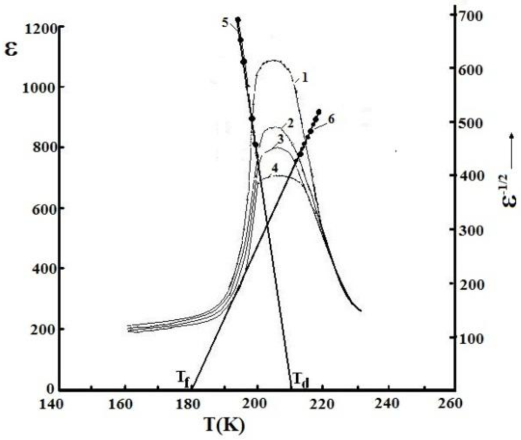

Fig. 1. Temperature dependence of the dielectric constant ε(T) of a $TlInS_2$<V> crystal, measured at frequencies: 1 kHz (curve 1); 10 kHz (curve 2); 100 kHz (curve 3); 1 MHz (curve 4). Curves 5, 6 – temperature dependence of $\varepsilon^{-1/2}$(T) for $TlInS_2$<V> (without irradiation)

An important feature of ferroelectrics with diffuse phase transitions is that in them the dielectric constant above the temperature T_m does not change according to the Curie-Weiss law, but according to the law $\varepsilon^{-1/2} = A + B(T - T_0)$. Fig. 1 (curves 5, 6) also shows the dependence $\varepsilon^{-1/2}$(T) for the $TlInS_2$<V> compound.

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On the side of the high-temperature phase, it intersects the temperature axis at T_f = 170 K. At this temperature, a phase transition occurs from the relaxor (nanodomain) state to the macrodomain (ferroelectric) state. Also, at a temperature T_d = 212 K (Burns temperature), a phase transition from the paraelectric to relaxor state occurs.

As is known [6–9], the diffuse character of the ε(T) dependence is a necessary condition for the existence of a relaxor state. A sufficient condition is that the dependence $\varepsilon^{-1/2}(T)$ varies linearly. During irradiation, T_c, as a rule, decreases, this indicates a common tendency for all ferroelectrics to weaken the ferroelectric properties with an increase the concentration of defects (Table).

Fig. 2 demonstrates this dependence $\varepsilon^{-1/2}(T)$ and ε(T). As can be seen from the figure, the $\varepsilon^{-1/2}(T)$ dependence intersects the temperature axis at T_f = 170 K (see Fig. 2, curve 5) and at T_d = 220 K (see Fig. 2, curve 6) in the irradiated crystal from the high-temperature and low-temperature regions accordingly, relative to the temperature of the curve maximum ε(T). In relaxor ferroelectrics, this is the temperature at which the polar dipoles freeze, and the crystal from the state of ferroelectric glass becomes an ordered ferroelectric state. This temperature is also characterized by the fact that when it occurs temperature filling of trap centers, and localized charged impurities are neutral.

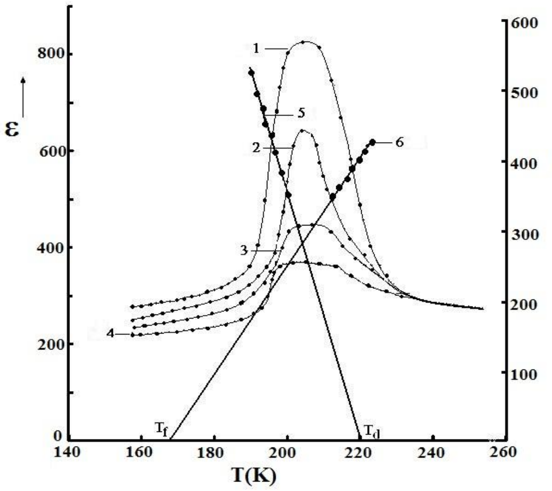

Fig. 2. Temperature dependence of the dielectric constant ε(T) of a $TlInS_2$<V> crystal, measured at a frequency of 1 kHz (curve 1); 10 kHz (curve 2); 100 kHz (curve 3); 1 MHz (curve 4). Curves 5, 6 is the temperature dependence of $\varepsilon^{-1/2}(T)$ for $TlInS_2$<V> (irradiation with a dose of 4 MGy)

As is known [8], the main cause leading to a smearing of the phase transition is the presence of an unordered charge distribution in the crystal. The increase in blurring when irradiated with a dose of 4 MGy indicates that dipole charge centers appear in the bulk of the crystal upon irradiation. At this stage of the study, one can make only an assumption about the nature of these dipole centers. These can be radiation defects formed due to the energy of electronic excitations created by radiation. In our opinion, the most likely mechanism for the formation of radiation defects in the $TlInS_2$<V> compound is multiple ionization of the vanadium impurity atom. A born defect increases the energy levels in the forbidden zone of the crystal; thermofilling of these levels occurs at a lower temperature compared to the non-irradiated compound, i. e. the region of existence of ferroelectric glass is expanding.

In [11], the effect of γ-irradiation on the dielectric constant of Rb_2ZnC_{l4} and Pb_2ZnBr_4 crystals in the transition region of the incommensurate-commensurate phase was studied. It is shown that with an increase in the irradiation dose, the magnitude of the dielectric constant for both crystals decreases and their width increases. It was established that with increasing dose, the phase transition temperature for Rb_2ZnC_{l4} decreases, and for Pb_2ZnBr_4 it increases and erodes. The dominant role in these processes is played by ionization-type defects (charged defects), which arise as a result of γ-irradiation. The smearing of phase transitions probably occurs due to the interaction of polar defects with the spontaneous polarization of the initial crystal [10–12]. According to [13], the decrease in the phase transition temperature with an increase in the irradiation dose is due to a decrease in the concentration of ferroelectric active dipoles in the crystal. Earlier, we studied the effect of γ-irradiation on the dielectric and electrical properties of $TlInS_2$ crystals in the transition region of the incommensurate-commensurate phase [14] and established the possibility of obtaining a relaxor state in these compounds. It is shown that, with two (or more) multiple ionizations, the anionic atom is positively charged and its normal position in the site surrounded by cations is unstable.

Analyzing the literature data and the results of our own experiments, we can say that the γ-irradiation strongly influences the relaxor state of the $TlInS_2$<V> compound and extends the temperature range of its existence. It is also shown that the Vogel-Fulcher temperature T_f shifts towards the low temperatures, and the Burns temperature T_d moves towards the high temperatures. Since $TlInS_2$<V> is both a ferroelectric and a semiconductor, the study of the electrical properties of this crystal is very interesting.

In this paper presents the results of a study of the temperature dependence of the electrical conductivity σ(T) and the dielectric constant of a $TlInS_2$<V> crystal in an alternating electric field in the frequency range 1 kHz…1 MHz.

The temperature dependences of the electrical conductivity σ(T) of the $TlInS_2$<V> crystal are shown in Fig. 3. In the temperature range T_d–T_f, the dependence σ(T) is satisfactorily described by the Mott law [15], and corresponds to the hopping conduction mechanism. It is in this temperature range that $TlInS_2$<V> is in a state of ferroglass. In the temperature range below T_f = 175 K, the conductivity is practically independent of temperature. Fig. 4 shows the results of studies of the frequency dependence of the electrical conductivity of a $TlInS_2$<V> crystal at a temperature T = 200 K. As can be seen from the figure, in the frequency range $10^3…10^6$ Hz, the electrical conductivity varies according to the law $\omega^{0.8}$. This indicates the hopping mechanism of charge transfer over states localized in the vicinity of the Fermi level [15].

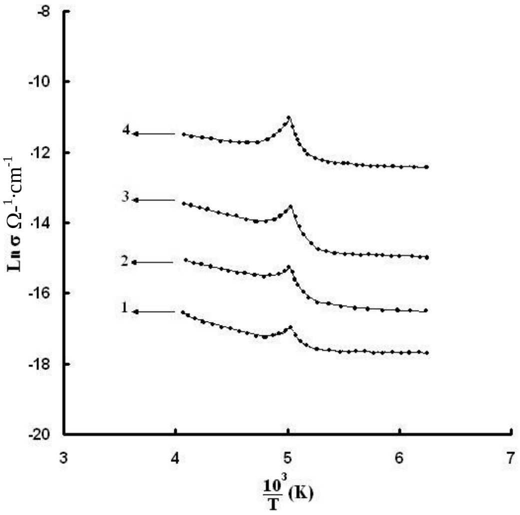

Fig. 3. Temperature dependence of electrical conductivity σ(T) for $TlInS_2$<V> crystals where V is 0.3%: 1 kHz (curve 1); 10 kHz (curve 2); 100 kHz (curve 3); 1 MHz (curve 4) (without irradiation exposure)

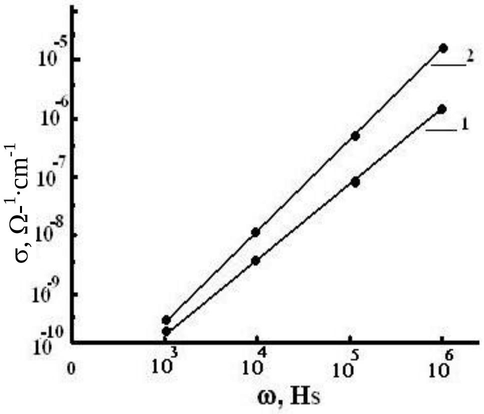

Fig. 4. Temperature dependence of electrical conductivity σ(T) for $TlInS_2$<V> crystals where V is 0.3 %: 1 kHz (curve 1); 10 kHz (curve 2); 100 kHz (curve 3); 1 MHz (curve 4) irradiation dose of 4MGy

Suppose that the eigenfunctions of an electron with energy E in a non-periodic field are given in the form Ψ(x, y, z) and normalized by one electron in the volume Ω. An alternating field acts on the electron, so that the potential energy is $exF\cos\omega t$

$$\sigma(\omega)=\frac{\pi^3}{96}e^2KT\left[N(E_F)\right]^2\alpha^{-5}\omega\left[\ln\left(\frac{\nu_{phon}}{\omega}\right)\right]^4 . \quad (1)$$

The frequency dependence of conductivity for hopping transport by carriers with energies near the Fermi level should be $\omega\left[\ln\frac{\nu_{phon}}{\omega}\right]$, i. e. approximately proportional to $\omega^{0.8}$, when $\omega \ll \nu_{phon}$ conductivity according to [15] is determined by the formula:

$$N^2(E_F)=\frac{96\sigma(f)\alpha^5}{\pi^3e^2KTf\left[\ln\left(\frac{\nu_{phon}}{f}\right)\right]^4}, \quad (2)$$

where e – is the electron charge; K– is the Boltzmann constant; N_F – is the density of localized states near the Fermi level; $a=\frac{1}{\alpha}$ – is the localization radius; α – is the decay constant of the wave function of the localized carrier $\Psi\sim e^{\alpha r}$; ν_{phon} – is the phonon frequency.

Formula (2) allows us to determine the density of states at the Fermi level N (E_F) of a $TlInS_2$<V> crystal.

$$N^2(E_F)=\frac{96\sigma(f)\alpha^5}{\pi^3e^2KTf\left[\ln\left(\frac{\nu_{phon}}{f}\right)\right]^4}. \quad (3)$$

If T = 190 K, $\nu_{phon} = 10^{12}$ Hz, $f = 10^6$ Hz, we obtain at temperature T = 190 K:

$$N_F^2=1{,}2\cdot10^{48}\sigma(f)\alpha^5. \quad (4)$$

The value of the density of states N_F at a temperature T = 190 K (nanodomain state) of $TlInS_2$<V> crystal is $7.89\cdot10^{17}$ $eV^{-1}\cdot cm^{-3}$ (non-irradiated) radius localization is defined as a = 30 Å and 1.8 10^{18} $eV^{-1}\cdot cm^{-3}$ (a = 25 Å, irradiated).

The theory of hopping conduction in alternating electric fields makes it possible to determine the average carrier jump length from one localized state of a localized state to another using the formula [15]:

$$R=(1/2\alpha)\ln(\nu_{phon}/f). \quad (5)$$

For $TlInS_2$<V>, the average jump length for unirradiated R = 207 Å and irradiated 172 Å. The difference between the energies of the states ΔE near the Fermi level can be determined by the formula:

$$\Delta E=\frac{3}{4\pi R^3N(E_F)}. \quad (6)$$

$TlInS_2$	N_F, $eV^{-1}\cdot cm^{-3}$	R, Å	ΔE, eV	a, Å
D = 0 MGy	$7.89\cdot10^{17}$	207	0.038	30
D = 4 MGy	$1.82\cdot10^{18}$	172.3	0.026	25

The calculated values of the hopping conductivity parameters $TlInS_2$<V> are tabulated. It is shown that below the Burns temperature (T_d) hopping conductivity takes place.

CONCLUSION

Investigations of the dielectric and electrical properties of $TlInS_2$ crystals doped with vanadium have established: the Vogel-Fulcher temperature (T_f – is the transition temperature to the relaxor state) and the Burns temperature (T_d – is the exit temperature from the relaxor state); it was established that γ-irradiation expands the region of existence of a relaxor state by 40 K; it is shown that the conduction mechanism in the relaxor phase region has a hopping character with a variable jump length and is carried out according to localized states near the Fermi level; the parameters characterizing this type of conductivity are determined before and after γ-irradiation.

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ВЛИЯНИЕ γ-ОБЛУЧЕНИЯ НА ДИЭЛЕКТРИЧЕСКИЕ И ЭЛЕКТРИЧЕСКИЕ СВОЙСТВА КРИСТАЛЛОВ $\mathrm{TlInS_2}$<V>

Р.М. Сардарлы, О.А. Самедов, Ф.Т. Салманов, Н.А. Алиева

Изучено влияние γ-облучения на релаксорные свойства соединения $\mathrm{TlInS_2}$<V>. Установлено, что в этом соединении температура Фогеля-Фулчера (T_f) смещается в сторону низких температур, а температура Бернса (T_d) – в сторону высоких температур. В результате температурный интервал существования релаксорного состояния расширяется на ~ 40 K. Установлено наличие прыжковой проводимости и определены параметры, характеризующие данный механизм.

ВПЛИВ γ-ОПРОМІНЕННЯ НА ДІЕЛЕКТРИЧНІ І ЕЛЕКТРИЧНІ ВЛАСТИВОСТІ КРИСТАЛІВ $\mathrm{TlInS_2}$<V>

Р.М. Сардарли, О.А. Самедов, Ф.Т. Салманов, Н.А. Алієва

Вивчено вплив γ-опромінення на релаксорні властивості з'єднання $\mathrm{TlInS_2}$<V>. Встановлено, що в цьому з'єднанні температура Фогеля-Фулчера (T_f) зміщується в бік низьких температур, а температура Бернса (T_d) – у сторону високих температур. В результаті температурний інтервал існування релаксорного стану розширюється на ~ 40 K. Встановлено наявність стрибкової провідності і визначено параметри, що характеризують даний механізм.