HOPPING CONDUCTIVITY ON RELAXOR FERROELECTRICS $TlInS_2$<V> EXPOSED GAMMA IRRADIATION

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ABSTRACT

The influence of γ-radiation on relaxing properties of $TlInS_2$<V> compound has been studied. It has been established, that the Fogel-Fulcher temperature T_f shifts to the side of low temperatures in this compound, and Bernce temperature T_d shifts to the side of high temperatures. In the result, the temperature interval of existence of relaxing state becomes wider on ~40K. Temperature dependences of the electrical conductivity $\sigma_{ac}(T)$ of the $TlInS_2$<V> crystal prior to and after gamma irradiation with a dose of 400 Mrad are investigated.

1.INTRODUCTION

Our previous investigations [1-5] show, that doping of $TlInS_2$ crystal by the some impurities leads to the strong relaxation of dielectric receptivity in the region of disproportionate phase. It has been established, the appearance of nano-sized polar domains, leading to the fact, that the state of dipole and ferroelectric glass precedes the ordered phase. The doping atoms, leading to the appearance of the relaxing state, create the capture levels in the forbidden band of semiconductor ferroelectric $TlInS_2$. The charge carriers, settling these levels, are spatially limited and in as the result the conductivity in this case is carried out by the tunneling through the potential barriers. This was observed at the investigation of the process of charge transfer in crystals $TlInS_2$, doped by atoms Fe, Mn, Cr, B, V, i.e. in these crystals in region of disproportionate phase the non-activated, temperature-independent hopping had been established.

In given paper the results of the investigations of the influence of γ-radiation on relaxing properties of $TlInS_2$<V> compound, where V – 0,3 atm.% are presented.

$TlInS_2$<V> monocrystals had been grown by the modified method of Bridgmen-Stockberger. The measurements were carried out on the borders, cut perpendicularly to polar axes. The borders had been polishing and covering by the silver paste.

The dielectric constant ε was measured with the help of the bridges of alternating current E7-8 (1 kHz) and E7-12 (1 MHz) in the temperature interval 150-250K. The velocity of temperature scanning was 0,1 K/min. The radiation of the samples (Co^{60}) was carried out at the room temperature. The radiation dose was accumulated in the one and the same sample and was 400 Mrad. The measurements $\varepsilon(T)$ were carried out after each radiation.

The temperature dependencies of dielectric constant $\varepsilon(T)$ of $TlInS_2$<V> crystal are given on the fig.1. The investigation of frequency dispersion was carried out on two frequencies of measured field. The shifting of degraded maximum $\varepsilon(T)$ in $TlInS_2$<V> crystal at the frequency increase was ~3K (fig.1, curves 1-2). As we suppose, the condition of the appearance of relaxing behavior in $TlInS_2$<V> crystal is the coincidence of the temperature of phase transition with temperature region of heat filling of local centers. The relaxing properties can be significantly changed by the introduction even the insignificant impurity quantity, influence on charge state of the compound [1,5]. Moreover, the temperature shift of maximum of dielectric constant can achieve the several degrees.

The important peculiarity of ferroelectrics with degraded phase transition is the fact, that the dielectric constant in them higher the T_m temperature changes not on Curie-Weis law, but on law $\varepsilon^{-1/2} = A + B(T - T_0)$. The dependence $\varepsilon^{-1/2}(T)$ for the compound $TlInS_2$<V> is also given on the fig.1 (curves 3,4). It crosses the temperature axes at T_f=170K from the side of the high-temperature phase. At this temperature the phase transition from relaxing (nano-domain) state macro-domain (ferroelectric) state is carried out. Also at the temperature T_d=212K (Berns temperature) the phase transition from paraelectric into relaxing state is carried out.

The temperature dependencies of dielectric constant $\varepsilon(T)$ at the radiation dose 400 Mrad is given on the fig.2. The radiation doses up to 200Mrad weakly influence on the dependence $\varepsilon(T)$, leading only to the decrease of maximum value of investigated dependence. These radiation doses of γ-radiation for these crystals are only slight ionizing radiation and plays the role of activating factor for such processes as the migration of point defects, impurities, domain borders and transitions of metastable states into stable ones. By other words, the radiation-stimulated senescence of the samples, not leading to the temperature changes of phase transitions and energetic spectrum of the crystal is observed. At the achievement of the expositional dose in 400 Mrad the radical change of $\varepsilon(T)$ dependency is observed. The strong degradation of the $\varepsilon(T)$ curve in temperature interval T_f-T_d and its widening in as the high temperature region, so the low one are observed (fig.2).

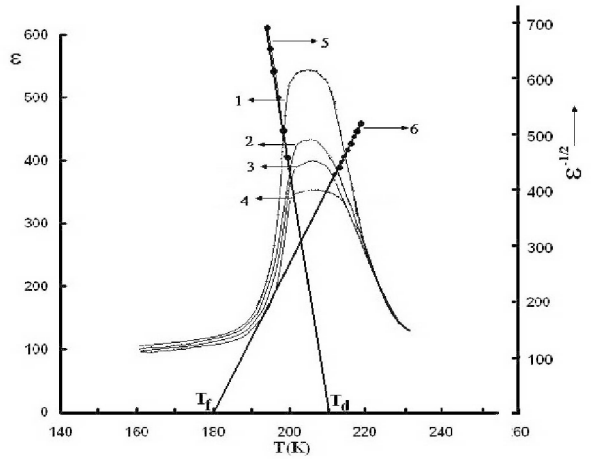


Fig. 1. The temperature dependence of dielectric constant $\varepsilon(T)$ of $TlInS_2$<V> crystal, measured on the frequencies: 1kHz (curve 1); 1 MHz (curve 2). Curve 3,4 – temperature dependence $\varepsilon^{-1/2}(T)$ for $TlInS_2$<V> (without radiation).

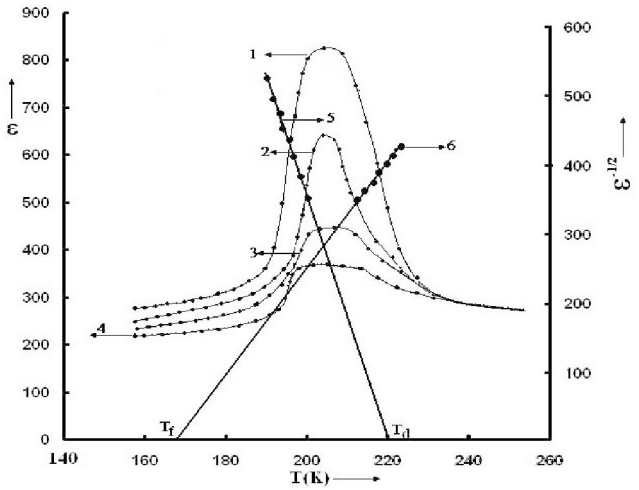


Fig. 2. The temperature dependency of dielectric constant $\varepsilon(T)$ of $TlInS_2$<V> crystal, measured on the frequency 1kHz (curve 1); 1 MHz (curve 2). Curve 3,4 – temperature dependence $\varepsilon^{-1/2}(T)$ for $TlInS_2$<V> (radiation by the dose 400 Mrad).

As it is known [1-8], the depredated character of $\varepsilon(T)$ dependency is the necessary condition of the existence of relaxing state. The enough condition is the fact that $\varepsilon^{-1/2}(T)$ dependency changes on linear law. This dependence is demonstrated by the fig.2. As it is seen from the figure, $\varepsilon^{-1/2}(T)$ dependence crosses the temperature axes at the T_f=140K (fig.2, curve 3) and at T_d=220K (fig.2, curve 4) in radiated crystal with high-temperature and low-temperature correspondingly, relatively to the temperature of maximum of $\varepsilon(T)$ curve. In relaxing ferroelectrics, this temperature is that one, at which the freezing of polar dipoles takes place and crystal from the state of ferroelectric glass transforms into ordered ferroelectric state. This temperature is also

characterized by the fact, that at this the temperature filling of trap centers and localized charged impurities are neutral ones.

As it is known [8], the existence of disordered distribution of the charges in the crystal is the main cause, leading to the degradation of phase transition. The increase of degradation at the radiation by the dose 400 Mrad shows on the fact that the dipole charge centers appear in crystal volume at the radiation. On the given stage of the investigation we can make the supposition about the nature of these dipole centers. These can be the radiation defects, created because of the energy of electron excitements, created by the radiation. On our opinion, the most probable mechanism of the creation of radiation defects in $TlInS_2$<V> compound is repeated ionization of boron impurity atom. The created defect increases the energy levels in forbidden crystal band, the heat filling of this level carries out at the more low temperature, in the comparison with non-radiated compound, i.e. the region of the existence of the ferroelectric glass widens.

In the ref [7] the influence of γ-radiation on dielectric constant of Rb_2ZnCl_4 and Pb_2ZnBr_4 crystals in the region of the incommensurate-commensurable phase transition had been investigated. It is shown, that the value of the peak of dielectric constant for both crystals decreases, and their value increases with the increase of the radiation dose. It is established, that the temperature of phase transition for Rb_2ZnCl_4 decreases, and for Pb_2ZnBr_4 it increases and widens with the increase of the radiation dose. The defects of ionizing type (charged defects), which appear in the result of γ-radiation, play in these processes the dominating role. The degradation of the phase transition probably is carried out because of the interaction of polar defects with spontaneous polarization of initial crystal. The decrease of the temperature of the phase transition with the increase of radiation dose is caused by the decrease of the concentration of ferroelectric active dipoles in crystal.

The influence of γ-radiation on dielectric and electric properties of $TlInS_2$ crystals in the region of incommensurable-commensurable phase transition [8] had been studied by us earlier and the possibility of the obtaining of relaxing state in these compounds had been established. It is shown, that the anion atom is charged positively and its normal position in the nod, surrounded by cations, is unstable at two (or more) divisible ionization. In the result of electrostatic interaction with positively charged cations, such positively charged anion is pushed into interstice, where further is neutralized.

Analyzing the literature data and results of own experiments we can say, that γ-radiation strongly influences on relaxing state of $TlInS_2$<V> compound and widens the temperature interval of its existence. It is also shown, that Fogel-Fulcher T_f temperature shifts to low temperature region and Berns T_d temperature shifts to the high temperature region.

In work [6] dielectric, polarizing and piroelectric property of $TlInS_2$ crystals, doping with 1 at. % Fe are investigated, also was shown, that these materials also concern to a class of ferroelectric-relaxor. Degradation of the temperature dependences of the dielectric permittivity in $TlInS_2$<V> is connected that the located charges create local electrical fields, thus, stimulating occurrence of polarization. Frequency dependences of susceptibility are determined by oscillatory properties of local condition and depend on dynamics of electrons on the capture levels. The existence of an impurity in a crystal results in high density of condition located near to a Fermi level. The conditions, located in a forbidden zone, are responsible for the majority of electronic processes proceeding in semiconductors.

At the same time there are $TlInS_2$<V> and ferroelectrics and semiconductor, the study of electrical properties of this crystal is represented with rather interesting.

In the present work the results of research of temperature dependence of electroconductivity of a $TlInS_2$<V> crystal in a variable electrical field in an interval of frequencies 1 kHz- 1MHz are presented. The conductivity in a variable field were measured by the alternating current bridge E7-8, E7-12, P5058, Q-METER BM560.

Temperature dependence of electroconductivity of a $TlInS_2$<V> crystal is shown in a fig. 3. In this dependence it is possible to allocate three temperature areas described by various mechanisms of conductivity. Up to temperature T_d=210K (downturn of temperature) dependence $\sigma(T)$ has a linear kind, that is characteristic for zoned conductivity. In an interval of temperatures T_d – T_f dependence $\sigma(T)$ is satisfactorily described by the Motts law [9], and corresponds hopping mechanism of conductivity. In this interval of temperatures $TlInS_2$<V> is in dipole glass condition. In a range of temperatures is lower T_f=175K conductivity practically does not depend on temperature.

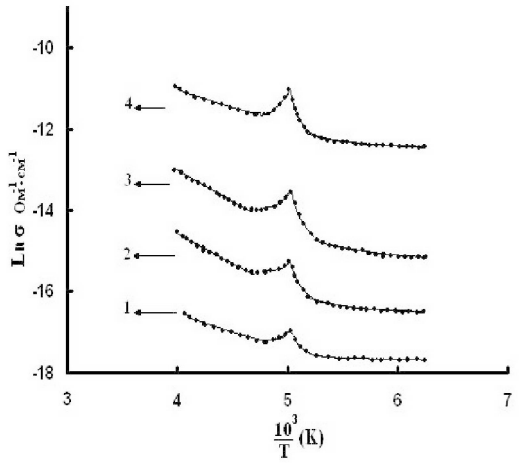


Figure 3. Temperature dependence of conductivity σ(T) in $TlInS_2$<V>: 1 – 1 kHz; 2 – 10 kHz; 3 – 100 kHz; 4 – 1 MHz (V=0,3 at.%).

In a fig. 4 the results of researches frequency dependencies of electroconductivity in an alternating field of a $TlInS_2$<V> crystal are given at temperature T=200K (radiation by the dose 400 Mrad). How it is seen from figure, in the frequencies region 10^3-10^6 Hz electrocurrent changes under the law $\omega^{0.8}$ (fig. 5). It testifies about hopping mechanism of carry of a charge on condition located in a vicinity of a Fermi level.

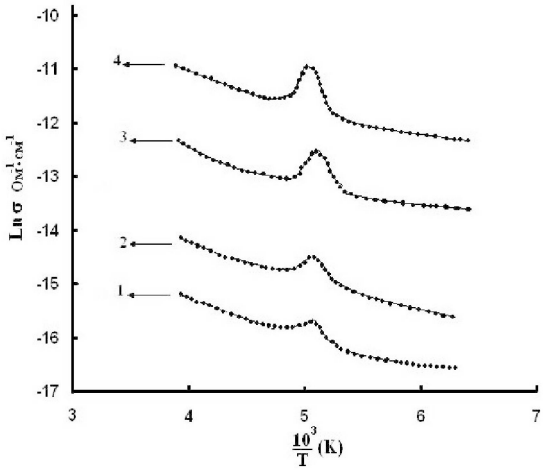


Fig. 4. Temperature dependence of conductivity σ(T) in $TlInS_2$<V> (V=0,3 at.%), radiation by the dose 400 Mrad: 1 – 1 kHz; 2 – 10 kHz; 3 – 100 kHz; 4 – 1 MHz.

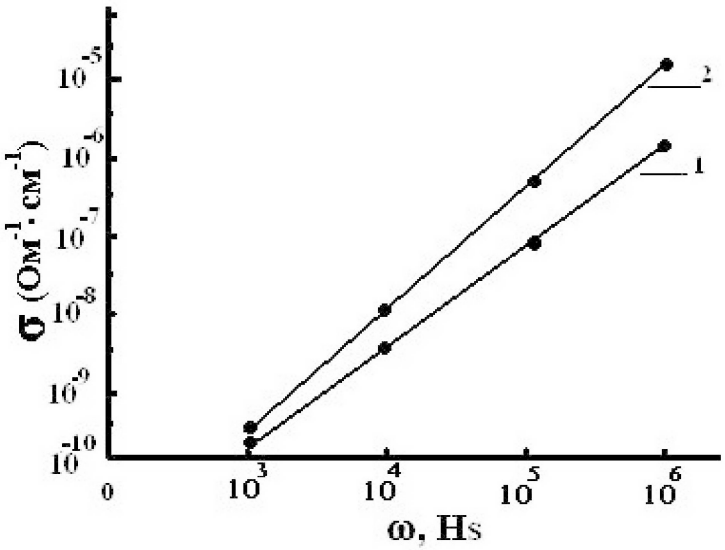


Fig. 5. Frequency dependences of the electrical conductivity $\sigma_{ac}(T)$ of the $TlInS_2$<V> (V=0,3 at.%): curve (1) prior to and (2) after gamma irradiation with a dose of 400 Mrad.

Conductivity according to works [9, 10] is defined by the formula:

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

Where e - electron charge, K - Boltsman constant, N_f - density of the located condition near to a Fermi level, $a = \frac{1}{\alpha}$ - radius of localization, α - constant recession of wave function of the located carrier of a charge $\Psi \sim e^{\alpha r}$, ν - phonon frequency.

The formula (1) allows to define density of condition at a Fermi level $N(E_f)$ of a $TlInS_2$<V> crystal.

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

If T=200K, $\nu_{fon}=10^{12}$ Hz, f=10^3 Hz, we obtain:

$$N_F^2 = \sim \sigma(\alpha) a^{-5} \qquad (3)$$

Thus, the results received at study electrocunductivity of a crystal $TlInS_2$<V> at the appendix of a variable electrical field, it has shown, that in it the temperature of Burns (T_d) is lower takes place hopping conductivity. Termoactivated conductivity is observed up to temperature of Vogel-Fulcher (T_f), and is lower T_f - nonactivated hopping conductivity. The energy of activation ΔW, density of condition $N(E_f)$, length of an average jump R, average time of a jump τ is determined and are resulted in the table.

Doze (Mrad)	T_f (K)	T_d (K)	T_{m1} (K)	T_{m2} (K)	P_S (Kl/cm²)	ΔE (eV)	N_F ($eV^{-1}\cdot cm^{-3}$)	R (Å)	A (Å)
0	180	210	199	207	$7{,}5\cdot10^{-8}$	0,038	$7{,}89\cdot10^{17}$	207	30
400	170	220	197	212	$7\cdot10^{-8}$	0,026	$1{,}82\cdot10^{18}$	172,3	25

Thus, we carried out comprehensive investigations into the temperature dependences of the permittivity ε(*T*) and the electrical conductivity σ(*T*) of $TlInS_2$<V> crystals exposed to gamma irradiation. It was established that there exists a correlation between the behavior of relaxors, in which the relaxor state is

formed as a result of inhomogeneous polarization in nanoregions due to the localization of charges at defects, and the electrical conduction, which has a hopping nature and is governed by thermal activation transitions from defects levels. The results obtained in the above investigations made it possible to determine the density of states of defect levels in irradiated $TlInS_2$<V> crystals, as well as the localization length and the hopping distance. It was demonstrated that the dielectric properties of relaxors can be controlled by varying the electronic subsystem. It was assumed that charge transfer in the temperature range of existence of a stable relaxor state is provided by tunneling from electron levels of the quantum dot through the potential barriers generated by the superlattice of the $TlInS_2$<V> crystal.

2. REFERENCES

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