PACS:71.23.An

DIELECTRIC RELAXATION IN GAMMA-IRRADIATED TlS CRYSTALS

S.M. Gahramanova

Institute of Radiation Problems of ANAS
ramil.azad@mail.ru

Abstract: Temperature dependences of the permittivity and conductivity of TlS crystals subjected 0.25 MGy and 0,75 MGy-irradiation are studied. The possible ionic conductivity, disorder, and electrical instability in TlS crystals are discussed.

Keywords: γ-irradiation, ionic conductivity, chain structure.

1. Introduction

TlS crystals are attracting attention in association with features of their crystal structure, more specifically, the pronounced chain structure. Weak links between chains result in the fact that such a structure is inclined to defect structure. For example, even in single crystals of this class of compounds, the density of uncontrolled defects can reach 10^{20} cm^{-3}. In this case, crystals exhibit hopping conductivity similar to that observed in amorphous or highly disordered crystals, which is well described within the Mott approximation.

In previous papers [1], it was shown that the conductivity of $TlInSe_2$ and $TlGaTe_2$ crystals above 300 K has superionic. It was assumed that Tl^{1+} ions diffusing via vacancies in the thallium sub-lattice between chains $(Ga^{3+}Te^{2-}{}_2)^{-}$ are responsible for the superionic conductivity.

Investigation of the temperature dependence of the conductivity σ(T) [2], measured in both experimental configurations (parallel and perpendicular to the chains, $\sigma_{II,}$ and $\sigma_{\perp}$) in the range of 90–300 K and current–voltage (*I–V*) characteristics of $TlGaTe_2$ single crystals showed that the dependence σ(*T*) in the ohmic region of the *I–V* characteristic possesses a hopping character and is described in the Mott approximation. The study of the *I–V* characteristics of $TlGaTe_2$ crystals subjected to various γ-irradiation doses in the region of a sharper current increase showed that this region is described within the Poole–Frenkel effect.

In this paper, we present the temperature dependences of the dielectric loss tangent (tgδ(*T*)), and conductivity of the TlS crystal, studied at various electric field strengths and γ-irradiation doses.

2. Experimental

The TlS compound samples were synthesized by alloying primary components (purity no less than 99.99) in evacuated quartz cells; the single crystals were grown by the modified Bridgman method. The tetragonal axis *c* of the freshly cleaved rectangular crystal samples prepared for the study was oriented in the cleavage plane. To measure the temperature dependences of the TlS crystal conductivity, capacitors with insulating plates made of the materials understudy were fabricated. Conductive layers were obtained by applying a silver paste onto the plate surface. The conductivity was studied using an E7-25 LCR meter in the temperature range 100–450 K. The measuring field amplitude did not exceed 1 V/cm. After preliminary measurements of tgδ(*T*) and ε(*T*), the samples were exposed to γ-irradiation from a standard ^{60}Co source. The irradiation dose was gradually accumulated in each sample by sequential gamma exposures to 0.25 and 0.75 MGy.

3. Experimental results and discussion

The temperature dependences of the conductivity σ_{II} (T) and $\sigma_{\perp}(T)$ of the initial samples and irradiated TlS crystals are shown in Figs. 1a and 1b.

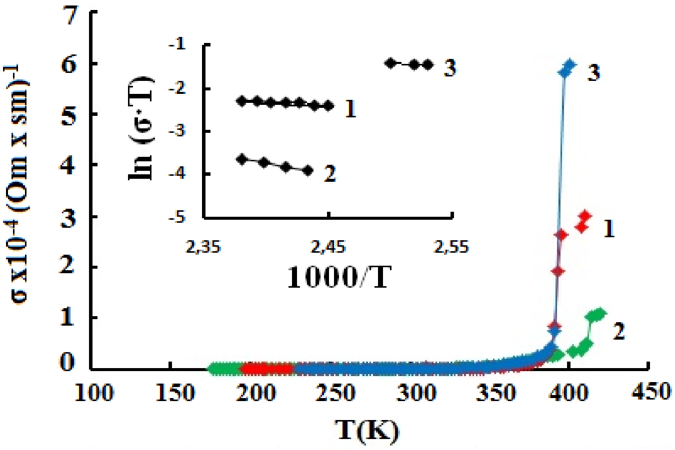

Fig. 1. Temperature dependences of the TlS conductivity σ(T). The γ-irradiation doses are 1- 0; 2- 0.25; 3-0.75 MGy. The insets show the dependences of ln(σ·T) on 1000/T

The γ-irradiation of crystals leads to the formation of radiation defects such as vacancies, interstitial atoms, and various defect clusters interacting with each other and with chemical impurities. As seen in Fig. 1, the conductivity decrease with an irradiation dose to 0.25 and 0.75 MGy in the measurements. The dominant role in these processes is played by ionization type (charged) defects resulting from γ-irradiation. The insets in Figs.1 show the temperature dependences in ln(σ·T)–1000/T coordinates. We can see that the experimental points are well fitted by a straight line according to the equation [3] for ionic conductivity

$$\sigma \cdot T = \sigma_0 \exp(-\Delta E^a/kT) \qquad (1)$$

where ΔE^a is the conductivity activation energy and $k$is the Boltzmann constant. Such behavior of the conductivity points to the dominance of ionic conductivity above the critical temperature [3].

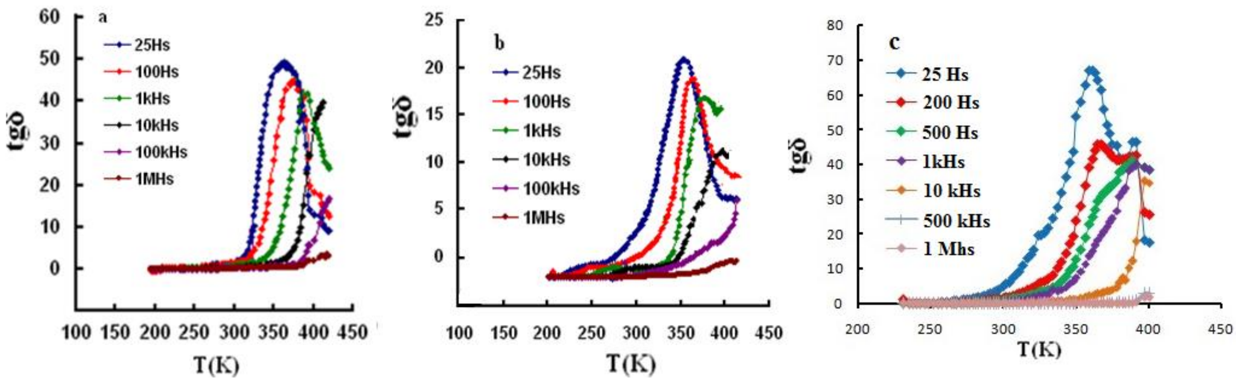

Fig.2. Temperature dependences of the dielectric loss tangent of the TlS crystal at frequencies the γ-irradiation doses are a- 0; b- 0.25; c-0.75 MGy.

The temperature dependence of the dielectric loss tangent of TlS crystal was studied for various frequencies and performed perpendicular and parallel to the ***c*** axis shown in fig.2. As shown in figure 2 the measuring field frequency f increases, tgδ(T) peaks shift to higher temperatures, while the values tgδ(T) decrease. The dependence of the temperature of the maximum on the measuring field frequency indicates the relaxed nature of the anomaly. The latter implies the existence of electric charges in the lattice, weakly bound to it. This suggests that the polarization in the TlS crystal is of a relaxation nature. To describe the permittivity relaxation peak, it is convenient to use the rapidly damping oscillator model [4]. The model considers the motion of n particles with the charge e in potential wells with the distance a between their minima and barrier height W. The natural oscillation frequency (ν) of particles in the well is much lower than the frequency of particle hopping between minima $(2\nu e^{-\frac{W}{kT}})$.

Figure 3 shows the temperature dependences of the frequencies of the maximum dielectric loss tangents (f_{max}) for the TlS crystal (in two measurement configurations, perpendicular and parallel to the ***c*** axis).

It is known that the temperature relaxation maximum (ε) is preceded by the tgδ maximum. Indeed, the latter is detected in $TlGaTe_2$ [5], and it is more easily studied experimentally since it appears inconvenient frequency ranges (500 Hz–1 MHz) and at low temperatures (200–450 K). Disregarding the through conductivity which is still insignificant in this temperature range, the anomaly of the dielectric loss tangent can be described by the expression from [6].

The extreme in temperature for tgδ is sought under the condition $\frac{f}{2\nu} << 1$ and $\frac{2E}{kT} >> 1$ which leads to the equation for the temperature maximum $\ln\frac{2\nu}{f_{max}} = \frac{E}{kT}$ from whence $f_{max} = 2\nu e^{-\frac{E}{kT}}$

The straight line extrapolation to $1/T$ determines the natural oscillation frequency in the potential well; the values for the two measurement configurations are $\nu_{II} = 4 \times 10^{12}$ Hz and $\nu_{\perp} = 3 \times 10^{12}$ Hz, which corresponds to the terahertz spectral region coinciding with the region of low frequency phonon modes of the vibrational spectrum of the TlS crystal [7].

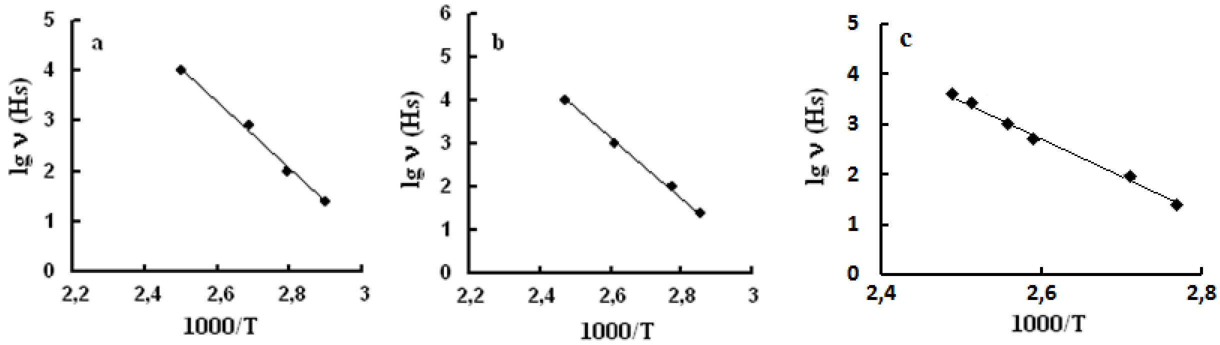

Fig. 3. Frequency of the relaxation maximum of the dielectric loss tangent as a function of the inverse temperature for TlS, the γ-irradiation doses are a- 0; b- 0.25; c-75 MGy.

The TlS compound structure can be presented as consisting of two subsystems: a rigid subsystem of negatively charged chains ($Tl^{3+}S_2$) lying in the (001) plane and a more mobile system of Tl^+ ions [8]. As follows from crystal-chemical considerations, Tl^+ cations should be the most mobile in the TlS structure. As noted above, the temperature dependence $\lg f_{max}$ in the case of straight line extrapolation to $1/T \rightarrow 0$ appears in the region of low frequency phonons in the phonon spectrum of the TlS crystal.

The space groups A_{2u} and E_u of these phonons [7] correspond to the vibrations of heavy Tl^{1+} atoms. Thus, specifically, thermal vibrations of the thallium subsystem and phonons with the space groups A_{2u} and E_u (vibrations of Tl^{1+}ions)result in the fact that the vibrational energy appears above the potential barrier after overcoming which the thallium subsystem "melts". In this case, the superionic transition occurs of the vibrational spectrum of the TlS crystal in the far infrared region [7] in the case of the light wave electric field vector **E** parallel to the tetragonal *c* axis detected the vibration whose frequency was below the lowest frequency phonon mode of the space group A_{2u}. This vibration was attributed to the liberation vibration of chains $(Tl^{3+}S^{2}{}_{2})^{-}$ during the superionic transition of the system, since the Tl^{+} sublattice begins to melt exactly at this temperature. In this case, the bond between the chains and Tl^{+} weakens, which is the cause of the libration vibrations of chains. We note that these low frequency vibrations are observed only in the $\mathbf{E} \parallel c$ configuration. Thus, proceeding from crystal-chemical considerations and the temperature dependence of the frequency of the maximum f_{max}, it can be assumed that the superionic transition of the TlS crystal is favored to the greatest extent by Tl^{+} ions mobility. This makes it possible to attribute the described vibration process to Tl^{+} cations.

Thus, in our opinion, the stepwise anomaly in the curves σ(T) (Figs. 1a and 1b) is mostly caused by Tl^{+} ion diffusion via vacancies in the thallium sub-lattice of the TlS crystals. This change results from the phase transition accompanied by disordering (melting) of the Tl sub-lattice of the TlS crystals. Such a pattern in the conductivity is typical of superionic conductors [9].

The activation energies ΔE_a were determined as $\Delta E_{aII=}$ 0.05 and $\Delta E_{a\perp=}$ 0.07 eV (initial sample) and $\Delta E_{aII=}$ 0.02 and $\Delta E_{a\perp=}$ 0.03eV (irradiated with a dose of 25Mrad) for measurements parallel and perpendicular to the tetragonal *c* axis, respectively. As is known, the ionic disorder in superionic crystals depends not only on the temperature but also, in the general case, can vary under external fields.

4. Conclusions

The results obtained show that the electronic conductivity component dominates in TlS at temperatures below 300 K. As the temperature further increases (above 300 K), a stepwise increase in the conductivity is observed, which is associated with an increase in the ionic component caused by the disordering of the Tl^{+} cations sub-lattice. The data obtained allow the determination of the hopping activation energy and its vibration frequency at which hopping over the potential barrier is possible. This frequency is determined by constructing the dependence $\lg f_{max}$ on $1/T$.

The vibration frequencies appeared to be 0 Mrad - $\nu = 4 \times 10^{12}$ Hz, 25 Mrad - $\nu_{\perp} = 3 \times 10^{12}$ Hz, 75 Mrad - $\nu_{\perp} = 2 \times 10^{12}$ Hz which corresponds to the terahertz region of the infrared spectrum and spans the low frequency vibrational spectrum of the TlS crystal. It is assumed that the Tl^{+} sub-lattice begins to melt and the bond between the chains and Tl^{+} becomes weaker during the superionic transition of the system; in this case, libration vibrations of chains $(Tl^{3+}S^{2-}{}_{2})^{-}$are possible.

References

1. R.M. Sardarly, O.A. Samedov, A.P. Abdullaev,F.T. Salmanov, O.Z. Alekperov, E.K. Guseinov, andN.A. Alieva, Semiconductors 45, 1387 (2011).
2. R. M. Sardarly, O. A. Samedov, A. P. Abdullaev,E. K. Guseinov, F. T. Salmanov, and G. R. Safarova,Semiconductors44, 585 (2010).
3. S. Parfen'eva, A. I. Shelykh, A. I. Smirnov, A.V. Prokof'ev, V. Assmus, Kh. Misiorek, Ya. Mukha, A. Ezhovskii, and I.G. Vasil'eva, Phys. Solid State 45, 2093 (2003).
4. A. B. Lidiard, in Handbuch der Physik, Ed. by S. Flьgge(Springer, Berlin, 1957), p. 246.
5. R. M. Sardarly, O. A. Samedov, A. P. Abdullaev,F. T. Salmanov, O. Z. Alekperov, E. K. Guseinov, andN. A. Alieva, Semiconductors 45, 1387 (2011).
6. S. Yu. Stefanovich, L. A. Ivanova, and A. V. Astaf'ev,Ionnic and SuperionicConductiviity in Segnetoelectics,Review, Ser. Scientific_TechnicalForecastings in Phys_icochemical Researches (NIITEKhIM, Moscow,1989) [in Russian].
7. A. M. Panich and R. M. Sardarly, Physical Properties of the Low Dimensional A3B6 and A3B3 Compounds (Nova Science, New York, 2010).
8. V. D. Muller and H. Z. Hahn, Anorg. Allgem.Chem.438, 258 (1982).

ДИЭЛЕКТРИЧЕСКАЯ РЕЛАКСАЦИЯ В γ-ОБЛУЧЕННЫХ КРИСТАЛЛАХ TlS

С.М. Гахраманова

Резюме: Исследованы температурные зависимости проводимости в *γ*-облученных кристаллах TlS. Обсуждаются возможные ионной проводимости, беспорядка, и электрической неустойчивости в кристаллах TlS.

Ключевые слова: γ-радиация, ионная проводимость, цепочечная структура.

γ-KVANTLARLA ŞÜALANDIRILMIŞ TlS KRİSTALINDA DİELEKTRİK RELAKSASİYA

S.M. Qəhrəmanova

Xülasə: γ-şüalara məruz qalmış TlS kristalının keçiriciliyinin və dielektrik xassələrinin temperatur asılılığı öyrənilmışdir. TlS kristalında, ion keçiriciliyinin, nizmsızlıq və elektrik dayanıqsızlığının mümkün mexanizimləri müzakirə edilmişdir.

Açar sözlər: γ-şüalanma, ion keçiriciliyi, zəncirvari quruluş.