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DIELECTRIC PROPERTIES OF $TlInS_2$(10%C) COMPOUND IRRADIATED WITH GAMMA QUANTA

O.A. Samadov[1], Kh.B. Orujova[1], N.M. Mehdiyev[1,3], A.I. Najafov[2], S.F. Samadov[1], R.N. Mehdiyeva[1], T.I. Kerimova[1]

[1]Institute of Radiation Problems of Ministry of Science and Education, Azerbaijan
[2]Institute of Physics of Ministry of Science and Education, Azerbaijan
[3]Azerbaijan State Oil and Industry University of Ministry of Science and Education, Azerbaijan
oktaysamedov9@gmail.com

Abstract: There are the same anomalies at temperatures T=410K, T=515K and T=571K in the temperature dependence of the dielectric permittivity (ε(T)) in the crystal $TlInS_2$<10%C>. It is shown that the experimental points of the ln(ε) dependence are collected on a straight line, which is typical for the ionic conductivity, and their activation energies are determined (ΔEa_1=0.54eV, ΔEa_2=0.32eV, ΔEa_3=0.22 eV). The activation energy of the hopping (ΔE=0.24 eV) and the oscillation frequency $\nu=8.10^{12}$ Hz were determined from the frequency dependence of the tangent tgδ(T) of the loss angle. At the same temperature, in $TlInS_2$<5%C> crystal, the permeability in the "c" direction is 34.5 times higher than that of the $TlInS_2$ crystal. It is also shown that the numerical value of the permittivity increases at radiation doses of 0-80Mrad and the temperature range related to ionic conductivity expands.

Keywords: ion conductivity, permeability, activation energy, radiation dose, gamma quanta, anomaly

1. Introduction

As is known, the $TlInS_2$ compound belongs to $A^3B^3C_2^6$ type semiconductor compounds, in which several consecutive ferroelectric and incommensurate phase transitions are observed at low temperatures [1-3]. For the first time, phase transitions were observed in $TlGaSe_2$ and $TlInS_2$ crystals at temperatures above 300K. The electrical conductivity in these phases was shown to be ionic [4, 5]. Also, in [6], there are some anomalies in the temperature dependence of the dielectric permittivity ε(T) in the compound $TlInS_2$<5%C> at temperatures (T) T=370K, T=415K, and T=532K. It was shown that the experimental points are collected on a straight line in the dependence of ln(ε), which is characteristic of ionic conductivity and their activation energies were calculated. The results obtained for tgδ(T) show that as the frequency of the measurement field increases, the tgδ(T) peaks are regularly shifted to higher temperatures and the value of tgδ decreases. The activation energy of the hopping (ΔE=0.24eV), and its oscillation frequency $\nu=8.10^{12}$ Hs were determined.

This study aims to investigate the dielectric properties of $TlInS_2$<10%C> crystal in the temperature range 300-600K, frequency range 25-10^6 Hz, and radiation doses 0-80Mrad.

2. Methods of the experiment

$TlInS_2$<C> single crystals were grown by the Bridgman-Stockbarger method. For measurements, 5×2×2×2 mm samples were used. Anisotropy of dielectric properties was not observed in the (001) plane, so electrodes were located on the surface of the crystals in the direction perpendicular to the layers. The silver paste was used as a contact. The complex dielectric permittivity and impedance were measured with an E7-12 AC bridge in the frequency range 25-106 Hz using a copper-constantan thermocouple at a step of 0.1 K/min.

3. Experimental results and discussion

Figure 1 shows the temperature dependence of the dielectric constant ε(T) of the $TlInS_2$ (10%C) compound above room temperature. There are anomalies in the ε(T) dependences for $TlInS_2$<10%C> crystals at temperatures T=410K, T=515K, and T=571K. As can be seen from Figure 1, dielectric dispersion is observed depending on the measurement frequency and the characteristic form of ε'(T) dependences corresponds to ionic conductivity and is determined by the following equation [7]:

$$\varepsilon = \varepsilon 0 \cdot \exp(-\Delta Ea / k\, T) \qquad (1)$$

At the same time, ln(ε)-1000/T dependence was established and the activation energies were calculated. In the ln(ε)-1000/T dependence, the experimental points are collected on a straight line and the dependence line changes. This is typical for ionic conductors, as we know from the literature. The activation energies were calculated from the ln(ε)-1000/T dependence (ΔEa_1=0.54eV, ΔEa_2=0.32eV, ΔEa_3=0.22 eV).

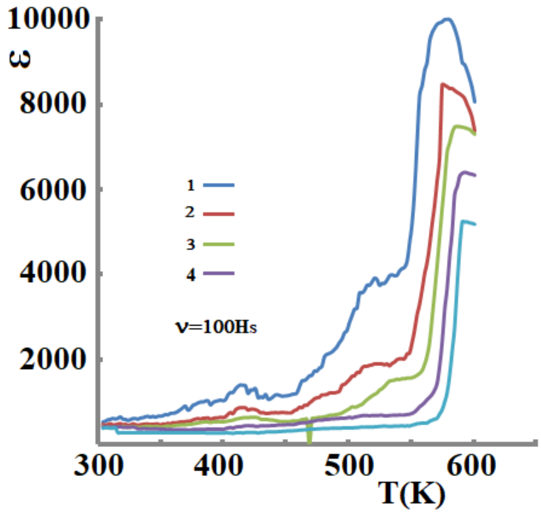

Fig. 1. Temperature dependence of permittivity ε(T) of $TlInS_2$ (10%C) crystal: 1 - 100Hz; 2 - 200Hz; 3 - 500Hz; 4 - 1kHz; 5-10kHz

Figure 2 shows the temperature dependence of the tangent of the dielectric loss angle (tg(T)) for the $TlInS_2$ (10%C) crystal. The activation energies of the relaxations were calculated from the displacement of the peaks of the tangent of the dielectric loss angle in the direction of increasing temperature depending on the measurement frequency: $E_a = \{kT_{peak1}\, T_{peak2}/(\, T_{peak2} - T_{peak1})\}\ln(\nu_2/\, \nu_1)$ (2).

Here, κ is Boltzmann constant, T_{peak1}, T_{peak2} – temperature of peaks, ν_1, ν_2 – measurement frequencies, respectively.

These results are consistent with those obtained in [8-11]. In these studies [8-11], it was shown that the conductivity in $TlInS_2$, $TlGaSe_2$, $TlInSe_2$, $TlInTe_2$, and $TlGaTe_2$ crystals above 300 K is mainly ionic. In the thallium sublattice, Tl+ ions diffusing into the gaps between $In^{3+}S_2^{2-}$, $Ga^{3+}Se_2^{2-}$, $In^{3+}Te_2^{2-}$ and $(Ga^{3+}Te^{2-}{}_2)^{-}$ $(Ga_3+Te^{2-}{}_2)^{-}$ nanochains were found to play a key role in ionic conductivity. The dielectric anomalies of a relaxation nature have been shown to be due to the presence of weakly bound electric charges in the crystal lattice. According to our investigation, the transition to the ionic state in $TlInS_2$, $TlGaSe_2$, $TlInSe_2$, $TlInTe_2$, and $TlGaTe_2$ crystals is due to Tl+ dipoles in $In^{3+}S_2^{2-}$, $Ga^{3+}Se_2^{2-}$, $(In^{3+}Te^{2-}_2)^{-}$, $(Ga^{3+}Te^{2-}_2)^{-}$ chains. This is caused by the melting of the thallium sublattice and the hopping of Tl+ ions from one localized state to another.

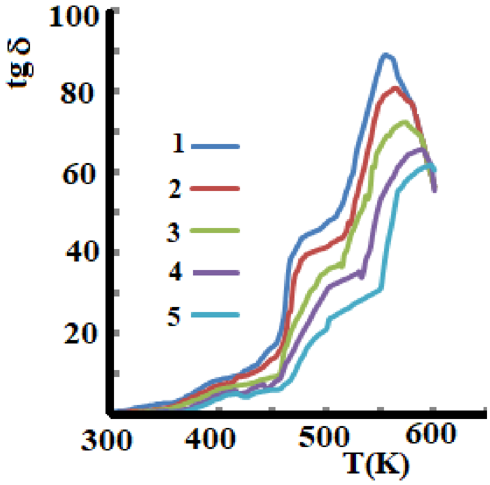

Fig. 2. Temperature dependence of dielectric loss angle tangent (tg(T)) for $TlInS_2$ (10%C) crystal: 1 - 100Hz; 2 - 200Hz; 3 - 500Hz; 4 - 1kHz; 5 - 10 kHz

In this case, a question arises about the place of localization of carbon atoms.

The high electronegativity of carbon atoms does not allow replacing indium atoms in the $TlInS_2$ compound. In all cases of substitution of indium with other substituent elements (B, Al, Mn, Cr, etc.), the dependence of ε(T) for this group of additives takes a typical characteristic of phase transitions. A decrease in the temperature of phase transitions is also observed [12].

In the case of a chaotic distribution of carbon atoms in the TlInS2 lattice, there should be a sharp decrease in the transparency of the crystals due to the formation of different types of additive levels in the crystals, which is not observed in this case. Using complex physicochemical methods of analysis, it has been determined that ~10 at.% carbon is dissolved in the $TlInS_2$ compound in monoclinic modification. $TlInS_2$ single crystals grown with 10 at.% carbon are transparent and light brown in colour, unlike the originals (the original colour is light yellow).

Due to the crystal-chemical parameters, additional carbon atoms can occupy the octahedral spaces between InS_4 tetrahedra within the tetrahedral complex of the $TlInS_2$ monoclinic lattice [InS10]. Due to the small size of carbon ions (0.2Å), the parameters of $TlInS_2$<C> crystals will differ from the parameters of the initial crystals. In this case, the introduction of an electropositive atom will weaken the bond with sulfur and thallium atoms, in this regard, after a certain value of temperature, an increase in the direction of the "c" axis (001) of the crystal, in electrical conductivity (relative to the ionic component of conductivity), as well as in permittivity in $TlInS_2$<C> crystals will be observed.

Figure 3 (1, 2, 3) shows the temperature dependence of the permittivity ε(T) for $TlInS_2$, $TlInS_2$ (5% C), and $TlInS_2$ (10% C) crystals (measurements were made in the "c" direction of the quadrilateral axis of the crystal). As can be seen from Figure 3, the permittivity of $TlInS_2$ (5% C) crystal in the "c" direction is 30 times higher than that of $TlInS_2$ crystal (at the same temperature). At the same time, the permittivity of $TlInS_2$ (10% C) in the same direction and at the same temperature is 1.15 times higher than $TlInS_2$ (5% C). The result obtained from the temperature dependence of the permittivity ε(T) in the direction of the tetragonal "c" axis confirms the assumptions made in point 3 above.

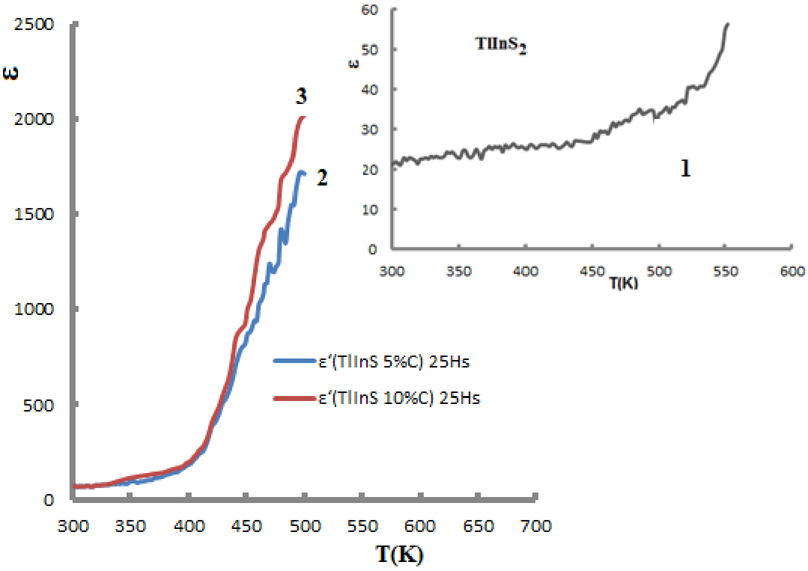

Fig. 3. Temperature dependence of the permittivity ε(T) of the crystals in the direction of the tetragonal "c" axis (measurements were made at a frequency of 25Hz):
1 - $TlInS_2$; 2 - $TlInS_2$ (5%C); 3 - $TlInS_2$ (10%C)

Figure 4 shows Cole-Cole diagrams for $TlInS_2$<10% C> crystal at temperatures of 350K, 480K, 550K, and 590K. As can be seen from Figure 4, monotone Cole-Cole diagrams were obtained at these temperatures. Monotonicity in the dependence of ε''(ε') is possible within the framework of Jonscher's law, which is universal based on the energetic approach for dielectrics [13]. In Johnscher's model, polarization is associated with the hopping of ions along long or short chains.

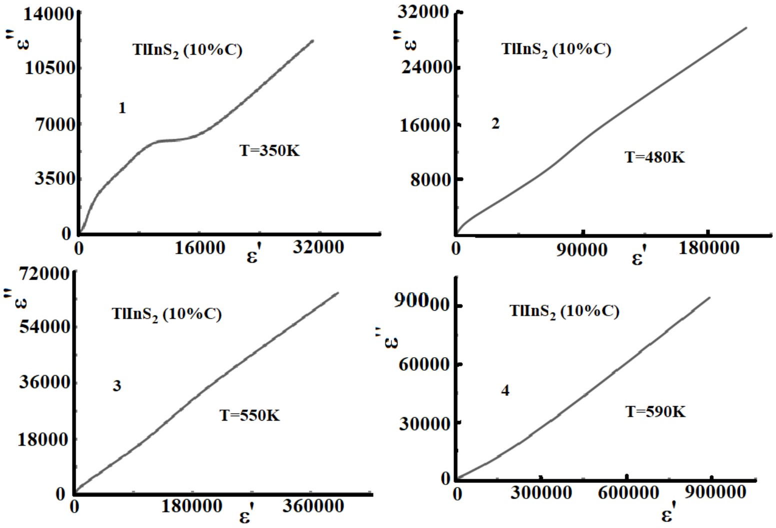

Fig. 4. Cole-Cole diagrams for $TlInS_2$<10% C> crystals (1 - 350K; 2 - 480K; 3 - 550K; 4 - 590K)

Figure 5 shows the temperature dependence ε(T) of the permeability of the $TlInS_2$ (10%C) compound irradiated with gamma quanta at doses of 20Mrad, 40Mrad, and 60Mrad (measurements were made at a frequency of 100Hz). As can be seen from Fig. 5, the value of permeability increases with increasing temperature, and its numerical value increases depending on the radiation dose, and the peaks change in the direction of increasing temperature. The reason for this is the increase in the concentration of free charge carriers depending on the radiation dose. The increase in permeability is related to the increase in the concentration of ionic charge carriers as a result of the increase in temperature and the generation of volume charges in the near field when applying an external potential difference to the electrodes.

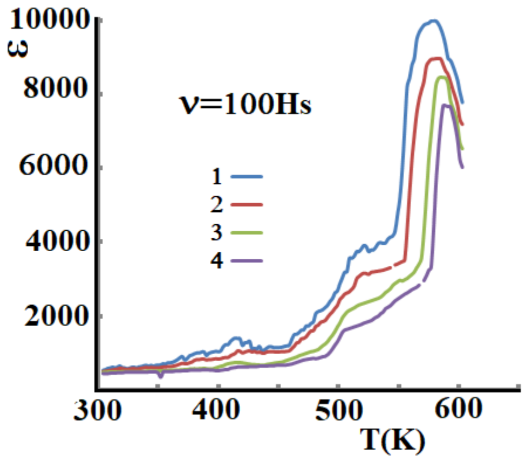

Fig. 5. Temperature dependence of permittivity ε (T) of $TlInS_2$ (10%C) crystal (measurements were made at a frequency of 100Hz): 1 - 0; 2 - 20Mrad; 3 - 40Mrad; 4 - 60Mrad

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ДИЭЛЕКТРИЧЕСКИЕ СВОЙСТВА СОЕДИНЕНИЙ $TlInS_2$(10%C), ОБЛУЧЕННЫХ ГАММА-КВАНТАМИ

О.А. Самедов, Х.Б. Оруджова, Н.М. Мехтиев, А.И. Наджафов, С.Ф. Самедов, Р.Н. Мехтиева, Т.И. Керимова

Резюме: В кристалле $TlInS_2$<10% C> наблюдались аномалии в температурной зависимости диэлектрической проницаемости (ε (T)) при температурах T=410K, T=515K и T=571K. Показано, что экспериментальные точки зависимости ln(ε) собраны на прямой, что характерно для случая ионной проводимости, и определены энергии активации (ΔEa_1=0.54 эВ, ΔEa_2=0.32 эВ, ΔEa_3=0.22 эВ).Определены энергия активации скачка (ΔE=0.24 эВ) и частота его колебаний ν= 8.10^{12} Гц из частотной зависимости тангенса угла потерь tgδ(T). При той же температуре диэлектрическая проницаемость в направлении «с» кристалла $TlInS_2$ <10% C> в 34.5 раза выше, чем у кристалла $TlInS_2$. Также показано, что численное значение диэлектрической проницаемости увеличивается при дозах облучения 0-80 Мрад и расширяется температурный интервал, связанный с ионной проводимостью.

Ключевые слова: ионная проводимость, диэлектрическая проницаемость, энергия активации, доза облучения, гамма-кванты, аномалия.

QAMMA KVANTLARLA ŞÜALANDIRILMIŞ $TlInS_2$(10%C) BİRLƏŞMƏSİNİN DİELEKTRİK XASSƏLƏRİ

O.Ə. Səmədov, X.B. Orucova, N.M. Mehdiyev, A.İ. Nəcəfov, S.F. Səmədov, R.N. Mehdiyeva, T.İ. Kərimova

Xülasə: $TlInS_2$<10% C> kristalında dielektrik nüfuzluğunun temperatur asılığıda (ε (T)) T=410K, T=515K və T=571K temperaturda anamaliyalar müşahidə olunmuşdur. Göstərilmişdir ki, ln(ε) asılılığının təcrübi nöqtələri düz xətt üzərində yığılır ki, bu da ion keçiriciliyi halı üçün xarakterikdir və aktivləşmə enerjiləri təyin olunmuşdur (ΔEa_1=0.54eV, ΔEa_2=0.32eV, ΔEa_3=0.22 eV). İtki bucağının tangensinin tgδ(T) tezlik asıllığından sıçrayışın aktivləşmə enerjisi (ΔE=0.24 eV), onun rəqs tezliyi ν=8.10^{12} Hz müəyyən edilmişdir.Eyni temperaturda $TlInS_2$ <10% C> kristalında “c” oxu istiqamətində dielektrik nüfuzluğu $TlInS_2$ kristalına nisbətdə 34.5 dəfə böyükdür. Həmçinin göstərilmişdir ki,0-80Mrad şüalanma dozalarında dielektrik nüfuzluğunun ədədi qiyməti artır və ion keçiriciliyinə aid olan temperatur intervalı genişlənir.

Açar sözlər: ion keçiriciliyi, dielektrik nüfuzluğu, aktivləşmə enerjisi, şüalanma dozası, qamma kvantları, anamaliya