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DIELECTRIC AND ELECTRICAL RELAXATION IN $TlInS_2$ CRYSTALS IRRADIATED BY γ- QUANTA

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Abstract: It has been studied impedance spectra of $TlInS_2$ crystals in alternating measuring field at temperatures of 100÷500K. Well-defined peak on the frequency dependence of the imaginary part of Z impedance is observed in the temperature interval of 215K-500K. It shifts to the high frequency area with increasing temperature. Under the influence of constant electric field from the kinetic changes in the electroconductivity of (σ) it is estimated ionic contribution conductivity (78% at T=470K). The experimental results show that the conductivity of the $TlInS_2$ crystal increases up to 82%. In the frequency range of 10-10^6Hz measured diagram in the complex plane of (Z-Z') is carried out with the using of equivalent circuits replacement method.

Keywords: Dielectric, semiconductor, electroconductivity, $TlInS_2$ crystal, frequency.

1. Introduction

Currently, $TlInS_2$ is one of the few semiconductor compounds, in which there is observed a sequence of inadequate and ferroelectric phase transitions (PT) [1-3]. According to neutron diffraction and X-ray studies [2,3], incommensurate phase, existing in the temperature of T_c = 201 K <T <T_i = 216 K, is characterized by the wave vector of ki = (δ, δ, 0.25), where δ = 0.012 - a parameter of inadequacy. Thus, in the temperature range of the inadequate phase existence of dynamics of the process is very complicated and very sensitive to defects of the structure. The nature of PT sequence in flaky compound of $TlInS_2$ is the subject of many studies. However, beliefs about the flow mechanism of PT in this crystal is not reached. The picture is complicated by the fact that, samples taken from different technological parties have different views of the temperature dependence of dielectric penetrability of ε(T) [4,5] In [6], we have shown that this feature is connected to the fact that the $TlInS_2$ compound belongs to the class berthollides, ie. in the homogeneity area has variable composition. Nevertheless, it can be considered as an established fact that $TlInS_2$ stoichiometric composition is improper ferroelectric with intermediate inadequate phase. It means that, in $TlInS_2$ with decreasing temperature it is realized the following sequence of PT; at 216 K there occurs a transition from the base paraphase to inadequate phase (symmetry of paraphase is set as $\mathbf{C^6_{2h}}$ [6]); feature on the curve of ε(T) at 201 K is identified as a transition to the ferroelectric commensurable structure with the occurrence of new inadequacy; at further cooling there occurs the final PT in commensurate phase [2].

Despite the above, it is not studied electrical and dielectric properties of $TlInS_2$ monocrystals in the paraelectric phase (T› Tc). The effect of radiation on these properties is not studied either.

In this paper we study the processes of ionic conductivity and the effects of volumetric-charge polarization in the $TlInS_2$ crystal. It is carried out the measurement of kinetic dependences of electroconductivity of σ (t) in a constant field and spectra of the complex impedance of Z*(f) and the module in the frequency interval of 10- 10^6 Hz and in the range of temperatures of 250-500K.

2. Experimental

$TlInS_2$ monocrystals were grown up by the modified Bridgman-Stockbarger's method. The samples in size of 5 × 2 × 2 mm were used for measurements. In the plane (001) anisotropy of dielectric properties was not observed, so, the electrodes deposited on the surface of the crystals in the direction of perpendicular layers. It was used silver paste as a contact. Measurements of the complex penetrability and impedance were carried out by means of the bridge of variable current of E7-20 in the frequency range of 25-10^6 Hz with the use of the copper-constantan thermocouple at 0.1 K / min step.

3. Results and discussion

Search of high-conductive ionic materials requires a comprehensive study of the dynamics of motion of the ions in a solid, which is conducted in interrelations with the synthesis conditions. For these purposes, the optimal method is impedance spectroscopy. The study of the response of system to a sinusoidal perturbation signal of small amplitude allows investigating in detail the processes of charge transfer in the material due to migration of ions and polarization effects. Modern methods of modeling processes, occurring in disordered systems, based on the data impedance spectroscopy allow broadening significantly our understanding of the diffusion mechanism of ions in them [7].

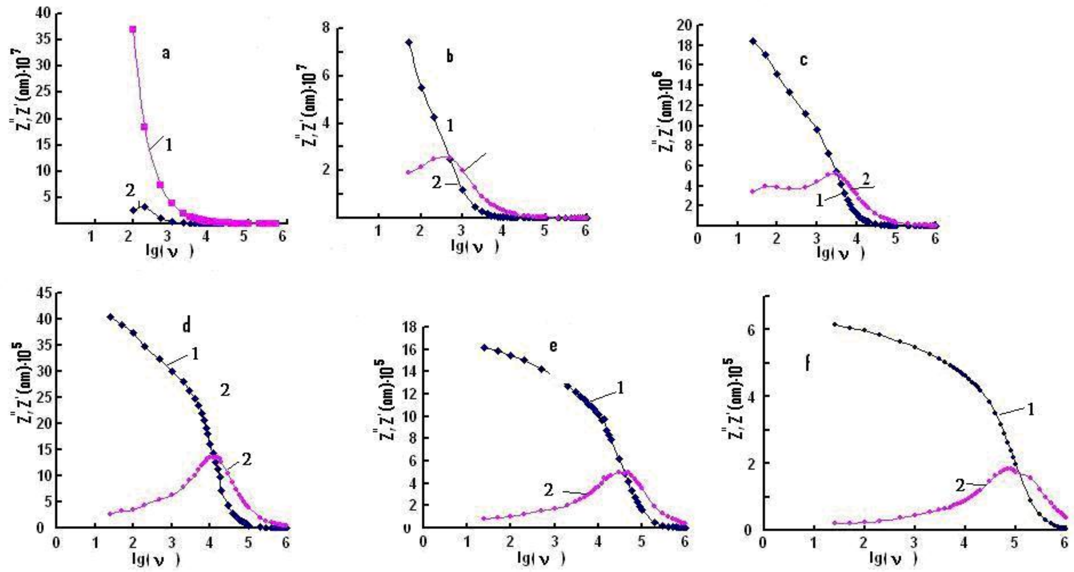

Fig.1 The frequency dependence of real (1) and imaginary (2) parts of the complex impedance of Z (f) of $TlInS_2$ crystal.a-200K; b-294K; c-340K; d-386K; e-429K; f-460K;*

In Fig. 1 it is shown for TlInS2 sample, isotherms of dependence on frequency of *Z*'– real and Z″- imaginary component of impedance. In Fig. 1 it is shown anomalies in the form of stepped variation of the real *Z′*(*f*) and maximum of imaginary Z″(f) part of impedance. Using the analysis results of frequency dependence of impedance, it can be determined the frequency range of alternating current, in which contribution of electrode impedance in experimentally determined parameters will be small [7-8]. By choosing frequency from this area, it is possible to make measurement of temperature dependence of electroconductivity and dielectric penetrability etc. and the obtained results will characterize true properties of this material.

It should be noted that the boundaries of indicated range may vary under the influence of external factors (for example, increase of temperature leads to a shift of border frequency to higher frequency).

As it is seen from Fig. 1, each curve is divided into three areas. The first low-frequency area shows a slow decline of the real parts of the complex impedance of Z*(f) and increase of conductivity with increasing frequency. This behavior is typical for the highly conductive ionic conductors and can be attached to the formation of space charge on blocking electrodes. The second mid-frequency area, in which the conductivity increases with frequency, occurs only at low temperatures. The third area - the frequency independent plateau, which is in the high frequency range and corresponds to the volume constant current conductivity. It should be noted that the plateau area is shifted from the low frequency area at low temperatures, in a high frequency area at high temperatures.

Fig. 2 shows the impedance spectra for $TlInS_2$ crystals which is constructed in the complex plane of (Z" = f (Z')). It highlighted two areas. The first, the main area corresponds to the contribution to the electrical response of the space-charge polarization of crystal. The presence of the second area, which is located in the right side of indicated semicircles, can be connected with the contribution of other electrical barriers in the sample. At high frequencies, Z" and Z' approach zero. In this case, the equivalent circuit can be represented by a contour with parallel connected capacitance of C and resistance of R (see inset to Fig.2). In the interpretation of experimental data the parameters of equivalent circuit can be calculated only when the maximum in dependence of $Z''(\omega)$, observed at $\omega_{\max} RC = 1$, in frequency range of 20 Hz < $\omega_{\max}$ > 1MHz available for measurement.

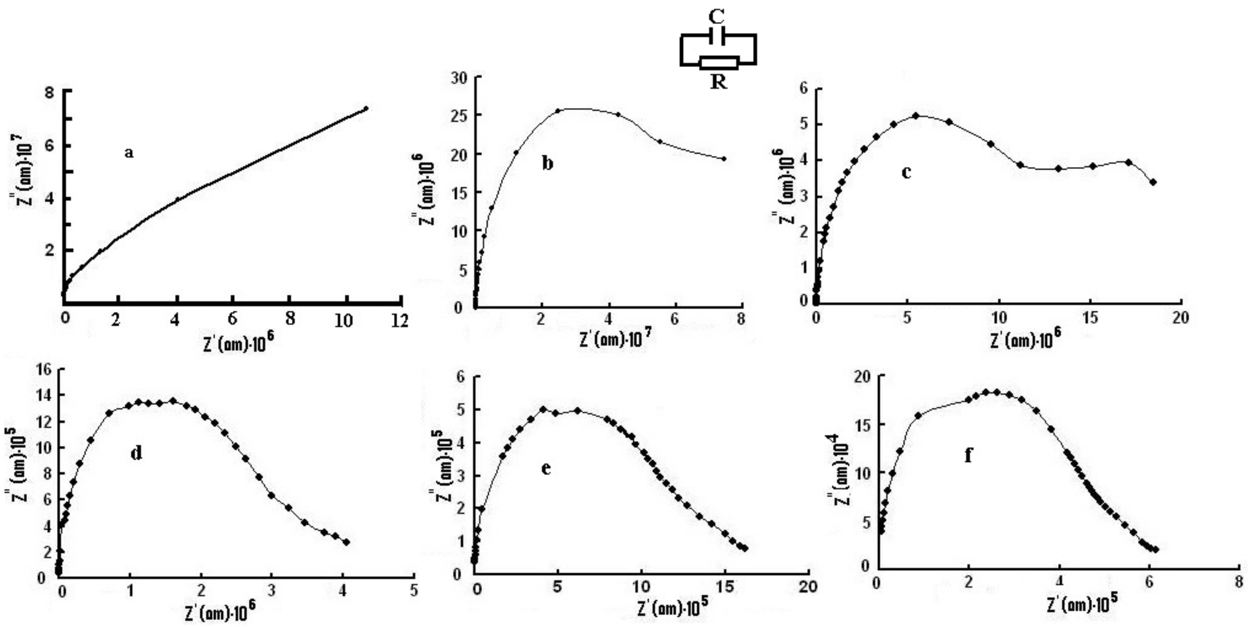

Fig.2. Impedance spectra for $TlInS_2$crystals. a-200K; b-294K; c-340K; d-386K; e-429K; f-460K.

The electronic component conductivity of $TlInS_2$ crystals was determined by means of the polarization method of Wagner. Wagner's method is based on the following phenomenon: a solid electrolyte with ionic or electron-ionic character of the charge transfer in the measuring of electroconductivity in constant current is observed change of conductivity over time. This phenomenon is caused by arise in a cell with sample polarization process, i.e. the formation on the border of the sample/electrode of double electric layer. As blocking electrodes retain ions, participating in the charge transfer on the border of the sample/electrode, mobile ions under the influence of a constant electric field accumulate in the negatively charge electrode, creating a concentration gradient in the sample volume [9-10].

The presence of a concentration gradient of positively charged ions leads to the appearance of diffused flow of ions, directed towards the opposite drift flow of ions side. In a stationary state drift and diffused flows compensate each other, and only the electron current flows through the sample. Thus, from the time dependence of the resistivity it can be determined the ratio of electron and ion components conductivity. In a constant field it was observed nonlinear decrease of electroconductivity over time, and decline of σ (t) occurs more rapidly at high temperatures (Fig. 3).

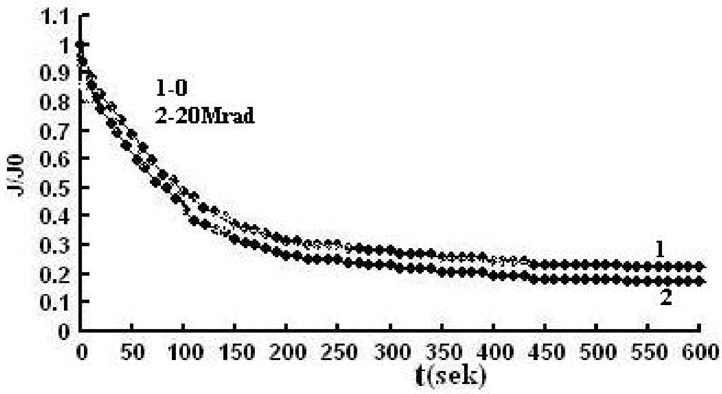

Fig. 3. Dependence of given electroconductivity on time of J (t) / J_0 at T = 470K: 1-0; 2-20Mrad.

Experimental results show that, 20Mrad irradiation doses of ionic conductivity of $TlInS_2$ crystal increases up to 82% (Fig.3 (2)). Unirradiated case the proportion of the ionic conductivity is 76% (Fig. 3 (1)).

In order to study the relaxation processes, flowing in the ion-conductive material, it is often used modular formalism. Complex electrical module can be represented as M * = 1 / ε * = M'+ jM". Representation of the impedance data as an electrical module is widely used by researchers in analyzing the electrical properties of ionic conductors, since it can be isolated the relaxation time of processes that contribute to the conductivity, at the same time, the effect of blocking electrodes is getting minimum [11]. On the frequency dependence of the imaginary part of the electric modulus of M" (Fig. 4) it is observed well defined peak in the temperature range of 200K-460K. It shifts to higher frequencies area with its increase.

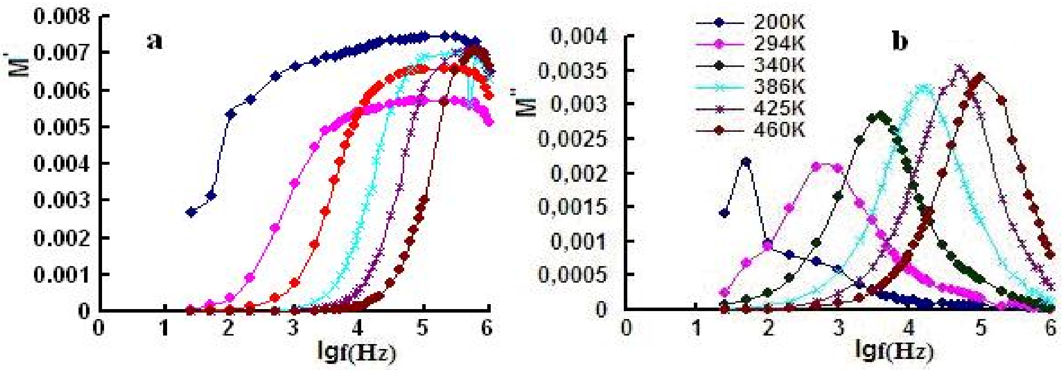

Fig. 4. The frequency dependence of the real (a) and imaginary (b) parts of the electric modulus of M" for the sample of $TlInS_2$ at temperatures: 200K; 294K; 340K; 386K; 423K; 460K.

M '(f) curves have usual S-shaped view, generally. However, they come to saturation more smoothly in high frequency area than in the low frequency area. From the value of the frequency, in which there is observed maximum (f_{max}) peak of the imaginary part of the electric module of M", it can be estimated so-called relaxation time of conductivity of τM in accordance with the formula of $2\pi f_{мак}\, \tau M = 1$.

For the complex electric modulus of M* it was drown up diagram of M″ from M' on the complex plane (Cole-Cole diagram). In Fig.5 it was represented M″ - M'- diagram of the complex electric modulus of M* for compound of $TlInS_2$. As it is seen from Fig.5 the frequency dependences of M″ (f) and M '(f) clearly identified in M″ - M'- diagram.

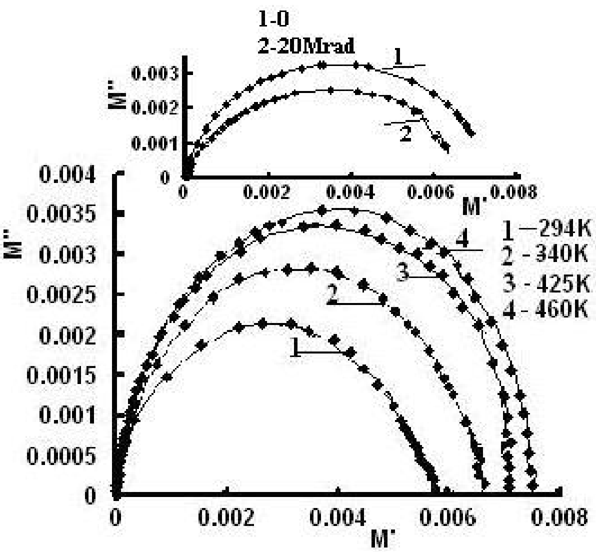

Fig. 5 M″ - M'- diagram for complex electrical module for $TlInS_2$ compound at different temperatures: 1-294K; 2-340K; 3-425K; 4-460K. The inserts to figure shows M″-M'-diagram at temperatures of 386K: 1-0; 2-20Mrad.

In the inserts to Fig.5, it was shown the dependence of M″ (M') as non-irradiated and irradiation of γ- quantum of $TlInS_2$ crystals at temperature of 386K. As it is seen in the inset of Fig.5, 20Mrad irradiation doses of $TlInS_2$ crystal of imaginary part of the electric module of M″ is killed.

Thus, in a constant field it is fixed a significant decrease of electroconductivity of σ with time. The obtained results show that at temperatures below 400K, it is dominated the electronic component in the conductivity. With further increase of temperature (above 400 K) it is observed discontinuous growth of conductivity, which is related to growth of ionic component. It is estimated ionic contribution of conductivity at temperature T = 470K (78%) under the influence of a constant electric field from kinetic changes of electroconductivity of (σ). Experimental results show that 20Mrad irradiation dose of ionic conductivity of $TlInS_2$ crystal increases up to 82%. The obtained results show that both irradiated and non-irradiated $TlInS_2$ RC equivalent combination scheme is the same. However, the frequency of maximum hologram increases compared irradiated with non-irradiated. It is connected with the increase of radiation defects of $TlInS_2$ crystal.

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ДИЭЛЕКТРИЧЕСКАЯ И ЭЛЕКТРИЧЕСКАЯ РЕЛАКСАЦИЯ В КРИСТАЛЛАХ $TlInS_2$ ОБЛУЧЕННЫХ γ–КВАНТАМИ

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Резюме: Исследованы импедансные спектры кристаллов $TlInS_2$ в переменном измерительном поле при температурах 100÷500К. На частотной зависимости мнимой части Z″ импеданса хорошо определяемый пик наблюдается при температурном интервале 215К-500К. С увеличением температуры он сдвигается в высокочастотную область. Под действием постоянного электрического поля от кинетического изменения электропроводности (σ) оценено ионный вклад проводимости (78% при Т=470К). Экспериментальные результаты показывают, что проводимость кристалла $TlInS_2$ возрастает до 82%. В диапазоне частот 10-10^6Гц измерение диаграммы в комплексной плоскости (Z″−Z′) осуществляется с использованием метода эквивалентных схем замещения.

Ключевые слова: Диэлектрик, полупроводник, электропроводность, кристалл $TlInS_2$, частота.

γ-KVANTLARI İLƏ ŞÜALANMIŞ $TlInS_2$ KRİSTALLARINDA DİELEKTRİK VƏ ELEKTRİK RELAKSASİYASI

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***Xülasə*:** $TlInS_2$ kristallarının impedans spektri dəyişən sahədə 100÷500K temperaturlarda tədqiq olunmuşdur. Z impedansının xəyali hissəsinin tezlik asılılığında dəqiq müəyyənləşdirilmiş pik 215K-500K temperatur aralığında müşahidə olunur. Temperaturun artması ilə pik yüksək tezlik sahəsinə doğru yerini dəyişir. Sabit elektrik sahəsinin təsiri altında elektrik keçiriciliyindəki (σ) kinetik dəyişikliklərdən ion qatqı keçiriciliyi qiymətləndirilir (78% T=470K temperaturda). Eksperimental nəticələr göstərir ki, TlInS2 kristalının keçiriciliyi 82%-ə qədər artır. 10-10^6Hz tezlik asılılığında kompleks müstəvidə ($Z''-Z'$) diaqramların ölçülməsi ekvivalent yerdəyişmə sxemi metodunun köməyi ilə həyata keçirilmişdir.

Açar sözlər: Dielektrik, yarımkeçirici, elektrik keçiricilik, TlInS2 kristalı, tezlik.