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RADIATION-STIMULATED CONVERSION TO SUPERIONIC STATE OF TlSe AND TlS CRYSTALS

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The electrical properties of TlSe and TlS compounds were studied in a constant and alternating measuring field when exposed to various doses of gamma radiation in the temperature range of 300…400 K. In a constant electric field, a decrease in electrical conductivity with time was detected. Complex impedance spectra were measured in the frequency range 20…10^6 Hz. It is shown that in the studied range of temperatures, frequencies and doses of γ-radiation, conductivity is ionic in nature. The electrical properties of TlSe and TlS crystals are determined by the conductivity of Tl^{+1} ions and the accumulation of charge carriers near the blocking silver electrodes.

INTRODUCTION

Ion transport in thallium chalcogenides was discovered by us relatively recently [1–4], among the crystals of which can be combined with the general formula $A^3B^3C^6_2$ and A^3C^6, the most promising in terms of creating supercapacitors and energy storage devices are the TlSe and TlS compounds. The impact of radiation on solids, through the induction of radiation defects, leads to a change in their phase states and physical properties. Currently, the main attention is paid to the physical nature of radiation-stimulated modifications of the properties of compounds and the creation of new structures.

The impact of radiation on solids leads to a change in their structural-phase states and physical properties. Radiation-stimulated methods of processing materials are based on a controlled change in electro-physical properties by creating structural defects in them that change the energy spectrum of the material and create new phases. Currently, the focus is on the physical nature of radiation-stimulated modifications of the properties of compounds and the creation of new structures.

The development of modern materials for the creation of ionistors, ion conductors, mini-accumulators, fuel cells and other devices, the operation of which is based on the properties of the conductivity of solid electrolytes (superionic conductors), depends on the search for new compounds that have an appropriate electronic and phonon spectrum, as well as an appropriate structure.

The characteristic features of superionic crystals are: the presence of mobile ions in the crystal, which should be more than the corresponding crystallographic positions; weak energy of ion disordering over positions; the existence of a connected grid of conduction channels.

The compound TlSe and TlS are isostructural, crystallizes in a volume-centered chain structure, symmetry D^{18}_{4h} (I4/mcm). X-ray phase studies of TlSe and TlS have shown that Tl atoms in its crystal lattice are located in two types of polyhedral with different valence states. Trivalent and monovalent thallium ions occupy two non-equivalent crystallographic sites. Tl^{3+} cations form covalent (sp^3) Tl-Se bonds and are located in the centers of the $Tl^{3+}Se_4^{2-}$tetrahedron, which are connected by common threads and form linear chains along the "c"-axis [5–8].

In the presented work, the results of studies of the temperature-frequency dependence of the ionic conductivity and impedance of the TlSe and TlS crystal under the influence of various doses of γ - radiation are presented.

1. EXPERIMENTAL TECHNIQUE

Synthesis of the TlSe and TlS compounds was carried out by direct fusion of high-purity initial components. Single crystals were grown by the vertical Bridgman method. Taking into account the high vapor pressure of selenium at the melting temperature, the synthesis of the compound was carried out in a two-zone mode. After synthesis, the sample was annealed at a temperature of 400 K. The synthesized samples were identified by differential scanning calorimetry (DSC) and X-ray phase analysis (XRD).

Single crystals were grown by the Bridgman-Stokbarger method. For measure the temperature dependence of the permittivity and electrical conductivity of TlSe and TlS materials. Measurements were made with an E7-25 digital immitance meter, at ranges of temperature into 100…450 K and frequency into 25…10^6 Hz.

2. RESULTS AND DISCUSSION

2.1. TEMPERATURE DEPENDENCE OF CONDUCTIVITY

Fig. 1 shows the temperature dependence of the electrical conductivity for TlSe and TlS crystals subjected to irradiation of γ-quanta. The inset to the figure shows the same dependence in the coordinates $\ln(\sigma \cdot T)$ on 1000/T. Measurements were made at doses γ-exposure 0; 0.25, and 0.75 MGy. As can be seen from the Fig. 1,a (curves 1, 2, 3) show a sharp increase in

conductivity with increasing radiation exposure dose for TlSe crystal.

As can be seen from Fig. 1,b (curve 2), when the TlS compound is irradiated, the electrical conductivity at a dose of 0.25 MGy decreases compared to the initial case, and at a subsequent dose of 0.75 MGy, the value of the conductivity starts to increase. The main role in these processes is played by the generation of ionized type defects (charged defects) as a result of radiation. That is, the reason for this is the creation of additional energy levels based on radiation defects in the forbidden zone of the crystal. The decrease in electrical conductivity of the crystal at a dose of 0.25 MGy is related to the recovery of radiation-stimulated structural defects. The increase in electrical conductivity in subsequent doses is due to the formation of new non-neutralizing radiation defects.

As can be seen from the inset to the figure, the experimental points of the temperature dependence of $\ln(\sigma \cdot T)$ on 1000/T in the region of a sharp jump in electrical conductivity fit well on a straight line, which for the case of ionic conductivity is described by the equation [9, 10]

$$\sigma \cdot T = \sigma_0 \exp(-\Delta E/kT).$$

Here ΔE is the activation energy of conduction, k is the Boltzmann constant.

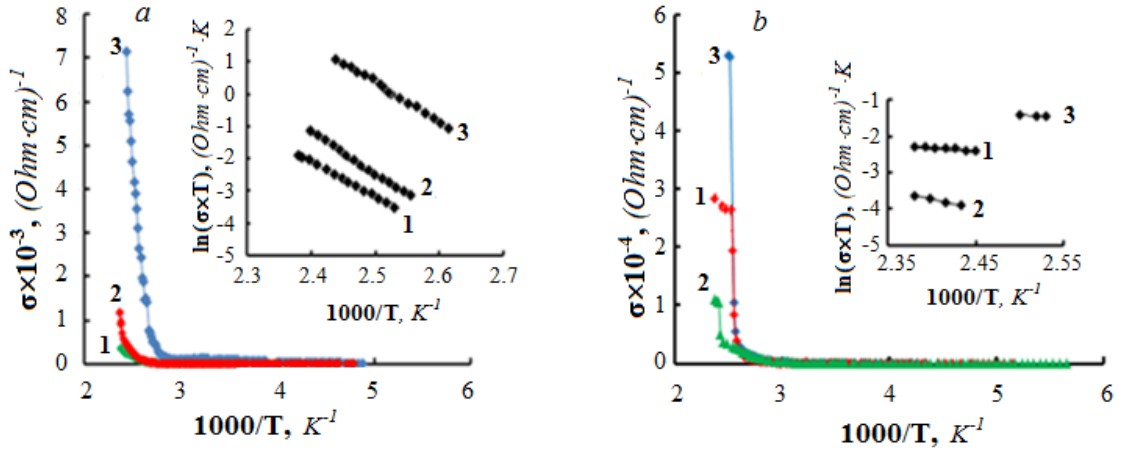

Fig. 1. Temperature dependence of the conductivity of the TlSe (a) and TlS (b) crystals subjected to irradiation of γ-quanta. The inset to the figures shows the same dependence in the coordinates ln(σ·T) on 1000/T. Curves 1–3 shows the doses of γ-irradiation, respectively 0; 0.25, and 0.75 MGy

The observed sharp increase in electrical conductivity in the TlSe and TlS crystals with increasing irradiation dose can be explained by a sharp increase in energy-equivalent crystallographic positions caused by radiation defects. In this case, the placement of mobile ions in the crystal becomes larger than the crystallographic octahedral positions themselves occupied by Tl^{+1} before radiation exposure. The compounds TlSe and TlS are isostructural. The crystallographic structure of the TlSe compound consists of anionic chains formed by $TlSe_4$ tetrahedral. Tl^{+1} ions are located in octahedral voids between $TlSe_4$ chains. It follows from crystal chemical considerations that the chain structure of TlSe crystals and the position of Tl^{+1} (Tl^{+1} is linked to chains of $TlSe_4$ tetrahedral by a weak van der Waals bond) ions are most conducive to the mobility of Tl^{+1}.

The inset of Fig. 1 shows the dependence of $\ln(\sigma \cdot T)$ on 1/T, at temperatures above the jump in conductivity for samples of TlSe and TlS crystals exposed to radiation doses: 0 (initial); 0.25, and 0.75 MGy. An increase in conductivity with an increase in the absorbed dose is observed. The presence of a chain structure of the TlSe and TlS crystals, as well as the existence of Tl^{+1} ions in octahedral voids, which are connected by a weak van der Waals bond with chains formed by $TlSe_4$ (TlS_4) tetrahedral, form conduction channels for Tl^{+1} ions.

2.2. TIME DEPENDENCE OF ELECTRICAL CONDUCTIVITY

The time dependence of electrical conductivity in a constant field in TlSe and TlS crystals irradiated with γ-quanta at doses of 0 and 0.25 MGy is studied. A constant electric field of intensity E ~ 1…10 V/cm was applied to the samples, and the current passing through the sample was measured at certain intervals [11, 12]. Silver contacts blocking the ionic contribution to the conductivity are used as electrodes.

In compounds with a mixed electron-ion character of charge transfer, when measuring the electrical conductivity at direct current, a time dependence of the conductivity is observed. The process is associated with the formation of a double electric layer in the near-surface layer of the sample. When blocking contacts are used as electrodes, mobile ions are delayed at the sample-electrode interface, as a result, under the influence of an electric field, a concentration gradient is created in the sample volume, which in turn leads to the emergence of a diffusion flow of ions directed in the direction opposite to the drift flow (ions). Thus, since the drift and diffusion fluxes of ions are compensated, a current flow through the sample, which is associated with charge transfer only by electrons.

Fig. 2 shows the time dependence of the conductivity of the electrochemical cell in the TlSe and TlS compounds irradiated with γ-quanta at doses of 0, 0.25 MGy at temperatures of 300, 350 K.

As can be seen from the figure, the time dependence of electrical conductivity in a constant field is nonlinear. Thus, at the initial moment of time, the value of conductivity decreases, and then it remains unchanged. As can be seen from the curves, the decrease of electrical conductivity σ(t) occurs faster at high temperature. Such a change is also observed after exposure to gamma rays. At a temperature of 350 K, the ion current passes ~ 20% in the initial samples, ~ 80% in the samples irradiated with a dose of 0.25 MGy for the TlSe crystal, and ~ 20% in the initial samples for the TlS crystal, and ~ 70% in the samples irradiated with a dose of 0.25 MGy.At the initial moment of time, the total current of ions and electrons flows, while in the stationary state charge transfer is carried out only by electrons. The time-dependent current drop in the constant electric field is due to the mutual compensation of the volume charges in the surface area of the blocking silver electrodes.

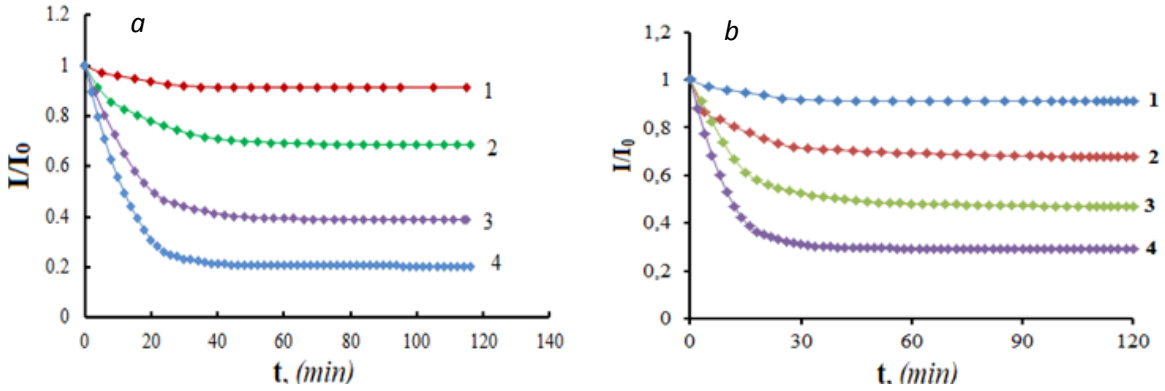

Fig. 2. Time dependence of electrical conductivity I/I_0 of TlSe and TlS compound. Measurements were carried out using silver electrodes at temperatures of 300 and 350 K and doses of 0, 0.25 MGy. Curves 1 and 2 – 300 K were 0 MGy, curves 3 and 4 – 350 K were 0.25 MGy

2.3. IMPEDANCE

The methods of impedance spectroscopy are used in the study of electro-physical processes occurring at the interface between an electrode and an ion-conducting material, the dielectric and transport properties of materials, the establishment of the mechanism of electrochemical reactions, and the study of the properties of porous electrodes. We have taken measurements real and imaginary parts of the impedance of the samples of the TlSe and TlS compounds at temperatures of 300, 350, and 400 K and doses of γ-irradiation 0; 0.25 and 0.75 MGy. The data obtained are presented as an impedance hodograph (Nyquist plots) on the complex plane. The measurements were made in the frequency range $20…10^6$ Hz.

In Figs. 3,a and 4,a show the dependence of (1) on Z"(Z') obtained at 300 K and 0 MGy, as can be seen from the figure, the dependence is a straight line. This dependence shows that at these temperatures and in the absence of radiation, the transfer of ions has not yet started, that is, the phase transition to the superionic state has not yet occurred.

Nyquist plots obtained at room temperature and after exposure to radiation at a dose of 0.75 MGy are shown in Figs. 3,b and 4,b (curves 1). As can be seen from these figures, the curve of the Nyquist graphs of the impedance of TlSe and TlS crystals is semicircular due to the effect of radiation dose.

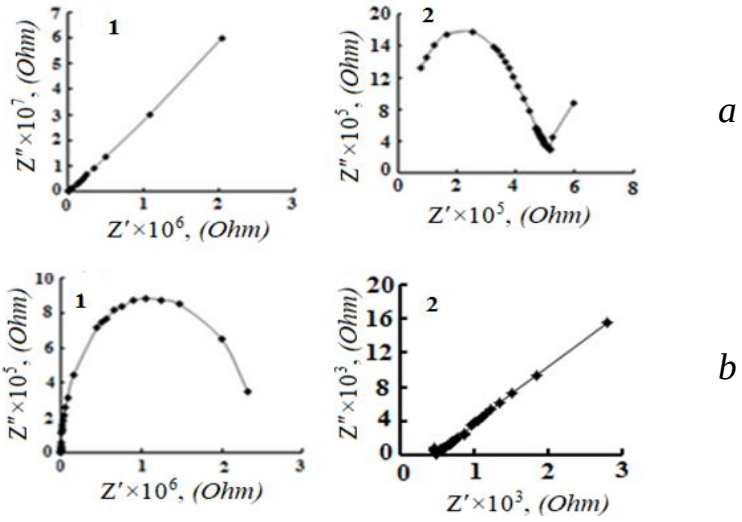

Fig. 3. Nyquist plots of the impedance Z''(Z') of the TlSe crystals. Measurements were made at temperatures: 1 – 300; 2 – 400 K, and at doses of γ-irradiation: a (1, 2) – 0 MGy; b (1, 2) – 0.75 MGy

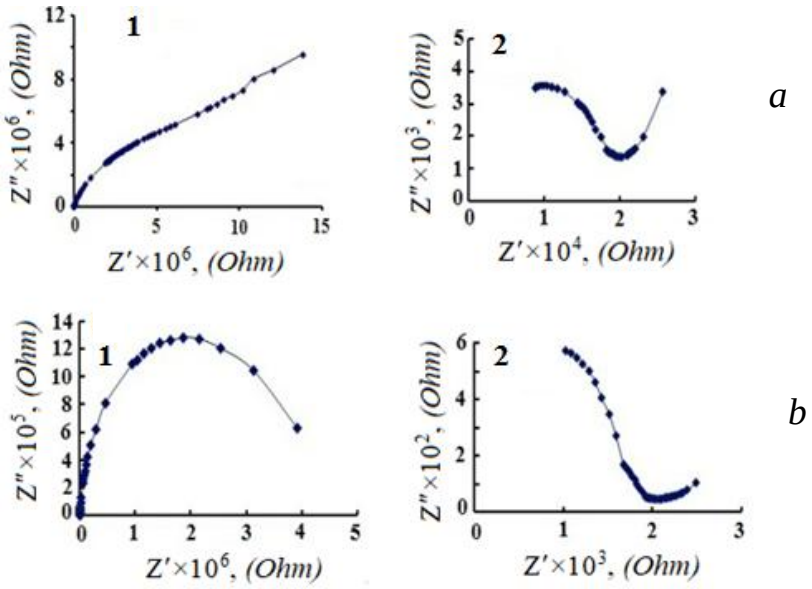

Fig. 4. Nyquist plots of the impedance Z''(Z') of the TlSe crystals. Measurements were made at temperatures: 1 – 300; 2 – 400 K, and at doses of γ-irradiation: a (1, 2) – 0 MGy; b (1, 2) – 0.75 MGy

As can be seen from Table and Figs. 3 and 4, the imaginary parts of the impedance show a maximum at frequencies f_{max} corresponding to the condition C_{eff} and R_{eff} and $\omega_{max} = 1$, where C_{eff} and R_{eff} are the effective parameters of the equivalent circuit, $\omega_{max} = 2\pi f_{max}$ is the circular frequency. On the non-irradiated samples in Figs. 3,a (curve 1) and 4,b (curve 1), the frequency f_{max} corresponding to the Z″ maximum increases with increasing temperature. As can be seen from Figs. 3,a (curve 1) and 4,a (curve 1), the dependence Z"(Z') is linear, such a dependence of the conductivity is characteristic of the zero-phonon (resonant) hopping conductivity of localized charge carriers.

Frequency values (f_{max}) corresponding to the Z"(Z') maximum and their relaxation times (τ), frequencies corresponding to the dispersion onset (f_{jump}) for TlSe crystals at 300; 350, and 400 K and doses of γ-exposure: 0; 0.25; 0.75 MGy.

Example	D, MGy	T, K	f_{max}, kHz	$\tau=1/2\pi f_{max}$, s	f_{jamp}, kHz
TlSe	0	300	–	–	2
		350	0.4	$3.9\cdot10^{-4}$	20
		400	30	$5.3\cdot10^{-6}$	60
	0.25	300	0.1	$1.5\cdot10^{-3}$	4
		350	0.6	$2.6\cdot10^{-4}$	30
		400	60	$2.65\cdot10^{-6}$	-
	0.75	300	1	$1.5\cdot10^{-4}$	50
		350	3	$5.3\cdot10^{-5}$	80
		400	–	–	–
TlS	0	300	–	–	–
		350	7	$1.05\cdot10^{-4}$	–
		400	600	$2.65\cdot10^{-7}$	–
	0.25	300	0.1	$1.5\cdot10^{-3}$	–
		350	0.8	$1.95\cdot10^{-4}$	–
		400	50	$2.16\cdot10^{-6}$	–
	0.75	300	0.4	$3.9\cdot10^{-4}$	–
		350	–	–	–
		400	–	–	–

Figs. 3,a,b (curve 2) and 4,a,b (curve 2) show the results of impedance measurements of TlSe and TlS crystals at 400 K and at irradiation doses of 0 and 0.75 MGy. Impedance Nyquist plots of TlSe and TlS crystals show "beams" in the low-frequency region. These observed rays indicate the presence of diffuse Warburg impedance [13]. As can be seen from curves 2 (see Figs. 3, 4) in non-irradiated samples at 400 K, an arc appears in the Nyquist plots, as well as a "beam" that we associate with diffuse ion transfer. In irradiated samples, the arc of the Nyquist plots shifts to the high frequency region. In this case, the beam in the impedance curve also moves to the high frequency region. Under irradiation with a dose of 0.75 MGy at a temperature of 400 K, the Nyquist plot arc continues to shift to the high-frequency region, and its measurement is beyond our experimental capabilities. At the same time, the previously observed "beam" remains in the low-frequency region of the Nyquist graphs, which we attribute to the polarization capacitance and resistance of the region near the electrode. That is, the Nyquist plots (curves 2) shown in Figs. 3,a,b and 4,a,b model the linear diffusion impedance known as Warburg diffusion impedance [13–16].

As can be seen from the curves of the impedance curves of the TlSe and TlS crystals shown in Figs. 3 and 4, "rays" in the low-frequency region of the diagrams appear both with an increase in temperature and with an increase in the irradiated dose. It is known [14] that the processes occurring at the interface between different conductive materials are described within the framework of the frequency response model, which is associated with the presence of both polarization resistances in the near-electrode region and polarization capacitance associated with charge accumulation in the region of the electrical double layer. The results obtained may indicate that TlSe and TlS crystals, at room temperature, and when irradiated with γ-rays at a dose of 0.75 MGy, experience a radiation-stimulated phase transition to the superionic state.

CONCLUSIONS

Temperature-frequency studies of the conductivity and impedance of the TlSe crystals subjected to various doses of γ-irradiation (0; 0.25, and 0.75 MGy) made it possible to establish the radiation-stimulating effect on the character of charge transfer in the crystal under study. It is shown that as a result of the impact of γ-quanta, in the bulk of the crystal, the nature of the conductivity changes. In samples not subjected to irradiation, charge transfer is carried out by electrons, and radiation exposure leads to the fact that the conductivity becomes predominantly ionic (superionic).

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РАДІАЦІЙНО-СТИМУЛЬОВАНА КОНВЕРСІЯ КРИСТАЛІВ TlSe І TlS У СУПЕРІОНИЙ СТАН

Р.М. Сардарли, Н.Н. Гаджієва, Н.А. Алієва, С.М. Гахраманова, Р.А. Маммадов

Електричні властивості сполук TlSe та TlS досліджені у постійному та змінному вимірювальному полі при впливі різних доз гамма-випромінювання у діапазоні температур 300…400 К. У постійному електричному полі виявлено зменшення електропровідності з часом. Спектри комплексного імпедансу вимірювалися у діапазоні частот 20…10^6 Гц. Показано, що у дослідженому діапазоні температур, частот та доз γ-випромінювання провідність має іонну природу. Електричні властивості кристалів TlSe і TlS визначаються провідністю іонів Tl^{+1} та накопиченням носіїв заряду поблизу блокуючих срібних електродів.