SUPERIONIC CONDUCTION IN $TlGaSe_2$ CRYSTAL INDUCED BY γ–IRRADIATION

R.M. SARDARLI, N.A. ALIYEVA, F.T. SALMANOV, A.P. ABDULLAYEV, M.Y. YUSIFOV, A.A. ORUDJEVA

Institute of Irradiation Problems of Azerbaijan National Academy of Sciences, B.Vakhabzade 9, AZ1143

The component frequency dependences of total complex impedance are measured in $25\div10^6$ Hz spectral region by impedance spectroscopy method and relaxation processes in $TlGaSe_2$ crystal before and after irradiation exposure by dose in 25 Mrad are investigated. The decrease of relaxation time in crystal after irradiation exposure is revealed. The obtained diagrams on complex plane ($Z''-Z'$) are analyzed using the method of equivalent replacement circuits. It is shown that the phase transition takes place with system transition into superionic state after γ – irradiation.

Keywords: impedance spectroscopy, γ – irradiation, equivalent circuit
PACS: 71.23.An

1. INTRODUCTION

Thallium chalcogenides of third group of Periodic table are characterized by laminar and laminar-chain structure and compounds based on these materials are widely researched [1-10] and also they are widely used in practices. The single crystals of these compounds are characterized by high sensitivity in IR, visible and roentgen region of electromagnetic wave spectrum and have the high tensosensitivity. Because of these properties, the compounds related to this group ($TlB^{III}C^{VI}{}_2$) are used and can be used as functional elements in optoelectronic systems as photoresistors, photodetectors, roentgenodetectors and nuclear radiation detectors and etc [11,12].

The electric conduction and dielectric properties of $TlGaTe_2$, $TlInSe_2$ and $TlInTe_2$ compounds at temperatures higher 300K are studied in works [2-4, 13-15]. The superionic conduction the mechanism of which is connected with Tl^+ ion diffusion is revealed. These compounds reveal the effect of negative differential resistance and voltage oscillation (the nature of which isn't established).

The decrease of electric conduction in electrostatic field is revealed at $TlInSe_2$ crystal investigation in constant and alternative electric field in temperature region 100-400K [18]. The complex impedance spectra are measured in $25\div10^6$ Hz frequency range, analysis of diagrams in complex plane ($Z''-Z'$) with use of method of equivalent circuits is carried out. These investigations show that electric properties of $TlInSe_2$ crystals are defined by hopping conduction in investigated interval of frequencies and temperatures and charge accumulation on limiting contacts takes place in this case. These investigations show that $TlGaTe_2$, $TlInSe_2$ and $TlInTe_2$ compounds have the enough high mobility of thallium ions and can be considered as materials with mixed electronic-ion conduction. Such conduction character shows on usage availability of these materials in the capacity of ionistors and accumulators.

The investigations of impedance characteristics of $TlGaTe_2$, $TlInSe_2$ and $TlInTe_2$ compounds in frequency region $25\div10^6$ Hz show that relaxation processes connected with charge transfer accelerate at increase of disorder degree. The crystal transition effect into superionic state induced by field is revealed in $TlGaTe_2$ crystal [15].

The analysis of earlier carried investigations shows that further investigations of thallium chalcogenide compounds joint by general formula $TlB^{III}C^{VI}{}_2$ presents is of big interest. The investigations of kinetic characteristics in $TlGaSe_2$ crystal are carried out with the aim of expansion of earlier carried investigations, understanding of superionic state nature and relaxation processes taking place there. The investigations are carried out before and after irradiation exposure by γ-quantums with energy≈1 MeV (1.17 and 1.33 MeV) on ^{60}Co at room temperature with use of impedance spectroscopy method.

2. EXPERIMENT

The solid solution samples are synthesized by alloying of initial components (purity not less 99.99) in evacuated quartz ampoules and their single crystals are grown up by Bridgeman modified method. The freshly cleaved samples in which "c" crystal axis is perpendicularly oriented to cleavage, prepared for investigation, have the rectangular form.

The condensers in which the plates of the investigated materials serve as dielectrics are prepared for measurements of temperature dependences of $TlGaSe_2$ crystal electric conduction. The capacitor plates are obtained by coating of argentum conducting contacts on the surface of cleaved plates. The sample electric properties are investigated by impedance spectroscopy method in frequency region $25\div10^6$ Hz. The electric conduction investigations are carried out by immittance measurer E7–25, the measurement precision is 0,1%. The samples are exposed by influence of γ–irradiation from standard irradiation source ^{60}Co after preliminary measurements. The irradiation dose is gradually accumulated by the means of the consistent expositions of γ–influence up to value 25 Mrad.

3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

As it is known, the impedance measurement data can be presented in the form of the hodograph impedance on

131 H.Javid ave, AZ-1143, Baku
ANAS, G.M.Abdullayev Institute of Physics
E-mail: jophphysics@gmail.com

complex plane. The obtained data are presented in the form of circular arcs which can be regular or irregular shapes. At the same time the equivalent replacement circuit from joint capacities and resistances describing the corresponding arc form. In such construction the current frequency in graphics isn't shown as a rule. The presence of the frequency dependences of impedance components in Bode diagram form allows us to detail analyze the spectral characteristics of real and imaginary impedance component.

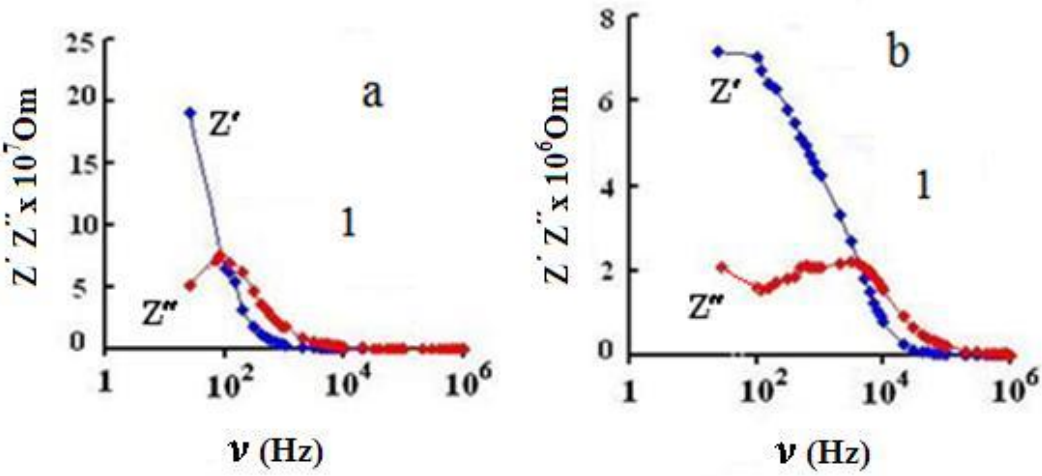

Fig.1. The frequency dependences of real (Z′) and imaginary (Z″) of impedance component for $TlGaSe_2$ sample. ***a*** figure are the measurements carried out before γ– irradiation and ***b*** figure are the measurements after γ– irradiation.

The frequency dependences of real (Z′) and imaginary (Z″) parts of impedance of $TlGaSe_2$ crystal are given in semilogarithmic scale in fig.1(a,b).

The presented dependences have the form corresponding to parallel equivalent replacement circuit. The measurements are carried out before and after γ – irradiation.

The frequency values (f_{max}), corresponding to Z″ maximum, (τ) relaxation times, frequencies (f_{jump}) corresponding to beginning of $TlGaSe_2$ frequency dispersion before and after γ–irradiation are shown in tables. The measurements are carried at room temperature.

Mrad	f_{max},kHz	$\tau=1/2\pi f_{max}$	f_{jump}, kHz
0	0.1	$1{,}6\cdot10^{-3}$	1
25	5	$3{,}18\cdot10^{-5}$	5 0

As it is seen from the figures, Z″ maximum value coincides with Z′ value at definite frequencies. This fact confirms that the hodograph arc (fig.2) describes the curve close to semicircle with maximum in intersection points of Z′ and Z″ and center situated on real axis. Such dependence type corresponds to parallel equivalent replacement circuit (fig.3a). Moreover, the charge transfer is characterized by same relaxation time.

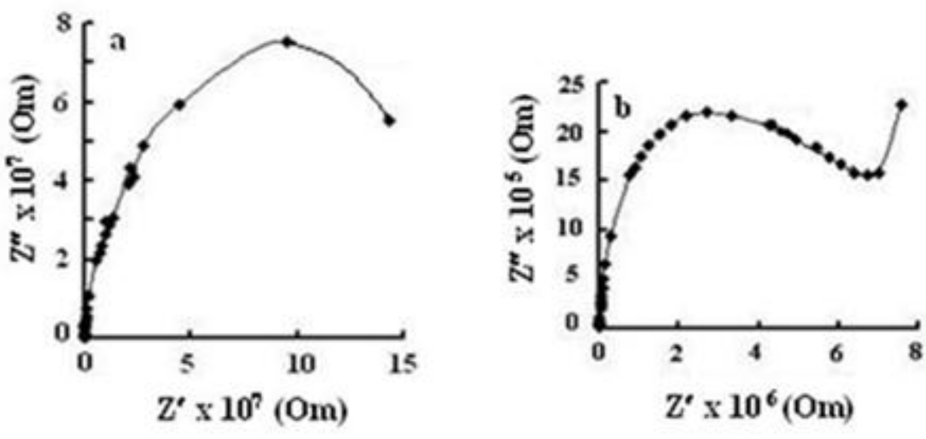

Fig.2. The diagram on complex plane (*Z″–Z′*) obtained on the base of fig.1. The figure **a** are the measurements carried out before γ– irradiation, figure **b** are the measurements after γ–irradiation.

The diagram on complex plane (Z''- Z') obtained on base of data fig.1 are presented in fig.2. The frequency values (f_{max}) corresponding to (-ImZ) maximum, relaxation times (τ), frequencies corresponding to frequency dispersion beginning (f_{jump}) for $TlGaSe_2$ samples before and after γ–irradiation, are given in table. As it is seen from the table, f_{max} frequency increase corresponding to Z'' maximum is observed. This means that charge transfer is accompanied by decrease of relaxation time (table). The spectrum analysis allows us to conclude that the relaxation process acceleration after irradiation influence is observed in $TlGaSe_2$ crystal samples.

As it is seen from fig. 1, the impedance imaginary parts reveal the maximum at f_{max} frequencies corresponding to condition $C_{eff}R_{eff}\omega_{max} = 1$, where C_{eff} and R_{eff} are effective parameters of equivalent circuit, $\omega_{max} = 2\pi f_{max}$ is circular frequency. The corresponding impedance hodographs of $TlGaSe_2$ crystal and the measurements are carried out at 300K before and after irradiation exposure by 25Mrad dose are given in fig.2. The top of hodograph arc corresponds to ω_{max} resonance frequency.

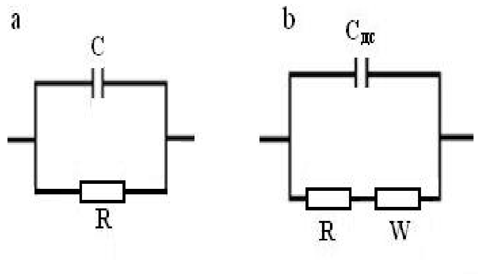

Fig.3. Equivalent circuit (***a*** is before γ – irradiation, ***b*** is after it) for electrode with capacity of C_{DL} double layer, W is Warburg diffuse impedance, R is sample resistance.

It is seen that arc has the form close to semicircle the center of which locates on real axis at measurements carried out before γ – irradiation; moreover, the charge transfer is characterized by same relaxation time. In this case the impedance hodograph of $TlGaSe_2$ crystal is qualitatively and quantitatively described in approximation of equivalent circuits with the help of impedance components of model electric circuit. Such hodograph form corresponds to homogeneous sample with low-ohmic and non-blocking contacts. The equivalent circuit of such hodograph is given in fig. 3***a***. The elements of equivalent circuit *R* and *C* can directly correspond to resistance and capacity of measurable sample.

The diagrams on complex plane (Z'' –Z') obtained from measurements after influence of γ–quantums, present themselves semicircles for one parallel RC–chain and beams in diagram low-frequency region (fig.2, curve ***b***). These beams on impedance diagram are probably connected with Warburg diffuse impedance on the basis of which the carrier diffusion doesn’t achieve the near-contact layer boundary in frequency range of applied sinusoidal signal. The crystal transition in superionic state is caused with system disorder in the result of irradiation influence can be responsible for appearance of Warburg diffuse impedance.

Earlier it has been shown in [2-4, 13-15] that the peculiarities connected with existence of ion conduction reveal at temperatures higher 300K in $A^{III}B^{III}C^{VI}_2$ crystal group. In this case Tl^{+1} ions diffusing in crystal can be responsible for existence of Warburg diffuse impedance in hodographs of investigated crystals after system transition in superionic state, moreover, the defects caused by irradiation influence are factor promoting ion mobility.

The observable difference in obtained hodographs and corresponding equivalent circuits can explain within framework of interaction theory between gamma quantums with substance.

As it is known [16], the irradiation influence on solid state leads to formation of non-equilibrium defects; this can be Frenkel couples, vacancies, interstitial atoms and etc. The weakening of beam intensity takes place at passing of γ –irradiation (in our case gamma quantum energy is ~1MeV) through the substance. The electrons which lead to defect formation in crystal lattice generate. The contribution in total scattering cross-section in this gamma-quantum energy region is the incoherent scattering on substance electrons (Kompton effect). The effective cross-section of Kompton scattering calculated per one atom proportionally to atomic number $\sigma'_c = Z\cdot\sigma_c$. As Tl is the largest atom in $TlGaSe_2$ crystal, then thallium atoms will be probable element which will shift. Note that the photonuclear reaction threshold isn’t achieved at gamma-quantum energy in ~1MeV.

4. IONIC CONDUCTION

The temperature dependence of electric conduction (σ(T)) for $TlGaSe_2$ crystal is given in fig.4). The measurements are carried out at electric field direction along crystal monoclinic axis, (**a**) is curve that represents the measurements carried out before the gamma irradiation, (**b**) is curve that represents the measurements carried out after gamma irradiation. As it is seen from the figure (**a** curve) the insignificant conduction increase at 450K is observed on crystals which aren’t exposured to gamma irradiation, however, the jump in σ(T) dependence and further conduction increase with activation energy 0.04eV at gamma influence 25 Mrad. As it is seen from figure insert the experimental points (in both before and after irradiation) of temperature dependence lnσ(T) in region of electric conduction strong jump well locate on direct line which is described by equation [17-19] for the case of ionic conduction:

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

here ΔE is electric conduction activation energy, k is Boltzmann constant.

The observable hopping change of electric conduction in $TlGaSe_2$ crystal exposured by gamma irradiation can be explained by strong change of ion number in states where they have the high mobility, i.e. phase transition in superionic state.

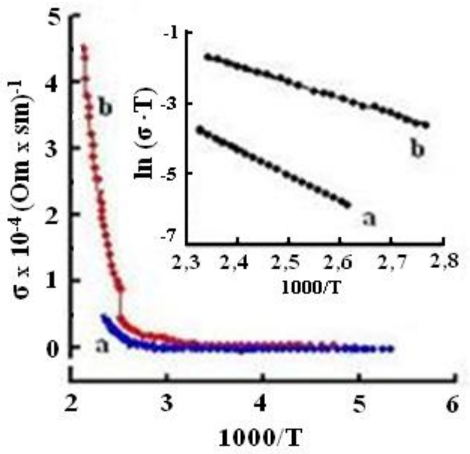

Fig.4. Temperature dependence of $TlGaSe_2$ crystal conduction in Arrhenius coordinates. ln(σ·T) dependence on 1000/T is given in insert. **a** curve represents the measurement results carried out before gamma irradiation, **b** curve represents the measurements after it.

$TlGaSe_2$ crystalline structure consists in anionic layers formed by Ga_4Se_{10} tetrahedrals which are consist in four $GaSe_4$ tetrahedrals [9]. Tl^+ ions locate in trigonal voids. It is supposed from chemical analysis of crystal that the layered structure of $TlGaSe_2$ crystal and Tl^+ ion position in trigonal voids mostly cause to thallium ion mobility.

The linear character of ln(σ·T) on 1/T is higher than temperature jump (insert to figure 1) shows the dominant character of ion conduction higher critical temperature. The presence of layers with weak Van-der-Waals interaction and also Tl^+ ion position in trigonal voids allows us to conclude that phase transition in superionic state caused by thallium ion diffusion by vacancies in thallium sublattice takes place. The gamma irradiation causes to disorder (melting) in thallium sublattice in $TlGaSe_2$ crystal. Such conduction is typical for materials with dominant ion conduction type [2,17-19].

4. CONCLUSION

The characteristic times of relaxation processes in $TlGaSe_2$ crystal before and after γ-irradiation are measured by impedance spectroscopy methods. The decrease of relaxation time in $TlGaSe_2$ after gamma irradiation is revealed. The energy loss mechanism in crystal in alternative field consists in both losses connected with through conduction and losses connected with relaxation polarization. The phase transition in superionic state at temperature 450K after γ-irradiation connected with disorder of thallium sublattice caused by irradiation influence, is revealed.

---

[1] *N. Mamedov, K. Wakita, S. Akita, Y. Nakayama.* ”1D- $TlInSe_2$: BandStructure, Dielectric Functionand Nanorods”, “Japanese Journal of Applied Physics” vol. 44, No.1B, 2005, pp. 1-6.

[2] *R.M. Sardarly, O.A. Samedov, A.P. Abdullaev, F.T. Salmanov, A. Urbanovic, F. Garet.* J-L. Japanese Journal of Applied Physics, 50 (2011) 05FC09 1-2.

[3] *P.M. Sardarly, O.A. Samedov, A. Sardarli, N.A. Aliyeva, R.Sh. Aqayeva, T. Musazade.* “Superionic Conduction and Specific Effects Induced by γ – Irradiation in Nanofibrous $TlGaTe_2$ Crystals”, “International Journal of Theoretical and Applied Nanotechnology”, Vol.1, Issue 1, 2012, pp.20-28.

[4] *P.M. Sardarly, O.A. Samedov, A.P. Abdullaev, F.T. Salmanov.* FTT, 2011, t.53, v.8, str. 1488-1492. (In Russian).

[5] *A.U. Sheleg, E.M. Zub, A.Ya. Yachkovskii, S.N. Mustafaeva and E.M. Kerimova.* “X-raydiffraction study of $(TlInSe_2)_{1-x}$ $(TlGaTe_2)_x$ crystal system” Crystallography Reports”, 2012, vol.57, no.2, pp.283-285.

[6] *S.N. Mustafaeva, E.M. Kerimova, S.S. Abdinbekov, L.N. Alieva, A.I. Hasanov, S.G. Jafarova*. “Electro physic sof $(TlInSe_2)_{0.1}$ $(TlGaTe_2)_{0.9}$” ICTRE-2012, N.68, pp.332-334.

[7] *K.R. Allakhverdiev, E.A. Vinogradov, N.M. Melnik, M.A. Nizametdinova, E.Yu. Salaev, R.M. Sardarly.* “Vibration Properties of TlSe” Phys.Stat.Sol.(b) 1978, v.87, pp.K115-K117.

[8] *R.M. Gasanly, A.F. Goncharov, B.M. Dzhavadov, N.M. Melnik, V.I. Tagirov, E.A. Vinogradov.* “Vibrational spectra of $TlGaTe_2$, $TlInTe_2$ and $TlInSe_2$ layer crystals” Phys. Stat. Sol.(b) 1980, v.97, pp.367-377.

[9] *A.M. Panich, R.M. Sardarly.* “Physical Properties of the Low Dimensional A^3B^6 and $A^3B^3C^6_2$ Compounds” <Nova Science Publishers> NY, 2010, p.310.

[10] *M.V. Belausov, P.M. Sardarly.* FTT, 1985, t.27, v.3 s.662-668. (In Russian).

[11] *E.Yu. Salaev, K.P. Allaxverdiev, Sh.G. Gas;mov, T.G. Mamedov.* Datchik gidrostaticheskogo davleniya. Avtorskoe svideetelstvo SSSR № 1182291, 1984. (In Russian).

[12] *I.V. Alekseev, S.V. Rozov*. Dedektor yadernogo izlucheniya. Patent № 80070, 2009. (In Russian).

[13] *R.M. Sardarly, O.A. Samedov, A.P. Abdullaev, E.K. Guseynov, F.T. Salmanov,* G.R. Safarova. FTT, 44, 610 (2010). (In Russian).

[14] *R.M. Sardarly, O.A. Samedov, A.P. Abdullaev, F.T. Salmanov,* O.Z. Alekperov, *E.K. Guseynov, N.A. Alieva*. FTT, 45,1441 (2011). (In Russian).

[15] *R.M. Sardarly, O.A. Samedov, A.P. Abdullaev, E.K. Guseynov, E.M. Godjaev, F.T. Salmanov*. FTT, 45, 1009 (2011). (In Russian).

[16] *V.V. Galavanov*. FTT, 1959, t.1, vip.3, s.432–441. (In Russian).

[17] *A.S. Nowick, A.V. Vaysleyb, I. Kuskovsky.* Phys. Rev. B **58**,8398 (1998).

[18] *Yu.Ya. Gurevich, Yu.I. Xarkach.* UFN, 136, 693 (1982). (In Russian).

[19] *Yu.I. Xarkach.* FTT, 23, 2190 (1981). (In Russian).

Recevied:08.02.2017