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INFLUENCE OF γ-IRRADIATION ON SUPERICONIC CONDUCTIVITY OF $(TIGaSe_2)_{1-x}$ $(TIInSe_2)_x$ SOLID SOLUTIONS

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Abstract: Samples of $(TIGaSe_2)_{1-x}(TIInSe_2)_x$ solid solutions are synthesized. The frequency dependences ($2*10^1$-10^6Hz) of components of the total complex impedance are studied by the impedance spectroscopy technique and relaxation processes are investigated depending on the composition of the $(TIGaSe_2)_{1-x}(TIInSe_2)_x$ solid solution in the solubility region (x=0-0.3). Corresponding diagrams on the (Z"-Z') complex plane are analyzed using the equivalent substitution circuit method. An anomaly in the temperature dependence of the electrical conductivity, which manifests itself in an abrupt increase in the conductivity, is found for the studied $(TIGaSe_2)_{1-x}(TIInSe_2)_x$ solid solution at 300K. This peculiarity is associated with the phase transition into the superionic state after 0.25 MGy gamma irradiation.

Keywords: solid solution, relaxation, impedance, conductivity

1. Introduction

Thallium chalcogenides of Group-III chemical elements of the periodic table have a chained and layered structure, while compounds based on these materials are studied widely [1-10]. They are highly sensitive in the IR infrared), visible, and X-ray spectral regions of electromagnetic waves and possess a high tensosensitivity. Due to these properties, compounds referring to the third group ($TIB^{III}C^{V}$) are used (and can be used) as functional elements in such an optoelectronic system as photoresistors, photodetectors, X-ray detectors, nuclear-radiation detectors, etc. [11,12].

The authors of [2-4, 3-5] studied the temperature- frequency dependences of the electrical conductivity and dielectric properties of $TIGaTe_2$, $TIInSe_2$ and $TIInTe_2$ compounds at above 300K. The character high mobility of thallium ions and can be considered as materials with mixed electron-ionic conduction. Such a character of the conduction indicates the prospects of using these materials as supercapacitors. The analysis of previous studies shows that further investigations into chalcogenide thallium compounds following the general formula $TIB^{||III|}C^{VI}$ are of doubtless interest. In order to extend previous investigations and understand accompanying mechanism of ionic conduction and relaxation processes, we study the frequency dependence of components of the total complex impedance and study the relaxation processes and temperature dependence of the conductivity at above 300 K for various compositions of the $(TIGaSe_2)_{1-x}(TIInSe_2)_x$ solid solution. İn contrast $TIGaTe_2$, $TIInSe_2$, and $TIInTe_2$ compounds, which crystallize in D_{4h}^{18} tetragonal space group, TIGaSe, teristic feature of these crystals is the fact that they C_{2h}^2 consist of Ga(In)-Te(Se) chains elongated along the $TIInSe_2$,and TIGaSe2 compound as well as solid solution tetragonal axis. Univalent thallium atoms have an octahedral surrounding made up of chalcogen atoms, ions based on them crystallize in the C^2 monoclinic and we can assume from crystal-chemical concepts that the structure of this class of compounds

is most favorable for the mobility of thallium ions. Superionic conductivity, the mechanism of which is often associated with the diffusion of TI^+ ions, was revealed for these compounds. The complex impedance spectra were measured in the frequency range of 20-10^6 Hz and diagrams in the (Z "-Z') complex plane were analyzed using the equilibrium substitution-circuit method. These studies show that $TIGaTe_2$, $TIInSe_2$, and $TIInTe_2$ compounds possess a crystal system and have a layered structure.

2. Experimental

The samples of solid solutions were synthesized by the fusion of the initial components (a purity of no lower than 99.99) in evacuated quartz cells, while their single crystals were grown by the modified Bridgman-Stockbarger method. Freshly cleaved samples prepared for investigation, in which the *c* axis is oriented perpendicularly to the cleavage, were rectangular shaped. To measure the temperature dependences of the electrical conductivity of the samples of the$(TIGaSe_2)_{1-x}(TIInSe_2)_x$ solid -solution crystals, we fabricated capacitors, in which plates of the studied materials served as the insulator. Capacitor plates were fabricated by deposition of silver current-leading contacts on the surface of cleaved plates. The electrical properties of the samples of the$(TIGaSe_2)_{1-x}(TIInSe_2)_x$ solid-solution were studied by impedance spectroscopy in a frequency range of 20-10^6 Hz. The electrical conductivity was measured using E7-25 digital immittance meter, the measurement accuracy was 0.1%.

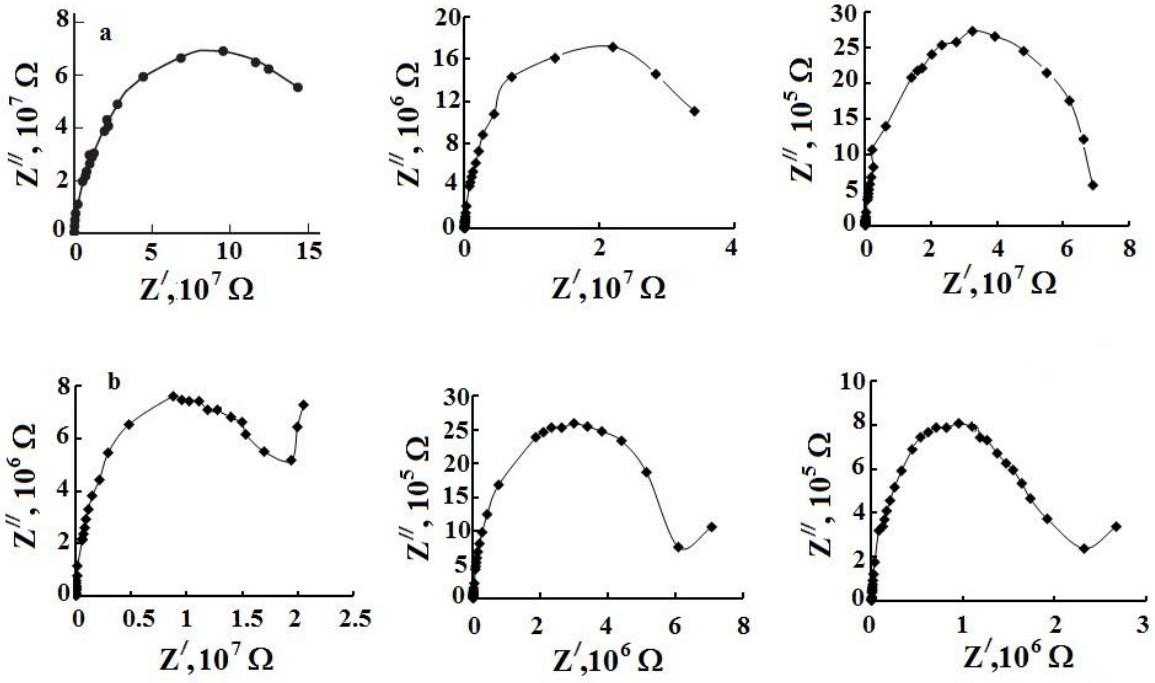

Fig.1. Impedance hodograph Z''(Z') for the$(TIGaSe_2)_{1-x}(TIInSe_2)_x$ solid solution; x=0,0.2,and 0.3 for curves a,b,and c,respectively.Measurements are performed at 300 K.Curves d,e,and f correspond to x=0,0.2,and 0.3. .Measurements are performed after 0.25 MGy irradiated.

3. Experimental results and discussion

Impedance spectroscopy methods are the most available methods for studying electrical processes at contacts of metals with ion-conducting materials. We measured the real and

imaginary parts of the impedance of the samples of the $(TIGaSe_2)_{1-x}(TIInSe_2)_x$ solid solution at 300 K. These data are presented in the form of an impedance hodograph on a complex plane (Fig.1).

It is seen from Figs.1. 1a,1b, and 1c that the hodograph arcs on a complex plane solid solution composition found from the measurements at 300 K circumscribe curves close to semicircles, the centers of which are located on the real axis; herewith, charge transfer has one relaxation time. İn this case, impedance hodograph of solid solutions with compositions 0,02, and 0.3 are qualitatively and quantitatively described in the equivalent-circuit approximation with the help of impedance components of a model electrical circuit. Such a hodograph from corresponds to a uniform sample with a low - ohmic and no blacking contact.An equivalent-circuit of such a hodograph is presented in Fig.2a.

Figures 1d, 1e and 1f show corresponding impedance hodograph of$(TIGaSe_2)_{1-x}(TIInSe_2)_x$ solid solutions at x=0,02, and 0.3 measured 300 K. Diagrams (Z''-Z') complex plane found from measurements at 300 K and after 0.25 MGy radiation, represent semicircles for one parallel RC chain and rays in the low-frequency diagram region (Figs. 1d, 1e, and 1f). Such a form of impedance hodographs measured at 300 K evidences the presence of additional contributions to the conductivity, which is apparently associated with the diffusion transfer of thallium ions near the interface between the solid electrolyte and electrode. These rays in the impedance diagram are characteristic of the Warburg diffusion impedance, which is based on the idea that carrier diffusion does not reach the diffusion layer boundary in the frequency range of the applied sinusoidal signal. It seems likely that the crystal transition to the superionic state at 300 K is responsible for the appearance of the Warburg diffusion impedance.

An equivalent circuit of the Warburg impedance is shown in Fig.2b. It has $Z_1=R_1$ is the active resistance and $Z_2=1/\omega C$ is the impedance of capacitance C (j is the imaginary unit and j is the frequency)

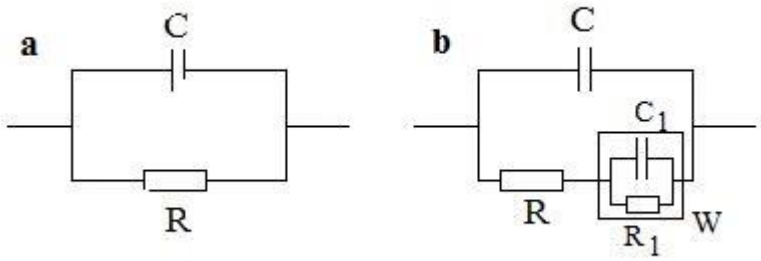

Fig.2.(a) Equivalent circuit for hodograph measurement at 300 K and (b) after 0.25 MGy irradiated. W is the Warburg diffusion impedance and R and C are the sample resistance and capacitance.

Thus, the Warburg impedance models a process ,in which the sinusoidal voltage supplied to an electrochemical cell leads to the diffusion of mobile ions from the electrode to the diffusion layer for one polarity and to the diffusions of In(σT) on 1000/T In the abrupt jump region of the electrical conductivity(curves b) lie well on a straight line, which is described by the following equation for the case of ionic conduction [16-18]: diffusion of mobile ions to the electrode for another polarity

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

Herewith, the process does not exit the diffusion layer region. Ions TI^{+1} are diffused here, ΔE is the activation energy of elecrtical conduction and k is the Boltzmann constant.The observed

jump-like variation in the electrical$(TIGaSe_2)_{1-x}(TIInSe_2)_x$ solid solution crystals at conduction in $(TIGaSe_2)_{1-x}(TIInSe_2)_x$ solid solutions 400 K are responsible for appearance of the Warburg impedance The transition to the superionic state is confirmed by measurements of the temperature dependence of the electrical conductivity; the results of these measurements are given below the text. Frequencies (f_{max}) corresponding to the maximum of Z“ relaxation times (Ţ) and frequencies corre-sponding to the frquency dispersion onset(f_{jamp}) for the$(TIGaSe_2)_{1-x}(TIInSe_2)_x$ solid solutions samples at 300 and 400 K are tabulated. It is seen from the Table 1 than a frequency f_{max} corresponding to the maximum of Z“in the solid solution is observed. Imaginary impedance parts manifest the maximum at frequencies of f_{max} corresponding to the condition C_{eff} R_{eff} $\omega_{max}=1.$, where C_{eff} and R_{eff} are the effective parameters of the equivalent circuit and $\omega_{max}=2\pi f_{max}$ the circular frequency.

Ionic conductivity

Figure 3 shows the temperature dependence of the electrical conductivity (σT) for $(TIGaSe_2)_{1-x}(TIInSe_2)_x$ solid solution crystals. Curves 1in Fig.3 reflects the measurements performed before radiated and curves 2, after radiation. It is seen in Fig.3 (curves *a*) that when applying an electric field perpendicularly to the layers, a certain increase in the conductivity at 300 K is observed. However, the jump in the dependence $\sigma(T)$ and a further increase in the conductivity with an activation energy of 0.04 eV are observed for measurements performed after radiation (curves 2). It is seen from the inset to Fig.3 that the experimental points of temperature depend at 400 K can be explained by an abrupt variation in the number of Tl^+ ions in states, where they possess a high mobility, i.e., the phase transition to the superionic state.

The crystalline structure two border components of the$(TIGaSe_2)_{1-x}(TIInSe_2)_x$ solid solution, i.e., $TIGaSe_2$ and $TIInSe_2$,as well as of the solid solutions themselves(in the solubility region),consist of anionic layers formed by $Ga_4Se_{10}(İn_4S_{10})$ tetrahedral, which is turned consist of four $GaSe_4(InS_4)$tetrahedral[9]. The Tl^+ ions are arranged in the trigon l voids between the Ga_4Se_{10} layers. It follows from crystal chemical concepts that the layered structure of the crystals of the solid solution under study and the site of Tl^+ in them largely promote the mobility of thallium ions.

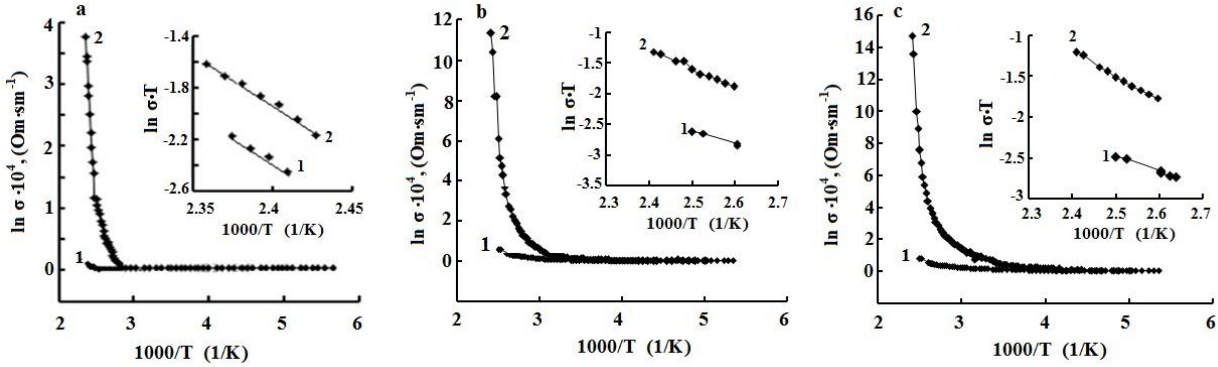

Fig.3. Temperature dependences of the conductivity of $(TIGaSe_2)_{1-x}(TIInSe_2)_x$ solid solutions at x=0, 0.2, and 0.3 consucutly a,b and c. Curves 1-reflect the measurements performed before radiated and curves 2-measurements performed after 0.25MGy.The dependence ln(σT) on 1000/T is presented in the insets.

The linear character of $\ln(\sigma T)$ on $1/T$ above the temperature jump (see insets to Fig.3) indicates the prevalent character of ionic conduction above the critical temperature. The presence of the layers and interlayer regions with a weak van der Waals inter-action serving as conduction

channels as well as the site of Tl^+ ions in trigonal voids between the layers allow us to affirm that the phase transition into the superionic state caused by the diffusion of thallium ions over vacancies in the thallium sublattice occurs in crystals after γ-irradiated.

4. Conclusion

The characteristic times of relaxation processess for the samples of the $TIGaSe_2)_{1-x}(TIInSe_2)_x$ solid solutions with x=0, 0.2, and 0.3 are determined using the impedance spectroscopy method. A decrease in the relaxation times in the solid solution is found. The energy loss mechanism in the alternate field for the solid –solution samples consists of both losses associated with the conduction and losses associated with relaxation polarization.

It is shown that the Tl^+ ions diffusing in the solid solution after the system transition into the state with increased superionic conduction are responsible for the presence of the Warburg diffusion impedance which manifests itself as rays in the hodographs of the studied $TIGaSe_2)_{1-x}(TIInSe_2)_x$ solid solutions after γ-irradiated. The phase transition into the superionic state after γ-irradiated is associated with the disorder of the thallium subllatice.

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ВЛИЯНИЕ γ-ОБЛУЧЕНИЯ НА СУПЕРИОННУЮ ПРОВОДИМОСТЪ В ТВЕРДЫХ РАСТВОРАХ $TIGaSe_2)_{1-x}(TIInSe_2)_x$

Ф.Т. Салманов

Резюме: Синтезированы образцы твердых растворов $TIGaSe_2)_{1-x}(TIInSe_2)_x$ методом импедансной спектроскопии измерены частотные зависимости ($2* 10^1$-10^6ГЦ) компонент полного комплексного импеданса и исследованы релаксационные процессы в зависимости от состава твердого раствора $(TIGaSe_2)_{1-x}(TIInSe_2)_x$. В области растворимости(x=0-0.3). С использованием метода эквивалентных схем замещения проанализированные полученные диаграммы на комплексной плоскости (Z “-Z’). В исследованном твердом растворе $(TIGaSe_2)_{1-x}(TIInSe_2)_x$ при 400 К обнаружена аномалия в температурной зависимости электрической проводимости, выражающаяся в резком росте проводимости. Эта особенность связная с фазовым переходом в суперионное состояние после гамма облучения 0.25МГр.

Ключевые слова: твердый раствор, релаксация, импеданс, проводимость

$(TIGaSe_2)_{1-x}(TIInSe_2)_x$ MƏHLULLARINDA SUPERİON KEÇİRİCİLİYİNƏ γ-ŞÜALARIN TƏSİRİ

F.T. Salmanov

Xülasə: 0.25 MGy γ-şüalanmaya məruz qalmış $(TlGaSe_2)_{1-x}(TlInSe_2)_x$ (x=0-0,3) bərk məhlulların impedans spektroskopiyası metodu ilə 2÷106 Hs tezlik oblastında kompleks immpedansı və relaksasiya prosesləri araşdırılmışdır. Radiasiyaya məruz qaldıqdan sonra relaksasiya müddəti azalır. Ekvivalent sxem əvəzləmələri üsulundan istifadə edərək ($Z''-Z'$) kompleks müstəvi diaqramları analiz olunmuşdur. $(TlGaSe_2)_{1-x}(TlInSe_2)_x$ bərk məhlulunuda 300K tempratur intervalında elektrik keçiriciliyinin tempraturdan asılılığında anomaliya müşahidə olunur və keçiricilik kəskin artır. Göstərilmişdir ki, $(TlGaSe_2)_{1-x}(TlInSe_2)_x$ bərk məhlulunda γ-şüalanmadan sonra 0.25 MGy superion halına faza keçidi baş verir.

Açar sözlər: bərk məhlul, relaksasiya, impedans, keçiricilik