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RADIATION-INDUCED DEFECTS IN GLASSES AND CERAMICS OF THE $CaO-Ga_2O_3-GeO_2$ SYSTEM

B.V. Padlyak[1,2], H. Jungner[3], K. Fabisiak[1] and S. P. Dubelt[4]

[1]Department of Physics, Kazimierz Wielki University of Bydgoszcz Weyssenhoff Sq. 11, 85-072 Bydgoszcz, Poland
[2]Institute of Physical Optics, 23 Dragomanov St., 79-005, L'viv, Ukraine
[3]Dating Laboratory, University of Helsinki, POB 64 Helsinki, Finland
[4]Department of Physics, L'viv Polytechnic National University, 79-013 L'viv, Ukraine

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Abstract. Electron spin resonance (ESR) and thermally stimulated luminescence (TSL) spectra of the *X* -, γ-, and β- irradiated glasses with $Ca_3Ga_2Ge_3O_{12}$ (garnet) and $Ca_3Ga_2Ge_4O_{14}$ (Ca-gallogermanate) compositions as well as glass and ceramics with $Ca_3Ga_2O_6$ composition are presented and analysed. The *X* - and γ- irradiation of Ge-contained glasses at room temperature induces simultaneously stable electron and hole paramagnetic defects, whereas the same irradiation of glasses with $Ca_3Ga_2O_6$ composition induces exclusively stable hole paramagnetic defects. Electron defects are assigned to ensembles of the *E'* (Ge) centres with different local environments and hole defects belongs to an ensemble of O^- centres, localized on different non-bridging oxygen of the glass network. TSL band, peaked at about 280 °C in the γ- and *X* - irradiated Ge-contained glasses is attributed to recombination of the *E'*(Ge) centres. TSL band with maximum about 230 °C in the γ- and *X*- irradiated Ge-contained glasses and glass and ceramics with $Ca_3Ga_2O_6$ composition is related to recombination of the O^- centres. TSL band, peaked at about 380 °C in the γ-, *X*- irradiated glasses and ceramics with $Ca_3Ga_2O_6$ composition as well as bands, peaked at 120, 220, and 380 °C in the same β- irradiated samples are assigned to non-paramagnetic radiation defects. Activation energies for β- induced defects in the glass and ceramics with $Ca_3Ga_2O_6$ composition are estimated.

1. INTRODUCTION

Studies of nature and formation mechanisms of radiation-induced defects in complex oxide compounds are current topics of solid-state physics and technology of novel materials for quantum electronics, in particular laser materials. Electron spin resonance (ESR) and thermally stimulated luminescence (TSL) provides powerful methods for study of the electron structure and local symmetry of the radiation defects in ordered (crystals) and disordered (compositionally or substitutionally disordered crystals, ceramics, glasses, *etc.*) solids. In comparison with crystalline solids, the electron and local structure of radiation-induced defects in glasses are studied insufficiently. This also concerns to compounds of $CaO-Ga_2O_3-GeO_2$ system, which can be obtained in both crystalline [1-3] and glassy (or vitreous) [4] states. Therefore, compounds of $CaO-Ga_2O_3-GeO_2$ system can be used for study of formation peculiarities and structure of radiation defects in crystals and glasses with the same chemical composition. From practical point of view glasses of the $CaO-Ga_2O_3-GeO_2$ system, activated with rare-earth ions are promising laser materials [5].

Corresponding author: B.V. Padlyak, e-mail: fizbp@ab.edu.pl

Three stable crystalline compounds: $Ca_3Ga_2Ge_3O_{12}$ (garnet structure, space group - *Ia3d*), $Ca_3Ga_2Ge_4O_{14}$ (Ca-gallogermanate structure, space group - *P321*), and $Ca_2Ga_2GeO_7$ (gelenite structure, space group $-P\bar{4}\,2_1m$) exist in the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ quaternary system [1-3]. Several crystalline compounds were found also in the $CaO\text{-}Ga_2O_3$, $CaO\text{-}GeO_2$, and $Ga_2O_3\text{-}GeO_2$ ternary systems, particularly $Ca_3Ga_2O_6$ crystal [6]. Glasses of high chemical purity and optical quality with $Ca_3Ga_2Ge_4O_{14}$, $Ca_3Ga_2Ge_3O_{12}$, and $Ca_3Ga_2O_6$ compositions were obtained according to [4]. During glass synthesis were obtained also ceramics with $Ca_3Ga_2O_6$ composition. The X-ray scattering and EXAFS (Extended X-Ray Absorption Fine Structure) studies of undoped glasses with $Ca_3Ga_2Ge_3O_{12}$, $Ca_3Ga_2Ge_4O_{14}$, and $Ca_3Ga_2O_6$ compositions show that their structure are characterised by short-range ordering similar as in the corresponding crystalline compounds and the $(Ga/Ge)O_6$ octahedra and $(Ga/Ge)O_4$ tetrahedra built the glass network [7,8].

ESR spectra of radiation-induced paramagnetic centres (PC) in crystals with $Ca_3Ga_2Ge_3O_{12}$ and $Ca_3Ga_2Ge_4O_{14}$ compositions were investigated earlier and described in [9,10]. Particularly, by ESR and optical spectroscopy it was shown that in the compositionally-disordered Ca-gallogermanate crystals the UV - and X-radiation at room temperature (RT) generates O^- centres, stable up to 380K [10], whereas in ordered $Ca_3Ga_2Ge_3O_{12}$ garnet crystals *X* - and γ-radiation at liquid nitrogen temperature induces Ge-related centres of $Ge^{3+}_{(d)}$ type, stable up to 220K only [9].

Previous results of ESR study of radiation-induced defects in the UV- irradiated glasses of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system were presented in [11], where intrinsic violet-blue photoluminescence of the undoped glasses was related to recombination of the UV - induced transient centres. ESR spectra of the UV -, X- and γ- irradiated glasses of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system were presented and interpreted in [12] and possible mechanism of intrinsic luminescence was proposed in [13]. First results of TSL investigations of the γ- and β- irradiated glasses of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system were presented in [14,15].

This paper presents the review of our studies of nature and structure of the radiation-induced defects in the glasses of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system. The obtained results are analysed in comparison with ESR and TSL referenced data for γ- and X- irradiated calcium-gallium-germanium garnet and Ca-gallogermanate crystals and glasses with different compositions.

2. EXPERIMENTAL DETAILS

The un-doped glasses of high chemical purity and optical quality with the $Ca_3Ga_2Ge_3O_{12}$, $Ca_3Ga_2Ge_4O_{14}$, and $Ca_3Ga_2O_6$ compositions were obtained by standard high-temperature synthesis according to [6]. Chemical composition of the glasses was controlled by X-ray microanalysis using a 'Camebax' apparatus. Paramagnetic centres in the non-irradiated glasses were controlled by ESR. Samples for TSL and ESR studies were cut to the size of $8\times4\times2$ mm^3.

The UV-irradiation of the samples was carried out at RT using a lamp of DKsEL-2000 type (P = 2000 W). The X- irradiation of the samples was carried out using an URS-55A apparatus (Cu K_α - radiation, U = 40 kV, I = 10 mA) at RT. Exposition time was equal to 1 h for both types of irradiation. The RT γ- irradiation (total dose $1.19\cdot10^4$ Gy) of the glass samples was realized in the Institute of Nuclear Research (Kyiv, Ukraine) using a ^{60}Co gun. The β-irradiation (total dose 1.5 Gy) was carried out at RT by a 40 mCi ^{90}Sr source in the Dating Laboratory of the University of Helsinki (Finland).

The X- band ESR measurements were carried out at room and liquid nitrogen temperatures using a computer controlled RADIOPAN SE/X-2544 spectrometer with cylindrical TM_{110} cavity, operating in the high-frequency (100 kHz) modulation mode of the magnetic field. The *g*- values of the observed PC were evaluated from experimental ESR spectra through resonance relationships using a Bruker computer simulation program 'SimFonia'. The microwave frequency of the ESR spectrometer was controlled by means of a diphenylpicrylhydrazyl (DPPH) *g*-marker (g=2.0036±0.0001).

The TSL glow curves were measured with a Ris∅ TL/OSL-DA-12 system. The samples were heated from RT up to 400 °C using a heating rate of 2 °C/s. In order to collect maximum of emitted light only a blue filter to absorb red glow during heating was used.

3. RESULTS AND DISCUSSION

3.1. ESR of the radiation-induced defects in UV-, γ- and X- irradiated glasses and ceramics

As was shown in [12,13] the UV -irradiation of the Ge-contained glasses with $Ca_3Ga_2Ge_3O_{12}$ and $Ca_3Ga_2Ge_4O_{14}$ compositions induces stable PC of the I type (Figs. 1a and 1b), whereas in the UV-irradiated glass with $Ca_3Ga_2O_6$ composition only

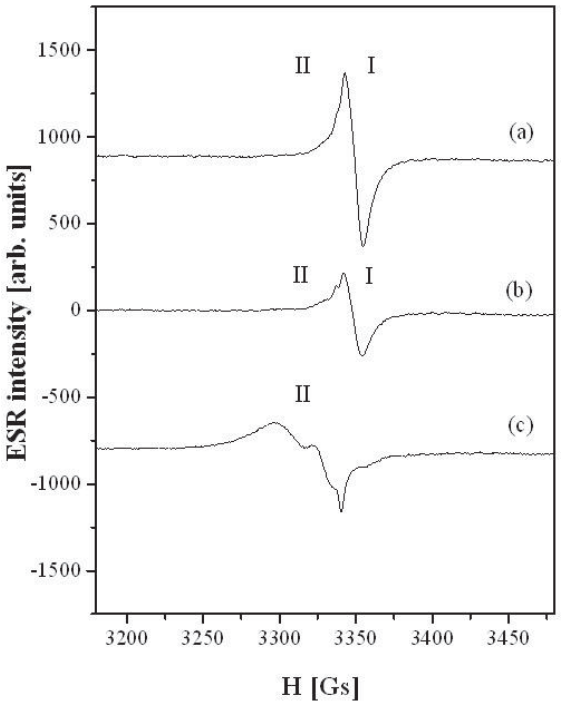

Fig. 1. X-band ESR spectra of UV - irradiated glasses with $Ca_3Ga_2Ge_4O_{14}$ (a), $Ca_3Ga_2Ge_3O_{12}$ (b), and $Ca_3Ga_2O_6$ (c) compositions, registered at RT. The ESR spectra of electron and hole centres are signed as I and II, respectively.

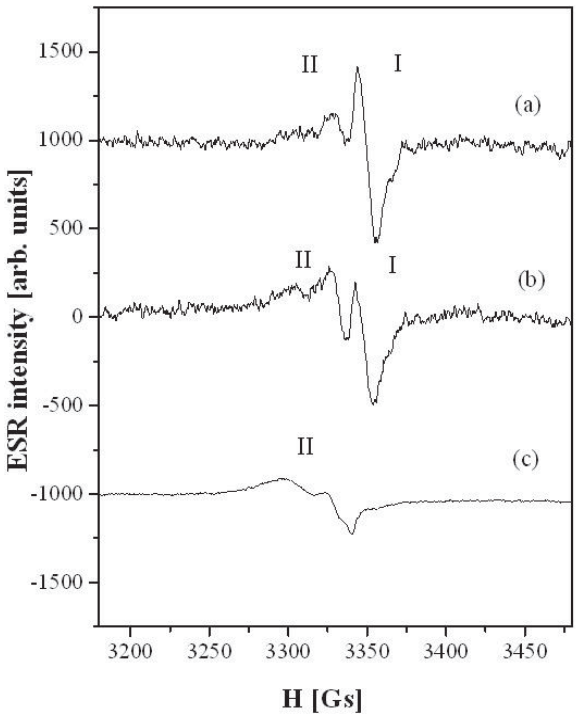

Fig. 2. X-band ESR spectra of X- irradiated glasses with $Ca_3Ga_2Ge_4O_{14}$ (a), $Ca_3Ga_2Ge_3O_{12}$ (b), and $Ca_3Ga_2O_6$ (c) compositions, registered at RT.

stable PC of the II type have been detected (Fig. 1c). The *X* - irradiation of Ge-contained glasses leads to generation of stable PC of both types (Figs. 2a and 2b), whereas in the glass with $Ca_3Ga_2O_6$ composition only stable PC of II type appear (Fig. 2c). In the γ - and X - irradiated glasses of CaO-Ga_2O_3-GeO_2 system the same ESR spectra of radiation-induced PC were observed. The number of both types of centres depends on the glass composition and the generation efficiency decreases for centres of the I type and increases for centres of the II type with decreasing of GeO_2 content in the glass composition (Figs. 1 and 2). The observed peculiarities of PC formation are characteristic also for CaO-Ga_2O_3-GeO_2 glasses, activated with the transition and rare-earth ions.

Detailed analysis of ESR spectra, presented in the Figs. 1 and 2, shows that these spectra really belong to centres of two different types. 'Pure' ESR spectrum of the I type is observed in the UV-irradiated glass with $Ca_3Ga_2Ge_4O_{14}$ composition (Fig. 1a), whereas 'pure' ESR spectrum of the II type is observed in the UV -, X-, and γ- irradiated glass with $Ca_3Ga_2O_6$ composition (Figs. 1 and 2c). These 'pure' ESR spectra are presented in Figs. 3 and 4 and were used for analysis and evaluation of the *g*-values for both types of centres. No better resolution of complex ESR spectra in all investigated glasses was observed at 77K (Figs. 3 and 4), that indicates significant inhomogeneous broadening of ESR lines for both types of PC, caused by statistical distribution of their local axes and spectroscopic parameters. Thus, the observed ESR spectra can be considered as a superposition of a number of spectra with statistically distributed *g*-values. Such spectra can be described by a suitable spin Hamiltonian with average *g*-values and their average-quadratic deviations. Using the experimental *g*-values, peak-to-peak derivative linewidths, and the lineshape, it was possible to simulate the ESR spectra. Best fit to the experimental spectra was obtained for *g*-values, given in Table 1. For comparison the Table 1 contains also *g*-values for radiation-induced PC in some germanate and silicate glasses as well as in

Table 1. The *g*-tensor principal values for hole and electron radiation-induced centres in the glasses and crystals of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system and in the some germanate and silicate glasses with different composition.

Glass and crystal compositions	Type of centres	*g* - tensor principal values			References
		g_{xx}	g_{yy}	g_{zz}	
GeO_2 (glass)	*E′*(Ge)	1.9944±0.0008	1.9944±0.0008	2.0010±0.0008	[16]
	E′(Ge3)	1.9945*	1.9945*	2.0011±0.0001	
Ge-doped silica	*E′*(Ge2)	1.9868*	1.9978*	2.0010±0.0001	[17]
fibre (SiO_2:Ge)	*E′*(Ge1)	1.9930*	1.9994*	2.0007±0.0001	
	E′(Ge0)	1.9943*	1.9943*	2.0009±0.0001	
$CaO\text{-}Ga_2O_3\text{-}GeO_2$ (glass)	Ensemble of *E′*(Ge) centres	1.996±0.002	1.996±0.002	2.001±0.002	Our results, [2]
$Ca_3Ga_2Ge_3O_{12}$ (crystal)	$Ge^{3+}_{(d)}$ #	2.008	2.008	2.008	Our results, [9]
$xMe_2O(1\text{-}x)SiO_2$ (glass)	HC_1	2.019*	2.009*	2.003*	[22,23]
(Me = Li, Na, K)	HC_2	2.019*	2.012*	2.010*	
$CaO\text{-}Ga_2O_3\text{-}GeO_2$ (glass)	Ensemble of O^- centres	2.017±0.002	2.009±0.002	2.0033±0.001	Our results, [2]
$Ca_3Ga_2Ge_4O_{14}$ (crystal)	O^- (1)	2.0180±0.001	2.0134±0.001	2.0029±0.0005	Our results, [10]
	O^- (2)	2.0186±0.002	2.0160±0.002	2.0053±0.002	

Notes: *Represents the maximum of a distribution of the g -values;
#The superhyperfine interaction ($a \cong 6$ G) with 2 nuclei of the ^{69,71}Ga isotopes ($I = 3/2$) was observed.

the $Ca_3Ga_2Ge_4O_{14}$ disordered and $Ca_3Ga_2Ge_3O_{12}$ ordered crystals. The ESR spectrum of the I type centres has been described by a spin Hamiltonian of axial symmetry with *g*-values, which are characteristic for electron centres (g_{xx}, g_{yy}, $g_{zz} < g_e = 2.0023$), whereas the ESR spectrum of the II type PC has been described by a spin Hamiltonian of rhombic symmetry with *g*-values, which are characteristic for hole centres (g_{xx}, g_{yy}, $g_{zz} > g_e = 2.0023$).

The observed electron PC can be identified as Ge-related centres, because these centres are induced in the Ge-contained glasses, exclusively. Similar centres were observed earlier in the GeO_2 glass and crystal [16], Ge-doped silica fibre [17] and other germanate glasses [18]. In according to referenced data, presented in Table 1, the Ge-related PC in the glass network are characterized by axially symmetric *g*-tensor and are assigned to *E′*(Ge) centres, i.e. electrons, trapped at the sites of oxygen vacancies in the dangling sp^3 hybrid or-

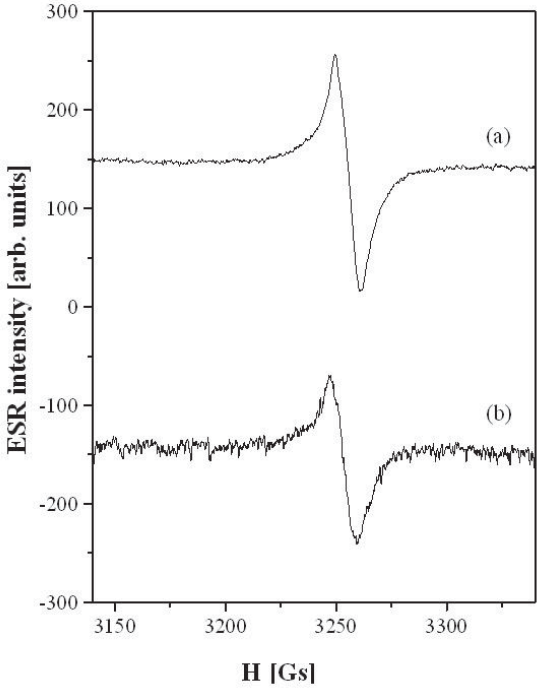

Fig. 3. X-band ESR spectra of UV - induced electron *E′*(Ge) centres, registered in glass with $Ca_3Ga_2Ge_4O_{14}$ composition at room (a) and liquid nitrogen (b) temperature.

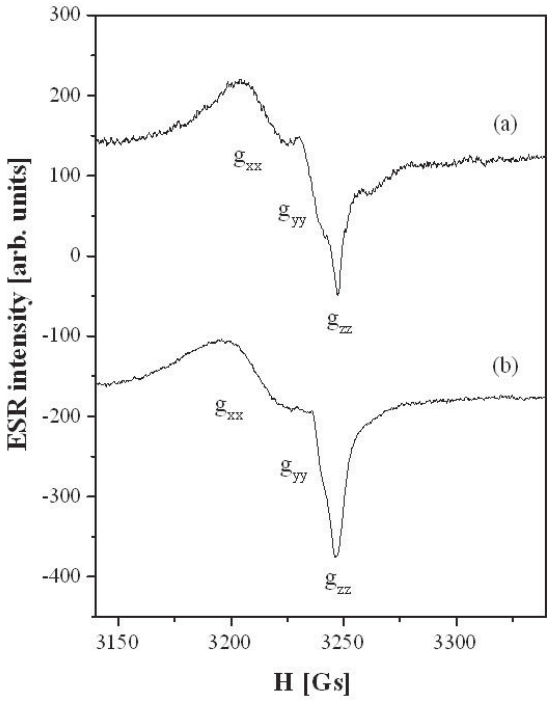

Fig. 4. X-band ESR spectra of X- induced hole O^- centres in glass with $Ca_3Ga_2O_6$ composition, registered at room (a) and liquid nitrogen (b) temperature.

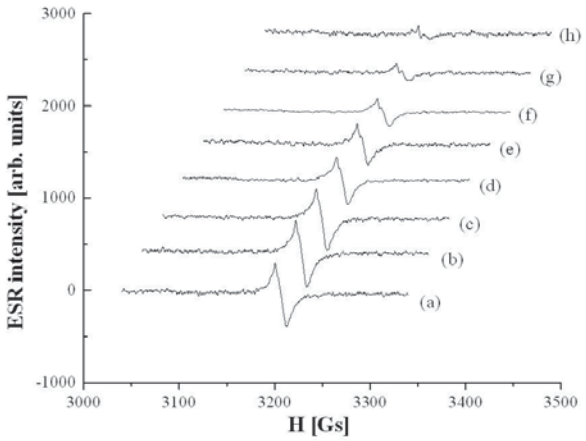

Fig. 5. ESR spectra of the *E′*(Ge) centers, registered at RT after isochronal annealing in the air at the following temperatures: 325K (a), 375K (b), 400K (c), 425K (d), 450K (e), 475K (f), 500K (g), and 550K (h).

bital of Ge. Geometry and theoretical calculation of the *g*-values for *E′*(Ge) centre are given in [17]. The *E′*(Ge) centres are analogous to well-known silicon E′(Si) centres [19,20].

The ESR spectrum of *E′*(Ge) centres in the CaO-Ga_2O_3-GeO_2 glasses is characterized by the largest linewidth in comparison with analogous centres in the GeO_2 glass and crystal [16] and Ge-doped silica fibre [17]. That are connected with the presence of a number (ensemble) *E′*(Ge) centres with different local environments, which give slightly shifted and statistically distributed *g*-values and form the observed ESR lineshape. Presence of the *E′*(Ge) centres with different local environments in CaO-Ga_2O_3-GeO_2 glass network clearly demonstrates isochronal annealing of the UV-irradiated samples (Fig. 5). With increasing of annealing temperature a better resolution of the ESR spectra was observed (Fig. 5), that is related with different thermal stability of the *E′*(Ge) centres with different local environments.

The ESR spectrum of X- and γ- induced hole centres in the Ge-contained glasses (Figs. 2a-2c) is similar to the spectrum of UV - induced hole centres in non-germanate $Ca_3Ga_2O_6$ glasses (Fig. 1c). Similar ESR spectra were observed in a number irradiated silicate glasses with different composition and were assigned in [21-23] to the HC_1 hole centres. The *g*-values of hole centres in CaO-Ga_2O_3-GeO_2 glasses are close to *g*-values of the HC_1 centres in silicate glasses and O^- centres in the $Ca_3Ga_2Ge_4O_{14}$ disordered crystals (see Table 1). Because the composition and local structure of CaO-Ga_2O_3-GeO_2 glasses and $Ca_3Ga_2Ge_4O_{14}$ disordered crystals are very similar [3, 6-8], the observed hole PC in the glasses were assigned to an ensemble of O^- centres, i.e., holes, trapped at non-bridging oxygen with different local environments. Better resolution in ESR spectra of the O^- centres was not observed with the increasing of temperature during isochronal annealing (Fig. 6). This result shows that different O^- centres in the glass network are characterized by a similar thermal stability.

So, the ESR spectroscopy shows that X- and γ-irradiation of glasses with $Ca_3Ga_2Ge_3O_{12}$ and $Ca_3Ga_2Ge_4O_{14}$ composition at RT induces simultaneously E′(Ge) electron and O^- hole PC, whereas the same X- and γ- irradiation of the glass with $Ca_3Ga_2O_6$ composition induces O^- hole centres, exclusively (Figs. 1–4). The UV - irradiation of Ge-containing glasses at RT leads only to generation of the *E′*(Ge) stable centres (Figs. 1a and 1b). The ensemble of electron *E′*(Ge) centres in the glass

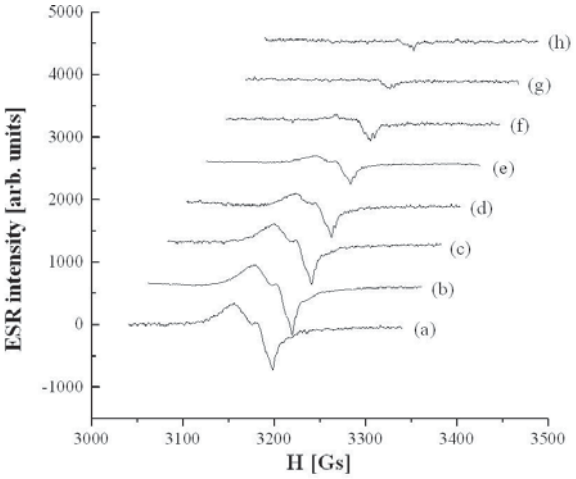

Fig. 6. ESR spectra of the O^- centers, registered at RT after isochronal annealing in the air at the following temperatures: 325K (a), 375K (b), 400K (c), 425K (d), 450K (e), 475K (f), 500K (g), and 550K (h).

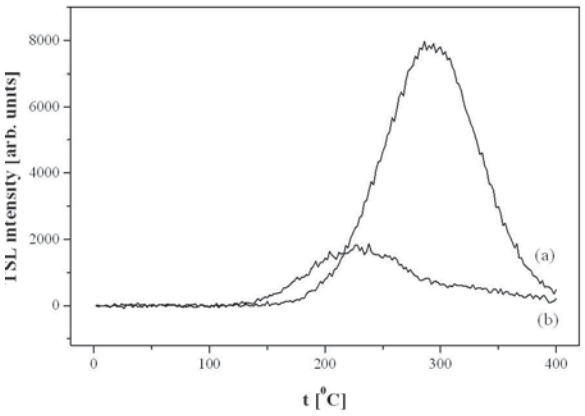

Fig. 7. TSL glow curves of the γ- irradiated glasses with $Ca_3Ga_2Ge_3O_{12}$ (a) and $Ca_3Ga_2Ge_4O_{14}$ (b) composition.

network is characterized by continuously distributed *g*-values, caused by different local environments. The ensemble of hole centres consists of O^- centres, localized on different non-bridging oxygen of the glass network [12,13]. Isochronal annealing shows that the ensembles of *E'*(Ge) and O^- centres are characterized by high thermal stability in the CaO-Ga_2O_3-GeO_2 glass network and their ESR spectra are still observed up to 550K (Figs. 5 and 6).

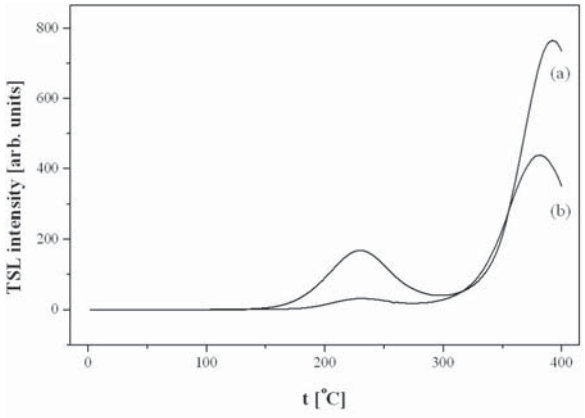

Fig. 8. TSL glow curves of γ- irradiated ceramic (a) and glass (b) with $Ca_3Ga_2O_6$ composition.

3.2. TSL glow curves of the γ- and β- irradiated glasses and ceramics

Because the γ- and X - irradiated glasses and ceramics of the CaO-Ga_2O_3-GeO_2 system show the same ESR and TSL spectra, below only the γ- irradiated glasses and ceramics are considered. TSL glow curves of γ- irradiated glasses with $Ca_3Ga_2Ge_3O_{12}$ and $Ca_3Ga_2Ge_4O_{14}$ compositions are presented in Fig. 7. For glass with $Ca_3Ga_2Ge_3O_{12}$ composition the glow curve represents an intense, almost symmetrical broad band at 280 °C, whereas for glass with $Ca_3Ga_2Ge_4O_{14}$ composition the glow curve is characterized by a broad complex asymmetric band with maximum about 230 °C. Detailed analysis shows that the glow curve for glass with $Ca_3Ga_2Ge_4O_{14}$ and $Ca_3Ga_2Ge_{43}O_{12}$ compositions (Fig. 7) is a superposition of two bands with maxima around 230 and 280 °C. The TSL band at 230 °C in the glass with $Ca_3Ga_2Ge_3O_{12}$ composition is relatively weak and is superimposed by a strong broad band peaked at 280 °C. The linewidth for all TSL bands in the Ge-contained glasses is similar. The band peaked at 280 °C in the glass with $Ca_3Ga_2Ge_4O_{14}$ composition is weaker than the band peaked at 230 °C, whereas in the glow curve of the glass with $Ca_3Ga_2Ge_3O_{12}$ composition the band at 280 °C dominates. TSL glow curves for γ- irradiated glass and ceramics with $Ca_3Ga_2O_6$ composition consist of two almost symmetrical bands, peaked at 230 and 380 °C (Fig. 8). The band at 230 °C is

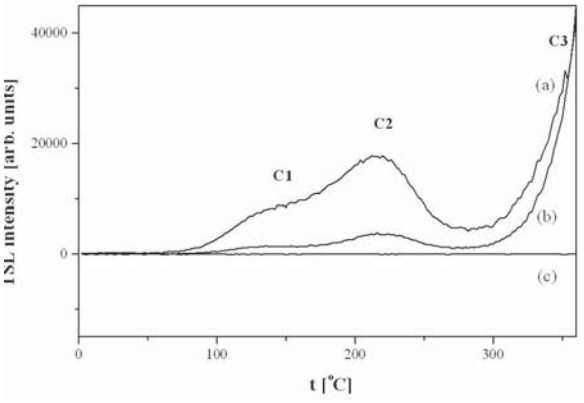

Fig. 9. TSL glow curves of β- irradiated ceramic (a) and glass (b) with $Ca_3Ga_2O_6$ composition and glass with $Ca_3Ga_2Ge_3O_{12}$ composition (c).

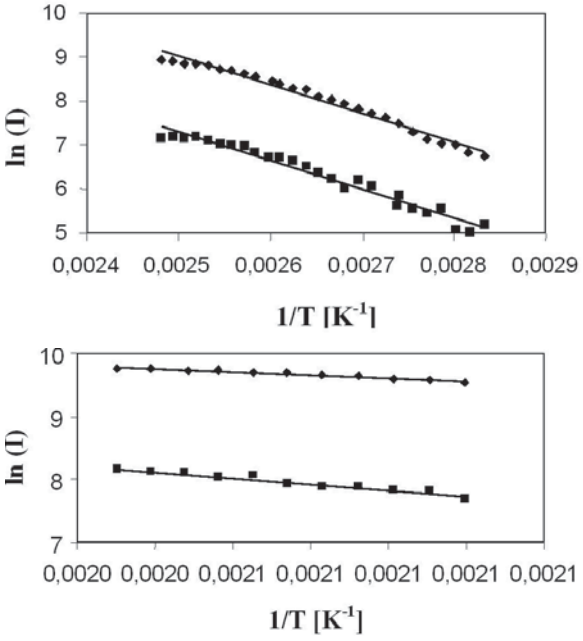

Fig. 10. Results of the glow curves analysis by linear fitting for β- irradiated ceramic (full diamonds) and glass (full squares) with $Ca_3Ga_2O_6$ composition in the 80 ÷ 130 °C (a) and 190 ÷ 210 °C (b) temperature range. The solid lines are the least-squares fitting to experimental results.

much weaker than the one at 380 °C. Because the TSL band around 230 °C was observed in the γ-irradiated glasses with $Ca_3Ga_2Ge_4O_{14}$, $Ca_3Ga_2Ge_3O_{12}$, and $Ca_3Ga_2O_6$ compositions we suppose that this band can be assigned to recombination of the same radiation-induced defects.

The observed TSL glow curves in the γ- irradiated glasses of CaO-Ga_2O_3-GeO_2 system can be identified on the basis of comparison with corresponding ESR spectra, detected in the same irradiated samples after isochronal thermal annealing. ESR shows that disappearance of the *E′*(Ge) and O^- centres is observed above 280 °C and 230 °C, respectively. Therefore, the pronounced TSL glow curves around 280 °C in the Ge-contained glasses are attributed to recombination of the *E′*(Ge) centres. In the γ- irradiated Ge-contained glasses as well as in the glass and ceramics with $Ca_3Ga_2O_6$ composition, the TSL glow curves with the maximum at about 230 °C are assigned to recombination of the O^- centres. The intense TSL band peaked at 380 °C available in the γ- irradiated glass and ceramics with $Ca_3Ga_2O_6$ composition (Fig. 8) could be related to recombination of non-paramagnetic radiation defects, because above 300 °C ESR spectra in the γ- and X- irradiated samples were not observed. Thus, we can conclude that the TSL shows good correlation with the ESR data, obtained for the same X- and γ- irradiated glasses.

In the β- irradiated at RT nominally pure Ge-containing glasses none TSL glow curves are observed (Fig. 9, curve c). In the β - irradiated glass and ceramics with the $Ca_3Ga_2O_6$ composition we observe a complex TSL glow curve, consisting of three bands with the maxima located at 120, 220, and about 380 °C, which correspond to C1, C2, and C3 centres, respectively (Fig. 9, curves a, b). In Figs. 10a and 10b the results of glow curves analysis for the β- irradiated glass and ceramics with $Ca_3Ga_2O_6$ composition are presented. Assuming a simple form:

$$I(t) = A\exp(-E / kT),$$

where A is a constant, k – the Boltzman constant, we obtain from Figs. 10a and 10b the following values of the activation energy: $E_1 \cong 0.56$ eV and $E_2 \cong 0.33$ eV for C1 and C2 radiation-induced centres, respectively.

The maximum of the TSL band at 220 °C in the β- irradiated glass and ceramics with $Ca_3Ga_2O_6$ composition, that corresponds to the C2 centres (Fig. 9, curves a, b), is close to the maximum of TSL glow curves at 230 °C for the O^- centres found in the γ- irradiated glasses and ceramics (Figs. 7 and 8). But the TSL band at 220 °C cannot be assigned to O^- centres, because the O^- and any other ESR spec-

tra in the β- irradiated glasses and ceramics of CaO-Ga_2O_3-GeO_2 system were not observed. Therefore, the TSL bands peaked at 120 and 220 °C as well as the band, located at about 380 °C may be related to recombination of the C1, C2, and C3 non-paramagnetic radiation defects.

4. CONCLUSIONS

Results from ESR and TSL spectroscopy show that the formation of radiation-induced defects in the glasses of CaO-Ga_2O_3-GeO_2 system strongly depends on the basic glass composition and on the kind of irradiation. Particularly, the electron excess *E'* (Ge) and hole trapped O^- centres stable at RT coexist in the X- and γ- irradiated glasses with $Ca_3Ga_2Ge_4O_{14}$ and $Ca_3Ga_2Ge_3O_{12}$ composition, whereas in the glasses with $Ca_3Ga_2O_6$ composition the UV -, X-, and γ- irradiation at RT induce only stable O^- centres. The structural disordering leads to a better stabilization of the radiation defects, because thermal stability of the radiation-induced paramagnetic centres in the ordered garnet ($Ca_3Ga_2Ge_3O_{12}$) and compositionally disordered Ca-gallogermanate ($Ca_3Ga_2Ge_4O_{14}$) crystals is lower in comparison with glasses of the same composition.

TSL glow curves show good correlation with ESR spectra of the same irradiated samples. Particularly, the TSL band with maximum at 230 °C in the γ- and X- irradiated Ge-contained glasses as well as in the γ-, X- irradiated glass and ceramics with $Ca_3Ga_2O_6$ composition is assigned to recombination of O^- centres. The TSL band peaked at about 280 °C in the γ- and X- irradiated Ge-contained glasses is attributed to recombination of the *E'*(Ge) centres. The TSL band, peaked at about 380 °C in the γ- and X- irradiated glass and ceramics with $Ca_3Ga_2O_6$ composition can be related to recombination of non-paramagnetic radiation defects.

No TSL bands was observed in the β-irradiated Ge-contained glasses, whereas in glass and ceramics with $Ca_3Ga_2O_6$ composition a complex TSL glow curve with maxima at about 120, 220, and 380 °C was observed. This glow curve is due to non-paramagnetic radiation defects, because no ESR spectra were observed in the β- irradiated glasses and ceramics of CaO-Ga_2O_3-GeO_2 system. Activation energies for β- induced non-paramagnetic C1 and C2 defects were estimated. Nature and electron structure of the C1, C2, and C3 defects in the β- irradiated glass and ceramics with $Ca_3Ga_2O_6$ composition needs more detailed study.

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