Thermally Stimulated Luminescence of Radiation-Induced Defects in the Glasses of CaO-Ga_2O_3-GeO_2 System

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Abstract

Thermally stimulated luminescence (TSL) and electron spin resonance (ESR) spectra of *X*-, *γ*- and *β*-irradiated glasses with garnet ($Ca_3Ga_2Ge_3O_{12}$), Ca-gallogermanate ($Ca_3Ga_2Ge_4O_{14}$) and $Ca_3Ga_2O_6$ compositions have been investigated and analysed. *X*- and *γ*-irradiation of the Ge-containing glasses induces simultaneously electron and hole paramagnetic defects, stable at room temperature, whereas the same irradiation of glasses with $Ca_3Ga_2O_6$ composition yields only in stable hole paramagnetic defects. The electron defects are assigned to ensembles of E′ (Ge) centres with different local environments. The hole defects belong to ensembles of O^- centres, localised at different non-bridging oxygens of the glass network. The pronounced TSL glow curves in the *γ*- and *X*-irradiated Ge-containing glasses peaked at about 280°C are attributed to recombination of the E′ (Ge) centres. The TSL glow curves with the maximum near 230°C in the *γ*- and *X*-irradiated Ge-containing glasses and the glass and ceramics with $Ca_3Ga_2O_6$ composition are related to recombination of the O^- centres. The TSL glow curve peaked in the vicinity of 380°C observed in the *γ*- and *X*-irradiated glasses with $Ca_3Ga_2O_6$ composition could be assigned to recombination of non-paramagnetic defects. No TSL glow curves are observed in the *β*-irradiated Ge-containing glasses, whereas the TSL glow curves with the maxima at about 120, 220 and 380°C are peculiar for the glass and ceramics with $Ca_3Ga_2O_6$ composition. The activation energy for the *β*-induced defects is estimated and their models are discussed.

Keywords: CaO-Ga_2O_3-GeO_2 glasses, radiation-induced defects, TSL, ESR, E′ (Ge) centre, O^- centre

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1. Introduction

Studies of nature and mechanisms for the radiation-induced defects in complex oxide compounds are among the current and urgent topics of solid state physics and technology of novel materials for quantum electronics, in particular, the laser materials. Thermally stimulated luminescence (TSL) and electron spin resonance (ESR) provide powerful tools for studying the electron structure and local symmetry of the radiation-induced defects in both the ordered (crystalline) and disordered (compositionally or substitutionally disordered crystals, glasses, ceramics, etc.) solids. A nature and structure of the radiation-induced defects in the compounds that can equally exist in either ordered or disordered state represent especially interesting problem within the topic. This also concerns to the compounds of $CaO-Ga_2O_3-GeO_2$ system, which could be obtained in both the crystalline and vitreous (or glassy) states and remain promising laser host materials.

Three stable crystalline compounds exist in the quaternary $CaO-Ga_2O_3-GeO_2$ system [1-4]: $Ca_3Ga_2Ge_3O_{12}$ (the 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 $P\bar{4}2_1m$). Several crystalline compounds have been also found in $CaO-Ga_2O_3$, $CaO-GeO_2$ and $Ga_2O_3-GeO_2$ ternary systems, in particular, in $Ca_3Ga_2O_6$ crystal [5]. We have obtained for the first time the glasses of high chemical purity and optical quality with the $Ca_3Ga_2Ge_4O_{14}$, $Ca_3Ga_2Ge_3O_{12}$ and $Ca_3Ga_2O_6$ compositions (see [6]). X-ray scattering and EXAFS (Extended *X*-Ray Absorption Fine Structure) studies of the undoped glasses with the $Ca_3Ga_2Ge_3O_{12}$, $Ca_3Ga_2Ge_4O_{14}$ and $Ca_3Ga_2O_6$ compositions have shown that the local structure of the investigated glasses is characterised by a short-range chemical ordering similar to that peculiar for the corresponding crystalline compounds [7,8].

The ESR spectra of the radiation-induced paramagnetic centres (PC) in the crystals with $Ca_3Ga_2Ge_3O_{12}$ and $Ca_3Ga_2Ge_4O_{14}$ compositions have been earlier investigated and described in detail in [9,10]. In particular, it has been shown with the aid of optical and ESR spectroscopy that UV- and *X*-radiation at the room temperature (RT) generates O^- centres in compositionally disordered Ca-gallogermanate crystals, which are stable up to 380 K [10]. At the same time, in the ordered $Ca_3Ga_2Ge_3O_{12}$ garnet crystals and at the liquid-nitrogen temperature, *X*- and γ-radiation induces Ge-related centres of $Ge^{3+}_{(d)}$ type, which turn out to be stable up to 220 K [9].

Some preliminary results of ESR studies for the radiation-induced defects in UV-irradiated glasses of $CaO-Ga_2O_3-GeO_2$ system have been presented in [11], where the intrinsic violet-blue photoluminescence of the undoped glasses is related to recombination of UV-induced transient centres. The ESR spectra of UV-, *X*- and γ-irradiated glasses of $CaO-Ga_2O_3-GeO_2$ system have been presented and interpreted in [12], and the possible mechanism for the intrinsic luminescence has been proposed in [13]. Finally, preliminary TSL studies in the γ-irradiated glasses of $CaO-Ga_2O_3-GeO_2$ system have been reported in [14].

The aim of this paper is to continue the studies for the nature and structure of the radiation-induced defects in the glasses of $CaO-Ga_2O_3-GeO_2$ system. Particularly, the TSL glow curves of γ- and β-irradiated glasses of the $CaO-Ga_2O_3-GeO_2$ system are obtained for the first time. Furthermore, we report here on their analysis and comparison with the ESR data derived earlier for the same γ- and *X*-irradiated glasses.

2. Experimental details

The undoped 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 a standard technique of high-temperature synthesis, performed according to [6]. The chemical composition of the glasses was controlled with *X*-ray microanalysis, using the "Camebax" apparatus. Paramagnetic impurities in the non-irradiated glasses were controlled with the ESR technique. The samples prepared for the TSL and ESR investigations were cut to the size of $8\times4\times2$ mm^3.

UV-irradiation of the samples was carried out at the RT, using a lamp of DKsEL-2000 type (P=2000 W). The samples were also *X*-irradiated at the RT with the URS-55A apparatus (Cu K_α-radiation, U = 40 kV, I =10 mA). The exposition was equal to 60 min for the both types of irradiation. The RT γ-irradiation (total dose 1.19×10^4 Gy) of the glass samples was performed at the Institute of Nuclear Researches (Kyiv, Ukraine), using a ^{60}Co gun. β-irradiation (total dose 1.5 Gy) was carried out at the RT with the aid of standard source at Dating

Laboratory of the University of Helsinki (Finland).

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

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

3. Results and discussion

3.1. TSL glow curves and ESR spectra of γ- and *X*-irradiated glasses and ceramics

The TSL glow curves of the γ-irradiated glasses with $Ca_3Ga_2Ge_3O_{12}$ and $Ca_3Ga_2Ge_4O_{14}$ compositions are presented in Fig. 1. For the glass with $Ca_3Ga_2Ge_3O_{12}$ composition, the glow curve represents an intense, almost symmetrical broad band centred at 280 ^{0}C, whereas in case of the glass with $Ca_3Ga_2Ge_4O_{14}$ composition the glow curve is characterised by a broad, complex and asymmetric band with the maximum about 230°C. Basing upon a detailed analysis, we have shown that the glow curve for the glass with $Ca_3Ga_2Ge_4O_{14}$ and $Ca_3Ga_2Ge_{43}O_{12}$ compositions (see Fig. 1) is a superposition of two bands with the 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, being covered by a strong and broad band peaked at 280^{0}C. The linewidths for all the TSL bands in Ge-containing glasses are similar. The band peaked at 280 ^{0}C in the glass with $Ca_3Ga_2Ge_4O_{14}$ composition is weaker than that peaked at 230 ^{0}C, whereas the band at 280°C dominates in the glow curve of the glass with $Ca_3Ga_2Ge_3O_{12}$ composition. The TSL glow curves for the glass and ceramics with $Ca_3Ga_2O_6$ composition γ-irradiated at the RT consist of two almost symmetrical bands peaked at 230 and 380°C (Fig. 2). The band centred at 230°C is much weaker than the band at 380°C. Since the TSL band around 230°C is observed in γ-irradiated glasses with the $Ca_3Ga_2Ge_4O_{14}$, $Ca_3Ga_2Ge_{43}O_{12}$ and $Ca_3Ga_2O_6$ compositions, we suppose that it should be assigned to recombination of the same radiation-induced defects.

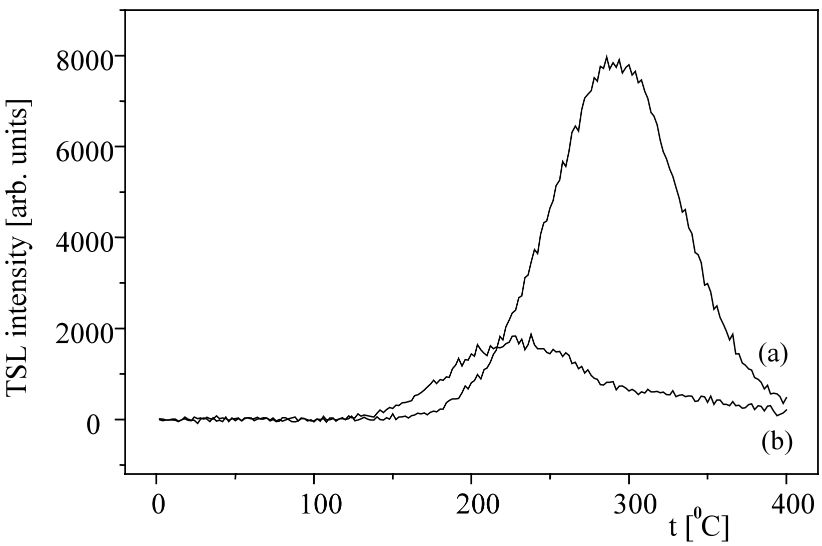

Fig. 1. TSL glow curves for γ-irradiated glasses with $Ca_3Ga_2Ge_3O_{12}$ (a) and $Ca_3Ga_2Ge_4O_{14}$ (b) compositions.

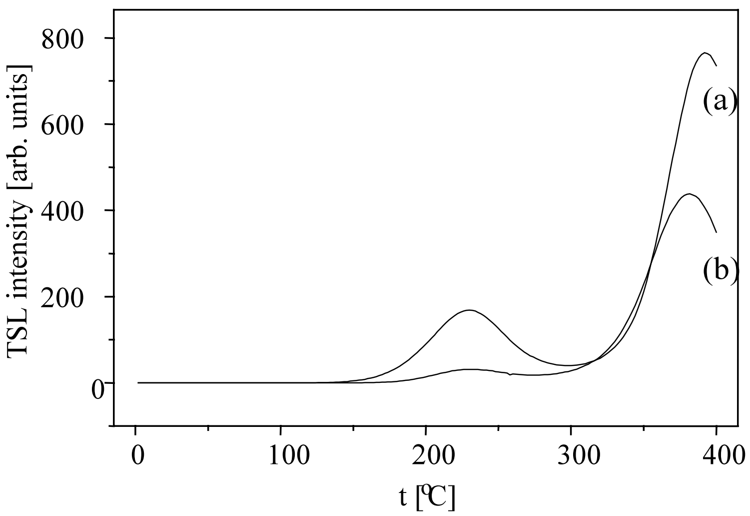

Fig. 2. TSL glow curves for γ-irradiated ceramics (a) and glass (b) with $Ca_3Ga_2O_6$ composition.

The observed TSL glow curves in the glasses of CaO-Ga_2O_3-GeO_2 system may be identified on the basis of comparison with the corresponding ESR spectra, detected for the same irradiated samples after isochronal thermal annealing [12]. The interpretation of the observed ESR and TSL spectra in *X*-and γ-irradiated glasses of CaO-Ga_2O_3-GeO_2 system will be given below.

X- and γ-irradiation of the glasses with $Ca_3Ga_2Ge_3O_{12}$ and $Ca_3Ga_2Ge_4O_{14}$ compositions induce simultaneously electron and hole paramagnetic defects, whereas the same irradiations of the glass with $Ca_3Ga_2O_6$ composition impose solely hole paramagnetic defects stable at the RT (Fig. 3). UV-irradiation of the Ge-containing glasses leads only to generation of paramagnetic defects of the electron type, which are stable at the RT (Fig. 4). According to the work [12], the electron defects are assigned to ensembles of E′(Ge) centres with continuously distributed *g*-values caused by different local environments, while the hole defects – to ensemble of O^- centres, which are localised at different non-bridging oxygens of the glass network. The ESR spectra of E′(Ge) and O^- centres are presented in Fig. 4 and 5.

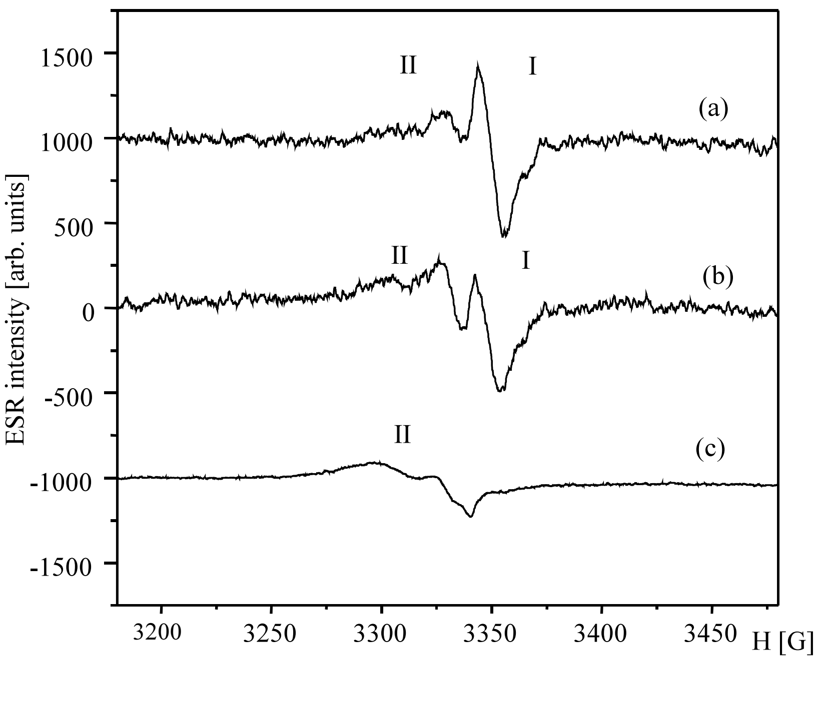

Fig. 3. X-band ESR spectra of *X*-irradiated glasses with $Ca_3Ga_2Ge_4O_{14}$ (a), $Ca_3Ga_2Ge_3O_{12}$ (b) and $Ca_3Ga_2O_6$ (c) compositions, detected at the RT. The ESR spectra of the electron and hole centres are denoted as I and II, respectively.

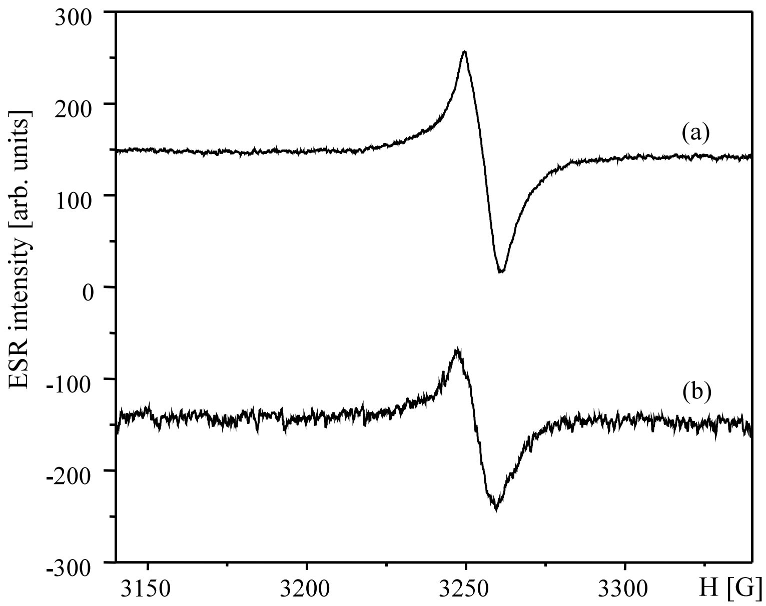

Fig. 4. X-band ESR spectra of UV-induced electron E′ (Ge)-centres, detected for the glass with $Ca_3Ga_2Ge_4O_{14}$ composition at RT (a) and liquid-nitrogen temperature (b).

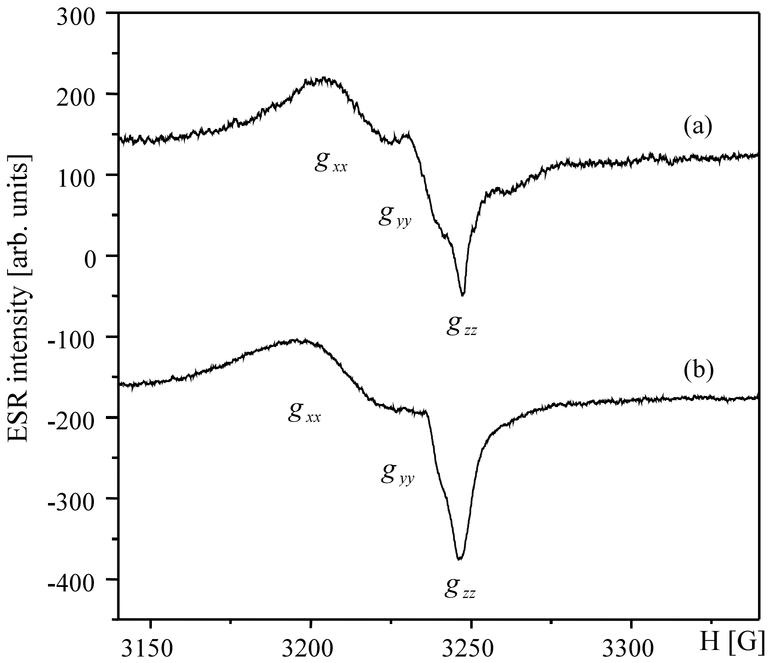

Fig. 5. X-band ESR spectra of *X*-induced hole O^--centres in the glass with $Ca_3Ga_2O_6$ composition, detected at RT (a) and liquid-nitrogen temperature

The ESR spectroscopy of the irradiated samples performed after isochronal annealing shows that the E′ (Ge) and O^- centres are characterised by a high thermal stability in the CaO-Ga_2O_3-GeO_2 glass network. Moreover, disappearance of the E′ (Ge) and O^- centres is observed above 280 and 230°C, respectively. Therefore, the pronounced TSL glow curves around 280°C in the Ge-containing glasses are attributed to recombination of the E′ (Ge) centres. In the γ-irradiated Ge-containing glasses and 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 main fraction of O^- centres. The intense TSL band peaked at 380°C available in the *X*- and *γ*-irradiated glass and ceramics with $Ca_3Ga_2O_6$ composition (see Fig. 2) could be related to recombination of non-paramagnetic radiation-induced or intrinsic defects, because their ESR spectra are 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.

3.2. TSL glow curves of β-irradiated glasses and ceramics and their analysis

In the nominally pure Ge-containing glasses, β-irradiated at the RT, none TSL glow curve is observed (Fig. 6, curve c). In the β-irradiated ceramics and glass 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 above 380°C. This corresponds to C1, C2 and C3 centres, respectively (see Fig. 6, curves a, b). In Fig. 7a and 7b, we present the results of glow curve analysis for the β-irradiated ceramics and glass with $Ca_3Ga_2O_6$ composition. Assuming a simple form

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

where A is some constant, k the Boltzman constant, we obtain from Fig. 7a and 7b the values of the activation energy ($E \cong 0.56$ eV and $E \cong 0.33$ eV for the C1 and C2 centres, respectively).

The maximum of the TSL band in the β-irradiated glass and ceramics with $Ca_3Ga_2O_6$ composition, that corresponds to the C2 centres (Fig. 6, curves a and b), is close to the maximum of the TSL glow curves for the O^- centres found for the γ-irradiated glasses and ceramics (see Fig. 1 and 2). It could be assigned to recombination of the O^- centres. The TSL band peaked about at 120°C and the band located above 380°C may be related to recombination of the radiation-induced C1 and C3 centres or the non-paramagnetic intrinsic defects. The nature and electron structure of the C1 and C3 defects in β-irradiated glass and ceramics with $Ca_3Ga_2O_6$ composition need a more detailed investigation involving the ESR and optical spectroscopy.

Conclusions

Using the methods of TSL and ESR spectroscopy, we have shown that the formation of radiation-induced defects in the glasses of CaO-Ga_2O_3-GeO_2 system depends on the basic glass composition and the kind of irradiation. In particular, the electron-excess E′ (Ge) and hole-trapped O^- centres stable at the RT coexist in X- and γ-irradiated glasses with the $Ca_3Ga_2Ge_4O_{14}$ and $Ca_3Ga_2Ge_3O_{12}$ composition, whereas the UV- and X-radiation induce only O^- centres in the glasses with $Ca_3Ga_2O_6$ composition, and these centres prove to be stable at the RT. The structural disordering leads to a better stabilisation of radiation defects, because the thermal stability of the radiation-induced centres in the ordered garnet ($Ca_3Ga_2Ge_3O_{12}$) and disordered Ca-gallogermanate ($Ca_3Ga_2Ge_4O_{14}$) crystals is lower, when compare with the glasses of the same composition.

The TSL glow curves show a good correlation with the ESR data. Particularly, the TSL band with the maximum near 230 – 220°C in γ- and X-irradiated Ge-containing glasses, as well as in γ -, X- and β-irradiated glass and

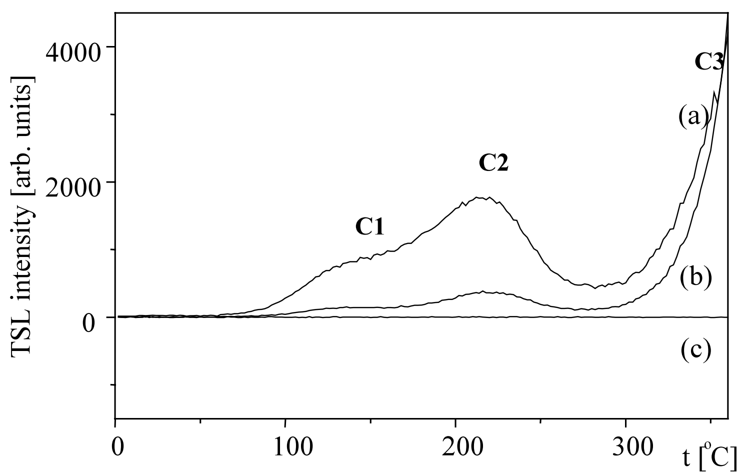

Fig. 6. TSL glow curves for β-irradiated ceramics (a) and glass (b) with $Ca_3Ga_2O_6$ composition.

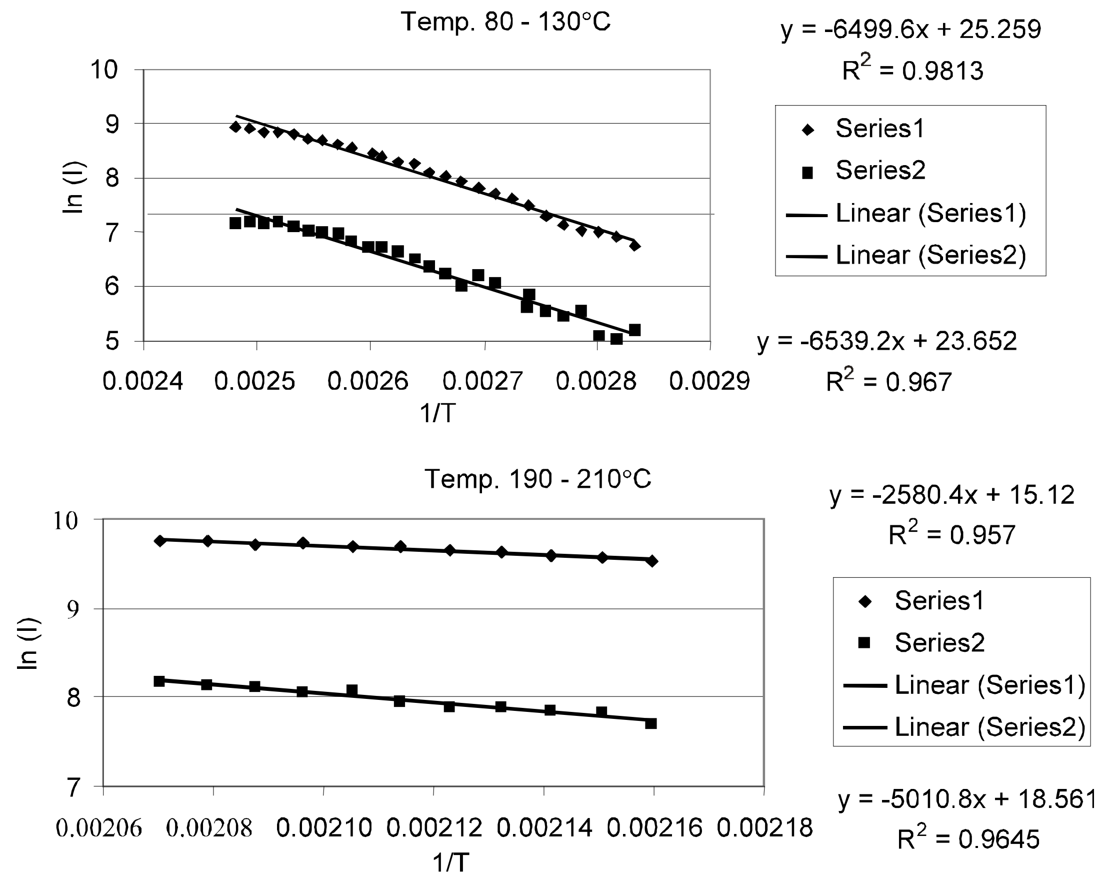

Fig. 7. Results of the glow curves analysis by linear fitting for *β*-irradiated ceramics (series 1 data) and glass (series 2 data) with $Ca_3Ga_2O_6$ composition in the 80 ÷ 130°C (a) and 190 ÷ 210°C (b) temperature range. Details of fitting are given in the Figures.

ceramics with $Ca_3Ga_2O_6$ composition, are assigned to recombination of the O^- centres. The TSL band for the *γ*- and *X*-irradiated Ge-containing glasses peaked in the vicinity of 280°C is attributed to recombination of the E′ (Ge) centres. The TSL glow curve for the *γ*- and *X*-irradiated glasses with $Ca_3Ga_2O_6$ composition, which is peaked at about 380°C, could be related to recombination of non-paramagnetic defects. The studies on the nature and electron structure of the C1 and C3 defects existing in the *β*-irradiated glass and ceramics with the $Ca_3Ga_2O_6$ composition will be a subject of a future work.

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