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# Laser- and $\gamma$ -induced transformations of optical spectra of indium-doped sodium borate glass

O V Kopyshinsky<sup>1</sup>, B A Okhrimenko<sup>1</sup>, S E Zelensky<sup>1,3</sup>, B A Danilchenko<sup>2</sup>  
and O P Shakhov<sup>2</sup>

<sup>1</sup> Physics Department, Kyiv University, 6 Glushkova Street, Kyiv 03680, Ukraine

<sup>2</sup> Institute of Physics of National Academy of Sciences, 46 Prospect Nauki, Kyiv 03028, Ukraine

E-mail: zele@phys.univ.kiev.ua

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## Abstract

The optical absorption and luminescence properties of indium-doped sodium borate glass irradiated by  $\gamma$ -rays and by powerful UV lasers within the impurity-related absorption band are investigated experimentally. It is demonstrated that both the laser- and  $\gamma$ -irradiation cause similar transformations of optical spectra in the UV and visible regions. The changes of the spectra observed are described with the use of a model which includes three types of impurity centres formed by differently charged indium ions.

## 1. Introduction

Heavy ions with the configuration of outer electrons  $nd^{10}(n+1)s^2$  ( $\text{In}^+$ ,  $\text{Sn}^{2+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Tl}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$ ) are usually referred to as mercury-like ions (MLI). Luminescent properties of MLI in various matrixes (alkali halide crystals, oxide glasses, aqueous electrolyte solutions) are nowadays investigated in detail. Luminescent properties of various MLI in various matrices are quite similar. As a rule, broad luminescence bands ( $\Delta\nu \sim 10^3 \text{ cm}^{-1}$ ) without visible structure are observed in the UV and visible spectral regions. MLI luminescence lifetimes vary within  $10^{-7}$ – $10^{-4}$  s. Most commonly, the luminescence of MLI impurity centres is ascribed to the transitions in the MLI outer electron shell, namely  $nd^{10}(n+1)s(n+1)p \leftrightarrow nd^{10}(n+1)s^2$ .

For all this likeness of luminescent properties of MLI in various matrices, certain differences are observed in the interpretation of luminescence and absorption bands of MLI impurity centres in crystals and in disordered matrixes. For example, investigations were carried out with aqueous electrolyte solutions and borate glasses doped with differently charged MLI [1–3]. The results of these investigations show that d-electrons of MLI play an important role in the formation of optical spectra, i.e. the optical transitions of d-electrons appear in the absorption and luminescence spectra observed. Further, on the basis of analysis of numerous

<sup>3</sup> Author to whom any correspondence should be addressed.

experimental data, the authors [3] made a supposition that the orbital collapse of excited f-electrons can manifest itself in the MLI optical spectra.

The use of powerful UV lasers for the excitation of MLI luminescence has expanded the scope of phenomena investigated. Under this powerful laser excitation, the laser-induced quenching of luminescence, the two-photon successive photoionization of MLI, and the laser-induced absorption were discovered and investigated [2–5]. For the borate glasses and alkali halide crystals doped with MLI, the irradiation by powerful UV laser light causes stability changes in the glass optical absorption and luminescence spectra that can be used for the purposes of optical recording and storage [5]. As for the borate glass, the above-mentioned laser-induced stable transformations of optical properties are the most pronounced in the glass doped with indium ions.

Alkali borate glass doped with  $\text{In}^+$  ions was first synthesized and investigated in [6]. It was discovered that the luminescence and absorption spectra include three overlapping spectral components which can be related to the transitions  $5s^2 \leftrightarrow 5s5p$  and  $4d^{10}5s^2 \leftrightarrow 4d^94f5s^2$  or  $4d^{10}5s^2 \leftrightarrow 4d^95s^25p$ . Later [2, 3, 5, 7, 8] the indium-doped borate glass was investigated under powerful UV laser excitation in the spectral region of  $\text{In}^+$  absorption. It was found that the powerful excitation caused reversible and irreversible changes in the absorption and luminescence spectra and kinetics. All of the data obtained in the experiments are interpreted using a single model. The reversible changes in the optical characteristics are attributed to the absorption of laser radiation by the excited indium centres. The irreversible changes result from the laser-induced recharging of indium centres,  $\text{In}^+ \leftrightarrow \text{In}^{2+} \leftrightarrow \text{In}^{3+}$ . The suggested model of interaction of indium-doped borate glass with powerful UV laser radiation is also confirmed by the investigations of recombination luminescence, thermoluminescence, and the kinetics of laser-induced absorption [5].

Indium-containing glasses and crystals have attracted the attention of physicists in various aspects. For example, the authors [9] have proposed indium disilicate as a new fast scintillator; the optical properties of  $\text{In}_2\text{O}_3$  nanocrystals and films have been investigated in [10, 11]; indium is used as a dopant in silicon [12] and ZnS [13]; and nanoparticles of indium oxide have been successfully embedded into porous silicon [14]. It should be noted that, in the present paper, we investigate glasses which are quite different from the indium-containing objects. The main differences are the following. First, we investigate a wide-band-gap glass in which the impurity-related energy levels lie within the band gap. Second, the glass investigated is doped with indium in a form of  $\text{In(I)}$ , but not  $\text{In(III)}$ . Third, the level of indium doping in the glass investigated is much lower than the indium content in  $\text{In}_2\text{O}_3$  crystals.

The goal of this paper is to investigate the effect of  $\gamma$ -irradiation on the spectral properties of indium-doped sodium borate glass and to compare the  $\gamma$ -induced and laser-induced changes of the glass spectral characteristics.

## 2. Experimental details

The investigations were performed with the following glass samples:  $\text{Na}_2\text{O}-7\text{B}_2\text{O}_3-0.1 \text{ wt\%In}$  and  $\text{Na}_2\text{O}-7\text{B}_2\text{O}_3$ , hereinafter referred to as Na7–In and Na7 respectively. The glass was melted in platinum crucibles at a temperature of 1300 K in air. The glass was cast into preheated aluminium moulds and was annealed for 8–10 h at a temperature of 600 K. After the annealing, the glass samples were gradually cooled down to room temperature over 15–20 h.

To ensure that the doping indium is uniformly distributed in the bulk glass, we compared the luminescence spectra of Na7–In glasses with indium contents of 0.01, 0.1 and 1%. The agreement of the spectra indicates the absence of indium aggregate centres or colloidal particles in the glasses investigated.

Spectral measurements were performed with a computer-controlled spectrometer. For the excitation of glass luminescence, the following light sources were employed: a YAG–Nd<sup>3+</sup> laser (third and fourth harmonics, wavelengths 355 and 266 nm respectively, pulse duration  $\theta = 25$  ns) and a nitrogen laser (337 nm, 8 ns). For the luminescence excitation, the surface power density of the laser radiation was approximately  $10^4$ – $10^5$  W cm<sup>-2</sup>. The luminescence was detected with a photomultiplier through a single grating monochromator. The non-uniformity of the spectral sensitivity was corrected with the use of a standard incandescent lamp. The time-resolved luminescence spectral measurements were performed using the nitrogen laser and a gated photomultiplier with a gating pulse width of 0.15–0.5  $\mu$ s.

In this paper, the laser radiation was used both for excitation of the glass luminescence and for UV irradiation of the glass samples. The parameters of the laser pulses at irradiation were as follows: wavelength 266 nm, power density  $10^7$ – $10^8$  W cm<sup>-2</sup>, pulse energy 0.25 mJ.

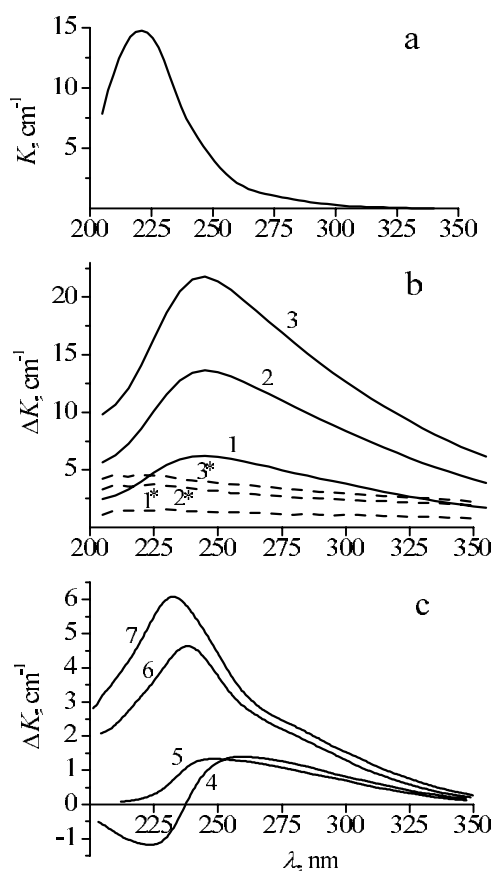
$\gamma$ -irradiation was carried out with a <sup>60</sup>Co source. In this paper, all of the measurements, irradiation and storage of the glass samples were performed at room temperature. The experimental data were obtained with a delay of at least 10 days after the irradiation.

### 3. Results and discussion

Figure 1(b) presents the  $\gamma$ -induced optical absorption spectra,  $\Delta K(\lambda)$ , of glass samples Na7–In and Na7 for three values of the irradiation dose, where  $\Delta K$  is the difference in the absorption coefficients of the  $\gamma$ -irradiated and non-irradiated glass samples. For the purpose of comparison, the absorption spectrum,  $K(\lambda)$ , of non-irradiated glass Na7–In is given in figure 1(a), where  $K$  is the absorption coefficient. As can be seen from figure 1(b), the  $\gamma$ -induced absorption takes place primarily in the UV spectral region. Further, the  $\gamma$ -induced absorption is much stronger in the indium-doped glass than in the non-doped glass. This indicates that indium ions in borate glass participate in the processes of  $\gamma$ -induced transformations of optical properties.

Figure 1(c) shows the laser-induced optical absorption spectra of glass sample Na7–In for different values of laser UV irradiation dose [2]. The photon energy of the UV laser employed is below the ionization threshold of both the glass matrix and the impurity centres; hence the non-doped glass does not show the laser-induced absorption. The mechanism of laser irradiation involves the ionization of indium impurity centres via sequential absorption of two laser photons by indium centres through the intermediate excited state. The optical absorption spectra of the laser-ionized centres (In<sup>2+</sup>, In<sup>3+</sup>) differ from the spectrum of initial In<sup>+</sup> centres; hence the laser-induced absorption is observed in the indium-doped glass Na7–In (figure 1(c)). The absorption spectra of In<sup>+</sup>, In<sup>2+</sup>, and In<sup>3+</sup> centres are wide overlapping bands in the UV spectral region. The laser irradiation changes the concentrations of the three types of indium impurity centres, which results in changes of the laser-induced absorption spectra with irradiation dose. As can be seen from figure 1(c), for small doses (curve 4), the laser-induced fading is observed in the region of 200–230 nm. With increasing laser irradiation dose, the fading disappears, the induced absorption band increases and its peak shifts towards shorter wavelengths (curves 5, 6 and 7 in figure 1(c)). The mentioned behaviour of the induced absorption spectra can be interpreted within the framework of the model involving the laser-induced recharging of impurity centres according to the scheme In<sup>+</sup>  $\leftrightarrow$  In<sup>2+</sup>  $\leftrightarrow$  In<sup>3+</sup> [2].

Concerning the In<sup>+</sup>, In<sup>2+</sup> and In<sup>3+</sup> overlapping absorption bands, the following considerations should be noted. As expected, the absorption spectra of In<sup>+</sup> and In<sup>3+</sup> centres are similar in shape, and the absorption cross-section of the In<sup>3+</sup> centres exceeds the appropriate values of the In<sup>+</sup> centres. This assertion is indirectly substantiated by the results in [1, 15], where the spectral properties are investigated for the aqueous electrolyte solutions doped



**Figure 1.** (a) Absorption spectrum of non-irradiated glass Na7-In. (b)  $\gamma$ -induced absorption spectra of Na7-In (1–3) and Na7 (1\*–3\*) for the irradiation dose of 1700 Gy (1, 1\*), 4250 Gy (2, 2\*), 8500 Gy (3, 3\*). (c) Laser-induced absorption spectra of Na7-In for the dose of  $10^4$  Gy (4),  $4 \times 10^4$  Gy (5),  $7.5 \times 10^4$  Gy (6), and  $1.5 \times 10^5$  Gy (7).

with MLI in different charge states corresponding to the electron configurations with and without s-electrons,  $nd^{10}(n+1)s^2$  and  $nd^{10}$ . As is shown in [1], the absorption spectrum of  $\text{H}_2\text{O-HCl-Sn}^{4+}$  solution to a first approximation is similar to the spectrum of  $\text{H}_2\text{O-HCl-Sn}^{2+}$  solution. Similar conclusions are drawn for solutions doped with  $\text{Tl}^{3+}$  and  $\text{Tl}^+$  [1],  $\text{Sb}^{5+}$  and  $\text{Sb}^{3+}$  [15].

Considering the laser- and  $\gamma$ -induced absorption spectra given in figure 1, the following should be noted. First, the presence of indium impurities in the glass accounts for the irradiation-induced absorption in the UV spectral region for both  $\gamma$ - and laser irradiation. Second, the effects of  $\gamma$ - and laser irradiation at large doses are similar to a first approximation. In both of these cases, the broad UV absorption band increases with increase of irradiation dose, which can be explained by the increase in the concentrations of the ionized indium centres ( $\text{In}^{2+}$  and  $\text{In}^{3+}$ ).

There are also considerable differences between the  $\gamma$ - and laser-induced absorption spectra given in figure 1. First, within the interval of  $\gamma$ -irradiation doses investigated, the fading at wavelengths of 200–230 nm is not observed. Second, the shapes of the spectra at large doses are slightly different. Third, the  $\gamma$ -induced absorption spectra are higher than

the laser-induced spectra, whereas the  $\gamma$ -doses are much smaller than the laser doses. For example, curves 1 and 7 in figure 1 are of the same order of magnitude ( $\Delta K \approx 6 \text{ cm}^{-1}$ ), whereas the appropriate doses differ by a factor of 100. These differences can be attributed to the differences in the mechanisms of ionization by laser and  $\gamma$ -irradiation. Indeed, the  $\gamma$ -irradiation involves a unaimed bombardment of the bulk glass, whereas the laser irradiation is 'aimed' directly at indium centres. As a consequence, the relative concentrations of  $\text{In}^+$ ,  $\text{In}^{2+}$  and  $\text{In}^{3+}$  centres are different for laser and  $\gamma$ -irradiation, even if the doses are equal.

As for the above-mentioned difference in the magnitude of the effects, consider the following estimations. For a  $1 \text{ cm}^3$  glass sample, the total energy absorbed during  $\gamma$ -irradiation can be approximately estimated as 20 J. Suppose this energy is spent on the creation of electronic excitations with an average energy of tens of electronvolts. Then the estimated total number of  $\gamma$ -induced electron-hole pairs created in the  $1 \text{ cm}^3$  glass sample during the irradiation is of the same order of magnitude as the number density of indium centres in the glass ( $10^{19} \text{ cm}^{-3}$ ). Thus we conclude that indium ions in the investigated glass effectively trap the  $\gamma$ -generated holes, whereas the  $\gamma$ -generated electrons are captured elsewhere in the glass.

For the UV laser irradiation of the Na7-In glass, the relatively low efficiency of creation of ionized indium centres can be explained with the following reasoning. For the two-step absorption transitions in  $\text{In}^+$  centres, consider the following population balance equations:

$$\begin{aligned} \frac{dn_1}{dt} &= -\sigma_1 F n_1 + \frac{n_1^*}{\tau} \\ \frac{dn_1^*}{dt} &= \sigma_1 F n_1 - \frac{n_1^*}{\tau} - \sigma_1^* F n_1^* \\ \frac{dn_1^{**}}{dt} &= \sigma_1^* F n_1^* \end{aligned} \quad (1)$$

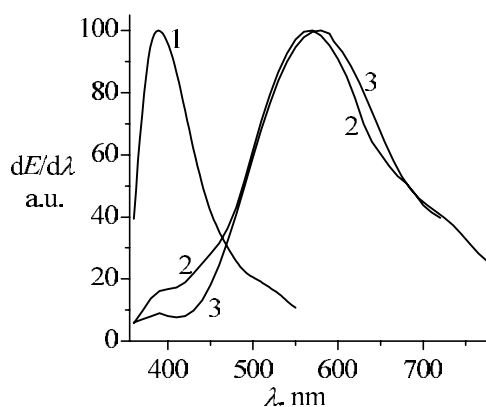
where  $n_1$  and  $n_1^*$  are the populations of the ground and excited states of  $\text{In}^+$  centres respectively,  $n_1^{**}$  is the number density of electrons detached from  $\text{In}^+$  centres,  $\sigma_1$  is the absorption cross-section,  $\sigma_1^*$  is the cross-section of absorption from the excited state of  $\text{In}^+$  centres,  $F$  is the laser intensity in photons  $\text{cm}^{-2} \text{ s}^{-1}$ , and  $\tau$  is the excited state lifetime. Here  $\sigma_1 = 10^{-19} \text{ cm}^2$  and  $\sigma_1^* \approx 5 \times 10^{-19} \text{ cm}^2$  [3] at the laser wavelength of 266 nm. The total number of electrons detached from  $\text{In}^+$  centres in a unit volume by a single laser pulse,  $N_e$ , can be calculated from (1) as  $n_1^{**}$  at  $t = \theta$ . The number of laser photons absorbed in a unit volume,  $N_q$ , can be estimated as

$$N_q = \int_0^\theta (\sigma_1 n_1 + \sigma_1^* n_1^*) F dt. \quad (2)$$

With the use of (1) and (2) at a laser power density of  $50 \text{ MW cm}^{-2}$ , we can estimate the value of  $N_e/N_q \approx 0.2$ . The value obtained is overestimated for the following reasons:

- (1) The UV laser radiation is absorbed in Na7-In not only by s-electrons of indium centres, but also by d-electrons. This absorption does not result in ionization.
- (2) The ionized indium centres ( $\text{In}^{2+}$  and  $\text{In}^{3+}$ ) absorb the laser light.
- (3) Each laser irradiation pulse is followed by recombination processes, which also reduce the efficiency of ionization.

The mechanisms are difficult to account for. However, their role in the decrease of ionization efficiency can be estimated as follows. Experiments [5] show that a single laser pulse causes a decrease in the number density of  $\text{In}^+$  centres in a non-irradiated glass sample by approximately 1% ( $\Delta n_1 \approx 0.01 n_1$ ). On the other hand, this value can be calculated with (1). As a result, for the laser irradiation of Na7-In we evaluate the ionization quantum efficiency as  $\Delta n_1/N_q \approx 0.05$ .



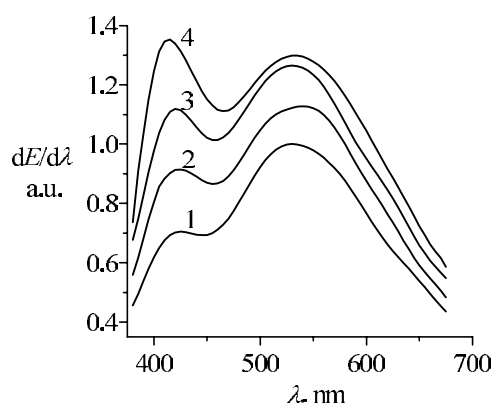
**Figure 2.** Luminescence spectra of non-irradiated (1), laser-irradiated (2) and  $\gamma$ -irradiated (3) glass Na7–In.

This value is an estimate for low doses, when the concentration of  $\text{In}^+$  centres does not change significantly with the dose. For larger doses, the ionization of  $\text{In}^{2+}$  centres and the recombination processes should be taken into account. Nevertheless, the estimate obtained is in agreement with the results given in figures 1(b) and (c), at least by an order of magnitude.

We now consider the results of the investigation of luminescent properties of laser- and  $\gamma$ -irradiated glass Na7–In. In this paper, the luminescence of undoped glass Na7 is neglected as far as possible by a factor of 0.05–0.01 as large as the luminescence of the indium-doped glass. The luminescence spectra of irradiated and non-irradiated glass Na7–In are given in figure 2. The excitation wavelength is 355 nm, and the spectra are normalized by maximal intensity. The ‘blue’ emission band of the non-irradiated glass (curve 1 in figure 2) can be attributed to the transitions in the external electron shell of  $\text{In}^+$  ions, as is done for indium-doped potassium borate glass in [6]. The laser UV irradiation of the glass gives rise to the formation of a ‘yellow’ luminescence band with a maximum at 560–580 nm (curve 2 in figure 2). As can be seen from figure 2, curve 3, the  $\gamma$ -irradiation of the glass also produces a long-wavelength luminescence band which practically coincides with the ‘yellow’ band of the laser-irradiated glass. It is reasonable to suggest that both the ‘yellow’ luminescence bands are of the same nature.

The ‘blue’ luminescence of MLI in alkali borate glass is usually ascribed to the transitions from the  $^3\text{P}_{0,1,2}$  level splitting in the ligands field. These transitions are spin forbidden; hence the appropriate lifetimes are relatively long ( $10^{-7}$ – $10^{-5}$  s). For example, the decay time of ‘blue’ luminescence of the non-irradiated glass Na7–In is about 10  $\mu\text{s}$ . According to [5], the ‘yellow’ luminescence of laser-irradiated indium-doped glass is attributed to the transitions in the external electron shell of  $\text{In}^{2+}$  ions. The possible transitions  $^2\text{P}_{1/2,3/2} \rightarrow ^2\text{S}_{1/2}$  are dipole allowed, and therefore we can expect that the lifetime of the ‘yellow’ luminescence will be shorter compared with the lifetime of the ‘blue’ luminescence. The appropriate measurements confirm this supposition. For both laser- and  $\gamma$ -irradiated glass, the luminescence decay time in the ‘yellow’ band does not exceed the length of the laser excitation pulse (25 ns), which can be considered as indirect confirmation of the proposed interpretation of the ‘yellow’ luminescence investigated.

Thus, to a first approximation, the changes in the spectral characteristics of glass Na7–In caused by  $\gamma$ -irradiation are similar to the changes caused by powerful laser UV irradiation performed in the spectral region of  $\text{In}^+$  absorption.



**Figure 3.** Luminescence spectra of  $\gamma$ -irradiated glass Na7–In for various intervals of UV illumination: 1, 0 min; 2, 8 min; 3, 20 min; 4, 40 min.

As is known for non-doped borate glass [16–18], the ionizing irradiation causes the formation of colour centres of two main types: BEC centres and BOHC centres. The BEC centres are electrons trapped at oxygen vacancies. For these centres, the average depth is about 0.2 eV, so BEC centres are unstable at room temperature. The BOHC centres are holes trapped at oxygen vacancies bridging a three-coordinated boron to a tetra-coordinated boron of the glass-forming network. The BOHC centres are stable at room temperature. Besides the BEC and BOHC centres, irradiated borate glasses usually contain other centres which can trap the electrons and holes produced by the ionizing radiation.

After the  $\gamma$ -irradiation, the glass samples become coloured. The coloration is visible to the naked eye as a slight brown tint in the bulk glass for a sample thickness of several millimetres. During the storage of  $\gamma$ -irradiated glass for several weeks, the  $\gamma$ -induced coloration remained practically unchanged. However, clearly visible photo-bleaching of the glass samples was observed during the recording of luminescence spectra. That is why in this paper the following measures were taken to reduce the errors caused by the photo-bleaching:

- (1) The luminescence spectra were recorded at the lowest possible intensity of photoexcitation.
- (2) The spectrometer was equipped with a computer-controlled mechanical gate, which shuts off the excitation beam while the monochromator's motor is operating.

As a result, the spectra presented in this paper were recorded under such conditions that the photo-bleaching can be neglected (the repeatedly recorded two spectra were practically identical).

Figure 3 illustrates the changes in the luminescence spectra of  $\gamma$ -irradiated glass Na7–In caused by the photo-bleaching. For the spectra in this figure, the excitation intensity of the nitrogen laser was about  $10^4 \text{ W cm}^{-2}$  with a repetition rate of  $50 \text{ pulses s}^{-1}$ . In the intervals between the recordings of the spectra, the glass sample was illuminated by the same nitrogen laser with an increased power density of about  $100 \text{ kW cm}^{-2}$ . Hereinafter we will refer to this laser treatment of  $\gamma$ -irradiated glass samples as illumination, in order to differentiate this process from the UV laser irradiation of  $\gamma$ -non-irradiated samples. As can be seen from figure 3, with an increase in the dose of UV illumination, the luminescence intensity increases. Further, the ratio of intensities of the  $\text{In}^+$  and  $\text{In}^{2+}$  luminescence bands (the 'blue' and 'yellow' bands respectively) also changes with illumination dose.

The observed illumination-induced transformations of luminescence spectra of the  $\gamma$ -irradiated glass can be interpreted as follows. The laser photons release the localized



electrons from the traps with subsequent capture of the released electrons by indium ions,  $\text{In}^{3+} + e^- \rightarrow \text{In}^{2+}$  and  $\text{In}^{2+} + e^- \rightarrow \text{In}^+$ . As a result, the increase in concentration of the  $\text{In}^+$  and  $\text{In}^{2+}$  luminescence centres causes an increase in the ‘yellow’ and ‘blue’ luminescence bands which is observed experimentally.

It should be noted that the experimental results described in this paper can be formally interpreted in another way as follows. First, suppose the electron configuration  $4d^{10}5s$  of the  $\text{In}^{2+}$  ion is unstable. One of the reasons for such a supposition is the fact that MLI in electrolyte solutions usually exist in two stable forms, e.g.  $\text{Tl}^+$  and  $\text{Tl}^{3+}$ ,  $\text{Sb}^{3+}$  and  $\text{Sb}^{5+}$ , corresponding to the configurations  $nd^{10}(n+1)s^2$  and  $nd^{10}$  [1, 15]. Second, suppose the ‘yellow’ luminescence band corresponds to the transitions  $4d^{10} \leftarrow 4d^95s$  or  $4d^{10} \leftarrow 4d^94f$  in  $\text{In}^{3+}$  ions, and also suppose that  $\text{In}^{2+}$  ions do not possess luminescence. On this basis, one can interpret the observed illumination-induced transformations of luminescence spectra as follows: the laser illumination causes transformation of  $\text{In}^{2+}$  ions to  $\text{In}^{3+}$  ions (by successive two-photon ionization of  $\text{In}^{2+}$  centres) and also to  $\text{In}^+$  ions (as a result of the recombination of photo-released electrons with  $\text{In}^{2+}$  centres).

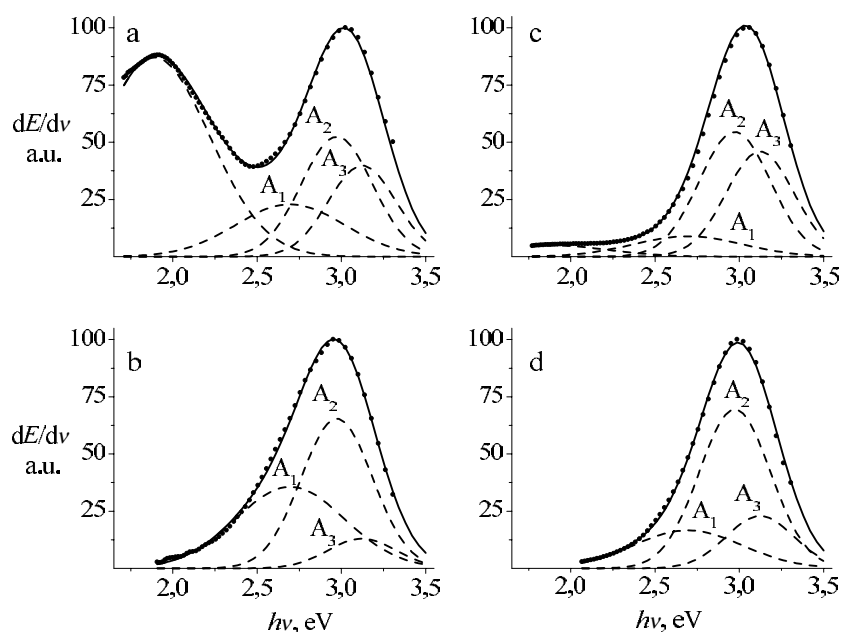
Since the latter model requires the two-photon ionization of impurity centres by laser radiation, we can choose between the above two models by performing the following experiment. For the illumination of  $\gamma$ -irradiated glass, we employed a continuous-wave He–Ne laser, whereas for the luminescence excitation the attenuated radiation of the nitrogen laser was used. The parameters of the He–Ne laser (632 nm, 3 mW) eliminate the possibility of two-photon absorption in indium centres, but enable the single-photon photo-release of trapped electrons. The experiment shows that the low-intensity light of the He–Ne laser causes a detectable increase in both the ‘yellow’ and ‘blue’ luminescence bands of  $\gamma$ -irradiated indium-doped glass. Thus we accept the first model,  $\text{In}^{3+} + e^- \rightarrow \text{In}^{2+}$  and  $\text{In}^{2+} + e^- \rightarrow \text{In}^+$ , that describes the observed illumination-induced transformations of luminescence spectra of  $\gamma$ -irradiated glass.

As is known for alkali halide crystals [19–21], both  $\gamma$ - and UV laser irradiation can also produce  $\text{In}^0$  and  $\text{Tl}^0$  centres. These centres are unstable at room temperature. Being generated by powerful UV laser irradiation, the  $\text{In}^0$  centres practically exist during the action of the laser pulse [21]. The absorption spectrum of  $\text{Tl}^0$  centres in alkali halide crystals is located in the visible region [20]. These reasons substantiate the absence of  $\text{In}^0$  centres in the model considered in this paper.

In order to reveal possible hidden changes in the luminescence spectra caused by  $\gamma$ -irradiation, we investigated the structure of the luminescence spectra observed. With the nitrogen pulsed laser excitation, the time-resolved luminescence spectra of  $\gamma$ -irradiated and non-irradiated glass were recorded. The experiments showed that the ‘blue’ luminescence band of Na7–In glass undergoes significant changes while decaying after the laser excitation pulse. The transformations of the ‘blue’ luminescence band are observed both for  $\gamma$ -irradiated and non-irradiated glass samples and indicate that this band hides its complex structure. As for the ‘yellow’ luminescence band of  $\gamma$ -irradiated glass, we did not discover its transformation during the luminescence decay because its lifetime is shorter than the shortest available gating pulse width (0.15  $\mu\text{s}$ ).

All of the luminescence spectra obtained at different delay times indicate that the ‘blue’ luminescence band consists of no less than three overlapping components with different lifetimes. We use the following function for fitting:

$$I(\omega, \Delta t) = \sum_{i=1}^3 I_{0i} \exp[-(\omega - \omega_{0i})^2 \Delta \omega_i^{-2} 4 \ln 2 - \Delta t \tau_i^{-1}] \quad (3)$$



**Figure 4.** Luminescence spectra and spectral components according to expression (1) for  $\gamma$ -irradiated (a), (b) and non-irradiated (c), (d) glass Na7–In for  $\Delta t = 0$  (a), (c) and  $15 \mu\text{s}$  (b), (d). Excitation wavelength 337 nm.

**Table 1.** Parameters of components of Na7–In luminescence.

	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>
$\omega_{0i}$ (eV)	2.70	2.97	3.12
$\Delta\omega_i$ (eV)	0.76	0.50	0.47
$\tau_i$ ( $\mu\text{s}$ )	18.02	12.69	6.36

where  $\Delta t$  is the delay between the excitation pulse and the gating pulse,  $I_{0i}$  is the peak value of the  $i$ th component at  $\Delta t = 0$ ,  $\omega_{0i}$ ,  $\Delta\omega_i$  and  $\tau_i$  are respectively the central frequency, half-width and lifetime of the  $i$ th component. The parameters of the components obtained are given in table 1. As an example, figure 4 shows the decomposition of the ‘blue’ luminescence band of the Na7–In glass. It should be noted that all of the spectra obtained for various gating delays can be fitted using expression (3) with the fixed values of  $\omega_{0i}$ ,  $\Delta\omega_i$  and  $\tau_i$  for both  $\gamma$ -irradiated and non-irradiated glass. Because the structure of the ‘yellow’ luminescence band is not resolved in our experiments, this band is presented in figure 4 only as a single Gaussian component.

It should be noted that the authors [6], using the luminescence excitation spectra, have also resolved three components in the luminescence spectrum of potassium borate glass doped with indium ions. Taking into consideration the similarity of properties of MLI in various matrices, the three components of ‘blue’ luminescence obtained in this paper (table 1) can also be assigned to the transitions in the external electron shell of  $\text{In}^+$  ions. The components A<sub>2</sub> and A<sub>3</sub> correspond to the transitions  $4d^{10}5s^2 \leftrightarrow 4d^{10}5s5p$  (s-bands), and A<sub>1</sub> corresponds to  $4d^{10}5s^2 \leftrightarrow 4d^95s^24f$  or  $4d^{10}5s^2 \leftrightarrow 4d^95s^25p$  (d-band). As can be seen from figure 4, the relative intensities of s-bands (A<sub>2</sub> and A<sub>3</sub>) are equal for both  $\gamma$ -irradiated and non-irradiated glass, whereas the relative contribution of the d-band (A<sub>1</sub>) in the  $\gamma$ -irradiated glass is 2.5 times

larger than in the non-irradiated glass. This seems surprising since all of the components  $A_1$ ,  $A_2$  and  $A_3$  are attributed to only one luminescence centre ( $\text{In}^+$  centre). We believe that the observed increase of the d-band in the irradiated glass is caused by the luminescence of the d-electrons of  $\text{In}^{2+}$  and/or  $\text{In}^{3+}$  centres. Unfortunately, the experimental data available do not enable us to distinguish the d-luminescence of the  $\text{In}^+$ ,  $\text{In}^{2+}$  and  $\text{In}^{3+}$  centres.

For the  $\gamma$ - and laser-induced transformations of indium centres in glass, the model under consideration in this paper implies that the concentration of  $\text{In}^+$  centres decreases with irradiation dose. The decrease in concentration manifests itself through the appropriate decrease in the 'blue' luminescence band. For example, at a  $\gamma$ -irradiation dose of 8500 Gy, the experiments show that the intensity of 'blue' luminescence decreases by a factor of  $N = 6$ . However, this does not mean that the concentration of  $\text{In}^+$  centres in the irradiated glass also decreases by the same factor  $N = 6$ . The decrease in the concentration of  $\text{In}^+$  centres is accompanied by an increase in the concentration of  $\text{In}^{2+}$  and  $\text{In}^{3+}$  centres; hence the absorption of laser excitation increases significantly (see figure 1). The irradiation-induced absorption does not result in 'blue' luminescence but causes a decrease in the spatially integrated signal of 'blue' luminescence registered experimentally. In order to estimate this decrease for the concentration of  $\text{In}^+$  centres using the measured value of  $N$ , we considered the following relations. For  $\text{In}^+$  centres, we denote by  $n_1$  and  $\sigma_1$  the concentration and the absorption cross-section at the wavelength of laser excitation, respectively. According to Bouguer's law, the following expression can be written:

$$F(z) = F_0 \exp[-(\sigma_1 n_1 + \beta)z] = F_0 \exp(-\alpha z) \quad (4)$$

where  $F$  is the surface power density of laser excitation,  $z$  is the coordinate along the laser beam,  $F_0 = F(0)$ ,  $\beta$  is the absorption coefficient of irradiated glass except for  $\text{In}^+$  absorption, and  $\alpha$  is the absorption coefficient of the irradiated glass Na7-In. For a differential of volume,  $dV = S dz$ , where  $S$  is the cross-section of the laser beam, the total power of the 'blue' luminescence emitted from the volume element  $dV$  is proportional to the amount of excited  $\text{In}^+$  centres, which can be derived from the population balance equations. Thus the intensity of the 'blue' luminescence,  $dI_L$ , emitted from  $dV$ , can be written as

$$dI_L = \text{constant } \sigma_1 n_1 F dV. \quad (5)$$

By substituting (4) into (5) and by integrating over  $z$  from 0 to  $l$ , the following expression for the intensity of luminescence emitted from the whole glass sample,  $I_L$ , can be derived:

$$I_L = \text{constant } \sigma_1 n_1 F_0 \alpha^{-1} [1 - \exp(-\alpha l)]. \quad (6)$$

We denote by  $n_1^0$  the concentration of  $\text{In}^+$  centres in the non-irradiated glass. With  $\beta = 0$ , the following expression can be written for the intensity of luminescence of the non-irradiated glass:

$$I_L^0 = \text{constant } F_0 [1 - \exp(-\sigma_1 n_1^0 l)]. \quad (7)$$

Dividing (7) by (6) gives

$$N = \frac{I_L^0}{I_L} = \frac{\alpha [1 - \exp(-\sigma_1 n_1^0 l)]}{\sigma_1 n_1 [1 - \exp(-\alpha l)]} \simeq \frac{\alpha n_1^0}{n_1 [1 - \exp(-\alpha l)]}. \quad (8)$$

With the values of  $N$  and  $\alpha l$  measured experimentally, expression (8) enables us to estimate the irradiation-induced relative decrease in concentration of the  $\text{In}^+$  centres,  $n_1^0/n_1$ . Here,  $l$  is the length of the light-emitting track located within the field of vision of the photodetector. For a  $\gamma$ -irradiation dose of 8500 Gy and for  $N = 6$ , the calculation gives a value of  $n_1^0/n_1 \approx 2$ .

The value of  $n_1^0/n_1 \approx 2$  obtained should be considered as a rough estimate. The primary sources of errors are the following:

- (1) the non-uniformity of sensitivity of the photodetector within its field of vision (which causes the uncertainty in the integration of (6));
- (2) the overlapping of luminescence spectra of  $\text{In}^+$  and  $\text{In}^{2+}$  centres (which causes the uncertainty in the determination of  $N$ ).

The method of calculating  $n_1^0/n_1$  can also be employed for laser-irradiated Na7–In glass samples. However, in this case, additional errors arise due to the non-uniformity of the distribution of indium centres in the irradiated glass (caused by the spatial non-uniformity of laser irradiation).

#### 4. Concluding remarks

The optical properties of  $\gamma$ - and laser-irradiated indium-doped sodium borate glass are similar. The observed transformations of luminescence and absorption bands can be interpreted on the basis of a single model. The spectral characteristics of irradiated glass are formed mainly by indium centres in different charge states.

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