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RADIOPHOTOLUMINESCENCE IN THE TISSUE-EQUIVALENT LiB_3O_5:Ag GLASSES

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Abstract. The absorption, photoluminescence (PL), and radiophotoluminescence (RPL) spectra in lithium triborate glass (LiB_3O_5:Ag), doped with 1% silver ions and irradiated with different doses of γ-radiation in the 0-20 Gy range have been investigated. The change of these spectra as a function of irradiation dose was also measured. The PL spectra of Ag^+ are dominated by an ultraviolet broadband at about 290 nm. The RPL band is centered at about 430 nm at the excitations in the 310-350 nm spectral region. The mechanism of RPL emission arises from a change in the charge state of silver to A^0-type centers when Ag^+-doped glass is exposed to radiation that generates electrons and holes.

Keywords: lithium triborate glass, γ-radiation, radiophotoluminescence, dosimetric response
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Introduction

Radiophotoluminescence (RPL) is a luminescent phenomenon caused by photoexcitation of centers formed by ionizing radiation, such as γ- or X-rays [1,2]. This phenomenon is exciting because it combines high sensitivity with reusability for dose-measuring, making it ideal for practical applications. The intensity of RPL is proportional to the absorbed radiation dose, and RPL is therefore used in passive dosimeters for personal monitoring, medical dosimetry, and radiation control to reliably measure cumulative dose without loss of information during reading [2,3].

In silver-doped glasses, ions mainly have a valence state of Ag^+, responsible for PL in the UV spectral region. At the same time, the RPL mechanism involves ionizing radiation interacting with the host material, forming electron-hole pairs. These charge carriers are trapped at Ag^+ dopant sites, forming stable RPL centers. In the case of Ag-doped phosphate glasses, these centers include neutral silver atoms (Ag^0), dimeric silver ions (Ag_2^+), and divalent silver ions (Ag^{2+}), which emit light in the visible region of the spectrum upon UV excitation. The process is highly dependent on the composition of the host matrix and the dopant concentration, which affects the efficiency and stability of the RPL centers [2-6].

Due to their promising dosimetric properties, the phosphate glasses doped with silver (Ag) have attracted considerable interest among various host matrices. The RPL centers, in particular, such as Ag^0 and/or Ag^{2+} ions, will not disappear unless the glass dosimeter is

annealed at high temperatures, which allows it to be used in cumulative dosimetry. In these Ag-doped glasses, RPL is characterized by emission peaks with maxima in the blue 430-440 nm, yellow 530-560 nm, and orange near 650 nm spectral region when excited in the 300-350 nm spectral range [6–10].

However, Ag-doped phosphate glasses have one, but rather significant, drawback: their effective atomic number Z_{eff} = 15 [11], while for human body tissues Z_{eff} = 7.42 [12]. This requires the introduction of appropriate coefficients when determining the actual dose received by a patient with cancer during radiotherapy. To avoid this, the dosimetric material's Z_{eff} should equal 7.42. As it turned out, lithium triborate (LiB_3O_5) has a Z_{eff} value of 7.39, which is close to the Z_{eff} of human body tissues [13]. Therefore, LiB_3O_5 has recently attracted more and more attention from researchers. For example, the luminescent properties of LiB_3O_5 polycrystalline powders doped with CuO, MnO_2, Fe_2O_3, $CoCO_3$ and MgO [14], Al_2O_3 [15] and rare earth oxides (Y, Ce-Lu) [16], as well as the luminescent properties of LiB_3O_5:Ag pyroceramics [17] and LiB_3O_5:Ag glasses [18] have been studied. The results of the PL and TL studies of LiB_3O_5:Ag glasses have demonstrated the prospects of this material for medical dosimetry. However, no reports have been made on the RPL emission properties in Ag^+-doped LiB_3O_5:Ag glass. This work aims to investigate the RPL phenomenon in Ag-doped lithium borate glasses, focusing on the formation and behavior of RPL centers under different doses of γ-radiation. Elucidating the spectral and dosimetric properties for the first time will provide a basis for optimizing LiB_3O_5 glasses for application in radiation monitoring.

Experimental

The starting materials were high-purity lithium carbonate (Li_2CO_3) and boric acid (H_3BO_3). These reagents were mixed in a specific ratio to form the LiB_3O_5 compound and synthesized using a solid-state reaction method in a ceramic crucible at 973 K. According to the chemical reaction:

$$Li_2CO_3 + 6H_3BO_3 \rightarrow 2LiB_3O_5 + CO_2 + 9H_2O, \quad (1)$$

was produced LiB_3O_5 in powder form, with a melting temperature (T_{melt}) of 1107 K. The doping of LiB_3O_5 charges with a concentration of 1.0% wt. Ag was achieved by introducing $AgNO_3$ into this powder. The mixture was then finely ground in an agate mortar. The powder was melted in a platinum crucible under an air atmosphere at 1200 K to prepare the glass for 1–2 hours. The molten material was poured onto a metal substrate at room temperature to form a glass block. Plates measuring approximately 6.0×7.0×1.5 mm^3 were cut from the block, with their surfaces ground and polished for further use.

The samples were exposed to γ-rays under realistic radiation therapy conditions using a γ-ray machine at the HALCYON unit of Varian (USA) at the Lviv Regional Oncology Treatment and Diagnostic Center. The applied radiation doses ranged from 3.0 to 20.0 Gy.

A CM 2203 spectrofluorometer was used to investigate the spectroscopic properties of the borate glasses. Excitation was provided by a 150 W pulsed xenon lamp, with the device controlled via a personal computer. The spectrofluorometer operated within a spectral range of 220–820 nm, with a minimum scanning step of 0.5 nm for excitation and detection monochromators.

Results and Discussion

Fig. 1 shows the PL spectra of LiB_3O_5:Ag glass samples γ-irradiated in the dose range from 3 to 20 Gy with a maximum of 290 nm.

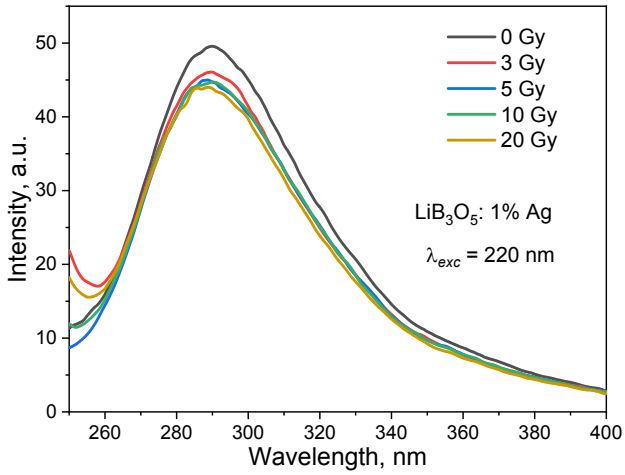

Fig. 1. Photoluminescence spectra of LiB_3O_5:Ag glasses at different irradiation doses under 220 nm excitation.

It is also noticeable from Fig. 1 that the intensity of radiation in the spectral region of 250-400 nm decreased slightly after γ-irradiation, and the luminescence spectra ceased to depend on the irradiation dose. This emission band is most probably associated with the PL from Ag^+ ion-based emission centers, and the decrease in its intensity can be explained by the recharging of some of these centers with free charge carriers formed during γ-irradiation.

In general, the role of Ag^+ ions in the LiB_3O_5 matrix and their PL mechanism in the LiB_3O_5:Ag glass samples are discussed in detail in [18,19]. As was shown in [18,19], the excitation spectra for this emission show a preponderant broad band peaked at about 220-230 nm, which coincides with the peak position of the shoulder displayed in the optical absorption spectra (Fig. 2).

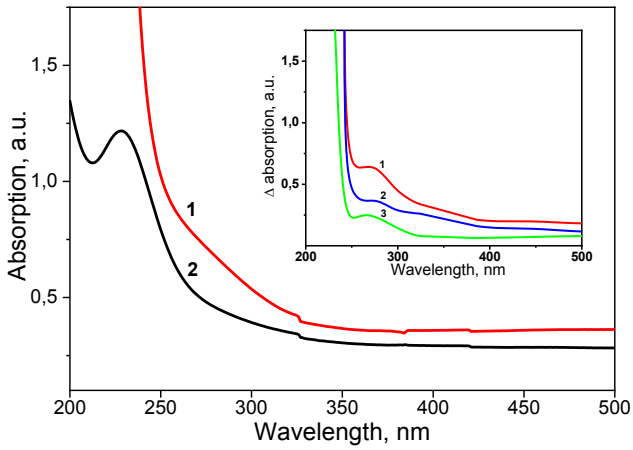

Fig. 2. Absorption spectra of unirradiated LiB_3O_5 glass: 1 - undoped, 2 - doped with 1% Ag. Inset shows the difference spectra between glasses: 1 - LiB_3O_5:Ag irradiated with 3 Gy and LiB_3O_5 unirradiated; 2 - LiB_3O_5:Ag irradiated with 3 Gy and LiB_3O_5:Ag unirradiated; 3 - unirradiated LiB_3O_5:Ag and LiB_3O_5.

The absorption band in the undoped LiB_3O_5 glass in the 220 nm region (curve 1 in Fig. 2) is responsible for charge transfer transitions, i.e., the formation of B^{2+} and O^- centers [20] in boron oxide complexes $(B_3O_7)_5$, which are the basis of lithium triborate compounds. A noticeable band in the region of 250-320 nm in the absorption spectrum of LiB_3O_5:Ag glass

(shown in an enlarged form in the inset of Fig. 2) is undoubtedly associated with the Ag impurity, since it is completely absent in the spectrum of undoped glass. At the same time, the small shoulder higher than 350 nm arises as a result of the influence of localized surface plasmon resonance in silver nanoparticles. The formation of Ag NPs is very typical for various silver-doped borate glasses [21]. The size of these Ag NPs can be estimated by the formula $R = V_F / \Delta\omega$, where V_F is the Fermi velocity (V_F = 1.39×10^6 m/s for metallic Ag) and $\Delta\omega$ is the half-width of the plasmonic absorption band [22]. Estimating the size of Ag NPs using this formula in our case gives a result of R at about 1 nm, corresponding to hundreds of Ag atoms in a nanoparticle. But more important for us is the information that, along with Ag NPs, various Ag aggregates are present in borate glasses, such as Ag^{2+}, Ag_3^{2+}, and Ag_4^{2+} nanoclusters [23], as well as clusters with a larger number of Ag^+ ions and Ag^0 atoms that can form Ag_m^{n+} centers [24]. It has been established that such Ag aggregates exhibit photoluminescence, usually in the spectral region of 400-600 nm [25].

It should be noted that we found luminescent emission (RPL) in γ-irradiated LiB_3O_5:Ag glass samples just in the spectral region of 400-500 nm with a maximum at 430 nm, which can also be associated with Ag_m^{n+} centers.

It should be noted that the formation mechanism of RPL centers in Ag-doped glasses involves the interaction of ionizing radiation with the host glass matrix. Ionizing radiation generates electron-hole pairs within the material. Electrons are subsequently trapped by silver ions (Ag^+) to form neutral silver atoms (Ag^0). Concurrently, holes become localized within the phosphate/borate glasses matrix, particularly at sites such as PO_4/BO_4 tetrahedra, forming phosphor/boron-related hole centers. Over time or through thermal processes, the trapped holes can migrate and combine with Ag^+ ions, forming Ag^{2+} ions. These Ag^0 and Ag^{2+} centers serve as RPL centers responsible for the blue and orange emissions observed in such materials, as indicated in many studies, particularly those provided by Kawamoto et al. and Miyamoto et al. [7,9].

The spectral characteristics of RPL in the investigated Ag-doped lithium-borate glasses (LiB_3O_5:Ag) indicate existing these specific electronic transitions related to RPL centers. In particular, the emission band at approximately 430-440 nm (see Fig. 3) can be attributed to Ag^0 and/or Ag_2^+ centers, consistent with results of other authors for Ag-doped phosphate

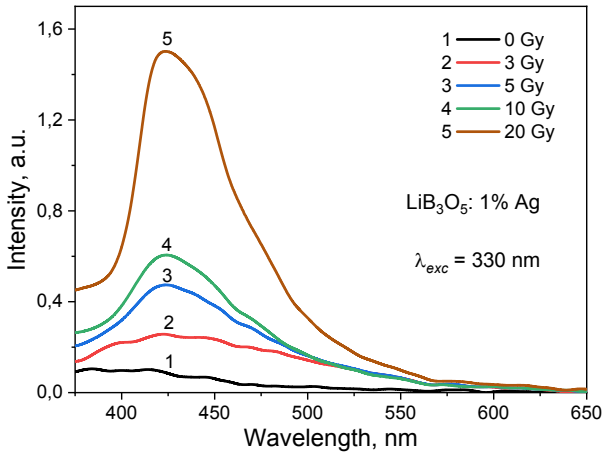

Fig. 3. The radiophotoluminescence spectra of Ag-doped lithium-borate glasses at different irradiation doses under 330 nm excitation.

glasses and observed emission from photoreduced silver ions. The excitation of RPL centers occurs predominantly in the ultraviolet range (300-350 nm), aligning with the energy absorption needed to excite these specific luminescence centers. It should be noted that the intensity of the RPL (Fig. 3) is several times lower compared to the intrinsic PL of Ag^+ ions (Fig. 1), which is excited at 220 nm.

The RPL spectra at an irradiation dose of 20 Gy and excitation with different wavelengths are shown in Fig. 4. These excitation wavelength dependences of RPL intensity (Fig. 4) reveal behavior similar to RPL spectra at different doses presented in Fig. 3.

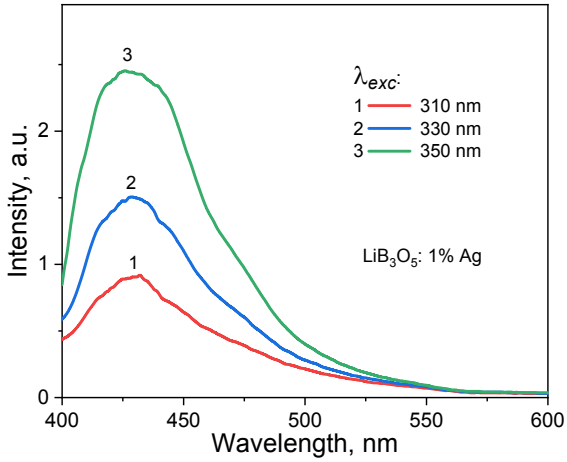

Fig. 4. The radiophotoluminescence spectra of Ag-doped lithium-borate glasses irradiated with a dose of 20 Gy under the excitation with different wavelengths.

An essential characteristic of RPL in Ag-doped lithium-borate glasses is its dose dependence. Experimental data demonstrate an apparent dose-dependent increase in RPL intensity at the γ-ray doses of 3, 5, 10, and 20 Gy (Fig. 5). Both the peak and integral intensities measurements further confirm the linear response, emphasizing the material's suitability for moderate-dose radiation dosimetry.

At the same time, this increase may be nonlinear at higher doses, which, in the case of phosphate glasses, has been attributed to saturation effects and higher-order molecular

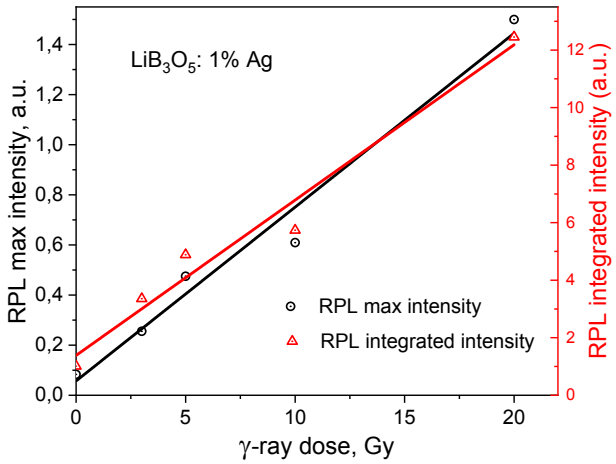

Fig. 5. Peak (circles) and integral (triangles) RPL intensities as a function of radiation doses (λ_{exc} = 330 nm). The solid lines represent linear approximations of the dose dependencies of RPL intensities.

silver clusters (Ag_m^{n+}) formation [9]. These clusters, formed due to the diffusion and aggregation of silver atoms or ions under high-power radiation, could contribute to deviations from linear dose-intensity behavior.

It should be noted that the build-up effect in Ag-doped lithium-borate glasses significantly influences the existence of blue RPL emission and the observed absence of yellow-orange emission. The build-up effect refers to the gradual transformation of RPL centers post-irradiation [8]. This involves two primary steps: (1) the formation of neutral Ag^0 centers through the trapping of electrons by Ag^+ ions and (2) the subsequent formation of Ag_2^+ centers via the association of Ag^+ and Ag^0. However, in lithium-borate glasses, the yellow-orange emission, commonly attributed to Ag^{2+} centers, is absent under specific conditions. This observation may be conditioned to the intensive Ag_2^+ formation via thermal heating of the glass matrix under γ-ray radiation. Such an effect may be explained by the enhanced mobility of Ag^+ ions and electrons at elevated temperatures, facilitating their interaction to form Ag_2^+ centers.

Consequently, the dominance of blue RPL at 430-440 nm is ascribed to transitions within Ag^0 and/or Ag_2^+ centers. An interesting observation in the presented study is the absence of yellow-orange emission, typically associated with Ag^{2+} centers. This phenomenon is likely due to the rapid formation and efficient stabilization of Ag^0 centers, as Ag^+ ions quickly trap the electrons formed by irradiation in the host glass matrix. Additionally, the enhanced mobility of Ag^+ ions and electrons under thermal conditions may contribute to this effect, facilitating recombination at Ag^0 centers. These peculiarities suppress the formation of Ag^{2+} species, hence limiting yellow-orange emission. This unique behavior underscores the importance of the glass matrix composition and processing conditions in determining the spectral characteristics of RPL.

Conclusions

The dosimetric response of blue RPL in lithium-borate glasses doped with 1% silver (Ag) has been investigated. The RPL mechanism was elucidated, emphasizing the formation dynamics of RPL centers and the spectral characteristics associated with blue emissions. This RPL phenomenon, primarily involving forming Ag^0 and Ag_2^+ centers, was characterized through spectroscopic analysis under varying γ-ray doses ranging from 3 to 20 Gy. The linear dose-dependent increase in RPL intensity provides valuable insights into LiB_3O_5:Ag for potential applications in radiation dosimetry for moderate radiation levels. Understanding the limitations in RPL intensity and the nonlinear dose response is crucial for optimizing these materials for practical use in precise and repeatable radiation measurements.

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Анотація. *Досліджено спектри поглинання, фотолюмінесценції (ФЛ) та радіофотолюмінесценції (РФЛ) у склі триборату літію (LiB_3O_5:Ag), легованому 1% іонами срібла та опроміненому різними дозами γ-випромінювання в діапазоні 0-20 Гр. Також вимірювали зміну цих спектрів як функцію дози опромінення. У спектрах ФЛ Ag^+ переважає ультрафіолетова широка смуга приблизно при 290 нм. Смуга РФЛ зосереджена приблизно на 430 нм при збудженнях в спектральній області 310-350 нм. Механізм випромінювання РФЛ виникає через зміну зарядового стану срібла до центрів типу A^0, коли скло, леговане Ag^+, піддається випромінюванню, яке генерують електрони та дірки.*

Ключові слова*: скло триборату літію, γ-випромінювання, радіофотолюмінесценція, дозиметричний відгук*