Mn$^{4+}$ concentration effect on spectral properties of lithium-germanate glass-ceramics

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Abstract. A series of lithium-germanate glasses with different manganese concentration is synthesized. Li$_2$Ge$_7$O$_{15}$ nanocrystals nucleate in the glass matrix via standard volume crystallization technique thus obtaining lithium-germanate glass-ceramics. The glass-ceramics possess intense emission near 660–670 nm under two-band excitation at 330 and 450 nm. The luminescence lifetime is 550 μs for 0.05 mol.% MnO$_2$-doped glass-ceramics. The glass-ceramics obtained can be used as a source of deep-red radiation.

1. Introduction

A narrow-band red emission has been major requirement in solid-state lighting technologies in terms of a white-light-emitting diode (w-LED) with an InGaN UV/blue LED chip [1]. Currently, there are two primary strategies to fabricate the w-LED. One is employing the blue LED with yellow-emitting phosphor Y$_3$Al$_5$O$_{12}$:Ce (YAG:Ce) and nitride red phosphor [2], the other is combining UV LED chips with tri-color (blue, green, and red) phosphors. Between these two methods, the red-emitting phosphor is the indispensable component to obtain the vivid and warm white light illumination.

There have been mainly reported two different ions, namely, Mn$^{4+}$ and Eu$^{2+}$, doped as the red-emitting activator ions in various hosts [3]. The general performances of Mn$^{4+}$ (Eu$^{2+}$) as an activator ion are peak emission at 600–650 nm, excitation peak edge of 450–500 nm, photoluminescence decay lifetime of a few milliseconds (a few microseconds or less), and quantum yield of 80–90%. With this regard and from an economic point of view, it seems that non-rare-earth Mn$^{4+}$ is superior than Eu$^{2+}$.

Herein, we successfully synthesized novel transparent lithium-germanate glass-ceramics doped with Mn$^{4+}$ with red emission under UV/blue excitation and studied its properties under the influence of manganese concentration.

2. Materials and methods

The initial glasses were synthesized with the following composition: xMnO$_2$-10Li$_2$O-(90-x) GeO$_2$ (where x=0.005; 0.05; 0.1; 0.25; 0.5; 1; 2) mol.%. The synthesis was carried out in air atmosphere at a temperature of 1250°C using corundum crucibles. For the synthesis of glass-ceramics based on germanate glass the samples were subjected to the heat treatment at 560°C in programmable muffle furnaces (Nabertherm).

The glass absorption spectra were measured by a Lambda 650 spectrophotometer (Perkin Elmer) in the spectral range of 200–900 nm with a step of 1 nm at room temperature. For the luminescence and
excitation spectra recording, we used the LS-55 spectrofluorimeter (Perkin Elmer). Based on the luminescence spectra recorded with different delays after the exciting pulse, the luminescence decay curves were obtained, and the luminescence lifetime was determined. The luminescence spectra were corrected considering the spectral sensitivity of the spectrofluorimeter photodetector. For the excitation spectra, no correction was conducted. Glass transition temperature and the crystallization temperatures were determined using an STA 449F1 Jupiter (Netzsch) differential scanning calorimeter (DSC) with an accuracy of ±10 °C in a temperature range of 30 – 700 °C. The occurrence of nanocrystalline phase in the glass bulk was revealed with X-ray diffraction (XRD) method. Diffraction patterns were recorded with Rigaku Ultima IV X-ray diffractometer using CuKα radiation. The diffractogram was taken in the angle range from 10° to 50° in the Bragg-Brentano geometry.

3. Experimental results

The absorption spectra shown in Figure 1b are dominated by an intense absorption band with a maximum at 500 nm, which belongs to a series of $^5\text{B}_1(5\text{E}) \rightarrow ^5\text{A}_2(5\text{T}2)$, $^5\text{B}_1(5\text{E}) \rightarrow ^5\text{B}_2(5\text{T}2)$ and $^5\text{B}_1(5\text{E}) \rightarrow ^5\text{A}_1(5\text{T}2)$ transitions in trivalent manganese ions [4,5]. With an increase in the manganese oxide content, the intensity of the band increases, and the color of the glass becomes dark purple. The initial glasses do not exhibit luminescence in the visible region.

The DSC results show glass transition temperature to be 490°C and two exothermal regions with maxima at 550-560 and 630°C. On the DSC curve of glass with no manganese, the first crystallization peak locates at 550°C, with an increase in the manganese content, it shifts towards 560°C. The position of the second crystallization peak does not change. Moreover, its intensity decreases with increasing MnO$_2$ content, and the intensity of the former increases. This indicates the possibility of the formation of two types of lithium-germanate crystals in the glass matrix; however, manganese promotes the crystallization of only one of them. Therefore, further synthesis of glass-ceramics was carried out at 560°C for 5 hours.

![Figure 1](image-url)

Figure 1. (a) The absorption spectra and (b) the DSC curves of initial lithium-germanate glasses with different MnO$_{2}$ content.

The glass ceramics structure was investigated by XRD, which showed the presence of Li$_2$Ge$_7$O$_{15}$ crystals in the matrix (Figure 2b). In the sample with 0.5% MnO$_2$ and after heat treatment at 560°C for 5 hours, the mean size of the nucleated crystals was 8 nm. It is known [4,6] that Mn$^{2+}$ ions have a characteristic absorption at 410-415 nm and 360 nm. Thus, the bands of divalent manganese cannot be identified unambiguously in the absorption spectra before and after heat treatment (Figure 2a). Nevertheless, in the spectrum of glass-ceramics, the maximum of the band in the visible region shifted by 450 nm, and in the region of 330-350 nm the absorption intensity increased. It is known [7,8] that the absorption corresponding to the $^4\text{A}_2 \rightarrow ^4\text{T}_1$ and $^4\text{A}_2 \rightarrow ^4\text{T}_2$ transitions of tetravalent manganese falls on 330 and 460 nm. It is also possible to determine the oxidation state of manganese ions by studying the luminescent properties.
Figure 2. (a) The absorption spectra of initial glass and glass-ceramics with 0.5% MnO$_2$; (b) the XRD results of lithium-germanate glass-ceramics with 0.5% MnO$_2$: x is denoted for Li$_2$Ge$_7$O$_{15}$ phase, o is denoted for Li$_{0.115}$MnO$_2$ phase.

The luminescence of divalent manganese locates at the red-orange region with a maximum at 580-620 nm upon excitation at 410-415 nm [9]. Under the influence of the environment, the luminescence band of Mn$^{2+}$ can shift up to 700 nm, but the large FWHM will remain its characteristic (~100 nm) [10]. The energy level diagram of Mn$^{4+}$ is described by the Tanabe-Sugano diagram for d$^3$ transition elements in an octahedral field [11]. In this regard, in the crystalline environment, Mn$^{4+}$ ions produce intense luminescence in the red region. There are many crystalline phosphors doped with tetravalent manganese, which have luminescence in the 660-670 nm region [1,3].

In Figure 3b, the luminescence spectra of the obtained glass-ceramics show a maximum at 667 nm, regardless of the activator content (excitation at 332 nm). Photoexcitation spectra are normalized to the level at 330 nm (luminescence at 667 nm). The spectra (Figure 3a) show the presence of three excitation bands with maxima at 332, 400, and 460 nm. With an increase in the manganese content, the contribution of the long-wavelength band increases. So, the specific location and shape of the luminescence and photoexcitation bands indicates that the manganese ions are in 4+ oxidation state.

Figure 3. The excitation (a) and luminescence (b) spectra of the lithium-germanate glass-ceramics with different MnO$_2$ content.

The luminescence lifetime of Mn$^{3+}$ ions depends on the environment; in crystalline phosphors it can vary from 1 to 6 ms at room temperature [12,13]. The decay curves were measured based on the luminescence spectra of glass-ceramics recorded with a delay after the exciting pulse (Figure 4). The luminescence decay curve has a two-exponential character. The luminescence lifetime for a glass-
ceramic sample with 0.05% MnO$_2$ was 550 μsec, which was unexpectedly small. With a further increase in the manganese oxide content, the luminescence lifetime decreases, which indicates concentration quenching.

Figure 4. (a) The luminescence decay curve for glass-ceramics with different MnO$_2$ content ($\lambda_{\text{lum}}$=667 nm); (b) the glass-ceramics luminescence spectra with 0.5% MnO$_2$ after different delays from the exciting pulse ($\lambda_{\text{ex}}$=332 nm).

4. Conclusion
A series of Li$_2$O-GeO$_2$ glasses with MnO$_2$ concentration from 0.005 to 2 mol.% was synthesized. Lithium-germanate glass-ceramics were synthesized using standard volume crystallization technique thus nucleating Li$_2$Ge$_7$O$_{15}$ nanocrystals in the glass matrix. The glass-ceramics possessed intense emission near 660-670 nm under two-band excitation at 330 and 450 nm. The luminescence lifetime was 550 μs for 0.05 mol.% MnO$_2$-doped glass-ceramic sample. The specific location and shape of the luminescence and photoexcitation bands indicated that the manganese ions in this matrix were in 4+ oxidation state. Due to this, lithium-germanate glass-ceramics doped with manganese ions were a promising material for the development of deep red radiation sources.

Acknowledgments
Research was funded by Russian Science Foundation (Agreement #19-72-10036).

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