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Regular Article

Persistent luminescent borosilicate glasses using direct particles doping method

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ABSTRACT

Persistent luminescence (PeL) was obtained, from the first time to the best of our knowledge, from borosilicate bulk glasses. The glasses were prepared using direct doping method. Commercial PeL $SrAl_2O_4:Eu^{2+},Dy^{3+}$ microparticles (MPs) were added in the borosilicate glass after melting. The persistent luminescence can be augmented when casting the glass 3 min after adding the MPs at 950 °C. Although the borosilicate glasses exhibit persistent luminescence, the glass melt has a corrosive behavior on the MPs leading to the diffusion of Al and Sr into the glasses.

The field of optical imaging, in which photons are the information source, has expanded rapidly due to its direct applications in pharmacology, molecular and cellular biology, and diagnostics. Recently, a new optical imaging technique was developed to image vascularization, tumors and grafted cells using persistent luminescent (PeL) nanoparticles [1]. Persistent luminescence (PeL) or afterglow is a form of emission which continues after the removal of the irradiation source [2]. As explained in [3], inorganic PeL particles, when excited prior to injection, can be used to follow their *in vivo* distribution in real-time for >1 h without the need for any external illumination source.

This source can be for example visible light, UV radiation or X-rays. PeL $SrAl_2O_4:Eu^{2+},Dy^{3+}$ microparticles (MPs) were first introduced in the early/mid 1990s [4]. The Eu^{2+} ion acts as a luminescent center whereas the co-doping with Dy^{3+} increases the number of traps in the structure leading to an extension of the persistent luminescence time. $SrAl_2O_4:Eu^{2+},Dy^{3+}$ shows unique persistent luminescent properties, such as long fading time [5] and mechanoluminescence [6].

The "frozen sorbet" method was the first technique developed to prepare persistent luminescent crystals in glass [7]. Using this technique, it is possible to precipitate $SrAl_2O_4:Eu^{2+},Dy^{3+}$ crystals in the glass within the SrO-Al_2O_3-B_2O_3 system using the elements from the glass network. Later, it was demonstrated that PeL glasses can be prepared by adding PeL MPs in the glass batch prior to the glass melting [8,9]. However, this technique cannot be used to prepare PeL borosilicate bulk glass with the composition $26.9SiO_2$-$26.9B_2O_3$-$22.7Na_2O$-$1.7P_2O_5$-$21.8CaO$ (in mol%) (referred as B50) due to its high glass melting temperature (1250 °C) at which the MPs are not thermally stable. However, we prepared persistent luminescent bodies (sintered powder) with this composition by adding the $SrAl_2O_4:Eu^{2+}{\cdot}Dy^{3+}$ MPs in the glass powder prior to sintering at a lower temperature than the melting temperature [10]. Such borosilicate bodies can have an application as biophotonic sensors to track dissolution and mineralization of the implant after implantation in the body with the changes in the PeL overtime.

Recently, upconversion was obtained from phosphate glasses which contain only 0.01 at.% of Er^{3+} and 0.06 at.% of Yb^{3+} by adding $NaYF_4:Er^{3+}$, Yb^{3+} nanoparticles (NPs) into the glass using the direct doping method [11]. In this paper, we demonstrate that this direct doping method can be used to successfully prepare PeL borosilicate bulk glasses, as well.

The borosilicate glass with the composition ($26.9SiO_2$-$26.9B_2O_3$-$22.7Na_2O$-$1.7P_2O_5$-$21.8CaO$) (in mol%) was melted using SiO_2 (Umicore, 99.99%), and Na_2CO_3 (Honeywell, >99.5%), H_3BO_3 (Sigma Aldrich, >99.5%), $CaCO_3$ (Alfa Aesar, 99%), and $CaHPO_4.2H_2O$ (Sigma Aldrich, 98%). A 20 g batch was melted in a Quartz crucible at 1250 °C for 30 min. After melting, 2 weight-% of commercial $SrAl_2O_4:Eu^{2+}{\cdot}Dy^{3+}$ MPs (Jinan G.L. New Materials, China, YG-101) were added at lower temperature and then the glass was poured onto a brass mold. After quenching, the glasses were then annealed for 6 h at 400 °C, which is below the glass transition temperature of the glass to remove any residual stress.

A scanning electron microscope (Carl Zeiss Crossbeam 540) equipped with Oxford Instruments X-Max^N 80 EDS detector was used

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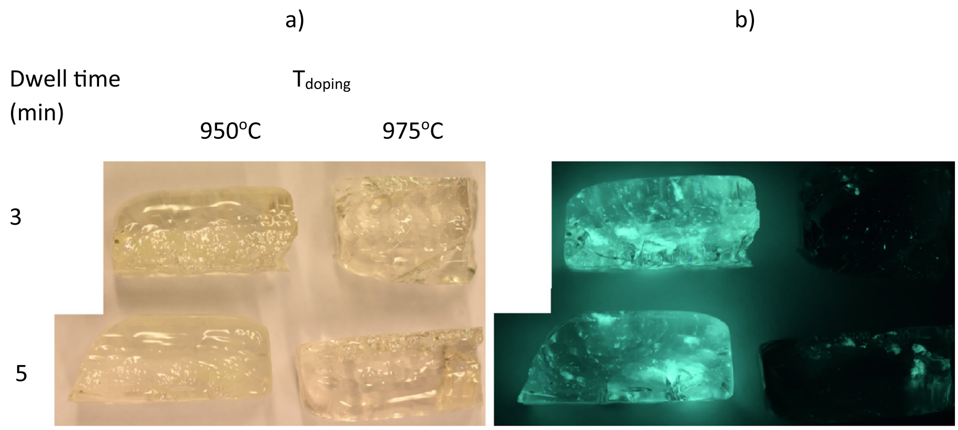

Fig. 1. Pictures of the investigated glasses observed under daylight (a) and after stopping UV irradiation (b).

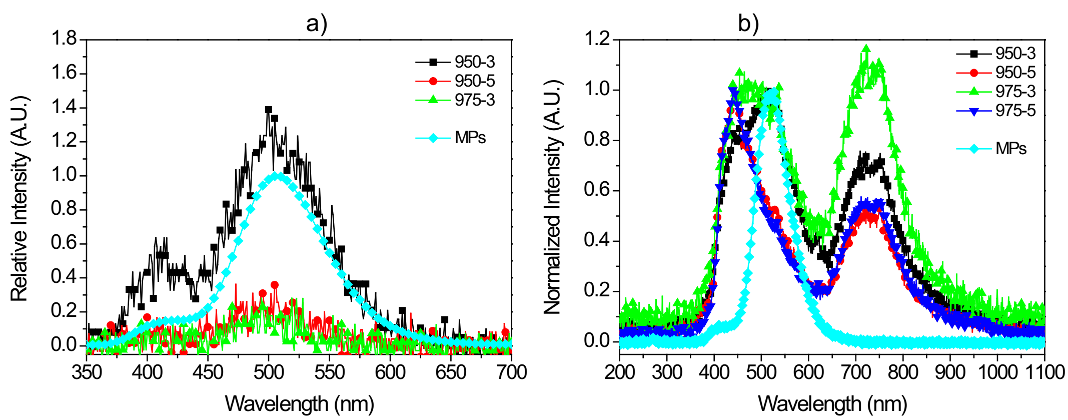

Fig. 2. PeL (a) and normalized PL (b) spectra of the investigated glasses.

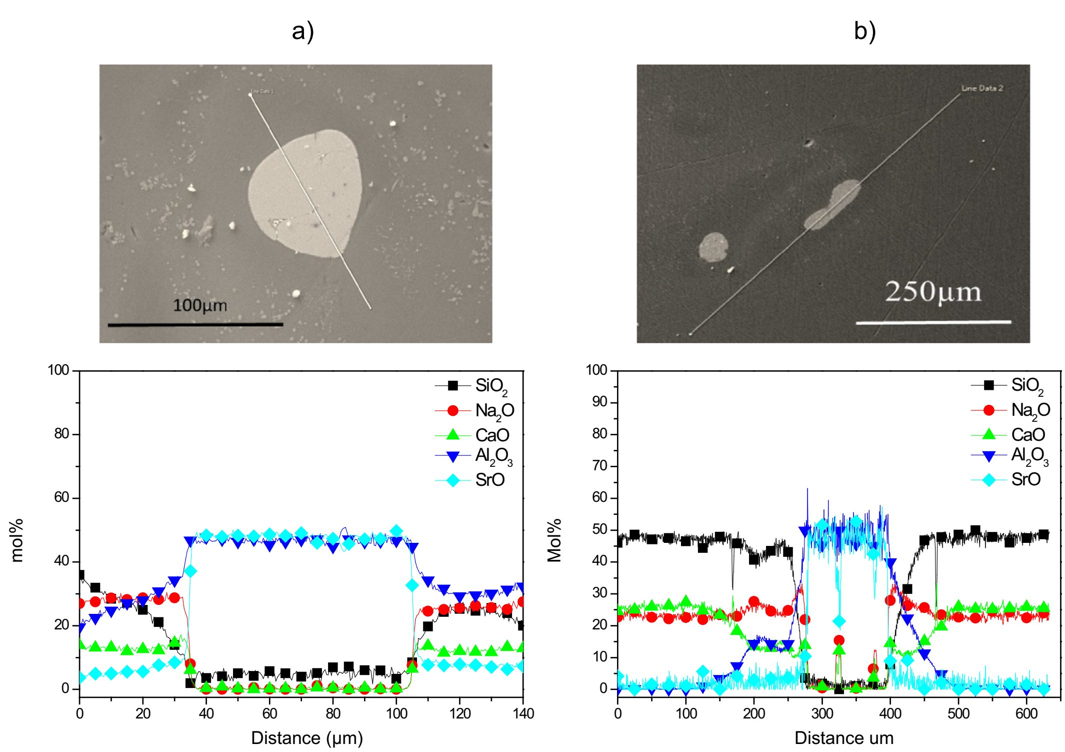

Fig. 3. SEM/EDS line profiles giving the elemental distribution across the MP diameter and interface with (950-3) (a) and (950-5) (b) glasses. The direction of scan starts at circle (corresponding to 0 μm).