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# Effect of the glass melting condition on the processing of phosphate-based glass–ceramics with persistent luminescence properties

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ABSTRACT

In this paper, we discuss the impact of the temperature and the duration of the melting on the persistent luminescence properties of phosphate glasses within the $P_2O_5$–$Na_2O$–CaO and $P_2O_5$–$Na_2O$–SrO systems prepared using a standard melting process in normal atmosphere by adding $Sr_4Al_{14}O_{25}$:$Eu^{2+}$,$Dy^{3+}$ microparticles in the glass batch before melting. Glasses with persistent luminescence properties can be successfully prepared if the melting conditions are carefully controlled.



## 1. Introduction

Persistent luminescence can be defined as emission obtained after the removal of an excitation source [1] which can be visible light, UV radiation, electron beam, plasma beam, X-rays, or even γ-rays. The emission can last from seconds to hours after the light source is removed. Persistent luminescent phosphors introduced in mid 1990s are the most recent commercial application where the luminescence of rare earth (R) ions is employed [2]. The most efficient of these materials employ $Eu^{2+}$ as the luminescent center and usually $Dy^{3+}$ as a co-dopant in matrices such as $SrAl_2O_4$ [3], $Sr_4Al_{14}O_{25}$ [4] or $Sr_2MgSi_2O_7$ [5].

There is an increasing demand for new persistent luminescent materials as potential replacement for the incandescent and fluorescent light sources due to their high luminous efficiency, energy-saving, long lifetime and good features for environment protection [6]. Because of excellent durability, thermal stability, easy fabrication and molding into any shapes, the inorganic glass–ceramic can be an excellent solution. Glass–ceramics which contain a glassy phase and $Eu^{2+}$,$Dy^{3+}$-doped $SrAl_2O_4$ persistent luminescence particles have been fabricated using the so called "Frozen sorbet method" by Nakanishi and Tanabe [7]. This method was found to be a useful technique for the design of new $SrAl_2O_4$-based phosphor composites which can be used under LED excitation (ca. 460 nm). In [8], this method was applied to the SrO–$Al_2O_3$–$B_2O_3$ system in order to fabricate glass ceramics. It was found that the $SrAl_2O_4$:$Eu^{2+}$,$Dy^{3+}$ crystals precipitating in the glass–ceramics show excellent long persistent luminescence and improved the excitation efficiency at ca. 460 nm in the photoluminescence excitation spectra compared to the $SrAl_2O_4$:$Eu^{2+}$, $Dy^{3+}$ phosphors prepared using a conventional solid state reaction. However, within this technique, the composition of the persistent luminescent microparticles depends on the composition of the glass matrix. Recently, we demonstrated that phosphate glasses with persistent luminescence properties can be prepared using a standard melting process in air by adding $Sr_4Al_{14}O_{25}$:$Eu^{2+}$,$Dy^{3+}$ microparticles in the glass batch before melting [6].

Here, we discuss the impact of the melting conditions (temperature and duration) on the persistent luminescence properties of phosphate glasses which contain $Eu^{2+}$,$Dy^{3+}$-doped $Sr_4Al_{14}O_{25}$ microparticles (MPs).

## 2. Experimental procedure

The glasses with the composition $50P_2O_5$–$10Na_2O$–40CaO (CaO glass) and $50P_2O_5$–$10Na_2O$–40SrO (SrO glass) (mol%) were prepared using a standard melting method. $NaPO_3$, $SrCO_3$ $CaCO_3$ and

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$(NH_4)_2HPO_4$ were used as the raw materials. The $Ca(PO_3)_2$ and $Sr(PO_3)_2$ precursors were first prepared independently using slow heating rate up to 900 °C. Glasses were prepared with 3 wt.% of commercial $Eu^{2+}$,$Dy^{3+}$-doped $Sr_4Al_{14}O_{25}$ microparticles (MPs) (Jinan G.L. New Materials, China, BG-01), corresponding to ~0.18 mol% of MPs in the CaO glass and to ~ 0.22 mol% of MPs in the SrO glass. The MPs were added in the glass batch which was then melted between 1000 and 1100 °C for 10–30 min in a quartz crucible in air. The melt was poured on a brass mold and the resulting glass was annealed at 40 °C below the glass transition temperature.

A scanning electron microscope (Leo 1530 Gemini, Zeiss) coupled with an Energy Dispersive X-ray Analyser (SEM/EDXA) (Vantage by Thermo Electron Corporation) was used to take overall images and to analyze the composition of the samples. The accuracy of the elemental analysis was ±1.5 mol%.

The photoluminescence and persistent luminescence properties of the $Sr_4Al_{14}O_{25}$:$Eu^{2+}$,$Dy^{3+}$ MPs and crushed MPs-containing CaO and SrO glasses were measured at room temperature using a Varian Cary Eclipse Fluorescence Spectrophotometer equipped with a Hamamatsu R928 photomultiplier (PMT). The conventional luminescence ($\lambda_{exc}$: 266 nm, Nd:YAG pulse laser, 8 ns, TII Lotis) was measured at room temperature using a CCD camera (Avantes, AvaSpec-2048x14). For persistent luminescence measurements, the samples were irradiated for 30 min at room temperature with a compact UV lamp (UVGL-25, 4 W, $\lambda_{exc}$: 365 nm). The first measurement was carried out 1 min after ceasing the irradiation and then every minute up to 2 h. Each individual measurement took 4 s. The luminescence intensity was calculated by integrating the area under the emission curve.

## 3. Results and discussion

Glasses with the composition $50P_2O_5$–$10Na_2O$–40CaO (CaO glass) and $50P_2O_5$–$10Na_2O$–40SrO (SrO glass) were prepared with $Eu^{2+}$,$Dy^{3+}$-doped $Sr_4Al_{14}O_{25}$ microparticles (MPs) using different melting conditions (temperature and duration) in normal atmosphere. In this paper, we discuss the impact of the melting conditions on the spectroscopic properties of phosphate-based glasses.

All the glasses which contain the MPs exhibit a green–blue persistent emission after ceasing the UV irradiation as seen in [9]. This green–blue emission from the samples confirms that some MPs remain in the glass. The intensity of the emission was found to depend not only on the glass matrix as discussed in [9] but also on the melting conditions: it could barely be seen when the glasses in both systems were melted for 20 or 30 min at 1000 °C or at higher temperature than 1000 °C for 10 min.

The persistent luminescence spectra of the CaO and SrO glasses, recorded at room temperature, are shown in Fig. 1a and b, respectively. The spectra exhibit a strong band centered at 490 nm and a weak one at 410 nm which is not present with irradiation at 365 nm in the spectrum of the MPs. However, this low-intensity band at 410 nm can be observed in the spectrum of the MPs if 254 nm was used (not shown here). These bands are due to the $4f^65d^1 \rightarrow 4f^7$ transition of $Eu^{2+}$ ions located in two different cation sites in the $Sr_4Al_{14}O_{25}$ structure. As explained in [9], the presence of the band located at 410 nm can be related to a diffusion of the Eu, Al and/or Sr from the MP to the glass and the subsequent weakened energy transfer between $Eu^{2+}$ ions. Otherwise, the shapes and band positions in the emission spectra are similar for both MPs-containing glasses and the MPs (Fig. 2b) confirming that it is the embedded MPs that show the persistent luminescence. One can also notice that the emission band of the MPs is slightly narrower than those of the glasses because some the $Eu^{2+}$ ions are suspected to diffuse to the glass outer surface and are in a weakened crystal field. In both glass systems, the intensity of the emission depends on the melting conditions: the intensity progressively decreases in the SrO glasses whereas it decreases dramatically in the CaO glasses when the temperature and the duration of the melting increase. No persistent luminescence was observed from the CaO glasses melted at 1000 °C for 30 min or at 1100 °C for 10 min. It should be pointed out that the SrO and CaO glasses melted at 1050 °C for 10 min have a stronger persistent luminescence emission than the glasses melted at 1000 °C for 30 min.

Fig. 1c shows the normalized persistent luminescence spectra of the MPs and of SrO glasses melted using different melting conditions. The shapes and positions of the bands in the emission spectra are similar for all samples confirming that it is the embedded MPs that show the persistent luminescence. However, the emission band of the MPs is slightly narrower than those of the glasses indicating that the site of the $Eu^{2+}$ is modified when the MPs are added in the glass network. One can notice that an increase in the temperature and duration of the melting increases the bandwidth of the main band, shifts its position to lower wavelength but has no impact on the intensity ratio of the band at 410 and 490 nm. These changes in the emission band can be related to the diffusion of the $Eu^{2+}$ ions to the glass with a weakened crystal field. Based on Fig. 1b and c, the increase in the melting temperature seems to have a bigger impact on the $Eu^{2+}$ ions diffusion in the SrO glasses than the increase in the melting duration. Because of the low emission intensity of the CaO glasses, it is not possible to determine which melting parameter (temperature or duration) has larger impact on the $Eu^{2+}$ ions diffusion.

Fig. 2a and b depicts the conventional emission spectra normalized to the band at 490 nm. All the glasses exhibit emission bands located between 575 and 650 nm which can be related to the emission from $Eu^{3+}$ ions. Some $Eu^{2+}$ ions are oxidized to $Eu^{3+}$ during the preparation of the glasses in agreement with our previous study [9]. One can notice that the intensity of those bands increases when the glasses are melted for a long time at 1000 °C or at higher temperature than 1000 °C. This indicates that in both glass systems, the number of $Eu^{3+}$ ions depends on the melting conditions. In the SrO glasses, the emission from the $Eu^{3+}$ is stronger when the glass is melted at 1000 °C for 30 min than when melted at 1050 °C for 10 min in agreement with data presented in Fig. 1b.

The spectra exhibit also two bands in the 350–575 nm range, the intensity of which also depends on the glass matrix and on the melting conditions. Those bands in the 350–575 nm range can be related to the luminescence of $Eu^{2+}$ located in two different cation sites in the $Sr_4Al_{14}O_{25}$ structure [10]. It should be noticed that the ratio between the intensity of these two bands changes progressively in the SrO glasses whereas it changes dramatically in the CaO glasses when the temperature and the duration of the melting increase. This seems to indicate that the $Eu^{2+}$ ions' sites in the SrO glasses change as the temperature and the duration of the melting progressively increase. On the other hand the $Eu^{2+}$ sites in the CaO are strongly modified when the glasses are melted at higher temperature than 1000 °C or longer than 10 min. In both glasses, the $Eu^{2+}$ ions sites are less impacted by the increase of the melting temperature from 1000 to 1050 °C than by the increase of the melting time from 10 to 30 min.

In summary, an increase in the temperature and duration of the melting in both CaO and SrO glasses leads to an oxidation of the $Eu^{2+}$ ions into $Eu^{3+}$ ions and also to a change of the crystal field strength acting on the $Eu^{2+}$ ions. This change in the structure around the $Eu^{2+}$ ions may be related to diffusion of Al and/or Sr from the MPs into the glass network. Accordingly, the structure of the MPs changes and may give new sites for $Eu^{2+}$.

The persistent luminescence decay curves of the CaO and SrO glasses at room temperature were registered. The luminescence decay of the 490 nm band measured at room temperature was found multi-exponential confirming that the emission comes