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New alternative route for the preparation of phosphate glasses with persistent luminescence properties

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Abstract

In this paper, we investigate a new alternative route for the preparation of phosphate glasses with persistent luminescence properties. Phosphate glasses within the P_2O_5–Na_2O–CaO and P_2O_5–Na_2O–SrO systems were prepared by a standard melting process in air by adding $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ microparticles in the glass batch before melting. We found that all the investigated glasses show persistent luminescence. It is clearly shown that conventional melting in air of $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ microparticles in phosphate glass batch can be a new technique to prepare phosphate glasses with persistent luminescence properties.

Keywords: Phosphate glasses; $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ microparticles; Persistent luminescence

1. Introduction

Persistent luminescence refers to the type of emission which lasts for a long time (from seconds to hours) after the removal of the irradiation source.[1] Materials capable of persistent luminescence function by collecting energy from the ambient sunlight and/or artificial lighting to trapping sites. The energy is then gradually released by the surrounding thermal energy as visible emission.[2] The effect is also called phosphorescence, afterglow, or long lasting phosphorescence (LLP). However, since the long lifetime of persistent luminescence is due to trapping of energy in defects, the term to be used for the phenomenon is not phosphorescence.[3] On the other hand, the afterglow can be considered an unwanted phenomenon in luminescent materials such as those used for TVs and other displays. Thus, persistent luminescence is the appropriate term. In the early/mid 1990s, the alkaline earth aluminates and silicates as $SrAl_2O_4:Eu^{2+},Dy^{3+}$ were introduced.[4] By now, they have replaced the traditional ZnS based ones in the applications, which include emergency signalization, micro-defect sensing, optoelectronics for image storage, detectors of high energy radiation and thermal sensors.[4,5] Recently, these materials have been used as an alternative optical imaging tool suitable for small animal imaging.[6]

The preparation of high quality transparent nanocomposites, ceramics or glasses based on rare earth doped luminescent materials of oxides and fluorides is still a challenge. Compared to rare-earth doped glasses, the fluorescence of the dopant rare-earth ions in glass–ceramics was reported to be enhanced considerably when the crystal phase acted as a sink for the dopant. During the annealing process, the rare-earth ions are typically precipitated together with the nanocrystal phase.[7,8] However, the use of transparent glass–ceramic for persistent luminescence applications has rarely been reported.

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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[9]. 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 light emitting diode (LED) excitation (ca. 460 nm). In Ref. 10, 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.

Phosphate glasses are biocompatible and thus suitable for biomedical purposes.[11] Even more, it is well known that the composition of the phosphate glasses can be tailored to possess a low melting temperature and a high concentration of dopant such as rare earths[12] or metals ions.[13] However, phosphate glasses are also known to have a fast dissolution rate limiting their biomedical application.[14] An in-depth dissolution study on phosphate glasses, conducted by Bunker et al., showed that the glass dissolution can be tailored and that these phosphate materials can even show dissolution rates similar to silicate glasses.[15] In Ref. 16, we showed that the substitution of SrO for CaO in phosphate glasses with the composition $50P_2O_5–10Na_2O–40(1-x)CaO–40xSrO$ (mol%) leads to glasses with better thermal stability upon crystallization and a wider temperature window between the end of the crystallization and the beginning of melting. We found that the strontium-containing glasses are promising as bioactive glass fibers.

In this paper, we present an alternative route to prepare phosphate glasses which contain Eu^{2+},Dy^{3+}-doped $Sr_4Al_{14}O_{25}$ microparticles (MP). $Sr_4Al_{14}O_{25}$:Eu^{2+},Dy^{3+} is a stable material[17] with high quantum efficiency[18] and excellent persistent luminescence intensity and duration.[19]

2. Experimental procedure

2.1. Glass processing

The glasses with the composition $50P_2O_5–10Na_2O–40CaO$ (CaO glass) and $50P_2O_5–10Na_2O–40SrO$ (SrO glass) (mol%) were elaborated using a standard melting method. $NaPO_3$, $SrCO_3$ $CaCO_3$ and $(NH_4)_2HPO_4$ were used as the raw materials. The $Ca(PO_3)_2$ and $Sr(PO_3)_2$ precursors were first independently prepared using slow heating rate up to 900 °C. Glasses were prepared with 2 ($x=2\%$) and 3 ($x=3\%$) wt% of commercial $Sr_4Al_{14}O_{25}$:Eu^{2+},Dy^{3+} microparticles (MPs) (Jinan G.L. New Materials, China, BG-01). The 2 and 3 wt% of MPs correspond respectively, to 0.12 and 0.18 mol% of MPs in the CaO glass and to 0.15 and 0.22 mol% of MPs in the SrO glass. The MPs were added in the glass batch which was then melted at 1000 °C for 10 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.

2.2. Structure and composition

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 image and analyze the composition of the samples. The accuracy of the elemental analysis was ±1.5 mol%. The samples were also studied using an X-ray diffraction analyzer (Philips X'pert) with Cu Kα radiation ($\lambda = 1.5418$ Å) to analyze the crystalline phases present. The scans were performed from $2\theta = 0$ to 60° with a step size of 0.02°.

Raman spectra were recorded between 400 and 1500 cm^{-1} at room temperature using a confocal micro-Raman (Renishaw Ramascope System 100) equipped with a Leica DMLM microscope (50× magnification) connected to a CCD camera. The spectra were collected at 90°. The excitation wavelength (λ_{exc}) of the laser was 514 nm and the power was set to $P_{avg} = 20$ mW. The spectral resolution was 2 cm^{-1}.

2.3. Luminescence

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 (λ_{exc}: 266 nm, Nd:YAG pulse laser, 8 ns, TII Lotis) was measured at room temperature using a CCD camera (Avantes, AvaSpec-2048×14). For persistent luminescence measurements, the samples were irradiated for 30 min at room temperature with a compact UV lamp (UVGL-25, 4 W, λ_{exc}: 365 nm). The first measurement was then 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 2 and 3 wt% ($x=2\%$ and 3%) of Eu^{2+},Dy^{3+}-doped $Sr_4Al_{14}O_{25}$ microparticles (MPs) using a standard melting process in normal atmosphere.

All the glasses which contain the MPs exhibit a green–blue persistent emission after stopping the UV irradiation (Fig. 1). The persistent luminescence intensity depends on both the MP concentration and the glass matrix. The green emission from the samples clearly indicates that it is possible to prepare a phosphate-based glass which contains $Sr_4Al_{14}O_{25}$:Eu^{2+},Dy^{3+} MPs using a one-step melting process in normal atmosphere. Our glasses exhibit a relatively long emission duration as the green luminescence of our glass could still be seen after 35 min.