

## PERSISTENT EXTINCTION EFFECT IN FLUORESCENT PHOTOSENSITIVE GLASS UNDER PULSED EXCIMER LASER IRRADIATION

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### 1. Introduction

Oxide glasses doped by rare earths are useful for many optical applications: light filters [1], laser media [2] and solid standards for narrow-band fluorescence [3]. Laser-induced gratings were recently observed in glasses doped by  $\text{Eu}^{3+}$  [4]. Fundamentals and applications of such glasses in nonlinear optics were reviewed by Aitchison [5].

### 2. Experimental results and discussion

We have studied the fluorescence properties of a sodium phosphate glass doped with the rare earths: europium and cerium. Bulk glassy samples of composition  $50 \text{ Na}_2\text{O}-49 \text{ P}_2\text{O}_5-0.5 \text{ Eu}_2\text{O}_3-0.5 \text{ CeO}_2$  were prepared. The details concerning the glass preparation are given in Ref. [6].

The investigated glass is colorless and transparent. It exhibits intense emission peaks situated at the wavelengths of 592 nm and 612 nm when excited with the radiation of wavelength 465 nm. The emission peaks were assigned to the  ${}^5\text{D}_0-{}^7\text{F}_{1,2}$  transition of  $\text{Eu}^{3+}$ .

We investigated the effect of the prolonged multipulse irradiation with ultraviolet (UV) light. A KrF\* excimer-laser source ( $\lambda = 248 \text{ nm}$ ;  $t_{\text{FWHM}} \geq 20 \text{ ns}$ ; repetition rate: 1-2 Hz) generating  $E = 80 \text{ mJ/pulse}$  (corresponding to a fluency of  $100 \text{ mJ/cm}^2$ ) was used.

As a result of irradiation with multiple laser pulses (7000-10000 pulses) we observed an exponential decay of the fluorescent emission at 612 nm. Fig. 1 shows the evolution of the fluorescent emission intensity as a function of laser pulse number. A similar evolution was observed in reduced silicate glasses with color centers at  $\lambda = 570 \text{ nm}$  [7].

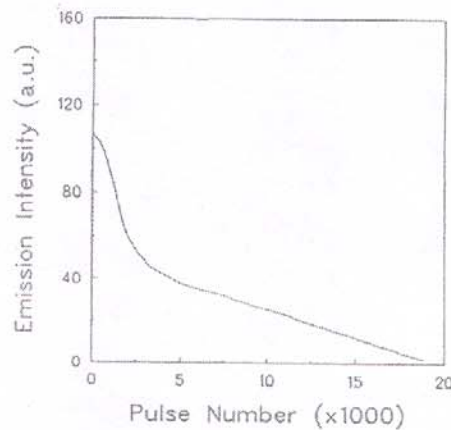


Fig. 1 Evolution of the  $\text{Eu}^{3+}$  fluorescent emission intensity at  $\lambda = 612 \text{ nm}$  versus the number of laser pulses applied to the fluorescent glass.

The persistency of the fluorescent extinction was still observed after 20 months after irradiation. To our knowledge the persistent extinction of the fluorescence emission of  $\text{Eu}^{3+}$  in glasses activated with europium and cerium was not yet reported in the literature by other authors.

We have measured the excitation spectra for the 420 nm emission line before and after the multipulse excimer-laser irradiation (Fig. 2). The intense UV laser light causes the ionization of  $\text{Ce}^{3+}$  ions [7,8]. The peak due to  $\text{Ce}^{3+}$  ions is identified in the vicinity of  $\lambda = 308 \text{ nm}$  in both spectra. This peak is related to the electronic transition between  ${}^2\text{F}_{7/2}$ ,  ${}^2\text{F}_{5/2}$  and  ${}^5\text{D}_0$  states. The peak appearing at 250 nm after the laser treatment is assigned to  $[\text{Ce}^{3+}]^+$  ions [7,9]. In our opinion [10] the electrons released by photoionization of the  $\text{Ce}^{3+}$  ions produce the observed extinction of the  $\text{Eu}^{3+}$  fluorescence as a consequence of the transitions of the  $\text{Eu}^{3+}$  ions to  $[\text{Eu}^{3+}]^-$  ions. For details concerning the  $[\text{Eu}^{3+}]^-$  and  $[\text{Ce}^{3+}]^+$  see the papers [8,9].

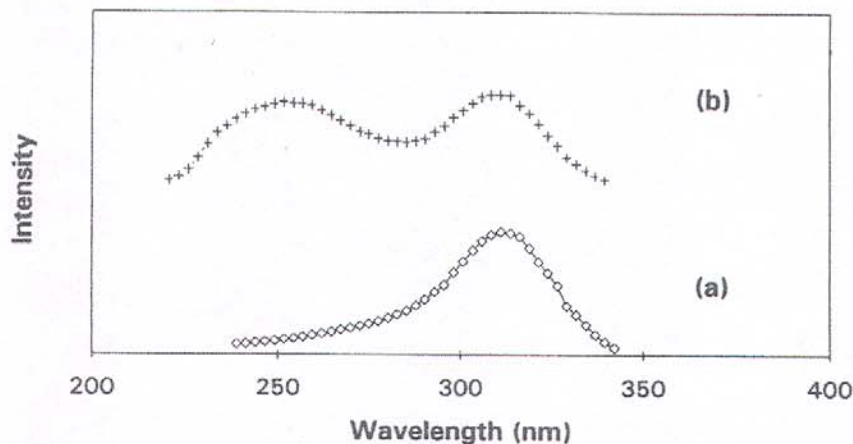


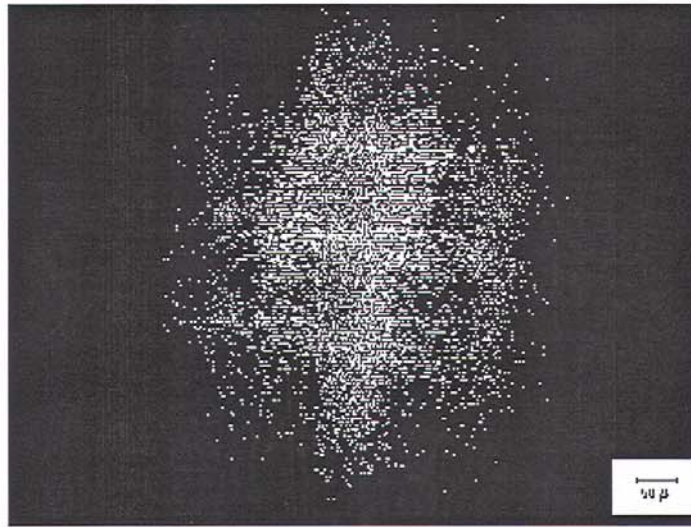
Fig. 2 Excitation spectra of the fluorescent photosensitive glass for emission at 420 nm: a. before and b. after the multipulse excimer-laser treatment.

In our opinion, the application the effect of persistent extinction of fluorescence can be extended to the development of a 3D memory of very high density of information.

A test to prove the recording capacity of the above-discussed materials and methods concerning the persistent extinction effect was conducted with a fine grid placed in front of the glass target. A good contrast image of the grid was recorded both on the surface as well as deep inside the glass target, due to the effect of the multipulse excimer-laser treatment.

To imprint the image at a certain depth within the sample, a short-focal length, corrected for aberrations, was used. The image was read with an Olympus BH-2 microscope equipped with a Sony Hyper HAD CCD camera.

Fig. 3 shows the fluorescence image recorded at 600  $\mu\text{m}$  beneath the surface of the sample. The dark areas correspond to the regions subjected to laser pulses while the light areas correspond to the region protected by the grid bars. The fluorescence characteristics inside the irradiated regions exhibit excellent fading characteristics.



*Fig. 3 Fluorescence image of a grid imprinted into the depth of a fluorescent photosensitive glass at 600  $\mu\text{m}$  beneath the surface of the photosensitive glass sample.*

### 3. Conclusions

In conclusion, a persistent extinction effect of fluorescent emission of  $\text{Eu}^{3+}$  in sodium phosphate glasses doped with europium and cerium was observed after irradiation with excimer-laser pulses. On this basis, a 3D-memory effect in these glasses has been demonstrated. Easy writing and reading can be conducted through a special confocal microscope [11].

The development of fluorescent photosensitive glasses could be of importance in the field of holography and for optical memories of very high storage density.

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