

# Three-dimensional memory effect in fluorescent photosensitive glass activated by europium and cerium

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The persistent extinction of fluorescence emission of  $\text{Eu}^{3+}$  in glasses activated with europium and cerium is reported for the first time to the authors' knowledge. The glass samples containing  $\text{Eu}^{3+}$  and  $\text{Ce}^{3+}$  were initially colorless and transparent and exhibited intense emission peaks at 592 and 612 nm assigned to the  ${}^5D_0$ - ${}^7F_{1,2}$  transitions of  $\text{Eu}^{3+}$ . The complete extinction of the  $\text{Eu}^{3+}$ -ion emission was obtained as an effect of multipulse excimer-UV-laser ( $\lambda = 248$  nm,  $\tau_{\text{FWHM}} \geq 20$  ns) irradiation of the glass samples. Fluorescence microscopy, Mössbauer spectrometry, and electron spin resonance were applied for investigation of the modifications induced by the laser treatment. As a decisive proof of the extinction of fluorescence we succeeded in recording three-dimensional fluorescent photographic patterns within the activated samples.  
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It has been recognized that glasses that contain rare earths are useful for many optical applications (as light filters,<sup>1</sup> laser media,<sup>2</sup> solid standards for narrow-band fluorescence,<sup>3</sup> etc). Recently, laser-induced gratings were observed in  $\text{Eu}^{3+}$ -doped glasses.<sup>4</sup> New research results on the applications of glasses in nonlinear optics were reviewed by Aitchison.<sup>5</sup>

We show that use of fluorescent photosensitive glass activated with rare earths (Eu, Ce) is a promising method for achieving three-dimensional optical memory.<sup>6,7</sup> Thus, on one hand, as a host material for rare-earth ions the enclosure in glass is superior to the enclosure in single crystals in terms of its higher transparency and easy mass production. We further note that, in addition having good storage capabilities, fluorescent photosensitive glasses are a subject of interest for fluorescence holography.

Europium and cerium are present in fluorescent photosensitive glasses as  $\text{Eu}^{3+}$ ,  $\text{Eu}^{2+}$ ,  $[\text{Eu}^{3+}]^-$ ,  $\text{Ce}^{3+}$ , and  $\text{Ce}^{3++}$  ionic states. The use of sodium phosphate glass<sup>8</sup> prevents the formation of  $\text{Ce}^{4+}$  ions. The ionic states  $\text{Ce}^{3++}$  and  $[\text{Eu}^{3+}]^-$  were defined and studied in Refs. 9–12. The state  $\text{Ce}^{3++}$  forms when  $\text{Ce}^{3+}$  captures a hole, whereas the state  $[\text{Eu}^{3+}]^-$  appears when  $\text{Eu}^{3+}$  traps an electron. We noticed that the  $\text{Ce}^{3++}$  centers, which are similar but not identical to  $\text{Ce}^{4+}$  ions, exhibit an absorption band with a maximum near 250 nm, whereas the maximum of the absorption band of  $\text{Ce}^{4+}$  peaks at 240 nm. We also noticed that the absorption and electron spin resonance (ESR) spectra of  $\text{Ce}^{4+}$  are different from those of  $\text{Ce}^{3++}$ , those of  $\text{Eu}^{2+}$  are different from those of  $[\text{Eu}^{3+}]^-$ . Finally, the  $\text{Eu}^{2+}$  ion is fluorescent, whereas the  $[\text{Eu}^{3+}]^-$  ionic state is not.<sup>12</sup>

The glass samples were subjected to multipulse UV laser irradiation in atmospheric air. We used a  $\text{KrF}^*$  excimer-laser source ( $\lambda = 248$  nm,  $\tau_{\text{FWHM}} \geq 20$  ns), which delivered an energy  $E_0 = (40\text{--}100)$  mJ/pulse at a repetition rate of (1–2) Hz. The incident laser fluence was set within the range 50–125 mJ cm<sup>-2</sup>. We usually applied series of a few tens to 20,000 subsequent laser pulses. Most of the irradiation was performed with parallel light beams. To test the threshold behavior of the recording capability of the glass, in some experiments we used a cylindrical lens with a focal length of 9 cm. The fluorescence and absorption spectra of the glass samples were recorded with an Amico-Bowman spectrophotofluorometer and a Perkin-Elmer Lambda 2S UV-VIS spectrometer, respectively, both before and after the multipulse laser treatment. The ESR spectra of both irradiated and unirradiated samples were recorded with a JES-ME-3X spectrometer operated in the X band (~9 GHz). The measurements were carried out in air at room temperature. The  ${}^{151}\text{Eu}$  Mössbauer experiments were performed on powder samples at room temperature. We used a (100-mCi)  ${}^{151}\text{Sm}_2\text{O}_3$  source and a Doppler drive in the triangle mode together with a proportional counter to detect the 21.6-keV gamma rays. The fluorescence and absorption investigations were carried out on samples with a composition (wt. %) of 50  $\text{Na}_2\text{O}$ –49  $\text{P}_2\text{O}_5$ –0.5  $\text{Eu}_2\text{O}_3$ –0.5  $\text{CeO}_2$ . The glass preparation is described elsewhere.<sup>6</sup>

The inset of Fig. 1 shows the emission spectrum of  $\text{Eu}^{3+}$  in our glass samples before UV-laser irradiation. The spectrum was obtained by excitation with the  ${}^7F_0$ – ${}^5D_2$  line at 465 nm. The fluorescence bands are assigned to transitions from the  ${}^5D_0$  to the  ${}^7F_j$  ( $j =$

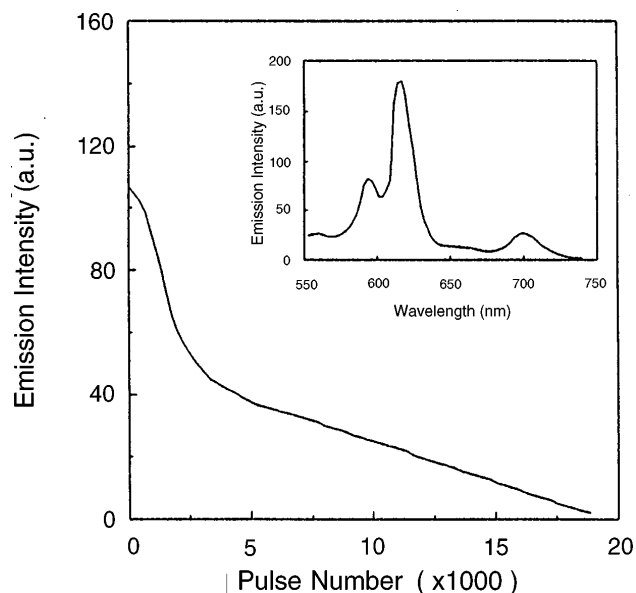


Fig. 1.  $\text{Eu}^{3+}$  emission intensity at 612 nm as a function of the number of applied UV-laser pulses. Inset, emission spectrum of  $\text{Eu}^{3+}$  in fluorescent photosensitive glass before UV-laser treatment ( $\lambda_{\text{ex}} = 465 \text{ nm}$ ).

0, 1, 2, 3, 4) level. As an effect of prolonged UV-light irradiation the emission of  $\text{Eu}^{3+}$  decreases at a low level (Fig. 1). In this experiment the excimer-laser source supplies an energy of  $E = 80 \text{ mJ/pulse}$  at a fluence of  $100 \text{ mJ cm}^{-2}$ . An exponential decay of as much as  $n < 5 \times 10^3$  pulses (where  $n$  is the number of subsequent laser pulses) can be observed. It is followed by a linear regression for  $n > 5 \times 10^3$  pulses. The two evolutions can be described by

$$I(n) = \begin{cases} A \exp(-n/N_1) & n < 5 \times 10^3 \\ Bn + C & n > 5 \times 10^3 \end{cases} \quad (1)$$

The best fit was obtained for  $A = 96.4$ ,  $N_1 = 4.1 \times 10^3$ ,  $B = -2.2 \times 10^{-3}$ , and  $C = 44$ . An analogous evolution was observed in reduced silicate glasses with color centers at  $\lambda = 570 \text{ nm}$ .<sup>13</sup>

In Fig. 2 the excitation spectra for the 420-nm emission before and after multipulse UV-laser irradiation are shown. The  $\text{Ce}^{3+}$  ions are photoionized under the action of intense UV light.<sup>9,13</sup> The peak that is due to  $\text{Ce}^{3+}$  can be identified near 308 nm in both spectra. The peak that appears at 250 nm after the laser treatment is attributed to  $\text{Ce}^{3++}$  ions.<sup>10,13</sup> In our opinion the electrons released by the photoionization of the  $\text{Ce}^{3+}$  ions produce the observed extinction of the  $\text{Eu}^{3+}$  fluorescence as a consequence of the transitions of  $\text{Eu}^{3+}$  ions to  $[\text{Eu}^{3+}]^-$  ions.

These hypotheses were first verified by a direct comparison of the absorption spectra of a sample before and after prolonged laser treatment. From the absorption spectra we observed that the band at 250 nm is missing in the case of the laser-treated sample. On the other hand, the unirradiated sample has an absorption spectrum with a maximum at 308 nm. After the multipulse laser equipment, this maximum disappears. The oscillations that are present in the UV part of the same spectrum are an indication of

the existence of trapped electrons. To check further on the plausible formation of  $[\text{Eu}^{3+}]^-$  states after laser treatment, we carried out ESR and Mössbauer spectrometry studies on a sample with a higher Eu content:  $50 \text{ Na}_2\text{O}-44 \text{ P}_2\text{O}_5-3 \text{ Eu}_2\text{O}_3-3 \text{ CeO}_2$ .

The ESR spectrum of the unirradiated sample (Fig. 3) consists of a narrow line located at  $g = 2.045$  (assigned to  $\text{Eu}^{2+}$  ions) superposed over a broad line located close to  $g = 2$ . Here  $g$  is the spectroscopic splitting constant. The narrow line presents a hyperfine structure that consists of six lines almost equally separated and of the same intensity. This behavior is the effect of the interaction between the uncoupled electronic spin and the Eu nucleus.<sup>14</sup> The average hyperfine interaction constant  $A$  is  $\sim 90 \text{ G}$ . The complexity of the resonance line is due to the superposition of two sextets ascribed to  $^{151}\text{Eu}$  and  $^{153}\text{Eu}$  isotopes, both with  $I = 5/2$ , as well as to the quadrupole effect. After the UV treatment (Fig. 3) the structure of the line ascribed to  $\text{Eu}^{2+}$  is practically independent of the number of applied pulses (as many as  $n \leq 9000$ ). However, in case of the irradiated samples a narrow resonance line without structure was observed close to the free-electron  $g$  value. A similar ESR spectrum was observed for  $[\text{Eu}^{3+}]^-$  in silicate glass.<sup>12</sup> The intensity of the central line increases with the number of applied pulses. Also, after multipulse irradiation, two shoulders were observed. They may be ascribed

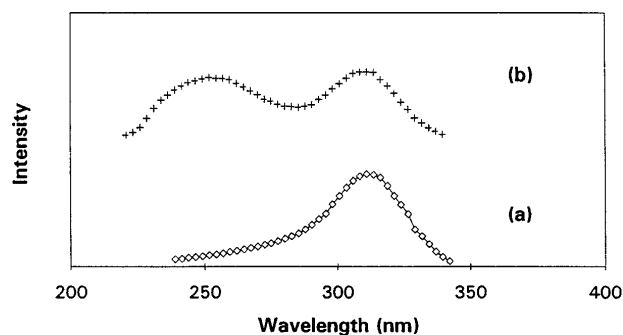


Fig. 2. Excitation spectra of fluorescent photosensitive glass for the 420-nm emission (a) before and (b) after multipulse UV-laser irradiation.

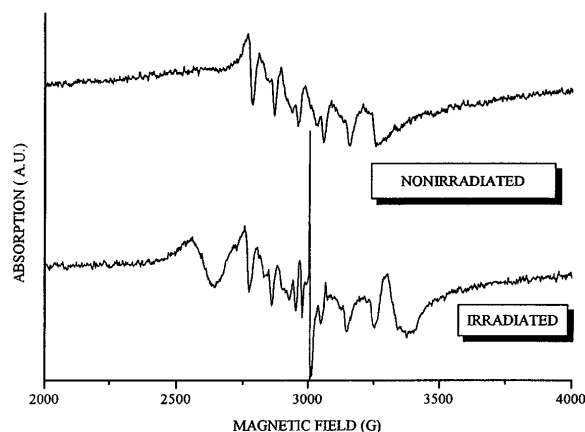


Fig. 3. ESR spectra of nonirradiated and irradiated  $50 \text{ Na}_2\text{O}-44 \text{ P}_2\text{O}_5-3 \text{ Eu}_2\text{O}_3-3 \text{ CeO}_2$  fluorescent photosensitive glass samples.

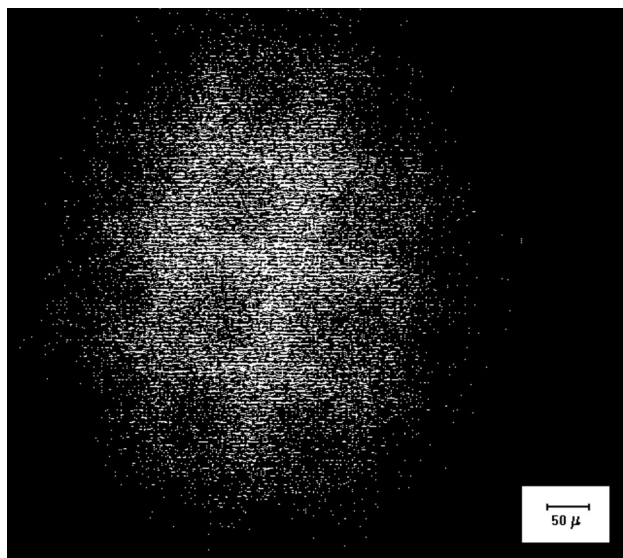


Fig. 4. Fluorescence image of a grid recorded into the depth of a fluorescent photosensitive glass at 600  $\mu\text{m}$  beneath the surface of the glass sample.

to an exchange coupling or may be considered to arise from a superhyperfine interaction.

A least-squares fit performed under the hypothesis of a Lorentzian shape of the Mössbauer spectrum of an unirradiated sample recorded at room temperature reveals a single line only, with a linewidth of  $\sim 2.1$  mm/s, which is close to the characteristic value for the source used. The presence of a single straight line in the Mössbauer spectrum suggests a nearly cubic and homogeneous neighborhood of Eu ions in the sample. The isomer shift of approximately  $-0.21$  mm/s ( $\pm 0.07$  mm/s) with respect to the  $^{151}\text{Sm}_2\text{O}_3$  source corresponds to  $\text{Eu}^{3+}$  ions in oxides.<sup>15,16</sup> In the irradiated sample the isomer shift decreases to  $-0.63$  mm/s, indicating a decrease of the electronic density at the Eu nucleus. The electronic traps created by irradiation could expand the wave function of 5s electrons, this decreasing the electronic density at the nucleus. This behavior confirms the presence of  $[\text{Eu}^{3+}]^-$  ions. At this stage of our studies we cannot completely rule out the formation of defect centers in the visible-wavelength region as a complementary mechanism leading to the persistent extinction of the fluorescence emission.

A final test to prove the recording capability of our glass samples was conducted with the aid of a fine grid placed in front of the glass target. A good contrast image of the grid was recorded both on the surface and in the bulk of the sample as an effect of the multipulse UV-laser treatment. To imprint the image at a certain depth inside the sample we used a short-wavelength aberration-corrected focusing lens. The image was read with an Olympus BH-2 microscope

equipped with a Sony Hyper HAD CCD camera. We used a BP360-370 excitation filter and a BA420 barrier filter.

In Fig. 4 we present the fluorescence image recorded at 600  $\mu\text{m}$  beneath the surface of the glass sample. The dark areas in Fig. 4 correspond to the zones subjected to the action of the laser irradiation, and the light areas correspond to the zones protected by the grid bars. The information stored inside the UV-laser-irradiated specimens exhibited excellent fading characteristics. The extinction of fluorescence has been preserved even 8 months after irradiation.

In summary, a three-dimensional memory effect in fluorescent photosensitive glass samples has been demonstrated. The composition of the recording media as well as possible mechanisms for the fluorescence extinction were presented. In our opinion, the development of fluorescent photosensitive glasses could produce a significant breakthrough in the fields of optical and holographic recording and storage.

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