

Fluorescent photosensitive glass-ceramics – a novel media for optical data storage

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A fluorosilicate glass-ceramic containing rare earths such as europium (Eu) was realized in order to be used as information 3D optical data storage media. Photosensitive agents: silver (Ag) and cerium (Ce) has been used for obtaining the photosensitivity properties. The material structure and properties were investigated by XRD, SEM, AFM, TEM, confocal microscopy and photoluminescence spectroscopy. The measurements revealed the presence of NaF nanocrystals having dimensions in the range of tens of nanometer. The zones having high nanocrystal population densities present a higher fluorescence. The results suggest that the fluorescent photosensitive glass-ceramics are promising candidates in the class of 3D information storage materials.

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1. Introduction

Three-dimensional optical memories have generated considerable interest for their potential application to high-density optical data storage [1]. For instance, the surface storage density accessible with focused beams of light (without near-field techniques) is roughly $1/\lambda^2$. With green light of roughly 0.5 micron wavelength, this should lead to 4 bits/sq. micron or more than 4 Gigabytes (GB) on each side of a 120mm diameter, 1mm thick disk. But by storing data throughout the volume at a density of $1/\lambda^3$, the capacity of the same disk could be increased 2000-fold, to 8 Terabytes (TB).

Fluorescent photosensitive materials such as fluorescent photosensitive glasses [2] and fluorescent photosensitive glass-ceramics [3] have interesting properties useful for 3D optical data storage [4].

A version of fluorescent photosensitive glass-ceramic is obtained starting from oxyfluoride glasses. These glasses have created much interest as host materials for optical devices, such as lasers and optical amplifiers which utilize f-f transitions of rare earths ions [5-7]. After a thermal treatment close to the crystallization temperature it is possible to obtain a glass-ceramic, in which fluoride nanocrystals are embedded in a primary oxide glass matrix. Thus, if the rare earths ions are incorporated into the crystalline phase, the glass-ceramic combine the particular optical properties of these ions in fluoride hosts,

with the elaboration and manipulation advantages of oxide glasses, suitable for industrial production.

In this paper we present structural and optical properties of the fluorescent photosensitive glass-ceramics doped with Eu. The properties were investigated by XRD, SEM, AFM, TEM, confocal microscopy and photoluminescence spectroscopy

2. Experimental

2.1 Preparation

The samples used in this study were prepared with the following composition in wt% : 69SiO₂ - 15.8 Na₂O-4.8 ZnO-6.3Al₂O₃-0.5Eu₂O₃-0.05CeO₂-0.2Sb₂O₃-0.05SnO-2.3F⁻-0.01Ag⁺, from stoichiometric quantities of SiO₂, NaCO₃, Al₂O₃, Eu₂O₃, ZnO, sodium fluorosilicate, Sb₂O₃, SnO, CeO₂ and AgF which were thoroughly mixed in a ball mill. The rare earths oxides were of 99.99% grade. All other reagents were c.p. grade. The chemical mixtures were melted at 1400°C in alumina crucibles, and these melts were kept at that temperature for about an hour and then poured on a graphite stage and annealed at 450°C. Precursor glass discs 1mm thick and 9 mm diameter were produced after cutting and polishing processes. The UV light irradiation were carried out with a 125W Hg lamp. The transparent fluorescent photosensitive glass-ceramics were obtained just by thermal treatment at

550 °C for 10 hours to precipitate NaF fluorescent nanocrystals without loss of transparency.

2.2 Characterization

X-ray powder diffraction data were collected on a D8 Advance Bruker diffractometer using Cu K α ($\lambda = 1.54178$ Å) radiation and a secondary beam graphite monochromator. Diffraction patterns were collected in the 2θ range from 10° to 100° . Samples of fluorescent photosensitive glass-ceramics were analyzed using a Hitachi S-2600 SEM operating at 25 kV. Surface morphology was studied by Atomic Force Microscopy using a Scanning Probe Microscope (Veeco Instruments) in tapping mode scanning a typical surface of $3.35 \mu\text{m} \times 3.35 \mu\text{m}$. The dimensions of surface corrugations measured by AFM is influenced by the finite size of the probe tip. Particles swept onto the TEM grids were analyzed using a JEOL 200-CX. The photoluminescence (PL) spectra were obtained from discs of fluorescent photosensitive glass ceramics, mounted in a Perkin Elmer 204 spectrofluorometer. All PL spectra were recorded at room temperature. 3D images of NaF fluorescent nanocrystals were studied by confocal microscopy with a Scanning Laser Microscope Leica SCP. The laser source was an Ar-ion laser operating at 488 nm.

3. Results and discussion

The process for producing a fluorescent photosensitive glass-ceramics requires an ultraviolet exposure of the precursor glass followed by a heating treatment to grow a photographic image containing photonucleated silver particles. These particles, in turn, nucleate the growth of NaF nanocrystals doped with rare earth ions, like Eu^{3+} .

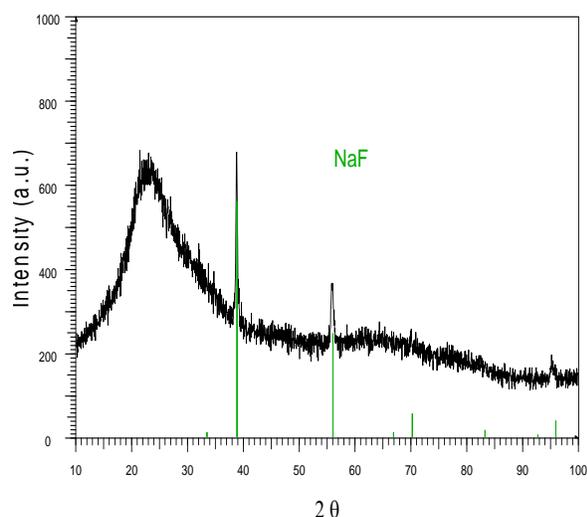


Fig. 1. X-ray diffraction pattern of a fluorescent photosensitive glass-ceramic sample.

X-ray diffraction measurements (Fig. 1) of the power obtained from fluorescent photosensitive glass-ceramic, show that during the thermal treatment fluoride nanocrystals of NaF precipitate in the precursor glass matrix. It is observed that two phases coexist in the glass-ceramic: (i) an oxyfluoride vitreous and (ii) a fluoride nanocrystalline phase (NaF).

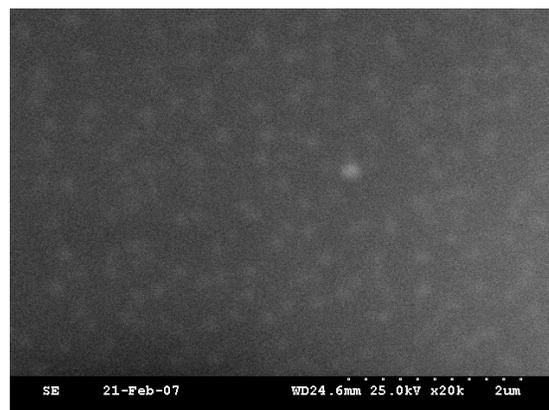


Fig. 2. SEM image of fluorescent photosensitive glass-ceramic.

The size of the nanocrystals precipitated into fluorescent photosensitive glass-ceramics was investigated by SEM, AFM and TEM. SEM image of Fig. 2 shows the presence of grown nanocrystals on the disc surface. Clear images of nanocrystals were realized by AFM (Fig. 3) and TEM (Fig. 4). Results indicate that nanocrystals average size is around 50 nm.

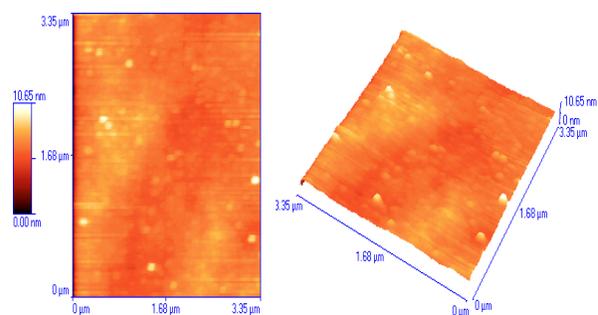


Fig. 3. AFM images of the surface of a disc realized by fluorescent photosensitive glass-ceramic.

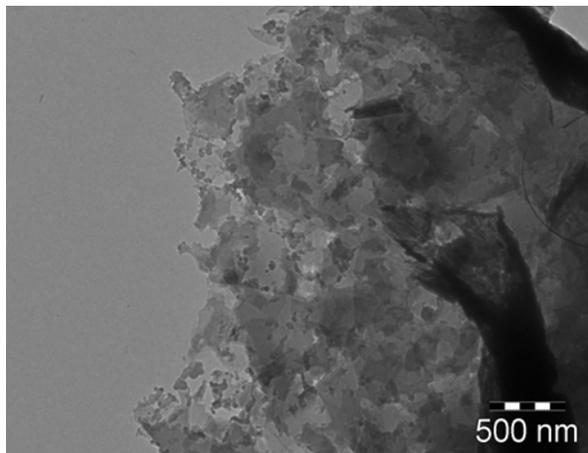


Fig. 4. TEM image of a particle of fluorescent photosensitive glass-ceramic.

In order to obtain information about the origin of 614nm fluorescence emission, excitation spectrum have been recorded (Fig. 5). The spectrum revealed four excitation bands of Eu^{3+} : ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$ (534 nm); ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ (463 nm); ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ (394 nm); ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$ (363 nm) and one excitation band of Ce^{3+} situated at 308 nm:

${}^2\text{F}_{5/2} \rightarrow {}^2\text{D}_{5/2} / {}^2\text{D}_{3/2}$ [9]. The emission spectra (Fig. 6) display three emission transitions of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (592 nm); ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (614 nm); ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ (653 nm). Due to the shielding effect of $4f^6$ electrons by 5s and 5p electrons in outer shells in the Eu^{3+} ion, narrow emission bands are produced. The changes in the Eu^{3+} environment can be monitored by optical spectroscopy. For this purpose, emission spectra of Eu^{3+} ions before (Fig. 6a) and after (Fig. 6b) thermal treatment corresponding to the transitions ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ($J = 1 - 3$) by exciting at 394nm the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transition have been obtained at room temperature. There are important changes in the relative intensities of the different transitions. It is especially interesting to note the decrease in the intensity of the hypersensitive electric dipole ${}^5\text{D}_0 - {}^7\text{F}_2$ transition in the glass-ceramic relative to the magnetic dipole ${}^5\text{D}_0 - {}^7\text{F}_1$ transition. The ratio of the electric to the magnetic dipole transition has been considered a measurement of how much closer the local site is to be centrosymmetric, for which the odd crystal field Hamiltonian is null [10]. From the results for this ratio, about 3.05:1 in the glass precursor (Fig. 6a) and about 3.02:1 in the glass-ceramic (Fig. 6b), it can be concluded that the local symmetry for the Eu^{3+} ions is higher in the glass-ceramic. These results suggest that Eu^{3+} ions are in higher concentration in NaF nanocrystals than in glass. Confocal microscopy image (Fig. 7) completes the previous results showing fluorescent nanocrystals inside a sample of fluorescent photosensitive glass-ceramic.

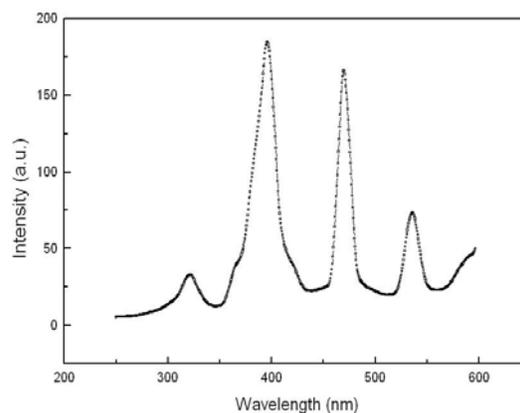


Fig. 5. Excitation spectrum ($\lambda_{em} = 614$ nm) of the fluorescent photosensitive glass-ceramic.

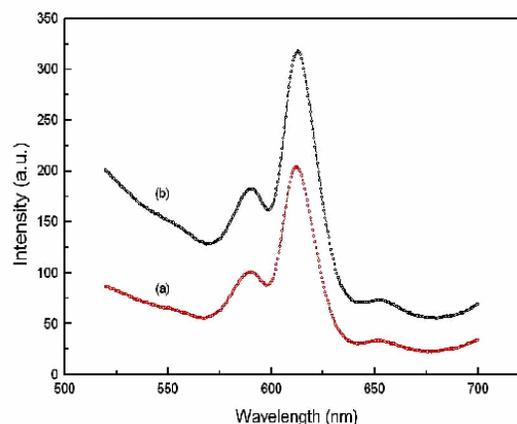


Fig. 6. Emission spectra ($\lambda_{ex} = 394$ nm) of the fluorescent photosensitive glass-ceramic before (a) and after thermal treatment (b).

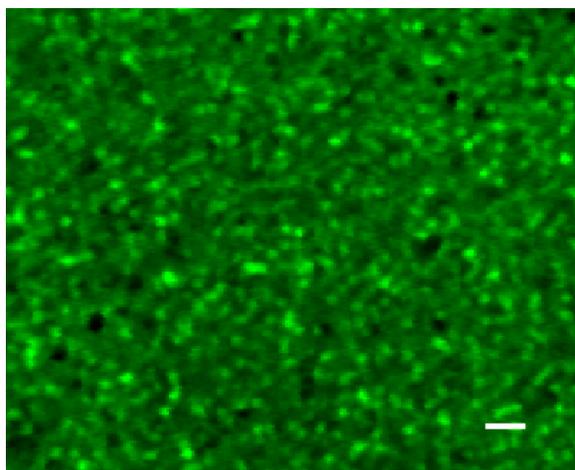


Fig. 7. Confocal image of the nanocrystals inside fluorescent photosensitive glass-ceramic. Inserted white bar represents 4 μm .

In summary, rare earth ions such as Eu^{3+} are preferentially incorporated into crystalline phase during thermal treatment.

4. Conclusions

A preparation method of fluorescent photosensitive glass-ceramic has been developed. The precursor glass contains Ag which acts as seed for the nucleation of NaF nanocrystals. After a thermal treatment, nanocrystals doped with Eu^{3+} were obtained. The optical properties of the rare earth ions in fluorescent photosensitive glass-ceramics are ruled by the final environment of the ions in these matrices. Measurements carried out by photoluminescence spectroscopy and confocal microscopy sustain the presence of Eu^{3+} in high concentration inside NaF nanocrystals. Therefore, these materials will be useful in developing next generation 3D optical memory devices with an ultrahigh storage density.

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