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Durability study of a fluorescent optical memory in glass studied by luminescence spectroscopy

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A B S T R A C T

Thermal stress at 100 °C for more than 3168 h of a fluorescent optical memory composed of laser written silver nano clusters embedded in glass has been performed. Measurements of luminescence spectra have been carried out at different times, showing a decreasing and an increasing evolution of the red and the blue part of the spectrum, respectively. This evolution has been attributed to the diffusion and the reor ganization of different silver species inside the matrix, altering the internal electric field. Stark effect based modeling enables the degradation mode of the memory.

1. Context and objectives

The innovations of recent decades have largely increased stor age capacity on the media, CD, CD R and DVD R up to Blu Ray, but in contradiction, the lifetime of such new supports is not as good as the innovation could be engaged. In comparison with the Egyptian scribes let us one of the first archive that could be read after 5000 years. Taking into account reliability aspect, we are, in 2012, 5000 years behind compared to the Egyptian technology. But if we use the Egyptian technology to record all actual data it will take us more than 1 billion pyramids, which is not possible. The first time to failure of actual digital support is around 20 years, which does not meet the archivist requirement [1].

This last point is a real huge societal high stake because nowa days, no perennial solution for more than 20 years of storage ex ists. Many sectors in the economic and social life are directly affected by this problem. In particular we must mention the archi vists. Their interest is to find a media for storing information for a long term. From the PSN (Pérennité des Supports Numériques) group report "It becomes urgent to develop innovative materials for a long term information storage" (12/2009) [1].

The main objectives of the project consists in the determination of the sustainability of Ag doped glass material structured by fem tosecond laser regarding environmental stresses applied to archi val of digital data.

The structuration of glass matrix is based on silver clusters structured under the femtosecond laser beam leading to a fluores cence contrast (under the laser excitation) between the glassy ma trix and the aggregate phase dots. Some results of the LOMA, IMS and ICMCB Laboratories about silver elements in glassy matrix gave some positive return to engage the reliability study.

The solution proposed in this study could be used on new optical memory glass based structured by femtosecond laser in the bulk. The advantage of this new technics resides in the fact that memory is composed by only one material (Glass). No delamina tion, shear stresses, etc. could be observed in this structure. The only one phenomenon is the diffusion of silver clusters. This publication answers to this specific issue.

2. Experimental setup

Silver clusters are created by a pulse train from a near infrared (NIR) femtosecond laser focused with a microscope objective in side a femto photo luminescent (FPL) glass (Fig. 1). Such a photo sensitive glass belongs to the phosphate family and was initially designed for gamma irradiation dosimetry [2,3]. In the present case, the composition is slightly modified: It is a zinc phosphate glass containing silver ions [2] presenting an ultraviolet (UV) absorption band below 280 nm. Detailed descriptions of its fabrica tion and properties can be found in the Methods. Following expo sure to a high repetition rate femtosecond pulse train, the glass presents a broad excitation band (300 450 nm). When excited by NUV radiation, it emits homogeneous white fluorescence that specifications (intensity, spectrum and lifetime) depend on the irradiation dose (fluency, number of pulses and repetition rate) [4 6]. This fluorescence is attributed to the presence of $Ag_m x^+$ sil ver clusters with the number of atoms $m < 10$ and the ionization degree x [5]. These silver clusters are created inside the focusing voxel (cf. Fig. 1A) and are arranged into a pipe shape along the propagation axis, with a length corresponding to the Rayleigh range (10 μm) and a wall thickness of about 80 nm. For a given

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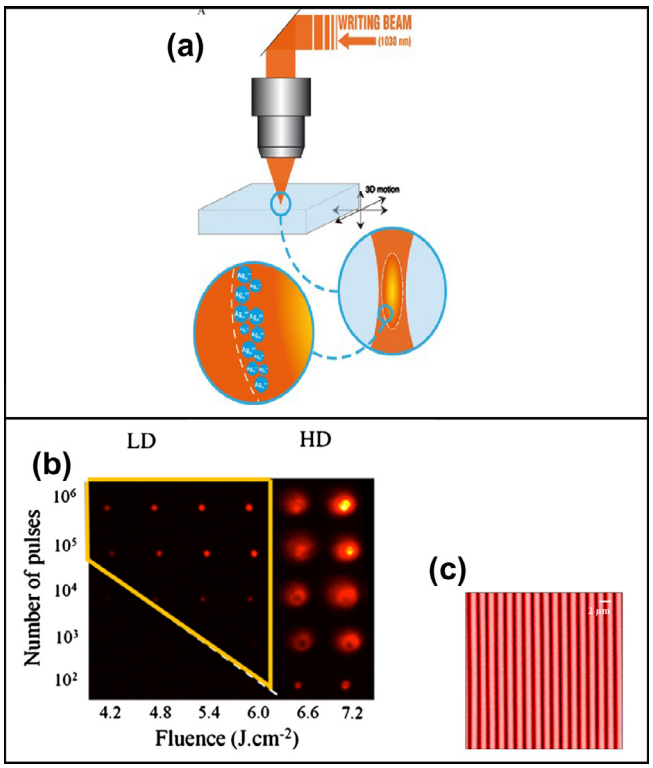


Fig. 1. (a) The laser interaction on Rayleigh range, (b) the separation between high dose (HD) and low dose (LD), and (c) the multiline structured by laser for each samples.

fluence range (from 2 J cm ^{2} to 6 J cm ^{2}), the silver clusters are produced without significant linear refractive index change (<10 ^{4}), while they exhibit appreciable fluorescence and nonlinear optical properties. This glass has already shown its potential for 3D optical data storage taking advantage of the third order susceptibility contrast of the photo induced clusters with respect to the glass matrix [6,7].

The silver clusters can emit fluorescence intensities much higher (50 times) than fluorescent molecules such as dyes (Rhodamine 6G at 10 ^{4} mol L ^{1}). The quantum yield of these species is very high, on the order of 17%. In the FPL glass, the emission can be tuned from yellow to red colors. The fluorescence time decay of the clusters is on the order of a few nanoseconds [4], allowing a reading speed as high as 500 MHz. In the FPL glass, the fluorescence intensity of the silver clusters varies linearly with the irradiance and logarithmically with the deposited number of pulses, within the range of interest. This last behavior is well known in photographic processes [4]. Therefore, by adjusting properly the dose, the fluorescence intensity of the photo induced species can be controlled exactly like in silver photographic films.

2.1. Glass preparation

The glasses were made using a standard melt quench technique. Glass constituents in powder form were used as raw materials and the proper amount was placed in a platinum crucible. A heating rate of about 1 °C min ^{1} was used up to 1000 °C. The melt was then kept at this last temperature (1000 °C) from 24 to 48 h. Following this step, the liquid was poured into a brass mould after a short increase of the temperature at 1100 °C in order to reach the appropriate viscosity. The glass samples obtained were annealed at 320 °C (55 °C below the glass transition temperature) for 3 h, cut (0.5 1 mm thick) and optically polished.

The silver zinc phosphate glass and the silver silicate glass have the following compositions, respectively:

- $40P_2O_5$ $4Ag_2O$ 55ZnO $1Ga_2O_3$ (mol%).
- $69.98SiO_2$ $1.27Ag_2O$ $16.37Na_2O$ 12.38CaO (mol%).

These glasses possess an absorption cut off wavelength at 280 nm (due to the silver ions associated absorption band around 260 nm) and emit fluorescence mainly around 365 nm when excited at 260 nm. This intrinsic fluorescence is due to Ag^{+} ions isolated in the glass.

2.2. Sample exposure

The glass samples were irradiated using a femtosecond laser oscillator source (t Pulse 500, Amplitude Systèmes) emitting 500 fs, 10 MHz repetition rate pulses at 1030 nm. The laser mode is TEM_{00}, M^2 = 1.2 and the output polarization is TM. The maximum output average power is close to 6 W, which results in a maximum energy per pulse of 600 nJ. Acousto optic filtering permits the tuning of the pulse energy, the number of pulses and the repetition rate for control of the cumulated effects. The laser beam was focused using a microscope objective (Zeiss Plan Apochromat 40×; NA = 0.75) at a depth of 150 μm in the glass. The beam waist was estimated to be 0.7 μm. The sample was manipulated using a micro precision *xyz* stage (MicroControle MFA CC) with a repeatability of 2 μm.

The 2 mm × 2 mm sample is structured with 1000 lines separated about 2 μm, at 150 μm under surface. The speed recording is 1 mm s ^{1}. There are two different samples A and B:

- Sample A: The fluency is close to 6 J cm^{2} and the modification of refractive index is not effective (10 ^{5} 10 ^{4}). It is the low dose sample (LD)
- Sample B: The fluency is close to 7 J cm ^{2} and the modification of refractive index is effective (10 ^{2} 10 ^{1}). It is the high dose sample (LD)

2.3. Fluorescence measurements

The fluorescence measurements are performed with single mode blue laser diode (364 nm) and a Jobin Yvon TRIAX 320 spectrometer. The resolution of spectrometer is 2.35 nm/mm and the width of the laser diode is around 0.5 nm. The reproducibility of measurement is estimated with a reference filter (Thorlabs FGL400). The optical spectra of sample have been corrected taking into account the reference white lamp and normalized to compare the spectral distribution. Fig. 2 gave the scheme of band structure of metal cluster.

2.4. Reliability tests

The ageing test are performed on Heraus climatic test chamber at 100 °C 3100 h corresponding to reference of passive storage realized by Laboratoire National de Metrologie et d'essais (LNE) [8].

The fluorescence measurements are realized before and after ageing test.

3. Results and discussion

3.1. Model of luminescence

Metal Ag clusters are molecular entity composed by few atoms and considered to be too small (<2 nm) for plasmonic resonance but having some specific fluorescence properties (Fig. 2). The

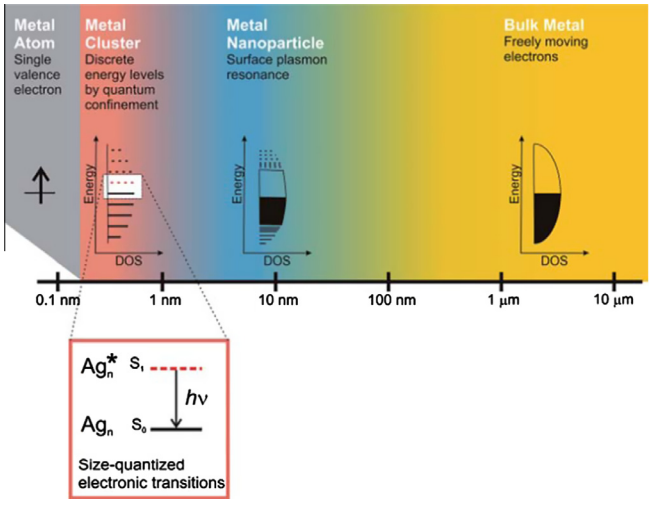


Fig. 2. Band structure of metal cluster.

interaction with light is operated by electronic transitions between different single energy level (as atomic level energy). In this case, the spontaneous emission rate is given by the following equation

$$R_{trans}(E) \propto \frac{\hbar^2\Gamma/2}{(E_0 \quad E)^2 + \hbar^2(\Gamma/2)^2} \tag{1}$$

Γ represents the spectral bandwidth (FWHM) and E_0 is the band position.

The emission spectrum of nanoclusters depends on the host matrix where they are stabilized.

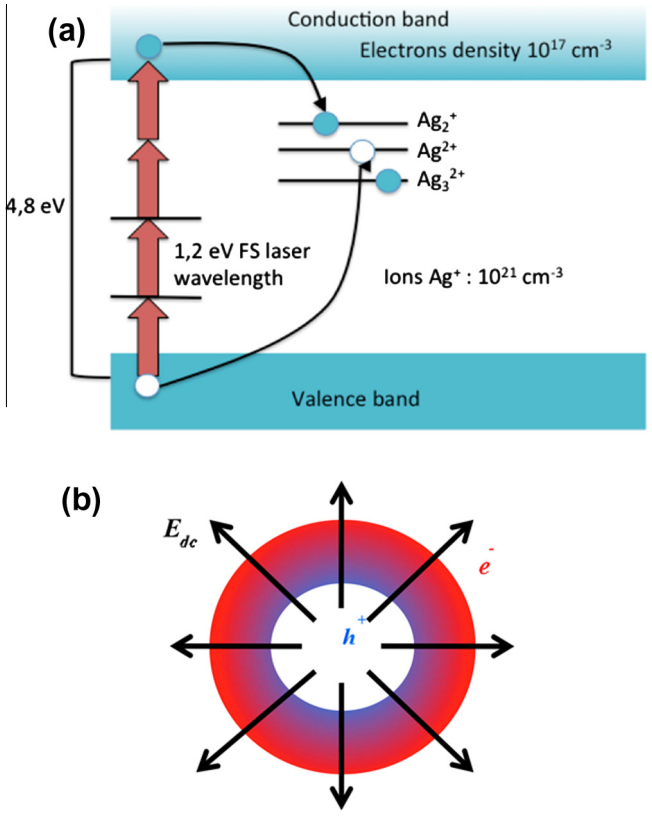


Fig. 3. Photoionisation process: band structure (a) electrical field direction in elementary structure (b).

The laser femtosecond interaction with matrix is driven by four photons absorption phenomenon (Fig. 3 a). The non linear absorp tion phenomenon generates electrons (10^{17} cm ^{3}) in the equiva lent conduction band of matrix. The Ag^+ ions (10^{21} cm ^{3}) located in the matrix (few percent) are:

Aggregated in Ag_2^{2+} with one electron come from conduction band and gives Ag_2^+.
the Ag^+ form with hole generated in the equivalent valence band Ag^{2+}.
3 Ag^+ are aggregate with one electron come from the equivalent conduction band.

These different charges generated by femtosecond laser diffused in the matrix to generate a donut as Fig. 3 b exposed and attached to the laser beam profile. This phenomenon is helped by the thermal heating of matrix due to the electron located in con duction band and thermally activated. After femtosecond laser pulse and thermal effect ended, the Ion located in the matrix give the electrical field presented in Fig. 3 b. Outside donut, the positive charges (aggregate) are fixed and activated by electrons during structuration while inside donut, the concentration in Ag^+ de creases and the equivalent charge became negative.

The luminescence phenomenon, activated by 325 450 nm laser sources and given in Eq. (1), is modified by the electrical field by Stark effect [9] and the spontaneous emission is given by the fol lowing equation:

$$R_{Stark}(\quad E) \propto \left\{ \left[\frac{dA_i(\quad \xi)}{d\xi} \right]^2 + \xi A_i^2(\quad \xi) \right\} K\, exp\left[\frac{4}{3}(\quad \xi)^{3/2} \right] [(\quad \xi)^{5/2} + 8(\quad \xi)^{1}] \tag{2}$$

where ξ is given by: $\xi \quad \frac{E_\xi E_g^{eff}}{\xi}$ and $\xi \quad \left(\frac{2m_r}{\hbar^2 q^2 E_{dc}^2}\right)^{1/3}$.

The equivalent spectrum given by model, developed by Eqs. (1) and (2), considering different Ag clusters is given in Fig. 4. The dif ferent part associated to different phenomenon is underlined with wavelength correspondence. For Stark effect, the best fitting is ob served for wavelength ranging from 570 to 700 nm. The inter level transition is given by Lorentzian curve (see Eq. (1)) observed for wavelength ranging from 350 to 570 nm. In optical spectrum, the most important cluster concentration is generally repeated. Gener ally, one can only observed a typical Lorentzian curve.

3.2. Experimental results

The results of fluorescence response before and after ageing tests are shown in Fig. 2. For high dose (HD) samples (Fig. 5 a),

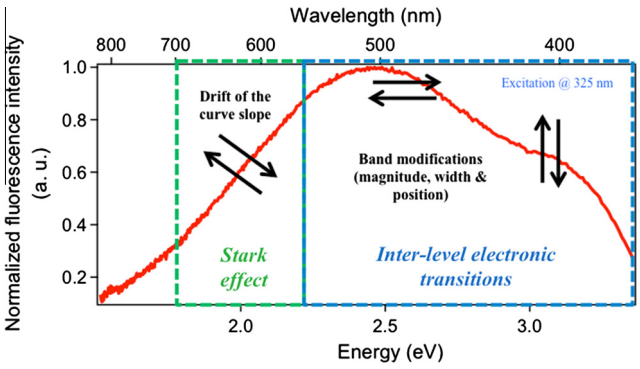


Fig. 4. Failure signatures on optical spectrum related to Ag_{xm} species modifications.

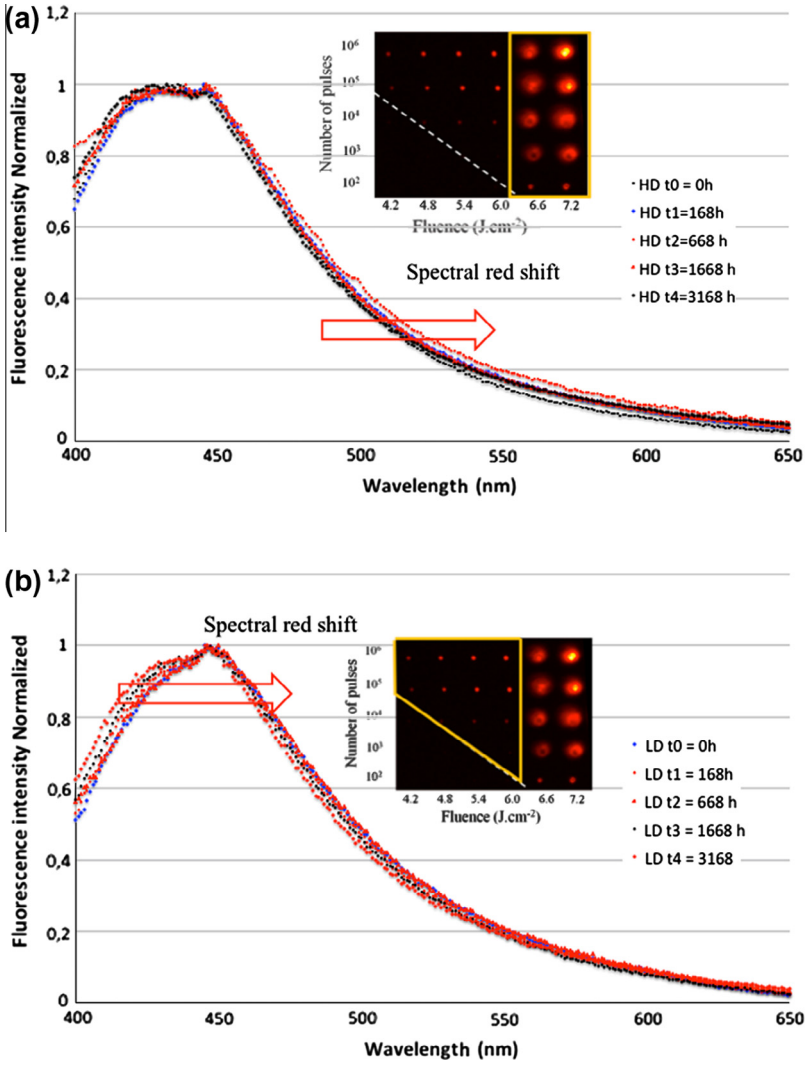


Fig. 5. Comparison between optical spectrum of HD (a) and LD (b) samples @ 300 K before and after ageing tests.

the impact of the spectral response is weak and only the red shift of high wavelength is observed. In this case, the Stark effect is modi fied in relation with electrical field. The modification of electrical field is closely related to the charge distribution in the matrix. The red shift is closely related to an increase of electrical field. The increase of electrical field is directly related to the diffusion of cluster. The diffusion of the cluster is in the good direction to in crease concentration of Ag cluster around the donut and increase the optical response of the system. System improves these perfor mances. There is no degradation but an increase of optical performances

For low dose (LD) samples (Fig. 5 b), the impact of the spectral response is weak and only a red shift of optical spectrum is ob served. In this case an Ag cluster is gradual change and explain the drift of E_0 position of the central energy. The modification of clusters no gradual changes optical performances of the system (less than 1% of the fluorescence).

4. Conclusion

These specific results are consistent with a long term reliability of optical memories. The spectral gradual change is mainly due to the modification of Ag cluster but the impact on optical perfor mances is very weak.

The impact on the performances is directly related to the elab oration and structuration of the samples. Both chemical composi tion and femtosecond laser parameters have been adjusted to find the optimized structure for reliability point of view. This pro cess is related to design for reliability, well established in industrial development. This original work shows that the design for reliabil ity is develop in the fundamental research for new optical memo ries. Based on these first results, many investigations will be engaged to find an industrial and long term optical memory based on commercial glass and laser.

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