Influence of pulsed laser irradiation on precipitation of silver nanoparticles in glass

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ABSTRACT

The effect of a high power Nd:YAG laser radiation on silver ion-exchanged glasses is investigated. Exposure time, spot size and energy have been varied in order to modify the size and the distribution of the metallic nanoaggregates which are formed under the laser irradiation. Optical absorption spectroscopy has been used to confirm the formation of the nanoaggregates by plasmon resonance apparition and the intensity and the decay of the resonance have been observed with the laser irradiation parameters. Quantitative composition of the samples, before and after irradiation, has been determined by energy dispersive X-ray analysis. Desorption of Na atoms and size reduction have been observed. TEM measurements have been carried out to verify the formation of silver nanoparticles.

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1. Introduction

Metallic nanopowders have been widely studied because they have interesting physical properties which are considerably different from the bulk phase. These nanoscale materials are expected to have many potential applications such as heterogeneous catalysts, surfaces of heat exchangers, memory devices, gas sensors, optical waveguides or optical switches [1–4]. Especially, extensive studies have been conducted on silver nanosized particles owing to their commercial applications for construction of medical tools and appliances and health care products [5,6].

Such heterogeneous materials, being composed of metallic nanoclusters in amorphous matrices, are fabricated by variety of methods. Among the most successful we have low energy ion-beam mixing [7], sol–gel [8], direct metal ion implantation [9], annealing of ion-exchange glasses in hydrogen atmosphere or evaporation-condensation [10–12].

In recent years, great effort has been taken to the processing of such nanocomposites using pulsed laser irradiation of ion-exchange glasses. The electric field intensity of a focused laser beam can reach even 100 TW cm⁻² in the case of femtosecond lasers. Therefore various microstructures are created when the laser pulse is focused into transparent materials due to
multiphoton processes. A number of experimental works with pulsed Nd:YAG laser irradiation concern metal polymer nanostructures, photochromic glasses, optical waveguides which all consist in the ion-exchange process in soda lime glasses [13–16].

In this work we investigate the effect of high power laser irradiation on sodium–silver ion exchange glasses at room temperature which promotes the formation of silver nanoparticles by diffusion and aggregation. The second harmonic of the Nd:YAG laser at 532 nm was selected as a light source since this wavelength is not absorbed by the dielectric host medium. Modification of the structure of the dielectric medium is studied by scanning and transmission electron microscopy and UV–Visible absorption measurements. Three principal parameters are varied during our investigations: the immersion time, the fluence of the single laser shot E and the number Nb of laser shots which determines the total fluence Et deposited to the sample.

2. Experiment

2.1. Preparation of the sodium–silver ion exchange glasses

In our investigations we used commercial homogeneous soda lime glass slides (76 × 25 × 1 mm³) with composition of 0.7167SiO2–0.1493Na2O–0.0428K2O–0.054CaO–0.0372BaO (mol%). Six sets of samples were prepared by silver–sodium exchange process immersing the slides in a molten salt bath of the 6% molar concentration of AgNO3 in NaNO3 at temperature T = 400°C. The immersion time, t, was ranging from 1 to 6 min for the consecutive sets of samples. In such conditions part of the sodium ions, at the glass surface, is replaced by silver ions and AgO is formed. One should notice that the process does not concern deposition on the surface of the glass but the exchange of the ions inside the glass matrix.

The thickness of the layers with exchanged ions (Ag) was estimated on the basis of the Scanning electron microscopy (SEM) patterns obtained in the back scattering mode. Such image of the sample immersed for 2 min in the salt bath is shown in Fig. 1. The bright part, about 2 μm wide, corresponds to the region containing silver particles resulting from interaction between the slide and the bath. Additional structures, particularly evident close to the surface of the sample (see upper part of Fig. 1), are defects due to the sample’s preparation (cut and polishing) after the ion exchange.

![SEM image of an ion-exchange sample for τ = 2 min immersion time and before laser irradiation.](image)

**Fig. 1.** SEM image of an ion-exchange sample for τ = 2 min immersion time and before laser irradiation.

2.2. Precipitation of Ag nanoparticles

The ion-exchange glasses were irradiated by the second harmonic (λ = 532 nm, photon energy = 2.33 eV) of the pulsed Nd:YAG laser. The laser delivered pulses of energy up to 450 mJ of about 5 ns duration, at a repetition rate of 10 Hz and of the Gaussian cross-sectional area. The beam was focused to the spot...
with the diameter of about 500 μm by means of the lens with the 1 m focal length and a 8 mm diameter diaphragm. The fluence of the single laser shot, incident onto the sample, was adjusted by changing the pulse energy and by placing the sample at different locations between the lens and its focal spot (in the range 60–80 cm). The diameter $\phi_{\text{spot}}$ of the spot was measured using photosensible paper, and its surface $\Sigma_{\text{spot}}$ was calculated assuming a circular shape.

The total fluence $E_T$ deposited to the sample was in the range from 1.1 to 723.3 mJ/cm$^2$ depending on the number of the laser shots. The experimental parameters concerning the immersion time $\tau$ ($\tau = 1–6$ ns), irradiation area ($\phi_{\text{spot}} = 8.25, 5.00$ and 6.00 mm, for $\Sigma_{\text{spot}} = 8.30, 19.63$ and 28.27 mm$^2$, respectively), the pulse energy ($E = 158$ and 300 mJ), its fluence ($E = 0.56, 1.06, 1.53$ and 3.62 J/cm$^2$) as well as the number of laser shots ($Nb = 1–400$, corresponding to cumulative exposure times $\tau = 5 \text{ ns}–2 \mu\text{s}$) are listed in Table 1.

No effect of the laser on the simple glass plate was observed for the studied range of parameters that was verified in a separate experiment: the beam crosses then the sample, without generating laser breakdown on the sample. Therefore, observed interactions during the laser irradiation of samples are clearly linked to the existence of the layer of ionic exchange see table in Fig. 3.

On the other hand, at sufficiently high laser intensities ($>300$ MW cm$^{-2}$), laser plasma was generated near the surfaces of the investigated ion-exchange samples. The luminosity of the plasma and the intensity of the noise produced during the plasma generation were changing with successive pulses. This effect can be explained by variations of the optical absorption of the samples with the number of laser shots and could serve as the method to control production of nanoparticles.

### 2.3. Investigations of Ag nanoparticles

The laser irradiated samples were studied with respect to their optical absorption, surface morphology and composition and the size of nanoparticles.

- Absorption spectra were acquired by using a UV–VIS/NIR dual beam spectrophotometer JASCO V-530 (accuracy of ±0.004% on absorbance measurements in the range 0.5–1.0) with 2 nm spectral resolution (accuracy of ±0.3 nm).
- Surface observations by SEM were carried out with a LEO 1430 VP electron microscope at room temperature in variable pressure mode and with a resolution of several micrometers. Investigated samples were metallised with a thin (5 nm) Au layer which was evaporated under high vacuum. This way the charged particles drifted away while the measurements were unaffected.
- TEM observations for the size of the precipitated nanoparticles were performed with a Philips CM-20 electron microscope operated at 200 kV. The samples for TEM measurements were prepared in a special way: the laser irradiated samples were first polished with a diamond paper in order to obtain powder with several microns thick grains which contain the silver nanoparticles. The nanoparticle powder was then diluted in ethanol and the solution was agitated by ultrasound for 5 min. Finally, the sample for observations, in the form of the droplet, was deposited on a carbon coated copper grid.
- Energy dispersive X-ray spectrometer (EDS) was used for analysis of chemical composition near the surface of the sample with accuracy of several atom percent (except for oxygen that is close to the detection limit and for which

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$\lambda = 532$ nm; max energy: 450 mJ/pulse; pulse duration: 5 ns; repetition rate: 10 Hz.

### Table 1

*Experimental conditions for the laser irradiation of Ag-exchanged samples Nd:YAG laser.*
uncertainty is more important). The interaction volume was 1 mm$^3$ which made the depth under analysis ($\lambda$/C25) smaller than the ion-exchange depth.

In our analysis we discarded all laser irradiated samples either without evident laser impact or with highly inhomogeneous laser irradiated zones which induced large uncertainties in the measured absorption spectra. These selected and unselected samples are indicated by different colours of the cells in table of Fig. 3.

3. Results

3.1. Optical absorption

3.1.1. Ion-exchanged samples before laser irradiation

The optical absorption spectra of the ion-exchange samples for different immersion times $\tau$ are shown in Fig. 4. The absorption of the prepared glasses varies significantly in the range of 350–600 nm and its magnitude corresponds to the thickness of the layers with exchanged ions. The weak “bumps” around 400 nm are not really significant (see the inset of Fig. 4, where the uncertainties were indicated), and no surface plasmon resonance (SPR) seems to take place in the visible. Nevertheless, the atomic silver and hole trap centres at non-bridging oxygen (NBO) near Ag$^+$ ions, respectively, absorption wavelengths of approximately 240 and 318 nm [17,18] that induces the high increase of optical absorption spectra below 400 nm. On the other hand, for all studied samples, only the minor absorption was detected at wavelengths larger than 600 nm.

3.1.2. Effect of the laser irradiation of ion-exchanged samples

Fig. 5 shows the optical absorption spectra of the Ag-exchange glasses before and after laser irradiation and for different immersion times $\tau$ (in mn), different total fluences $E_T$ (in mJ/cm$^2$) deposited to the sample and powers $P$ by laser shot (in MW cm$^{-2}$).

After laser irradiation, the irradiated area of the sample changes its colour from colourless through yellow and amber to white with increasing the laser intensity (see example on central part in Fig. 10). It is evident that after laser irradiation the absorption of the samples significantly increases for almost all wavelengths. Moreover, laser irradiation induces a wide absorption band centred at about 425 nm which is assigned to plasmon band. This band results from the light absorption by Ag nanoparticles and direct excitation of the surface plasmon waves [19,20].

The Ag atoms formation and precipitation mechanism of silver nanoparticles solely by laser irradiation are not fully understood, and generally multiphoton process is proposed [21]: under excitation of the laser irradiation (2.33 eV), the electrons of the valence band could absorb two or more photons and be excited to the conduction band. The free electrons quickly move to the surface of which gets negatively charged. Such conditions enhance the probability of adsorption of the Ag$^+$ cations. The free electrons then react with the adsorbed Ag$^+$ ions which, after receiving the electron, are reduced into Ag atoms. But in our experiment, the radiation with centred wavelength of 535 nm (2.33 eV) is not appropriate to generate the charge carrier of SiO$_2$ with bandgap of $\approx$ 8.9 eV.

Another mechanism was proposed by Qiu et al., [18]: in the as-exchanged glass, silver (essentially Ag$^+$ with a minor population of Ag$^0$ atom) are bound to NBO. Under laser irradiation, electrons were driven out from the 2p orbital of the NBO and are captured.

### Table 1

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Fig. 3. Observed effects for the laser irradiation of Ag-exchanged samples Nd:YAG laser: $\lambda = 532$ nm; max energy: 450 mJ/pulse; pulse duration: 5 ns; repetition rate: 10 Hz. (Grey barred boxes: not quite visible effect; grey boxes: experimental data not usable—see text.)
by silver ion to form Ag atom, while the glass microstructure changes and defects occurred.

The substrate temperature $T$ play a fundamental role in the formation and aggregation of Ag atoms: during thermal annealing, more Ag–O bonds are broken to form neutral silver atoms that become the dominant state. Furthermore, the thermal relaxation of the surface tensile stress introduced by the size difference between Ag$^+$ (ionic radius ≈ 1.26Å) and Na$^+$ (ionic radius ≈ 1.02Å) during the ion exchange process [16,22], causes diffusion of silver into the matrix, with consequential precipitation. The development of appreciable colour occurs only after the aggregation of Ag atoms to form nanoclusters ($\text{Ag}_n^0$) larger than 1 nm [23].

It is recognised that such aggregation of silver nanoclusters is allowed only at high temperature ($T \geq 500{\degree}\text{C}$ in air). But in the case of laser induced nanoclusters, the temperature of the laser irradiation area is certainly far less than 500{\degree}.C.

Recently, Sheng et al., [22] suggests that during excimer-laser irradiation (ArF: 193 nm), more Ag$^+$ acquire sufficient energy to overcome the static barrier potential produced by oxygen bonding, and move towards the stressed surface where there is nucleation with resultant aggregation.

It is also necessary not to neglect the influence of thermal effects from different origins, that should not only governed by the laser pulse duration, but also by the peak intensity and repetition rate with possible processes of thermal energy accumulation in the medium. Rashidi-Huey and Palpant [24] has studied the thermal response of nanocomposite materials made of matrix-embedded noble metal under pulsed laser excitation. The light pulse is partially absorbed by the electron gas of the particle surrounded by the transparent host. Then, they have shown that, following working conditions, it could exist a large discrepancy between electron and lattice temperatures, in the earliest moments of the irradiation, before thermal equilibrium can be achieved. The morphologic parameters of the material play a crucial role in the thermals behaviour, and a thermal lensing effect can be generated, the magnitude of which is particularly sensitive to the metal concentration of the material.

In all the case, the formation of silver nanoparticles can be described as follows:

$$\text{Glass} + n h\nu \rightarrow h^+ + e^- \ (n \geq 2)$$

$$\text{Ag}^+ + e^- \rightarrow \text{Ag}^0$$

$$n\text{Ag}^0 \rightarrow (\text{Ag}^0)_n$$

(4)

where $n$ is the number of photons; $h^+$ is a hole; $e^-$ is an electron; and $n$ is the number of Ag atoms forming the nanoparticle.

The absorption peaks are due to the SPR of these silver clusters. The size distribution particles are dominated by a mean size $R$, increasing with time, which volume fraction $N$, greater than the other, gives the absorption intensity $A$ as a function of the absorption cross-section $\sigma$:

$$A(\lambda, R) = \sigma(\lambda, R) N = N\sigma(\lambda, R)$$

(5)

where $N$ is the particle density in the matrix, $l$ is the thickness of the sample, and $\sigma = N\sigma$ is the total absorption coefficient of silver nanoclusters.

According to the Mie’s model [25], total absorption coefficient $\sigma(\lambda, R)$ of very small silver nanoclusters ($R < \text{10 nm}$) at wavelength $\lambda$ in an inhomogeneous medium is approximated by

$$\sigma(\lambda, R) = \frac{18\pi\varepsilon_0^3}{\lambda^2} \frac{\varepsilon_{2D}}{(\epsilon_{1D} + 2n_0^2)\lambda^2 + \varepsilon_{2D}}$$

(6)

where the Drude equations [26] can be used for the metal dielectric function:

$$\varepsilon_{\text{Drude}}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\Gamma_{\text{Bulk}}} \equiv \varepsilon_{1D}(\omega) + i\varepsilon_{2D}(\omega)$$

(7)

with

$$\varepsilon_{1D}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \Gamma_{\text{Bulk}}^2}$$

$$\varepsilon_{2D}(\omega) = \frac{\omega_p^2\Gamma_{\text{Bulk}}}{\omega(\omega^2 +\Gamma_{\text{Bulk}}^2)}$$

(8)
Fig. 5. Absorption coefficient versus wavelength for the irradiated ion-exchanged samples for different total fluences $ET$, as a function of the ion-exchanged duration $t$ (from the top to the bottom) and power by shot $P$ (from left to right). Before laser irradiation, Ag-exchanged: (a) $P = 111.76\text{MW cm}^{-2}$; (b) $P = 212.21\text{MW cm}^{-2}$; (c) $P = 723.26\text{MW cm}^{-2}$; after laser irradiation, total fluence $ET$ (in mJ cm$^{-2}$): $\bigcirc$, 5.31; $\blacktriangle$, 5.59; $\downarrow$, 15.26; $\blacktriangledown$, 21.22; $\blacktriangleleft$, 30.56; $\blacktriangleleft$, 36.16; $\blacktriangleright$, 53.05; $\blacktriangleleft$, 55.88; $\blacktriangleleft$, 72.33; $\square$, 76.39; $\bigcirc$, 106.10; $\blacktriangle$, 111.76; $\blacktriangledown$, 152.79; $\blacktriangleleft$, 180.82; $\downarrow$, 212.21; $\blacktriangleleft$, 223.52; $\blacktriangleleft$, 305.58; $\blacktriangleleft$, 361.63; $\blacktriangleleft$, 723.26; dot line corresponds to the laser radiation (532 nm). (For the readability of the figure, the experimental uncertainties are not indicated.)
\[ \omega_0 = \frac{2\pi}{\lambda} \]

\( \epsilon_{1p} \) and \( \epsilon_{2p} \) are the real and imaginary part of the dielectric function of silver nanoparticles; \( V \) is the volume fraction of metallic silver per unit of irradiated area, linked to the size \( R \) of the nanocluster; \( \omega \) the angular frequency; \( n_0(\omega) \) is the frequency dependant effective linear index of the matrix, linked to its effective linear dielectric function by \( n_0 = \epsilon_0^{\text{eff}} \); \( \Gamma_\text{Bulk} \) is the effective damping parameter for the free electrons in the bulk metal; and \( \epsilon_0 \) is the plasmon resonance frequency:

\[ \omega_p = \sqrt{\frac{4\pi N_e e^2}{m_e}} \]

(10)

where \( N_e \) and \( m_e \) are the density and mass of the free charges, respectively.

Taking into account the interband transitions of the metal in the expression of \( \epsilon \), and the quantum effect of reduction of electron mean free path when confined in particles whose size is smaller than the bulk mean free path (\( \approx 52 \text{ nm} \) at 273 K [27]), we have

\[ \epsilon_1(\omega, \epsilon) = \epsilon_1 + \epsilon_1(\omega) = \epsilon_1 + 1 - \frac{\omega_0^2}{\omega^2 + \Gamma(R)^2} \]

\[ \epsilon_2(\omega, \epsilon) = \epsilon_2 + \epsilon_2(\omega) = \epsilon_2 + \frac{\omega_0^2 \cdot \Gamma(R)}{\omega(\omega^2 + \Gamma_\text{Bulk})} \]

(11)

with

\[ \Gamma(R) = \Gamma_\text{Bulk} + \frac{V_f}{R} \]

(12)

\( \epsilon_1 \) and \( \epsilon_2 \) are the real and imaginary parts of the total dielectric function \( \epsilon \) of the nanoparticles; \( \epsilon_1 \) and \( \epsilon_2 \) are the real and imaginary part of the frequency-dependant dielectric function of bulk silver due to the inter-band transitions; \( \gamma \) is a model-dependant parameter (\( \gamma = 2.00 \) [30] to 0.25 [23]); \( \Gamma_\text{Bulk} \) is the absorption coefficient of the plasmon electron and the second term in the expression of \( \Gamma \) is used to introduce a size-dependant term in the damping frequency with the nanoparticle size \( R \) [28,29]; \( V_f \) is the fermi velocity of electrons in bulk silver (\( V_f = 1.39 \times 10^5 \text{ cm s}^{-1} \) in the case of silver [26]).

According to Eq. (7), the absorption intensity \( A(\omega) \) has a maximum value \( A_m \) at the resonance frequency \( \omega_m \) defined by

\[ \epsilon_{1p}(\omega_m) = -2n_0(\omega_m)^2 \quad \text{with} \quad \omega_m = \frac{2\pi}{\lambda_m} \]

(13)

After linearisation in the vicinity of \( \omega_m \), we can find that the absorption intensity has a lorentzian shape [31] whose the full-width at half-maximum \( \Delta \omega_m \) should vary inversely to the average radius \( R \) of the metallic clusters (Doyle’s formula):

\[ \Delta \omega_m \sim \gamma \frac{V_f}{R} \quad \text{with} \quad \Delta \omega_m = 2\pi \frac{\Delta \lambda_m}{\lambda_m} \]

(14)

Fig. 6 shows the absorption intensity obtain after two different treatment of the as-exchanged glass sample: thermal annealing at 500° during 2 h (a) or laser irradiation with total fluence \( E_f \approx 723 \text{ mJ cm}^{-2} \) (b) in the both cases, the profiles are very close of lorentzian shapes (full red lines), even if the lorentzian is not strictly valid far from the peak because de dielectric constant is not constant with wavelength [32]. Then, the mean radius of nanoparticles calculated using Doyle’s formula for \( \gamma = 2 \) is \( R \approx 2.7 \text{ nm} \) for thermal annealing and \( R \approx 1.9 \text{ nm} \) for laser irradiation, with a 10% experimental uncertainties. However, these results must be taken with caution: Doyle’s formula, if it is valid, gives only an estimate of the average nanoparticle size, and is highly dependent on the gamma-parameter.

We must note that, contrary to what is suggested for example in Ref. [16], unacceptable fits are obtained using Gaussian shapes (dashed blue curves in Fig. 6).

Direct comparison between the annealed sample and irradiated sample cannot be applied because in the first case the heat absorption is the result of an equilibrium process, while in the second, the energy absorption is concentrated in a reduced region in a non-equilibrium process. Nevertheless, the most important broadening of the absorption band in the case of thermal treatment is certainly also due to a larger distribution of nanoparticle sizes.

The size evolution of the metallic nanoaggregates formed under the laser irradiation seems to be the principal reason of the observed SPR effects: according to Eq. (12), the changes in the absorption band after irradiation are linked to the modification of \( \Gamma(R) \) through \( \Gamma_\text{Bulk} \) and \( R \) [30].

- A more homogeneous spatial distribution of particles in the host matrix and the decrease of defects concentration result in the weakening of \( \Gamma_\text{Bulk} \).

Fig. 6. Comparison between thermal annealing and laser irradiation. Dashed blue lines: results of Gaussian fitting curve; full red lines: results of lorentzian fitting curve: (a) exchanged time: \( \tau = 5 \text{ h} \) with \( T_{\text{anneal}} = 400° \); thermal annealing: 2 h with \( T = 500° \); \( \lambda_m = (427.12 \pm 0.10) \text{ nm} \) and \( \Delta \lambda_m = (98.28 \pm 0.35) \text{ nm} \); (b) exchanged time: \( \tau = 6 \text{ min} \) with \( T_{\text{anneal}} = 400° \); laser irradiation: \( P = 723.26 \text{ MW cm}^{-2} \); \( \lambda_m = (434.25 \pm 0.06) \text{ nm} \) and \( \Delta \lambda_m = (148.08 \pm 0.25) \text{ nm} \).
• The size evolution of nanoparticles induced by laser irradiation results in a decrease of the damping constant when \( R \) increases.
• A better crystalline quality and an increase of the particle size give rise to the plasmon band enhancement and narrowing.

But the resonance position \( \lambda_m \), bandwidth \( \Delta \lambda_m \) and intensity \( A_m \) of the absorption bands \( A(\lambda) \) for the different samples in Fig. 5 are governed by different other concomitant effects [30]:

• The porosity of the matrix that can modify the local environment of the particles and thus their optical response.
• The influence of the metal concentration that is directly correlated to the mutual interactions between particles.
• The dependence of the absorption bandwidth to the size distribution of the nanoparticles [4].

![Fig. 7](image1)
**Fig. 7.** Change of the wavelength position \( \lambda_m \) of the plasmon resonance versus total fluence \( E_T \) as a function of exchanged time \( t \): \( \square \), \( t = 1 \text{ min} \); \( \circ \), \( t = 2 \text{ min} \); \( \triangle \), \( t = 3 \text{ min} \); \( \triangledown \), \( t = 4 \text{ min} \); \( \diamond \), \( t = 5 \text{ min} \); \( \bigstar \), \( t = 6 \text{ min} \); red full line: polynomial regression model of the third order for all the experimental data points. (For the readability of the figure, not all the experimental uncertainties are indicated.)

![Fig. 8](image2)
**Fig. 8.** Absorption coefficient versus wavelength for the \( t = 1 \text{ min} \) irradiated ion-exchanged samples for different total fluences \( E_T \). After laser irradiation, total fluence \( E_T \) (in mJ cm\(^{-2}\)) = 5.31; \( \bigstar \), 5.59; \( \triangle \), 5.26; \( \square \), 21.22; \( \diamond \), 30.56; \( \bigstar \), 36.16; \( \triangle \), 53.05; \( \diamond \), 35.88; \( \square \), 72.33; \( \bigstar \), 76.39; \( \triangle \), 106.18; \( \square \), 111.76; \( \bigstar \), 152.79; \( \diamond \), 180.82; \( \square \), 212.21; \( \bigstar \), 223.52; \( \triangle \), 305.58; \( \diamond \), 361.63; \( \square \), 723.26; dot line corresponds to the laser radiation (532 nm). (For the readability of the figure, the experimental uncertainties are not indicated.)

![Fig. 9](image3)
**Fig. 9.** Influence of the power by shot \( P \) on the absorption spectra at the same total fluence \( E_T \) as a function of immersion time \( t \): \( \square \), \( t = 1 \text{ min} \); \( \circ \), \( t = 2 \text{ min} \); \( \triangle \), \( t = 3 \text{ min} \); \( \bigstar \), \( t = 4 \text{ min} \); \( \diamond \), \( t = 5 \text{ min} \); \( \bigstar \), \( t = 6 \text{ min} \); dot line corresponds to the laser radiation (532 nm). (For the readability of the figure, not all the error bars are indicated.)

• A quantum size effects, like described above. Particularly, the absorption band observed in the visible domain is essentially due to the Drude term in expression of the metal dielectric function \( \varepsilon(\omega, R) \). But it exists an other well-visible band in the UV-region (below 350 nm) whose one can distinguish the beginning for low total deposited energy \( E_T \) in Fig. 5.
• The bandwidth size dependence of the absorption band to the reduction of the electron mean free path when confined in particles whose size is smaller than the bulk mean free path (close to 52 nm for silver).
• The influences on resonance position of clusters with non-spherical shape, and of the surrounding medium (modification of refractive index, chemical interactions, etc.).

There is no clear consensus as to what is expected for the resonance frequency but because in metal \( \varepsilon_{1p} \) is negative and \( \varepsilon_{2p} \) is positive, the magnitude of absorption coefficient \( A_m \) at the resonance frequency \( \lambda_m \) will increase with particle size \( R \), while this growth must lead to a shift to the higher wavelength (red shift) of \( \lambda_m \). The observed blue shift could be attributed either to a particle dissolution and size reduction, a matrix refractive index evolution or a particle shape change during treatment [4].

Maximum resonance wavelengths \( \lambda_m \) in the absorption spectra of the irradiated glasses for the six immersion times \( t \) exposed to
total deposited fluence $E_T$ increasing from 1.1 to 723.3 mJ cm$^{-2}$ are plotted in Fig. 7. Despite the scattering of the experimental values observed for few $E_T$ values, a systematically decrease toward the shorter wavelength is observed with the increase of total deposited energy. A similar behaviour is observed at given deposited energy, when the immersion time $\tau$ increases, and the value of $\lambda_m$ passes through a maximum value when immersion time $\tau$ increases. Then, the optimal choice for $E_T$ is directly linked to the ionic exchanged depth in the Ag-exchanged sample: too weak and all ions cannot receive electron to be reduced to Ag$^0$ and form nanosized clusters (Ag$^0$)$_n$; too high and the formed nanosized clusters are degraded by the flux of energy, like it seems to be the case for the higher values of $E_T$ (see also in Fig. 5).

3.1.3. Influence of the total deposited energy $E_T$ on the 1 min ion-exchanged sample

For the 1 min ion-exchanged sample, the increasing of the energy $E_T$ leads to the progressive appearance of the peak of absorption from the "weak bumps" detected on the unirradiated glass sample (see Fig. 4) with progressive increase of its intensity (see Fig. 8). The peak wavelength shifts first of all toward longer wavelength (see arrow in Fig. 8) and, in a second step, slightly to the short ones. When total deposited energy is too high, the intensity of the peak of absorption decreases to finally disappear in the increase of absorption coefficient below 350 nm.

This can be attributed first to the formation and growth of silver nanoparticles [9] from the migration of the silver atoms induced by the laser irradiation. Then the average (Ag)$_n$ particle size increase gradually and the plasma resonance peak shifts to a longer wavelength as the diameter of the metal particles increases [19]. In the second step, the blue shift of the absorption peak indicates that laser irradiation probably destroyed large colloids into small ones [14], while the increase of the peak implies that the number of precipitated nanoparticles by irradiation enlarges. Then, it seems that the nanoparticles does not grow on the Ostwald ripening mechanism in which the smaller particles dissolve and the larger are growth [33]. Finally, the disappearance of the plasmon resonance peak to even higher deposited energy, points out that the (Ag)$_n$ nanoparticles dissolve and/or disappear. Pinchuk et al., [23] suggests such result: to observe the surface resonance plasmon effect, the nanoparticle size must be higher than 1 nm.

3.1.4. Influence of the power by shot $P$

The observed behaviour on the 1 min ion-exchanged sample appears less systematic on the other samples, to less to take into account.
account as parameter the total deposited power $P$ by laser pulse. Indeed, the effect of the power by pulse is clearly visible on curves of Fig. 5 (line by line): the laser irradiation is more efficient increasing $P$, at least so that it does not induce a destruction of the sample and a vaporisation of the matter by surface breakdown. Furthermore, to deposited total energy $E_T$ almost constant and for a same immersion time, the optical absorption spectra of the ion-exchanged samples depend strongly on the power $P$ of laser shot (see Fig. 9).

Thus, the apparition of the plasmon resonance effect is directly related to the ion-exchanged time but also to the $P$ value: for example it does not appear for the 1 min exchanged time exposed to a power by shot below 306 MW cm$^{-2}$ (see table in Fig. 3 and Fig. 5).

The behaviour to the absorption spectra of the different samples at given immersion time $\tau$ and deposited power by pulse $P$, as a function of total energy $E_T$, is then completely similar to that described previously in the general case for $\tau = 1$ mn (see Figs. 5 and 9): laser irradiation promotes the reduction of Ag$^+$ ions to silver atoms and diffusion; first deposited energy $E_T$ induce particle’s size growth and the resonance peak wavelength and intensity increase simultaneously; then shift of the peak toward the shorter wavelength, well visible in Fig. 9(a), indicates a reduction in size of the particles; if the $E_T$ value becomes to high, disappearance of the plasmon resonance peak.

We can remark in Fig. 10 that the resonance systematically appears at shorter wavelength for the 1 min exchanged sample and
is decayed to the longer wavelength with the increasing of the exchanged time.

The effect of the laser power does not seem linear: it is going to depend on the history of the sample, and particularly of the number and the frequency of pulses. Qiu et al. [18] suggests a direct proportionality to the square root of the average power of the laser beam, but it is difficult to verify this hypothesis.

3.2. Qualitative composition: SEM results

TEM measurements on ion-exchanged glasses show that no silver particles can be observed in the unirradiated samples. After laser irradiation, small well-separated dark particles can be observed. An example is given in Fig. 11(a) for \( t = 3 \text{ mn}, \) \( E_T = 223.5 \text{ mJ cm}^{-2}, P = 112 \text{ MW cm}^{-2} \); we can see particles with

\[
\begin{align*}
\text{Calcium concentration} \\
\text{[arb.units]} \\
\text{X [mm]} \\
\text{0} & \quad \text{1} & \quad \text{2} & \quad \text{3} & \quad \text{4} & \quad \text{5} \\
\text{0} & \quad \text{100} \\
\end{align*}
\]

\[
\begin{align*}
\text{Silver concentration} \\
\text{[arb.units]} \\
\text{X [mm]} \\
\text{0} & \quad \text{1} & \quad \text{2} & \quad \text{3} & \quad \text{4} & \quad \text{5} \\
\text{0} & \quad \text{100} \\
\end{align*}
\]

\[
\begin{align*}
\text{Sodium concentration} \\
\text{[arb.units]} \\
\text{X [mm]} \\
\text{0} & \quad \text{1} & \quad \text{2} & \quad \text{3} & \quad \text{4} & \quad \text{5} \\
\text{0} & \quad \text{100} \\
\end{align*}
\]

\[
\begin{align*}
\text{Silicium concentration} \\
\text{[arb.units]} \\
\text{X [mm]} \\
\text{0} & \quad \text{1} & \quad \text{2} & \quad \text{3} & \quad \text{4} & \quad \text{5} \\
\text{0} & \quad \text{100} \\
\end{align*}
\]

\[
\begin{align*}
\text{Oxygen concentration} \\
\text{[arb.units]} \\
\text{X [mm]} \\
\text{0} & \quad \text{1} & \quad \text{2} & \quad \text{3} & \quad \text{4} & \quad \text{5} \\
\text{0} & \quad \text{100} \\
\end{align*}
\]

Fig. 14. X-ray analysis of the Ag-exchanged samples with \( t = 3 \text{ mn}, \) as a function of the total fluence \( E_T, \) for two different powers by shot \( P. \) The legends for \( E_T \) values are given in the first figure of each column. (a) \( \Phi_{spot} = 5.00 \text{ mm}; P = 306 \text{ Mw cm}^{-2} \) (b) \( \Phi_{spot} = 3.25 \text{ mm}; P = 723 \text{ Mw cm}^{-2} \)
size less than 50 nm, lower than the electron mean free path in bulk silver ($\approx 52 \text{ nm}$): we are well in a quantum confinement regime (cf. Eq. (11)).

They are pure silver and diffraction analysis in Fig. 11(b) shows that they are crystallised in face-centred cubic lattice. Nevertheless, in case of highest deposited powers, such metallic nanoclusters disappear.

Optical and SEM images of the ion-exchanged samples show the rings which appear around the irradiated zones with the increase of the deposited power (see Figs. 12 and 13). Typical height of this ring is about 10 μm; it proves the vapourisation induced by the laser which leads to a redeposition around the irradiation zone. X-ray analyses with a typical interaction volume of $1 \mu$m$^3$ as shown in Fig. 14(a) and (b) prove that the highest deposited powers lead to a desorption of sodium and certainly to a reduction of the silver nanocrystals with the apparition of the rings [15,14,18]. This phenomenon is clearly observed by the observation of a white colour in the centre of the spot, in Fig. 12, and confirmed by the TEM analysis on high irradiated sample.

4. Discussion

According to the MIE theory [26] the apparition of the plasmon resonance band around 400 nm suggests that the pulsed laser processing of glasses leads to the formation of silver nanoparticles. The shift observed in the absorption coefficient band certainly results in a decrease in the mean size of this nanoparticles with the increasing energy or can be attributed to a decrease in the filling factor of the glass by the formation of the nanoparticles; in fact a decrease of the fraction of silver which leads to the formation of the nanoparticles. The increasing energy also leads to the desorption of the sodium observed by SEM investigations and an apparition of a white colour which is correlated to the shorter wavelength decay.

The increasing energy first leads to the particles growth and in a second way to a reduction in size which can be attributed to vapourisation effects which is visible on absorption curves by a move of the resonance towards the shorter wavelength. The decay is more marked for the shortest ion exchanged samples where the quantity and depth penetration of the silver ions is lower.

The power by pulse is an important parameter for the space-selective precipitation of silver nanoparticles in glass. Its principal effect is to locally warm up the sample, and it could have been compared to the heat treatment proposed by Zeng et al., [14] to promote the reduction of $\text{Ag}^+$ ions to silver atoms and the growth of the silver nanoparticle.

During the laser processing and the exposure of the Ag-exchanged glass to the Nb successive laser shots, the sample’s absorption is continuously modified since $E_f$ increases with Nb (see in Fig. 15, the evolution of absorption coefficient to 532 nm according to total deposited energy $E_f$): in the first time, the absorption of laser radiation at 532 nm increases with the time and passes by a maximum corresponding almost to the $E_f$ value for the maximum of plasmon resonance peak. Then it decreases before to increase again when the resonance peak begins to disappear. Consequently, the effect of the available power during each laser pulse on the Ag-exchanged sample is certainly not linear.

We can remark that this effect would have to be more or less important according to the used wavelength for the laser irradiation: for an 800 nm Ti:Sapphire laser, the absorption will be weak during all the irradiation process and the warm-up effect not significant; on the contrary, it will become rapidly very high by using a frequency-tripled Q-switched Nd:YAG laser at 355 nm.

Furthermore, this effect could be correlated with the evolution of the noise generated during the interaction of the laser radiation with the sample: indeed, it seems that the maximum of signal corresponds to the best treatment before destruction of the aggregates by ablation. This effect leaves the framework of this study and should give place to complementary work.

The various parameters (immersion time $t$, power by shot $P$, and total deposited energy $E_f$ from the number of shots Nb and available laser energy) are thus directly correlated and must be precisely adjust to not destroy the sample by surface breakdown and laser induced plasma.

5. Summary and conclusions

The laser irradiation of ion-exchanged glasses is a relatively new and original method to generate a space-selective precipitation and aggregation of metal nanoparticles inside a vitreous matrix, to modify their optical characteristics and allow a process control.

In this article we have investigated the influence of the pulsed Nd:YAG laser radiation on the ion-exchange glasses by using the optical absorption/extinction measurements as well as the transmission and scanning electron microscopy. The irradiation of the glass samples by the laser pulse promotes precipitation of the nanoparticles in multiphoton processes. These nanoparticles produce the absorption bands with maximum at about 420 nm which are attributed to the surface plasmon resonance (SPR). The absorption spectra change with the immersion time but also with the laser intensity, fluence, and with the number of the laser shots due to the heat treatment effects. Modifications of the extinction spectra are related to variations of the damping constant $\Gamma$, predominantly with the size and the shape of the nanoparticles. The larger nanoparticles the more enhanced and the narrower is their absorption spectrum. Determination of the relation between the peak absorption and the size of the nanoparticles, as measured by TEM, is the principal goal of our future investigations.

Furthermore, photoluminescence studies may be helpful to estimate quantity and size variations of the silver nanoparticles with the laser parameters and ion-exchange conditions.

With increasing the laser intensity and the irradiation time, the colour of the irradiated area was changing from colourless through
yellow to white. Apart from the colour variations, deposited laser energy and power were correlated to the evolution of the amount of noise generated during the laser interaction with the sample. This latter effect could provide an interesting method to control precipitation of the nanoparticles: first, absorbed laser energy leads to an increase in size of the particles and consequently of the optical absorption of the sample and generated noise; but further increase of energy destroys the larger particles, and the generated noise decreases.

The linear optical properties of nanocomposites consisting of silver nanoparticles embedded in a dielectric host medium are due to the excitation of SPR. The SPR is responsible for the enhancement of the local electromagnetic field in the particles, which amplifies their nonlinear properties as compared to those of bulk metal. Thus it is advisable to study such materials in terms of their nonlinear properties and to correlate them with their morphologic parameters.

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