Appl Phys A (2010) 98: 879–884
DOI 10.1007/s00339-009-5468-8

Applied Physics A
Materials Science & Processing

Structural changes induced on strontium barium niobate glass by femtosecond laser irradiation

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Received: 14 March 2009 / Accepted: 20 October 2009 / Published online: 12 November 2009

Abstract Localized modification of the optical properties of erbium doped strontium barium niobate (SBN) glass has been performed using femtosecond laser irradiation. The samples, with composition SrO–BaO–Nb_2O_5–B_2O_5 and doped with 5%mol of Er^{3+}, were fabricated using a melt-quenching method. The samples were irradiated with different number of pulses per spot (1–50 pulses) at two different laser fluences (2.6 and 5.6 J/cm^2) by using an fs laser amplifier operating at 800 nm and generating pulses with a duration of 120 fs.

Micro-luminescent microscopy, using an Ar^+ laser as excitation source, has been used to analyze the modifications of the luminescent properties of the sample upon fs laser exposure. The emissions of the Er^{3+}: $^4I_{11/2} \rightarrow {}^4I_{15/2}$ and $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions allow appreciating the structural modifications caused by femtosecond laser exposure. The lifetimes of the levels involved in these transitions were measured inside and outside the laser irradiated region. These measurements have been compared with those obtained in bulk glass ceramic sample, which is obtained from the glass precursor by a thermal treatment in order to estimate the optimal conditions to produce nanocrystals in a localized region by ultrafast laser irradiation.

PACS 42.62.Fi · 42.70.Mp · 52.38.Mf

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1 Introduction

Non-linear processing of dielectrics with ultrashort laser pulses has been proven as an excellent tool to modify and functionalize a variety of transparent materials, leading to applications like the formation of three dimensional optical memories [1, 2] and multicolor images [3], direct writing of waveguides [4–6], waveguide couplers and splitters [7, 8], waveguide optical amplifiers [9], and optical gratings [10, 11].

When a femtosecond pulse is focused in a transparent material, energy is deposited in a limited volume around the focus due to a combination of multiphoton absorption and avalanche ionization. The photogenerated hot electron plasma transfers its energy to the lattice, producing high temperatures and pressures [13]. When compared to cw and long pulsed laser pulses, the use of fs laser pulses [12] allows minimizing undesirable thermal diffusion effects due to the extremely short energy deposition time and induces a variety of non-linear processes associated to the high localization of laser photons both in time and space domains.

As a consequence of the energy deposition by non-linear absorption, the structural modification of the irradiated volume can be induced. In the particular case of glassy materials, crystallization can be induced by the excess energy released from the plasma into the surrounding media [14]. Since the electron plasma is generated only at the focal region, where the peak power of the laser beam exceeds the threshold of non-linear absorption, the crystallization process induced by femtosecond-pulsed radiation can be considered as superior in terms of control over the modified region shape/volume when compared with crystallization processes induced by conventional means (via linear absorption or heat treatment [15]).

The aim of this work is to analyze the structural and luminescence changes produced in erbium doped strontium barium niobate glasses upon irradiation with a femtosecond laser pulses. The properties of these glasses and the changes induced by a cw laser radiation have been studied in previous works [16–18] which show that changes in the luminescent behavior of the irradiated material can be correlated to changes in its structure. In this work, the effect of fs laser irradiation on glass samples is compared to the behavior of glass ceramic samples obtained by thermal treatment in order to determine the optimal conditions to produce nanocrystalline material upon laser exposure.

2 Experimental

The Er_2O_3–SrO–BaO–Nb_2O_5–B_2O_3 (SBN) glasses were prepared using the melt quenching method [16] with the following composition in mol%: 5 Er_2O_3, 11.25 SrO, 11.25 BaO, 22.5 Nb_2O_5, and 50 B_2O_3. Commercial powders of reagent grade (99.9% pure) oxides were mixed and melted in a platinum crucible for 1 h in an electric furnace at 1400°C. The melt was poured onto an iron mould to obtain samples with a thickness of 1.6 mm. The glass ceramic samples were obtained by thermal treatment of the precursor glass at 620°C for 2 hours. These samples were used to compare the luminescent behavior of glass ceramics with that exhibited by the glass exposed to fs-laser radiation.

A commercial chirped pulse amplification (CPA) Ti:sapphire laser system (Spectra Physics, Spitfire), providing s-polarized pulses, with pulse duration of 120 fs at a wavelength of $\lambda = 800$ nm, was used for irradiation. The laser pulse energy was measured by means of a pyroelectric detector (Ophir, PE-9). In the fs-irradiation setup, the sample was placed at 54° of the normal incidence in the focal plane of a 15 cm lens, resulting in an elliptical laser spot on the surface. The samples were irradiated at two different (peak) laser fluences (2.6 and 5.6 J/cm^2) and with a number of pulses ranging from 1 to 50 pulses.

The scheme of the confocal micro-luminescence setup used to characterize the samples is shown in Fig. 1. The sample is located at the focal plane of a 20× microscope objective (Mitutoyo, M-Plan NIR, numerical aperture (NA) = 0.26) on a motorized translation stage. The sample is excited using an Ar^+ cw laser by means of a dichroic mirror, while the luminescent emission is detected using a TRIAX-180 monochromator with a resolution of 0.5 nm and a photomultiplier. Optical emission spectra were located in regions inside and outside the fs-laser irradiated area. The corresponding emission lifetimes involved in these transitions were obtained using a mechanical chopper, and by recording the photomultiplier signal with an oscilloscope.

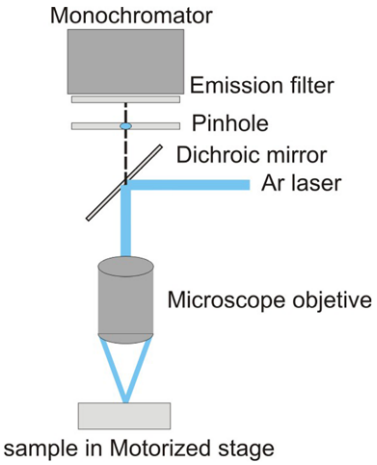

Fig. 1 Confocal micro-luminescence set up

3 Results and discussion

Localized zones of the SBN glass doped with Er^{3+} were irradiated with femtosecond laser pulses at two different peak fluences and with a variable number of pulses per spot. The emission spectra of the Er^{3+}: $^4S_{3/2}(^2H_{11/2}) \rightarrow {}^4I_{13/2}$, $^4I_{11/2} \rightarrow {}^4I_{15/2}$ and $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions were recorded inside and outside the laser exposed regions.

Er^{3+} ions have an absorption band at about 800 nm, coincident with the output wavelength of the femtosecond laser. Due to the absorption of the laser energy by the Er^{3+} dopants, the irradiated volume near to the focal point of the objective was heated to an elevated temperature, which apparently resulted in nucleation and growth of Er^{3+} doped nanocrystals in the volume near to the focal point at determined pulse power of the laser [17, 19, 20].

The results obtained for a laser fluence of 5.6 J/cm^2 are shown in Fig. 2 for the Er^{3+}: $^4I_{11/2} \rightarrow {}^4I_{15/2}$ transition (around 975 nm) with different number of pulses per spot. The emission spectra corresponding to 1 and 2 pulses shows a weak and broad emission band with a maximum at 975 nm, which is essentially similar to the one observed outside the irradiated region. This suggests that for these fluence and irradiation pulse numbers, the structure of the irradiated zone remains essentially unaltered. The emission corresponding to 5 and 10 pulses shows a clear indication for the occurrence of structural transformations, with the development of two different bands well separated and centered at 975 and 1005 nm, respectively. This latter can be considered as indicative for the presence of a new phase of the material, most likely a crystalline one. This can be inferred by comparing the spectra for 10 pulses at 5.6 J/cm^2 with those corresponding to the non-irradiated glass and to a glass ceramic obtained from the same glass. These are shown in Fig. 3. In a previous work, it was found that a fraction of the Er^{3+} ions stay in the glass ceramic environment due to the ceramic

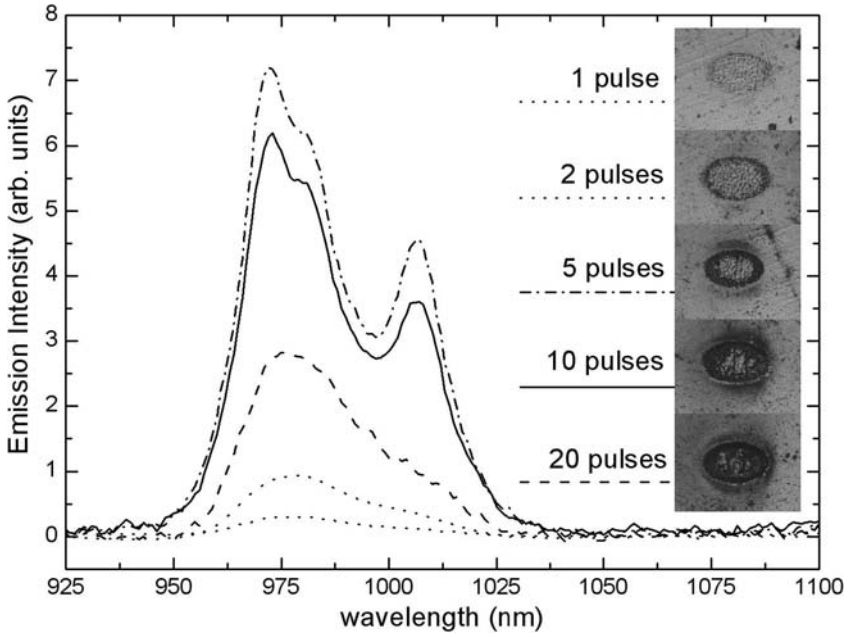

Fig. 2 Confocal micro-luminescence spectra under Ar^+ laser excitation corresponding to the Er^{3+}: $^4I_{11/2} \rightarrow {}^4I_{15/2}$ transition measured inside the irradiated area for different number of pulses at a fluence of 5.6 J/cm^2. *Inset* shows the optical images of the irradiated areas

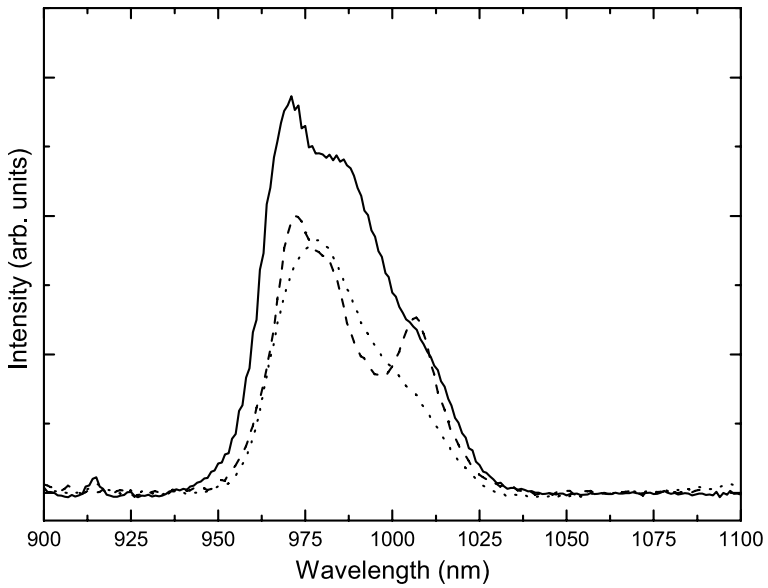

Fig. 3 Emission spectra under Ar+ laser excitation corresponding to the Er^{3+}: $^4I_{11/2} \rightarrow {}^4I_{15/2}$ transition in glass ceramic samples (*solid line*), inside the irradiated area (*dashed line*) and in the non-irradiated glass sample (*dotted line*)

formation induced by a thermal treatment at 620°C in a furnace, whereas the rest remains in the glassy phase [16–18]. The spectrum of the irradiated material in Fig. 3 resembles very much the one corresponding to the glass ceramic. They both show bands centered at 975 and 1005, although this latter is worst resolved in the glass ceramic specimen. This result could be explained on the basis of radiative transfer processes which change the shape of the emission bands. None of the indicated bands are observed in the glass (which shows a maximum of emission around 983 nm), indicating that they are correlated to the presence of crystalline material. In this respect, it is worthwhile noting that for a number of pulses beyond 5 the emission intensity decreases and the spectrum becomes structureless (with shape similar to that of the glass). This would be consistent with a process in which above a given dose the material partially crystallized with the initial pulses gets re-amorphized. This has been shown to occur in other matrices upon fs laser exposure [21, 22].

Figure 4 shows the corresponding spectra for the transitions Er^{3+}: $^4S_{3/2}(^2H_{11/2}) \rightarrow {}^4I_{13/2}$ and $^4I_{11/2} \rightarrow {}^4I_{15/2}$ transitions, for a laser fluence of 2.6 J/cm^2 and different number of pulses. In this case, the emission corresponding to the irradiated area for 1 and 2 pulses is nearly negligible, and similar to that of the non-irradiated glass matrix, indicating that the structure of the irradiated zone is not substantially

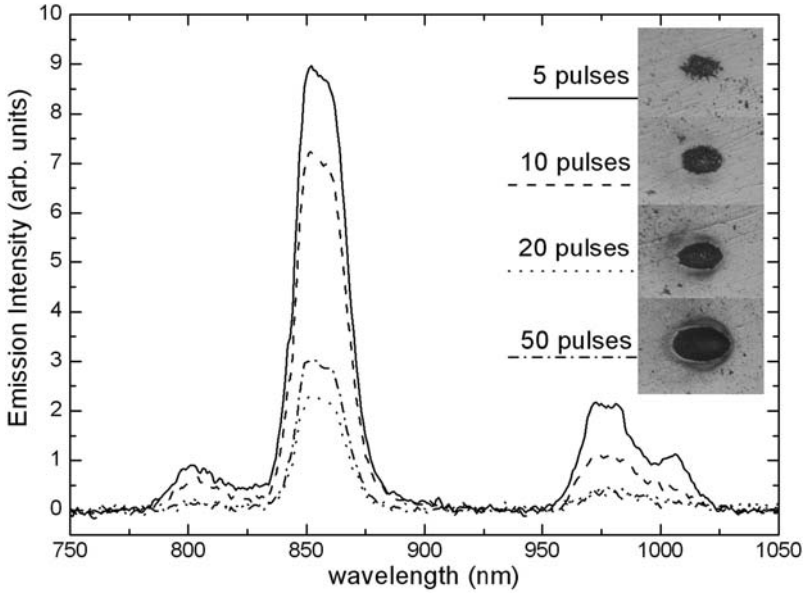

Fig. 4 Confocal micro-luminescence spectra under Ar^+ laser excitation corresponding to the Er^{3+}: $^4I_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2}(^2H_{11/2}) \rightarrow {}^4I_{13/2}$ transitions from samples irradiated with different number of pulses at the fluence of 2.6 J/cm^2. *Inset* shows the optical images of the irradiated regions

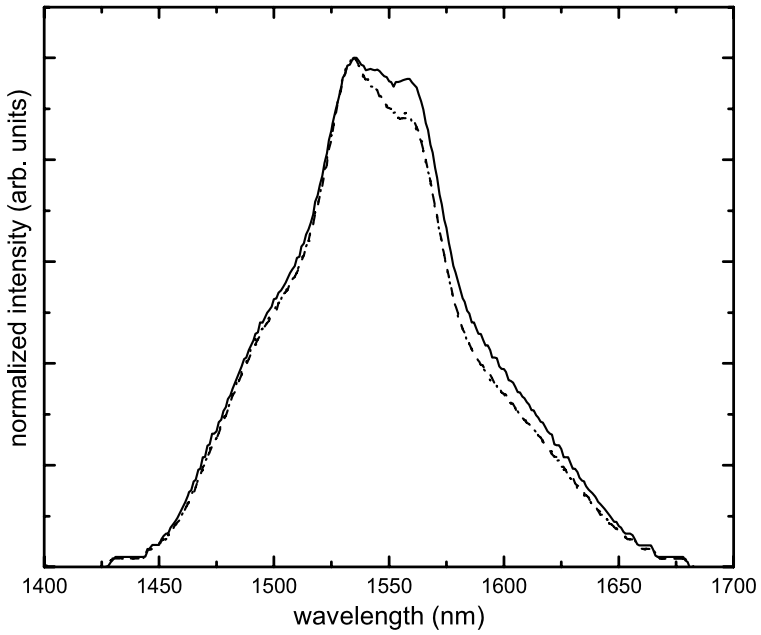

Fig. 5 Confocal micro-luminescence spectra under Ar^+ laser excitation corresponding to the Er^{3+}: $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition from samples irradiated with different number of pulses at a fluence of 5.6 J/cm^2. The *solid line* shows the spectra outside the irradiated area, and the *dashed and dot lines* show the spectra for the irradiated area at 10 and 5 pulses, respectively

modified. As for the bigger fluence (5.6 J/cm^2), the emission spectrum corresponding to 5 pulses shows clear structural differences, whereas the emissions with 10, 20 and 50 pulses are broader, without structure and less intense.

The emission band at 1550 nm corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions for the non-irradiated glass and regions irradiated with 5 and 10 pulses at a fluence of 5.6 J/cm^2 is shown in Fig. 5. There are differences between the emissions inside the irradiated area in comparison to the glass sample, although weaker than those observed at other emission bands.

Considering globally the analyzed emission bands, the results suggest that there are clear structural changes in the samples after the irradiation with 5 and 10 pulses for the two irradiation fluences used (2.6 and 5.6 J/cm^2). The mechanism of desvitrification is non-linear and of thermal origin [19]. Absorbing the laser energy by Er^{3+} ions results in the local temperature rise near to the focal point of the laser beam, where the power density is maximal. The temperature rise results in higher local phonon density, and therefore in a more efficient non-radiative decay of photo-excited Er^{3+} ions and subsequently in more effective heating [20]. For both fluences, the evolution of the luminescent bands with the number of pulses follows a similar trend: a small number pulses do not substantially affect the structure of the sample (heating might not be sufficient to form nanocrystals), while

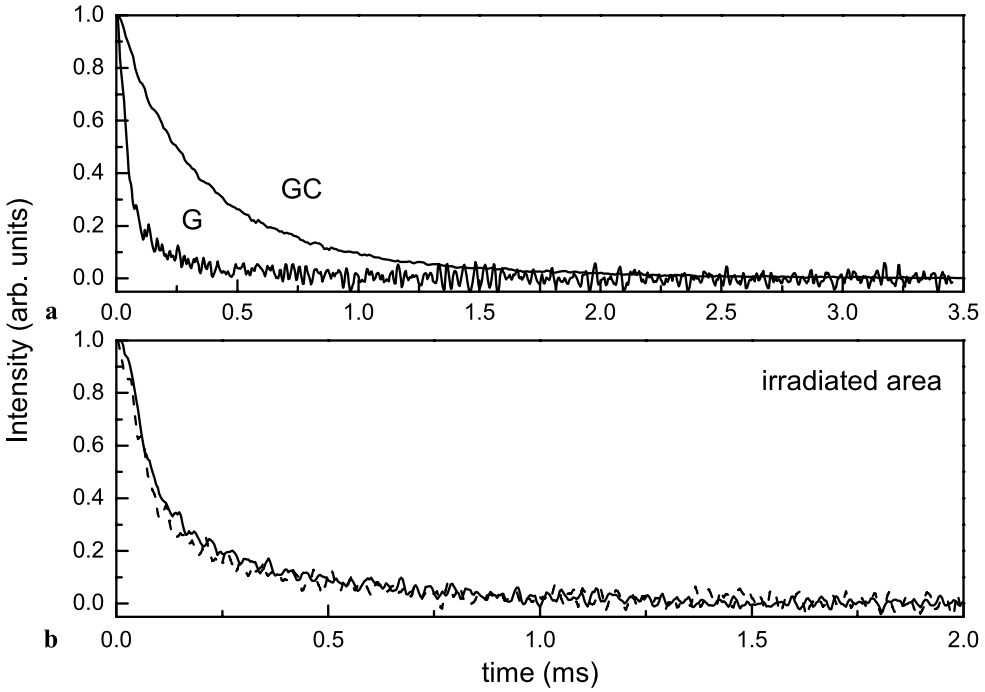

Fig. 6 Emission decay of the $^4I_{11/2}$ level (**a**) for the glass (G) and glass ceramic (GC) samples and (**b**) inside the irradiated area for 5 pulses at 2.6 J/cm^2 (*solid line*) and 5.6 J/cm^2 (*dashed line*)

a large number of pulses cause damage (re-amorphization) on the surface, suppressing the new phases [21, 22], most likely crystalline, induced for an intermediate number of pulses.

In order to investigate whether the observed changes are related to a devitrification process in the sample, the lifetime of the $^4I_{11/2}$ level has been measured. The decay of the luminescence of the corresponding transition is measured outside and inside the damage area with 5 pulses at the two different laser fluences. The corresponding plots are shown in Fig. 6. For comparison, the lifetime of the $^4I_{11/2}$ level for the glass ceramic sample obtained by a thermal treatment [16] is also shown. Inside the irradiated area, no matter the laser fluence, the decay curves show a double exponential behavior, while outside there is a single exponential decay. The glass ceramic sample, similarly to the fs-irradiated regions, shows two components. The fast component is attributed to the glassy phase of the samples and the slow one to the crystalline phase [16–18]. Inside the irradiated area, the slow component of the $^4I_{13/2}$ transition, corresponding to the crystalline environment, has a 395 and 420 µs lifetime for 5.6 J/cm^2 and 2.6 J/cm^2, respectively, whereas for the glass ceramic samples it shows a value of 289 µs. Good agreement between the decay constant of the slow component and the lifetime of the glass ceramic samples seems to confirm the presence of a crystalline phase after femtosecond irradiation. A comparison between the fast components cannot be made because of the temporal resolution limitations of our experimental setup.

4 Conclusions

A localized modification of the optical properties in Er^{3+} doped strontium barium niobate glasses has been induced by femtosecond laser irradiation using different fluences and number of pulses per spot. Confocal micro-luminescent measurements, using an Ar^+ laser as excitation source, have been carried out to spatially select a position inside and outside the irradiated area and to analyze its luminescent emission. The Er^{3+}: $^4I_{11/2} \rightarrow {}^4I_{15/2}$ and $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions and their lifetimes have been measured and shown to be correlated to structural modifications upon the femtosecond laser irradiation. It is shown that by using 5 or 10 pulses at two different fluences it is possible to modify the structure of the glass samples, leading to a crystalline environment for the Er^{3+} ions in the irradiated area, as evidenced by the luminescence measurements and their comparison to measurements obtained in glass ceramic samples. The result is thus consistent with the formation of a crystalline phase as a consequence of laser exposure.

Acknowledgements We would like to thank Comisión Interministerial de Ciencia y Tecnología (MAT 2007-63319 and MAT 2007-65990-C03-02), SEGAI Grant and FPI of Gobierno de Canarias, for financial support.

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