FEMTOSECOND LASER MODIFICATION ON STRONTIUM BARIUM NIOBATE GLASSES DOPED WITH Er$^{3+}$ IONS

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ABSTRACT

A localized modification of the optical properties in Er$^{3+}$ doped Strontium Barium Niobate (SBN) glasses using a femtosecond laser were carried out. The samples were irradiated with a different number of pulses per spot at two laser fluences. Confocal micro-luminescent has been developed to analyze the optical changes produced by exciting the sample with an argon laser. The emission of the Er$^{3+}$: $^4I_{11/2} \rightarrow ^4I_{15/2}$ and $^4I_{13/2} \rightarrow ^4I_{15/2}$ transitions are reported and shown structural differences after the femtosecond irradiation. The lifetimes of the levels involved in these transitions are measured inside and outside the damaged area. These measurements are compared with the bulk glass ceramic sample to estimate the optimal condition to produce nanocrystals in a localized area.

INTRODUCTION

The research in glass modification by use of short laser pulses is driven by scientific interest and their applications have been demonstrated for the formation of three dimensional optical memories$^{12}$ and multicolour images$^4$, the direct writing of waveguides$^{4,6}$, waveguide couplers and splitters$^{7,8}$, waveguide optical amplifier$^9$, and optical gratings$^{10,11}$.

The femtosecond laser has two apparent features compared with cw and long pulsed laser$^{12}$:

- Elimination of the thermal effect due to the extremely short energy deposition time.
- Participation of various non-linear process enabled by high localization of laser photons in both time and spatial domains.

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 structure, producing high temperatures and pressures$^{13}$. Structural modification, including 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 a threshold of the non-linear absorption, the crystallization process utilizing a femtosecond-pulsed laser is superior in terms of the internal modification of a transparent material such a glass, compared with crystallization which occurs via linear absorption or heat treatment$^{15}$. In this work, erbium doped strontium barium niobate glasses have been irradiated with a femtosecond laser. The properties of these glasses and the changes induced by a cw laser have been studied in a previous paper$^{16-18}$. Optical measurements show the changes of the local structure in a localized area after the irradiation and they are compared with the bulk glass ceramic sample obtained by thermal treatment with a furnace.

EXPERIMENTAL

The Er$_2$O$_3$-SrO-BaO-Nb$_2$O$_5$-B$_2$O$_3$ glasses were prepared using the melt quenching method$^{16}$ with the following composition in mol%: 5 Er$_2$O$_3$, 11.25 SrO, 11.25 BaO, 22.5 Nb$_2$O$_5$ and 50 B$_2$O$_3$.  

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Commercial powders of reagent grade were mixed and melted in a platinum crucible for 1 h in an electric furnace at 1400°C. The melt was poured between two iron plates and the thickness of the obtained sample was 1.6 mm. The glass ceramic was obtained by thermal treatment of the precursor glass at 620°C for 2 hours. It was used to compare with measurements in the locally damage zone by laser action.

A commercial chirped pulse amplification (CPA) Ti:sapphire laser system (Spectra Physics, Spitfire), providing linearly polarized pulses with pulse duration of 120 fs and at a wavelength of ~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 set-up, the sample was placed at 36° 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 laser fluences (2.6 and 5.6 J/cm²) with different number of pulses (1-50 pulses)

![Confocal Micro-luminescence set up.](image)

Confocal micro-luminescent was developed by using the following setup (see figure 1). The sample was situated in the focal plane of a 20X microscope objective (Mitutoyo, M-Plan NIR, numerical aperture (NA) = 0.26) in a motorized stage to displace at different positions. The detection system consists in TRIAX-180 monochromator with a resolution of 0.5 nm and detected with a photomultiplier tube.

The optical measurements were carried out inside and outside the irradiated area under Ar laser excitation for the emission spectra. The lifetimes involved in these transitions were obtained using a mechanical chopper and the signal was recorded by an oscilloscope.

RESULTS AND DISCUSSION

Localized zone of strontium barium niobate glass doped with Er³⁺ were irradiated by using a femtosecond laser at two different fluences and varying the number of pulses per spot. Inside these irradiated areas, the emission spectra of the Er³⁺: ⁴S_{3/2}(^{2}H_{15/2}) → ⁴I_{13/2}, ⁴I_{11/2} → ⁴I_{15/2} and ⁴I_{13/2} → ⁴I_{15/2} transitions were measured.

The results obtained with a laser fluence of 5.6 J/cm² are presented in the figure 2 for the Er³⁺: ⁴I_{11/2} → ⁴I_{15/2} transition with different number of pulses per spot. As it can see in this figure, the emission corresponding to 1 and 2 pulses are less intense than the rest. These spectra are compared with the emission outside of the irradiated area and there are no differences between both. It can be conclude that with 1 and 2 pulses do not produce or induce any different structure in the sample.
The emission corresponding to 5 and 10 pulses present structural changes. The emission spectra more resolved and the peak at 1005 nm seem to confirm the presence of a new phase. This spectrum is compared with the glass and glass ceramic emission spectra in figure 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 process using a thermal treatment at 620°C with a furnace, whereas the rest remains in the glassy phase$^{16,18}$.

![Figure 2](image.png)

Figure 2. Confocal Micro-luminescence spectra under Ar laser excitation inside the irradiated area of the Er$^{3+}$, $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition with different number of pulses at the fluence of 5.6 J/cm$^2$. The solid lines show the spectra for 5 and 10 pulses, the dashed line for the 20 pulses and the dot line for the 1 and 2 pulses.

By comparing the spectra showed in the figure 3, the emission for the irradiated area is in a good agreement with the glass ceramic sample around the peak of 975 nm. On the other hand, the peak at 1005 nm is not clearly observed in the glass ceramic sample. This result could be explained in basis to radiative transfer processes which change the shape of the emission bands. The emission

![Figure 3](image.png)

Figure 3. Emission spectra under Ar laser excitation on the glass ceramic samples (solid line), inside the irradiated area (dashed line) and on the glass sample (dotted line) of the Er$^{3+}$, $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition.
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The emission band at 1550 nm corresponding to the $^{4}I_{13/2} \rightarrow ^{4}I_{15/2}$ transitions is measured in the irradiated area at 5 and 10 pulses with a fluence of 5.6 J/cm\textsuperscript{2} which is given in the figure 5. There are differences between the emissions inside the irradiated area in comparison with the glass sample. The analysis of the presented results suggest that there are structural changes in the samples after the irradiation with laser fluence of 5.6 J/cm\textsuperscript{2} with 5 and 10 pulses in similar way with the results obtained with a laser fluence of 2.6 J/cm\textsuperscript{2}. Less number of pulses per spot does not affect the structure of the sample and a higher number of pulses causes damages on the surface whereas does not induce the formation of new phases.

In order to investigate if the changes have been obtained due to a desvitrification process on the sample, the lifetime of the $^{4}I_{11/2}$ level has been obtained. The decay of the luminescence of the $^{4}I_{11/2}$ level is measured outside and inside of the damage area with 5 pulses at two laser fluences. Inside the irradiated area the decays curves show a double exponential character, while outside there is one single exponential. From the fits of these curves, are obtained the constant decays of the slow and fast components and the values are presented in table 1.
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![Graph showing normalized intensity against wavelength](image)

Figure 5. Confocal Micro-luminescence spectra under Ar laser excitation inside the irradiated area of the Er\textsuperscript{3+}: \( ^4I_{1/2} \rightarrow ^4I_{15/2} \) transition with different number of pulses at the fluence of 5.57 J/cm\textsuperscript{2}. The solid line shows the spectra outside the irradiated area and the dashed and dot lines for the irradiated area at 10 and 5 pulses respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fast component (s)</th>
<th>Slow component (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass irradiated with 5 pulses at 5.57 J/cm\textsuperscript{2}</td>
<td>90</td>
<td>398</td>
</tr>
<tr>
<td>Glass irradiated with 5 pulses at 2.57 J/cm\textsuperscript{2}</td>
<td>70</td>
<td>420</td>
</tr>
<tr>
<td>Glass</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Glass Ceramic</td>
<td>4.5</td>
<td>289</td>
</tr>
</tbody>
</table>

Table I. Lifetime of The \(^4I_{1/2} \) Level

The lifetime of the \(^4I_{1/2} \) level for the glass ceramic sample, obtained by a thermal treatment\textsuperscript{16} is shown in the table to compare with the values obtained inside the irradiated area and in order to estimate the optimal condition to obtain glass ceramic environment under femtosecond laser excitation. In this sample were found the same double exponential behaviour. The fast component is attributed to the glassy phase of the samples and the slow component to the crystalline phase. The good agreement between the decay constant of the slow component with the lifetime of the glass ceramic samples seem to confirm the presence of a crystalline phase after the femtosecond irradiation. In against, the comparison between the fast components cannot be realized because the glassy phase is too fast for this experimental setup.

CONCLUSIONS

A localized modification of the optical properties in Er\textsuperscript{3+} doped Strontium Barium Niobate glasses using a femtosecond laser has been reported. The samples have been irradiated with a different number of pulses per spot at two laser fluences. Confocal micro-luminescent measurements have been carried out to spatially select a position...
inside and outside the irradiated area and to analyze the optical changes produced by exciting the sample with an argon laser. The emission of the Er$^{3+}$ $^{4}I_{11/2} \rightarrow ^{4}I_{15/2}$ and $^{4}I_{13/2} \rightarrow ^{4}I_{15/2}$ transitions and the lifetimes of these levels have been reported and shown the structural differences after the femtosecond irradiation. As conclusion, using 5 or 10 pulses at two different fluxes has been possible to modify the structure of the glass samples and the results seem to confirm the existence of crystalline environment for the Er$^{3+}$ ions in the irradiated area.

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REFERENCES