

## Local devitrification of Dy<sup>3+</sup> doped Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> glass by laser irradiation

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### ABSTRACT

The Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> (BTS) is a well known piezoelectric, ferroelectric and non-linear crystal. In this work, nanocrystals of BTS have been obtained by different thermal treatments of precursor glasses. The glasses were fabricated from BaO–TiO<sub>2</sub>–SiO<sub>2</sub> and doped with Dy<sub>2</sub>O<sub>3</sub> using the melt quenching method. Thermal treatment in an electrical furnace at 740 °C was used to obtain transparent glass ceramic samples, which are formed by an amorphous matrix containing BTS nanocrystals, with an average size of 35 nm confirmed by X-ray diffraction. Moreover, a localized area in the precursor glass has been irradiated by continuous wave (c.w.) Ar-laser or femtosecond (fs) pulsed laser. Evidence of the changes induced by laser irradiation is confirmed by spectroscopic comparison of irradiated regions with the precursor glass and glass ceramic samples. The emission spectra corresponding to the Dy<sup>3+</sup>: <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub> (578 nm), <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>11/2</sub> (670 nm) and <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>9/2</sub> (757 nm) transitions were obtained under laser excitation at 473 nm. These measurements confirm the incorporation of the Dy<sup>3+</sup> ions into the BTS nanocrystals which produces an enhancement of luminescence and makes it an attractive material for optical amplification.

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### 1. Introduction

Optically transparent glass–ceramics containing rare-earth ions [1] or non-linear optical crystals [2,3] have received considerable attention, because such materials have high potential applications in photonic devices such as phosphors and ultra-fast optical switches [1–3]. From the viewpoint of practical application in integrated optics, it is important to fabricate active ions-doped transparent glass–ceramics with controlled patterns e.g. dots, lines, which can serve as laser waveguide, grating, and wavelength conversion devices. Laser irradiation of glass materials has received much attention, because this technique has been regarded as a new process for spatially selected structural modification and/or crystallization in glass [4–7]. It is of particular interest for performing various optical functions to form crystalline phases in glass through laser irradiation.

Fresnoite crystal Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> (BTS), belonging to P4bm group, has TiO<sub>5</sub> square pyramidal structure, which is the origin of the polarizability of this crystal [8]. Since Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> crystal shows piezoelectric properties [9], this crystal is thought to be a candidate for surface-acoustic-wave devices [10]. Also Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> crystal shows

pyroelectricity [11], ferroelectricity [12–14], fluorescence [12], and non-linear optical property [15]. On BTS glasses, recently Maruyama et al. [16], reported the possibility of synthesizing transparent glass ceramic samples by heat treatment. Those transparent nanocrystallized materials have important applications in ultrafast optical switching but it is necessary to make complex structures of small size that are only possible by laser irradiation techniques.

The aim of this work is to analyse the luminescence changes produced in Dy<sup>3+</sup>-doped BTS precursor glasses upon irradiation with c.w. Ar-laser and with fs-laser pulses. In this work, the effect of laser irradiation on glass samples is compared to the behaviour of glass ceramic samples obtained by thermal treatment in order to determine the optimal conditions to produce nanocrystalline material upon laser exposure.

### 2. Experimental

A glass with the composition of 40BaO–20TiO<sub>2</sub>–40SiO<sub>2</sub> and doped by 1.5 Dy<sub>2</sub>O<sub>3</sub> (in mol.%) was prepared using a conventional melt-quenching method. Commercial powders of reagent grade BaCO<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub> and Dy<sub>2</sub>O<sub>3</sub> were mixed and melted in a platinum crucible at 1500 °C for 1 h in an electric furnace. After that, the melt was poured between two bronze plates at 200 °C. The samples were then annealed at 700 °C and cooled down slowly to room temperature about 24 h. The samples were polished to obtain a

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smooth and flat surface in both faces, in order to ensure that the laser does not diverge when irradiates the sample.

The glass ceramic (GC) sample was obtained by thermal treatment of the precursor glass at 740 °C for 30 min. This GC sample was formed by a glassy phase and a crystalline phase of Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> nanocrystals. This sample was used to compare the behaviour of glass ceramics with that exhibited by the glass exposed to laser radiation.

In the c.w. laser irradiation experiment, a multiline c.w. Ar-laser was focused on the surface of the glass sample, increasing the laser power beam until 4 W. The laser beam has a Gaussian profile with a FWHM of 1.4 mm. It was focalized on the sample using a 20 mm focal lens. The diameter of the focalized spot  $d_1$  at  $1/e^2$  intensity is given by the formula:

$$d_1 = \frac{\lambda f}{\pi d_2} \quad (1)$$

where  $\lambda$  is the excitation wavelength,  $f$  the focal length of the lens and  $d_2$  the diameter of the collimated pumping beam before the lens. A mean diameter of about 22  $\mu\text{m}$  is obtained for the pump spot on the sample. Therefore, at the maximum laser power in this experiment (about 4 W), the corresponding power density is about 26 MW/cm<sup>2</sup>.

In the fs-laser irradiation experiment, was used a commercial chirped pulse amplification (CPA) laser, it uses a Ti:sapphire laser system (Spectra Physics, Spitfire), providing s-polarized pulses, with pulse duration of 120 fs at a wavelength of 800 nm. 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 54° respect to the laser, in order to allow perpendicular observation of the sample during the process using a microscope. Laser was focalized by 15 cm lens, resulting in an elliptical laser spot on the surface. The samples were irradiated with a laser fluence of 4.5 J/cm<sup>2</sup> (power density  $3.7 \times 10^7$  MW/cm<sup>2</sup>) and pulses ranging from 1 to 50.

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) = 0.40) on a motorized translation stage. The samples are excited using c.w. diode laser excitation at 473 nm and the luminescent emission is detected using an Andor Newton CCD spectrograph. Optical emission spectra were recorded

in regions inside and outside the laser irradiated area. The observed volume is a prolate spheroid of about 1.35  $\mu\text{m}^3$ .

### 3. Results and discussions

X-ray diffraction measurements have been performed on the glass ceramic and on the precursor glass, samples. They are given in Fig. 2(a) and (b) respectively. A broad diffraction curve is clearly observed for the glass structure. However, the diffraction pattern of the glass ceramic shows the characteristic narrow peaks associated to the presence of nanocrystals. All XRD peaks are assigned to the so-called fresnoite Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> crystalline phase (space group P4bm, JCPDS No. 022-0513), indicating the formation of only Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> crystals (BTS) [16]. The average size of the precipitated BTS nanocrystal has been estimated to be around 35 nm using the Scherrer formula [17].

Luminescence spectra have been performed on the precursor glass and on the glass ceramic sample, as shown in Fig. 3. These spectra were recorded in the range of 500–900 nm under c.w. diode laser excitation at 473 nm and normalized for a better comparison. Four emission bands associated to the  $f-f$  transitions of Dy<sup>3+</sup>:  $^4F_{9/2} \rightarrow ^6H_{13/2}$  (578 nm),  $^4F_{9/2} \rightarrow ^6H_{11/2}$  (670 nm),  $^4F_{9/2} \rightarrow ^6H_{9/2}$  ( $^6F_{11/2}$ ) (757 nm) and  $^4F_{9/2} \rightarrow ^6H_{7/2}$  ( $^6F_{9/2}$ ) (845 nm) are observed. Although, there are not any significant changes in the shape of these emissions between the precursor glass and the glass ceramic sample, the relative intensities in these bands change. For the precursor glass sample, there is a nearly linear dependence of the maximum emission intensity of each band with the wavelength while for the glass ceramic sample the dependence is not linear. There is a decrease of the relative intensities of the Dy<sup>3+</sup>:  $^4F_{9/2} \rightarrow ^6H_{13/2}$  (578 nm) and  $^4F_{9/2} \rightarrow ^6H_{9/2}$  ( $^6F_{11/2}$ ) (757 nm) transitions with respect to the Dy<sup>3+</sup>:  $^4F_{9/2} \rightarrow ^6H_{11/2}$  (670 nm) transition. Fig. 3a and b show the relative intensities of the maxima of the emission bands as a function of wavelength for the precursor glass and glass ceramic sample, respectively. For notation purposes, we will call 1:1:1 the intensity relationship for the glass sample (which is a linear behaviour) and 1:2:1 for the glass ceramic sample (not-linear behaviour) where the Dy<sup>3+</sup>:  $^4F_{9/2} \rightarrow ^6H_{11/2}$  (670 nm) emission transition is the most intense one.

In Fig. 4 is shown the absorption spectrum of the BTS precursor glass at room temperature, in which the schematic energy-level diagram of Dy<sup>3+</sup> ions for this sample is included. The typical

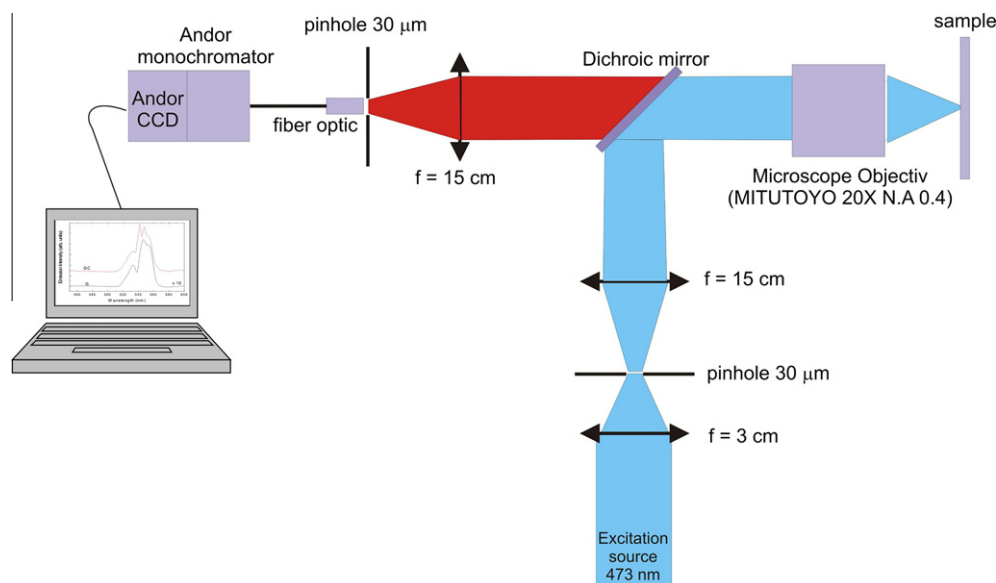


Fig. 1. Confocal luminescence microscope set-up.

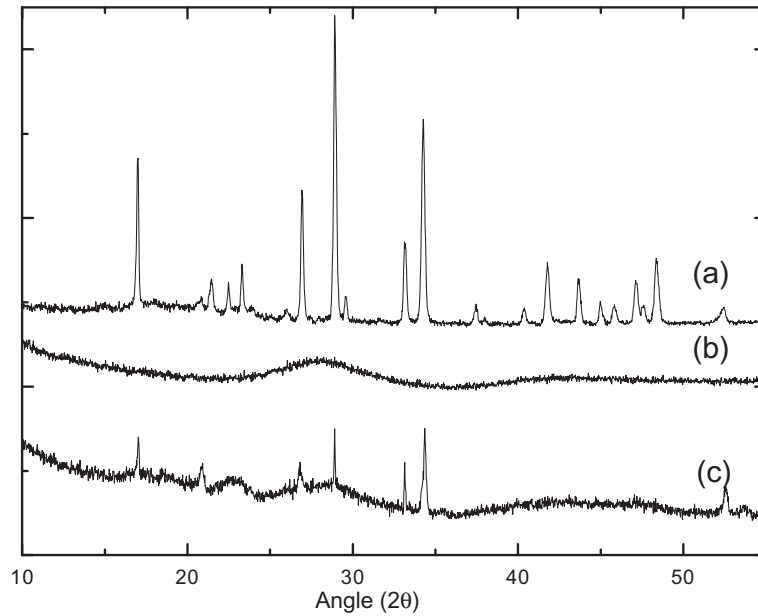


Fig. 2. XRD pattern for the glass ceramic sample (a), the glass sample (b) and the Ar-laser irradiated area (c).

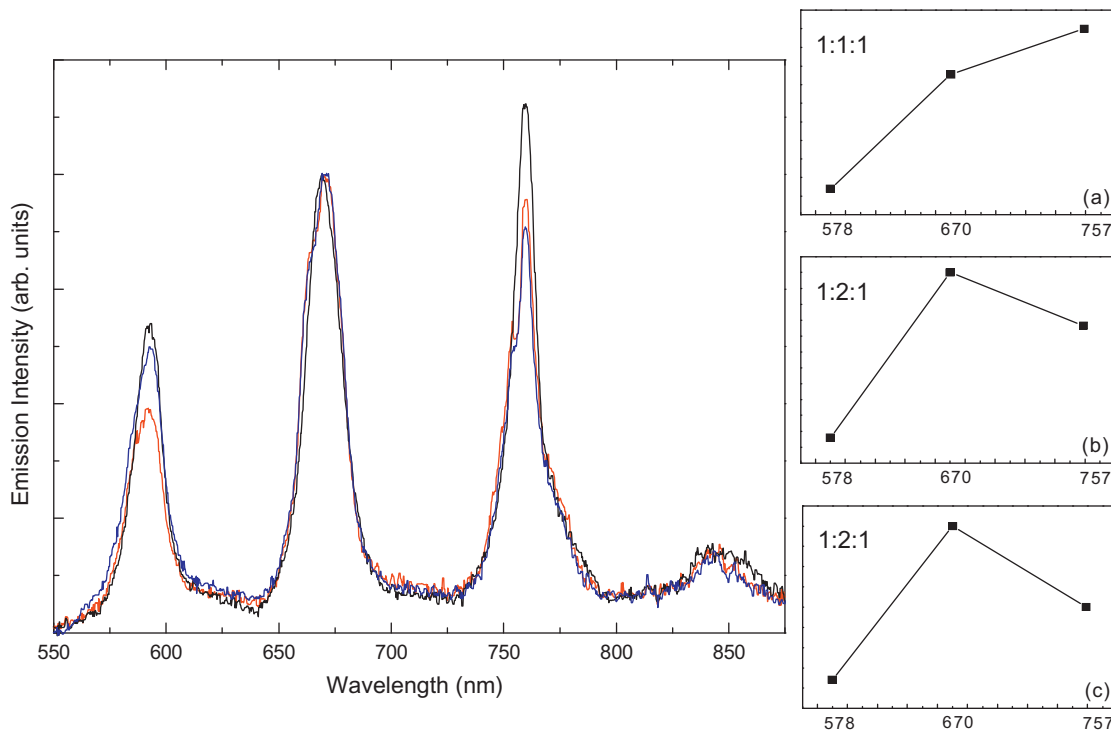


Fig. 3. Confocal emission spectra in the glass (black line), glass ceramic (red line) and inside the irradiated area by a c.w.: Ar-laser (blue line). (a) Relative emission intensities for the glass sample, (b) glass ceramic sample and (c) inside the irradiated area.

transitions between the ground state of  ${}^6\text{H}_{15/2}$  and the excited states of  $\text{Dy}^{3+}$  ions are observed in the sample, and the peak assignments are given in the figure.

As can be seen in Fig. 4,  $\text{Dy}^{3+}$  ions have low absorption bands coincident with the output wavelengths of a c.w. multiline Ar: laser (514, 488 and 458 nm). Therefore, when a glass sample doped with  $\text{Dy}^{3+}$  ions is irradiated with this laser a percentage of the incoming light is absorbed by these ions or the glass matrix. Due to the low absorption of the ions at these wavelengths it is necessary a high irradiation power (about 4 W) in order to induce a local

temperature increase at the focus of the laser beam. The temperature increase results in a higher local phonon density which produces an efficient heating [5–7,18]. After this irradiation process, the photoluminescence spectra in the range of 500–900 nm were recorded inside and outside of the irradiated area. As it is expected, there are not important changes in the shape of these emission bands, in similar way to the obtained ones for the glass and glass ceramic samples, where the shape of the emission bands remain unchanged although with different relative intensities. By comparing the intensities, it is found inside the irradiated area a decrease

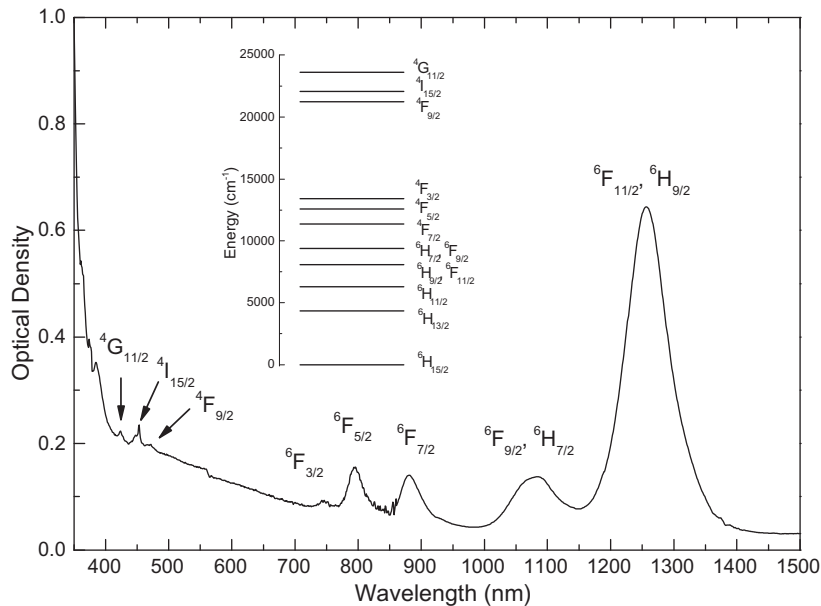


Fig. 4. Absorption spectrum for the glass sample at room temperature. The inset shows the energy level of the  $\text{Dy}^{3+}$ -ions.

of the  $\text{Dy}^{3+}$ :  $4\text{F}_{9/2} \rightarrow 6\text{H}_{13/2}$  (578 nm) and  $4\text{F}_{9/2} \rightarrow 6\text{H}_{9/2}$  ( $6\text{F}_{11/2}$ ) (757 nm) transitions respect to the  $\text{Dy}^{3+}$ :  $4\text{F}_{9/2} \rightarrow 6\text{H}_{11/2}$  (670 nm) transition (see Fig. 3). A 1:2:1 behaviour is observed inside the irradiated area (Fig. 3c). Moreover, in Fig. 2(c) is the XRD pattern of this Ar-laser irradiated area, it shows a broad diffraction curve as expected in a glass but some peaks appear corresponding to a nanocrystal phase. Due to some limitations in the XRD equipment, the volume measured is bigger than the irradiated area, this causes a big contribution of glass in the XRD pattern and a small contribution due to the nanocrystal phase. The change in the relative emission intensities (similar to the glass ceramic sample) and the XRD pattern obtained inside the irradiated area, allows us to conclude that BTS nanocrystals are formed upon irradiation with the c.w. Ar: laser.

Moreover, localized zones of the BTS precursor glass doped with  $\text{Dy}^{3+}$  were irradiated with femtosecond laser pulses, with a maximum local fluence of  $4.5 \text{ J/cm}^2$ , using a variable number of pulses per spot. The emission spectra of the  $\text{Dy}^{3+}$ :  $4\text{F}_{9/2} \rightarrow 6\text{H}_{13/2}$ ,  $4\text{F}_{9/2} \rightarrow 6\text{H}_{11/2}$ ,  $4\text{F}_{9/2} \rightarrow 6\text{H}_{9/2}$ ,  $6\text{F}_{11/2}$  transitions were recorded inside and outside the laser exposed regions by using confocal set-up. As can be seen in Fig. 4,  $\text{Dy}^{3+}$  ions have an absorption band around 800 nm, coincident with the output wavelength of the femtosecond laser. Due to the absorption of the laser energy by the  $\text{Dy}^{3+}$  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  $\text{Dy}^{3+}$  doped nanocrystals in the irradiated volume, as similarly observed in other matrix [6,19,20].

In a previous work, our research group found nanocrystals of strontium barium niobate after fs irradiation with a given number of pulses per spot [6]. It was concluded that a sufficiently low number of pulses does not affect to the sample, whereas an intermediate number of pulses induced the formation of new phase in the material, most likely a crystalline one. Moreover, high numbers of pulses return the sample to a glassy state.

After the fs irradiation, similar results were obtained for the BTS precursor glass. The emission spectra of the  $\text{Dy}^{3+}$  ions inside the irradiated area with different number of pulses per spot were obtained and their intensity relationships were studied (see Fig. 5). A low number of pulses does not affect the luminescent behaviour of the sample, whereas an intermediate number of pulses produce changes in the relative intensities of emission bands recorded in

the irradiated region. However, for a large increment in the number of pulses per spot, the irradiated area returns to a glassy behaviour. The fs-irradiated areas with 1 and 5 pulses per spot show a 1:1:1, consistent with a glassy state (Fig. 5a and b). This result suggests that for these pulse numbers, the structure of the irradiated zone remains essentially unaltered. In the emission corresponding to 10 pulses; it is found a 1:2:1 relationship between these intensities (Fig. 5c). For higher number of pulses, the relationship between these intensities is again 1:1:1 (Fig. 5d and e).

The changes between the relative intensities of these emission bands as function of the number of pulses per spot, let us to conclude that an intermediate number of pulses ( $\approx 10$ ) induce the formation of new structures on the fs-irradiated area which affects the luminescence properties of the sample. The nature of the induced changes is nowadays under study, but the present results indicate that correspond to BTS nanocrystals, as observed in the

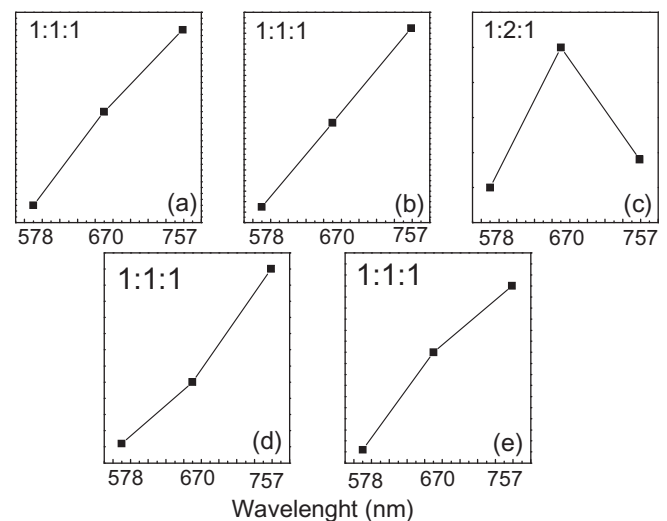


Fig. 5. Relationship between the emission intensities for the different  $\text{Dy}^{3+}$  transition bands inside the fs-irradiated area with different number of pulses. (a) 1 pulse, (b) 5 pulses, (c) 10 pulses, (d) 15 pulses, and (e) 20 pulses.

BTS precursor glass under furnace treatment and under c.w. laser irradiation.

Comparing our results with the literature in the sense of nanocrystal nucleation and growth, Cabral et al. [21,22], reported nucleation rates of few minutes at 750 °C. As we have nucleation and growth of nanocrystals in few seconds for c.w. Ar-laser and few milliseconds in the fs laser, we expect a greater temperature, probably together to another nucleation/growth mechanism.

The increase of the temperature at the center of the spot after an irradiation time, in laser heating experiments for semi-infinite bodies, could be estimated using the equation given in Ref. [23]. Some parameters needed on this equation have not been measured for BTS glasses. Moreover, during the heating the nucleation contributes by increasing the scattering of the incident irradiation and due to the irregular shape of the sample, a numerical estimation of the increase of the temperature is difficult to achieve. Therefore, new experiments based in the intensity ratio of thermalized levels are in progress in order to obtain an efficient estimation of the temperature of the irradiated area.

#### 4. Conclusions

Localized modifications in BTS precursor glass doped with Dy<sup>3+</sup> have been induced by laser irradiation. The glass used in this study (doped with 1.5% mol. of Dy<sup>3+</sup>) was fabricated by the melt quenching method. BTS glass ceramic containing nanocrystals with an average size of 35 nm, samples were obtained by a thermal treatment of this precursor glass. This BTS glass ceramic sample was used to compare with the results obtained inside the irradiated area.

Localized regions of the precursor glass were irradiated by c.w. Ar-laser or a pulsed femtosecond laser. Evidence of the changes induced by laser exposure was obtained by comparison of the spectroscopic properties and XRD patterns of irradiated regions with those corresponding precursor glass and glass ceramic samples. Confocal micro-luminescent measurements of emission spectra corresponding to the Dy<sup>3+</sup>: <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub>, <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>11/2</sub> and <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>9/2</sub> transitions were obtained under laser excitation at 473 nm. The results are consistent with the formation of a crystalline phase as a consequence of c.w. laser exposure. In the case of the fs laser, the behaviour of the regions exposed to an increasing number of pulses indicate that a for either a low or high number of irradiation pulses the material remains glassy, while for intermedi-

ate values (approximately 10 pulses at 10 mJ/cm<sup>2</sup> BTS nanocrystals) are locally formed.

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