

# Optical properties of transparent Dy<sup>3+</sup> doped Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> glass ceramic

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## ABSTRACT

The Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> is a well known piezoelectric, ferroelectric and non-linear crystal. Nanocrystals of Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> doped with 1.5 Dy<sup>3+</sup> have been obtained by thermal treatment of a precursor glass and their optical properties have been studied. X-ray diffraction patterns and optical measurements have been carried out on 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> (575 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 have been obtained under laser excitation at 473 nm. These measurements confirm the incorporation of the Dy<sup>3+</sup> ions into the Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> nanocrystals which produces an enhancement of luminescence at 575 nm. At this wavelength has been demonstrated a maximum optical amplification around 1.9 cm<sup>-1</sup> (~8.2 dB/cm).

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## 1. Introduction

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 [1]. Since Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> crystal shows piezoelectric properties [2,3], this crystal is thought to be a candidate for surface-acoustic-wave devices [4,5]. Also Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> crystal shows the pyroelectricity [6], ferroelectricity [7], fluorescence [8,9], and non-linear optical properties [10].

Trivalent Lanthanide Dy<sup>3+</sup> ions in transparent media are suitable as environmentally friendly phosphor due to yellow <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub> and blue <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub> transition ratio. Also, Dy<sup>3+</sup> ion is useful on studies about host properties due the well known hypersensitive transition <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub> and opposed to it, the <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub> transition is less sensitive to the host [11]. Those Dy<sup>3+</sup>-doped phosphors have important applications to produce white light from UV light emission diodes [12] whose yellow/blue ratio can be tuned by changes in the matrix.

In this work, oxide glasses have been prepared and doped with Dy<sup>3+</sup> ions. One interesting property of the BTS glass is that controlling the thermal treatment it is possible to produce transparent glass ceramic containing nanocrystals of BTS. Therefore, it has been obtained transparent glass ceramic samples and has been demonstrated optical amplification at 575 nm due to the emission of Dy<sup>3+</sup> ions.

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## 2. Experimental

A glass with the composition of 40BaO–20TiO<sub>2</sub>–40SiO<sub>2</sub> and doped by 1.5Dy<sub>2</sub>O<sub>3</sub> (in the molar ratio) was prepared using a conventional melt-quenching method. Commercial powders of ACS reagent grade (purity ≥ 99.9%) 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–rhodium crucible at 1500 °C for 1 h in an electric furnace. After that, the melt was poured between two bronze plates at 200 °C and then were annealed at 700 °C and cooled slowly to room temperature for about 24 h. The sample was polished to obtain a smooth and flat surface in both faces using 0.3 μm alumina, giving a thickness of 0.15 cm. 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 with a thickness of 0.12 cm.

Measurements of absorption spectra were done by a Perkin Elmer Lambda-9 spectrophotometer. For emission spectra of glass and glass ceramic samples a TRIAX-180 monochromator with 0.5 nm of resolution and a Hamamatsu R928 photomultiplier tube have been used. A laser diode at 473 nm was used as excitation source.

The optical amplification experiments were carried out in a pump and probe experimental shown in Fig. 1 [13]. The pump radiation was provided by an optical parametric oscillator (OPO) (EEKSPLA, NT 342/3/UVE) tuned at 475 nm with high energy pulses between 0.1 and 0.5 J/cm<sup>2</sup> with duration of 5 ns. The monochromatic probe beam was obtained by dispersing the light of Oriel Xenon 400 W lamp with a monochromator Oriel 7725 1/8 m, giving a signal power density of 195 μW/cm<sup>2</sup> at 575 nm with a spectral FWHM of 5 nm.

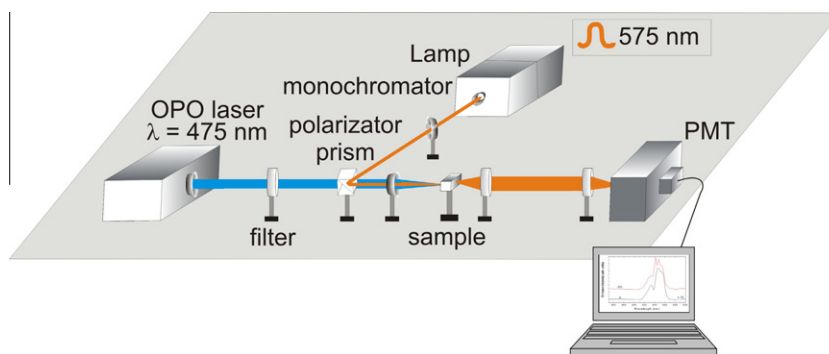


Fig. 1. Experimental setup for pump and probe optical amplification.

The incidence of pump and probe beams were parallel and normal to the surface of the sample that was located after a 1 mm diameter pinhole. In order to cover only the whole area of the pinhole, the pump and probe were focalized on pinhole area.

The detection system was made with the TRIAX-180 monochromator and registered by a digital oscilloscope TEKTRONIX-2430A.

### 3. Results and discussion

In Fig. 2 are shown the X-ray diffraction patterns obtained in the glass and glass ceramics samples. The glass spectrum shows broad bands characteristic of an amorphous phase. However, the pattern obtained for the glass ceramics sample coincide with the fresnoite  $\text{Ba}_2\text{TiSi}_2\text{O}_8$  crystalline phase. From the width of the obtained peaks, the crystal size of BTS was estimated by using Sherrer's equation. The average size of the precipitated BTS nanocrystals has been estimated to be around 35 nm.

Taking into consideration the ionic radius ( $r = 0.1027$  nm) of  $\text{Dy}^{3+}$  ions, one possible site in  $\text{Ba}_2\text{TiSi}_2\text{O}_8$  crystals for incorporation of  $\text{Dy}^{3+}$  ions is the site of  $\text{Ba}^{2+}$  whose ionic radius of  $r = 0.142$  nm is very similar to  $\text{Dy}^{3+}$ .

From density measurements, it is possible to estimate the proportion of nanocrystals in the glass ceramics samples using the equation  $d(\text{glass ceramics}) = (1 - f)d(\text{glass}) + fd(\text{crystal})$  where  $d$  is the density and  $f$  the volume fraction. Using the value  $d(\text{crystal}) = 4.446 \text{ g/cm}^3$  [14], it is obtained a value of  $f = 0.3$  for the studied sample.

The absorption spectra of glass and glass ceramic samples doped with 1.5 mol% of  $\text{Dy}^{3+}$  are shown in Fig. 3. As can be seen, the shape of both spectra are similar whereas the formation of

nanocrystals with an average size of 35 nm in the glass ceramics samples produce an important increase of the light dispersion at short wavelengths. The oscillator strengths and the Judd–Ofelt parameters (Table 1) have been obtained from these spectra. Moreover, from the Judd–Ofelt parameters have been calculated the spontaneous emission probability for the glass and glass ceramic samples for the  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$  transition. In the glass ceramics sample, the value for this transition has increased a factor about 1.5 respects to the glass matrix. However as can be seen in Fig. 4 the emission spectra obtained under excitation at 473 nm is quite similar between the glass and glass ceramic samples, it can be explained since the nanocrystal size does not produce quantum confinement. Moreover, the local crystalline field which affects to the  $\text{Dy}^{3+}$  ions incorporated to the nanocrystals, do not give to place to important spectroscopic changes respect to the glassy phase.

Due to these previous results and the good transparency of the glass ceramic sample, the transition at 575 nm could be very interesting for optical applications. Therefore, amplification measurements were obtained using the experimental setup shown in Fig. 1. In this experiment the OPO laser is used to excite the  ${}^6\text{H}_{15/2} \rightarrow {}^4\text{F}_{9/2}$  Ground State Absorption (GSA) centred at 475 nm, therefore it is excited the  ${}^4\text{F}_{9/2}$  level. In these conditions, a probe beam tuned at 575 nm can induce a relaxation process involving the stimulated emission of a photon at the same frequency. Therefore, two emission spectra are recorded: the first one with pump and probe present and the second one when the probe is blocked. These spectra are given in Fig. 5. An increase of the detected intensity at the signal wavelength 575 nm can be clearly appreciated. This increment is due to the stimulated emission associated with the  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$  transition that occurs at the probe wavelength

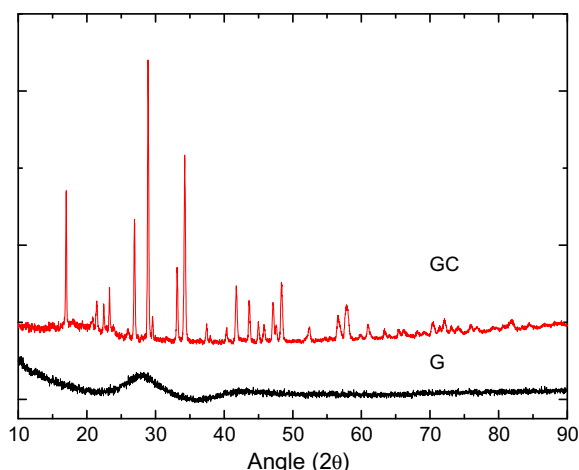


Fig. 2. X-ray diffraction patterns of glass (G) and glass ceramic (GC) samples.

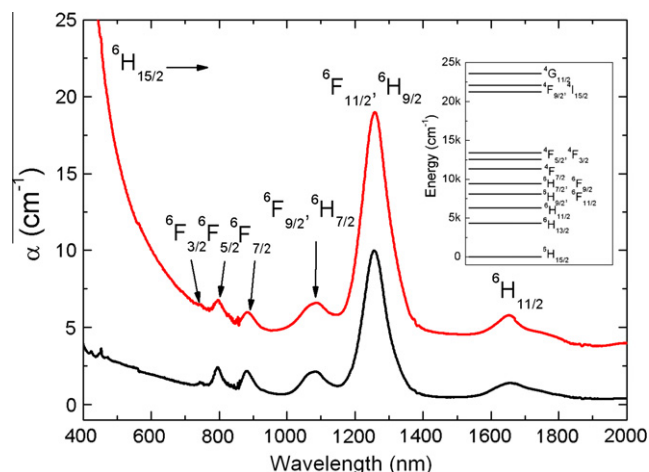


Fig. 3. Absorption spectra of glass (—) and glass ceramic (—) samples doped with 1.5%  $\text{Dy}^{3+}$  ions.

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