Optical properties of transparent Dy^{3+} doped $Ba_2TiSi_2O_8$ glass ceramic

L.L. Martin *, P. Haro-González, I.R. Martín [1]

Departamento de Física Fundamental y Experimental, Electrónica y Sistemas, Universidad de La Laguna, Av. Astrofísico Francisco Sánchez, s/n, E-38206 La Laguna, Tenerife, Spain

ABSTRACT

The $Ba_2TiSi_2O_8$ is a well known piezoelectric, ferroelectric and non-linear crystal. Nanocrystals of $Ba_2Ti-Si_2O_8$ doped with 1.5 Dy^{3+} 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^{3+}: $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (575 nm), $^4F_{9/2} \rightarrow {}^6H_{11/2}$ (670 nm) and $^4F_{9/2} \rightarrow {}^6H_{9/2}$ (757 nm) transitions have been obtained under laser excitation at 473 nm. These measurements confirm the incorporation of the Dy^{3+} ions into the $Ba_2TiSi_2O_8$ nanocrystals which produces an enhancement of luminescence at 575 nm. At this wavelength has been demonstrated a maximum optical amplification around 1.9 cm^{-1} ($\sim$8.2 dB/cm).

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1. Introduction

Fresnoite crystal $Ba_2TiSi_2O_8$ (BTS), belonging to P4bm group, has TiO_5 square pyramidal structure, which is the origin of the polarizability of this crystal [1]. Since $Ba_2TiSi_2O_8$ crystal shows piezoelectric properties [2,3], this crystal is thought to be a candidate for surface-acoustic-wave devices [4,5]. Also $Ba_2TiSi_2O_8$ crystal shows the pyroelectricity [6], ferroelectricity [7], fluorescence [8,9], and non-linear optical properties [10].

Trivalent Lanthanide Dy^{3+} ions in transparent media are suitable as environmentally friendly phosphor due to yellow $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and blue $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition ratio. Also, Dy^{3+} ion is useful on studies about host properties due the well known hypersensitive transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and opposed to it, the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition is less sensitive to the host [11]. Those Dy^{3+}-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^{3+} 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^{3+} ions.

2. Experimental

A glass with the composition of $40BaO–20TiO_2–40SiO_2$ and doped by $1.5Dy_2O_3$ (in the molar ratio) was prepared using a conventional melt-quenching method. Commercial powders of ACS reagent grade (purity $\geqslant$ 99.9%) $BaCO_3$, TiO_2, SiO_2, and Dy_2O_3 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 $Ba_2TiSi_2O_8$ 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^2 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 $\mu W/cm^2$ at 575 nm with a spectral FWHM of 5 nm.

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* Corresponding author. Address: Facultad de Física, Departamento de Física Fundamental y Experimental, Electrónica y Sistemas, Universidad de La Laguna, 38206 La Laguna, S/C de Tenerife, Spain. Tel.: +34 922318651; fax: +34 922319228.
   E-mail address: martin@ull.es (L.L. Martin).
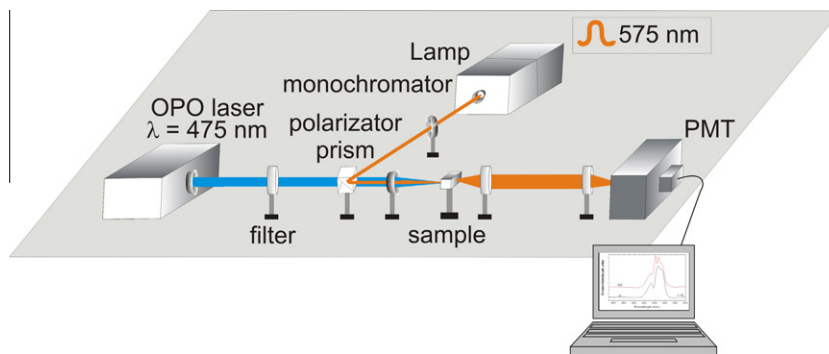   [1] MALTA Consolider Team.

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 $Ba_2TiSi_2O_8$ 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 Dy^{3+} ions, one possible site in $Ba_2TiSi_2O_8$ crystals for incorporation of Dy^{3+} ions is the site of Ba^{2+} whose ionic radius of $r = 0.142$ nm is very similar to 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 $d(\text{crystal}) = 4.446$ 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 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 $^4F_{9/2} \rightarrow {}^6H_{13/2}$ 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 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 $^6H_{15/2} \rightarrow {}^4F_{9/2}$ Ground State Absorption (GSA) centred at 475 nm, therefore it is excited the $^4F_{9/2}$ 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 $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition that occurs at the probe wavelength
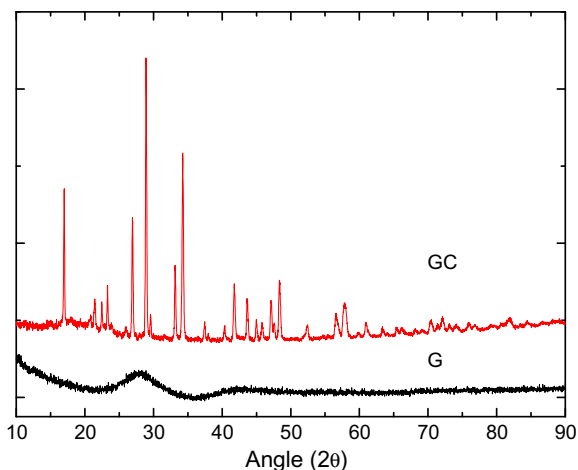

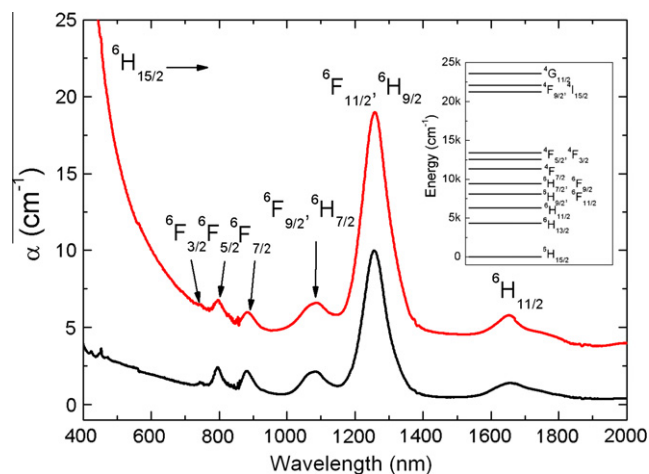**Fig. 2.** X-ray diffraction patterns of glass (G) and glass ceramic (GC) samples.

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

Table 1
Experimental and calculated oscillator strengths in glass and glass ceramic samples. The Judd–Ofelt parameters and spontaneous emission probability for the amplified transition are also included.

Levels	Glass		Glass ceramic	
$^6H_{15/2} \rightarrow$	f_{EXP} (10^{-8})	f_{CAL} (10^{-8})	f_{EXP} (10^{-8})	f_{CAL} (10^{-8})
$^6F_{3/2}$	12.3	9.2	0.6	5
$^6F_{5/2}$	94.4	48.7	77.9	27
$^6F_{7/2}$	94.6	116.2	73.9	101.7
$^6F_{9/2}$, $^6H_{7/2}$	170.6	165.3	227.6	220.2
$^6F_{11/2}$, $^6H_{9/2}$	848.0	846.7	1395.4	1394.5
$^6H_{11/2}$	81.4	98.7	104.3	116.2
		$A(s^{-1})$		$A(s^{-1})$
$^4F_{9/2} \rightarrow {}^6H_{13/2}$		957		1470
W_2 (10^{20} cm^2)		8.30		13.64
W_4 (10^{20} cm^2)		1.44		2.95
W_6 (10^{20} cm^2)		0.99		0.55
r.m.s. (10^{-8})		0.31		0.35

Fig. 6. Optical gain as function of the pump power density. The continuous line is a guide for the reader.

where α and L are the absorption coefficient and the length of the sample respectively ($L = 0.12$ cm). When the pump and the signal are simultaneously switched on, the intensity recorded after the samples at the signal wavelength, I_{pp} is given by

$$I_{pp} = I_p + I_o e^{(g_{int}-\alpha)L} \qquad (2)$$

where I_p is the spontaneous emission intensity induced by the pumping radiation and g_{int} is the internal gain coefficient. Then, the net optical gain coefficient g_{net} can be expressed as

$$g_{net} = g_{int} - \alpha \qquad (3)$$

The signal enhancement (SE) is defined as

$$SE = \frac{I_{pp} - I_p}{I_{probe}} \qquad (4)$$

By introducing (2) and (3) in the expression (4), SE can be related directly with the net optical gain coefficient as follow [13]

$$SE = \exp(g_{net}L) \qquad (5)$$

The intensities I_p, I_{pp} and I_{probe} can be experimentally measured. As we use a pulsed excitation source, I_p and I_{pp} are experimental curves that decay after the excitation pulse. Therefore, the values of SE and g are calculated by using Eqs. (4) and (5) from these experimental curves. The maximum of the detected intensity just after the pump pulse was used in order to obtain the g value. The gain coefficient as a function of the pump energy density is given in Fig. 6. A continuous growth of the net gain coefficient as a function of the pump power density can be observed in this figure. Finally, the maximum value for the net gain has been observed for a pump energy density of 0.36 J/cm^2 corresponding to 1.9 cm^{-1} ($\sim$8.2 dB/cm) during the maximum of the detected intensity.
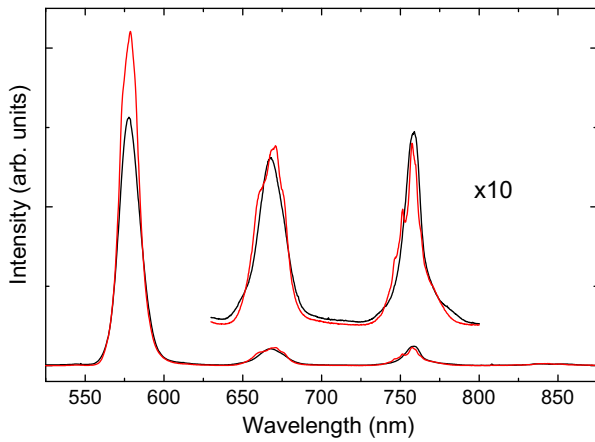

Fig. 4. Emission spectra of glass (−) and glass ceramic (——) samples doped with 1.5% Dy^{3+} ions under excitation at 473 nm.

and it is the physical basis of signal amplification. Under this pumping scheme, population inversion for $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition at 575 nm is expected at $t = 0$ s because $^6H_{13/2}$ is not initially populated. When a probe beam passes through a solid medium, its intensity decreases from the initial I_0 value to the final $I_{probe}(L)$ value according to the exponential law
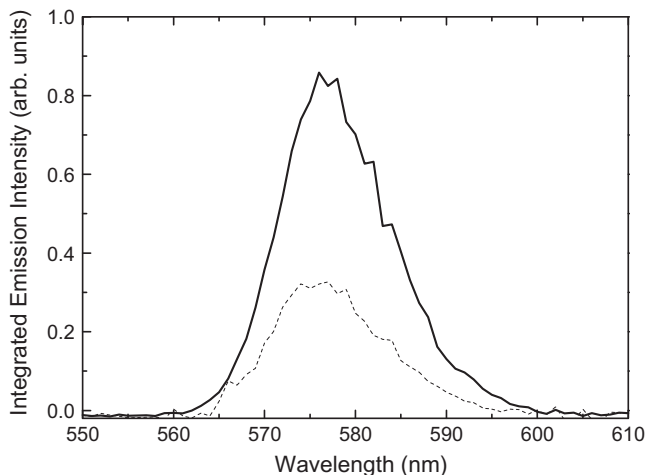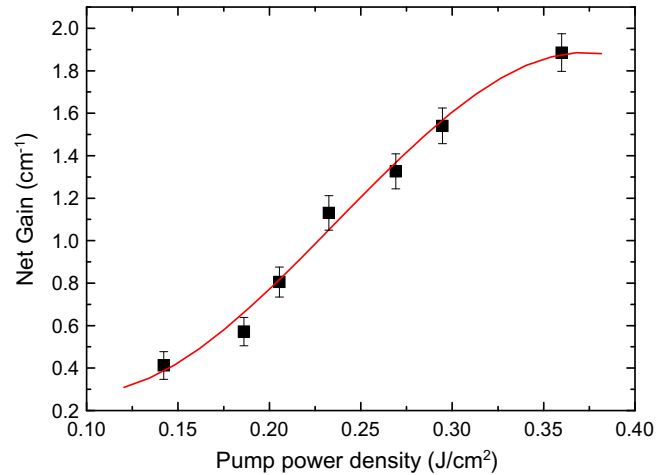
$$I_{probe}(L) = I_o e^{-\alpha L} \qquad (1)$$

4. Conclusions

Transparent glass ceramics containing nanocrystals of Ba$_2$Ti-Si$_2$O$_8$ doped with 1.5% Dy^{3+} have been prepared after thermal treatment of precursor glass. Due to the low average size of the nanocrystals (about 35 nm) these samples have a good transparency and their optical properties confirm that the Dy^{3+} ions are incorporated into the nanocrystals. Moreover, it is observed an increase of the emission at 575 nm in the glass ceramics sample due to the incorporation of the Dy^{3+} ions into the nanocrystals. The application of Dy^{3+}-doped BTS glass ceramic sample as an optical amplifier at 575 nm has been studied in a pump and probe

Fig. 5. Integrated emission intensity obtained using a pump at 475 nm and with (−) or without (- - - -) a probe at 575 nm.

set-up where a maximum gain around 1.9 cm^{-1} ($\sim$8.2 dB/cm) has been obtained pumping with 0.36 J/cm^2.

Acknowledgments

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