Stimulated emission and light amplification in Ho^{3+} doped oxyfluoride glasses and glass-ceramics

Fernando Lahoz [*] [a], Nestor. E. Capuj [b], Daniel Navarro-Urrios [b,c], Sergio E. Hernández [a]
[a]Dpto. Física Fundamental y Experimental, Electrónica y Sistemas, University of La Laguna, 38206 La Laguna, Tenerife, Spain;
[b]Dpto. Física Básica, University of La Laguna, 38206 La Laguna, Tenerife, Spain;
[c]Permanet address: Laboratorio Nanoscienze, Dipartimento di Fisica, Università di Trento, Via Sommarive 14, I-38050 Povo (Trento), Italy;

ABSTRACT

Stimulated emission and light amplification have been observed in Ho^{3+}-doped transparent oxyfluoride glasses and glass-ceramics. A pump and probe experiment has been designed to show this result. A doubled-frequency Nd-YAG pulsed laser oscillating at 532nm was used as the pump source to strongly populate the Ho^{3+} $^5S_2$:$^5F_4$ level. Low power laser radiation at 750nm was used as the probe beam to stimulate the Ho^{3+} $^5S_2$:$^5F_4 \rightarrow {}^5I_7$ electronic transition at the same wavelength.

The high power pump pulses provide population inversion between the Ho^{3+} $^5S_2$:$^5F_4$ and $^5I_7$ electronic levels and a net positive gain in the 750nm signal is observed both in the precursor glass and in the glass-ceramic. The highest optical gain was obtained for the glass-ceramic sample and corresponds to about 3.7cm^{-1} (~16dB/cm). The dynamics of the gain is also investigated.

Keywords: optical amplification, gain, holmium, glass-ceramics

1. INTRODUCTION

Oxyfluoride glass-ceramic materials are obtained when a precise thermal treatment is applied to a precursor glass. This thermal treatment causes that fluoride nanocrystals precipitate in the vitreous matrix. Most of the RE ions partition in the fluoride nanocristalline phase.[1] In fact, the main advantage of the oxyfluoride glass-ceramics is that they combine the good optical properties of RE ions in a low phonon energy fluoride host with the easy elaboration, manipulation in air atmosphere and suitability for industrial production of oxide glasses. Therefore, these materials combine various remarkable properties of oxides and fluorides in one material. The fact that the macroscopic properties of this material are characteristic of the oxide glass, except for the spectroscopic properties of the RE ions that are typical of low-phonon energy fluoride crystals, make this material unique in the field of optical material engineering.[2,3] Some interesting new optical properties have been found in these systems in the last years. Wang and Ohwaki [4] found that the upconversion emission of Er^{3+} ions in silica based oxyfluoride glass ceramics increases by about a factor of 100 compared to the precursor glass. Simultaneous photon avalanche upconversion in the three primary colours, red, green and blue, was observed in Ho^{3+} doped glass-ceramics.[5] Intense infrared emissions have been observed in Tm^{3+} or Er^{3+} doped glass-ceramics.[6,7] However, so far no demonstration of optical amplification has been reported in these materials.

In this paper, we report on the room temperature (RT) optical amplification of radiation at 750 nm in a Ho^{3+}-doped oxyfluoride glass and glass-ceramic. To the best of our knowledge, this is the first demonstration of net optical gain in a pump and probe experiment in a bulk glass-ceramic. Moreover, it is the first time that Ho^{3+} ions have ever been used to obtain optical amplification at this wavelength region.

[*] flahoz@ull.es; phone 34 922318654; fax 34 922318228

Photonic Materials, Devices, and Applications II, edited by Ali Serpengüzel,Gonçal Badenes, Giancarlo Righini
Proc. of SPIE Vol. 6593, 65930M, (2007) · 0277-786X/07/$18 · doi: 10.1117/12.721884

2. EXPERIMENTAL

The precursor glass was prepared from a homogeneous powder mixture with the following composition in mol %: 30 SiO_2, 15 Al_2O_3, 29 CdF_2, 22 PbF_2, 1.5 YF_3, 2.5 HoF_3. The glass was obtained by melting the powder at 1050ºC for 2 hours and quickly quenching the melt on a stainless-steel plate at RT. The transparent glass-ceramic was obtained after a thermal treatment of the precursor glass at 470ºC for 24 hours. X-ray diffraction measurements have confirmed the formation of nanocrystals of the β-PbF2 phase.[8]

Amplification experiments have been performed using a doubled-frequency Nd-YAG pulsed laser oscillating at 532nm as the pump source and a tunable Ti:sapphire laser for the probe beam. The end-polished sample was pumped with high energy pulses of about 5ns of duration at 532nm and the probe, or signal, was provided by a cw tunable Ti:sapphire laser. Homogeneous pump and signal beams were obtained after a 3mm diameter pinhole placed just in front of the sample. To cover the whole area of the pinhole, the signal beam was previously expanded with an optical system formed by a diverging and a converging lens. The signal was passed through a monochromator and then detected with a photomultiplier tube located at the output of the monochromator and analyzed in a digital oscilloscope. The incidence of the signal beam was normal to the surface of the sample, and that of the pump beam was at an angle of about 15º to avoid the high power pump pulses to enter into the detection system, while keeping a good overlap between the pump and probe beams along the 1.6mm long sample. Neutral density filters were placed in front of the signal beam to achieve an unsaturated signal regime, and in front of the monochromator to assure that the photomultiplier tube works in the linear regime.

3. EXPERIMENTAL RESULTS

3.1 Stimulated emission

The stimulated emission is the basis of any amplification or laser process. We have tried to verify if stimulated emission occurs in Ho^{3+} doped glass and glass-ceramic using a pump and probe scheme. A high power pump pulse excites the

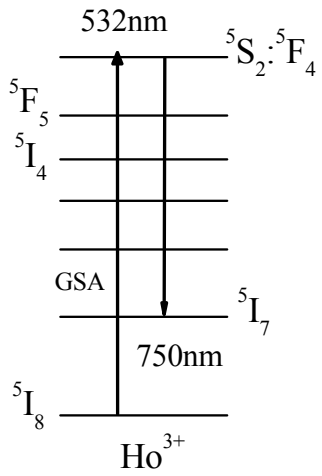

Fig. 1. Energy level diagram of the Ho^{3+} ions indicating the main transitions involved in the amplification process.

Ho^{3+} ions and they promote to an excited level. In the presence of an electromagnetic field (the signal or probe beam) that oscillates at the frequency of a given Ho^{3+} electronic transition, there is a probability that the Ho^{3+} ion relaxes by the

emission of a photon that is stimulated by probe beam. In fact, we have experimentally confirmed that this happens as follows.

The Ho^{3+} ground state absorption (GSA) $^5I_8 \rightarrow {}^5S_2{:}^5F_4$ is centered at about 536nm. When the sample is irradiated at 532nm, using a frequency-doubled Nd-YAG pulsed laser, a non-resonant GSA occurs and the $^5S_2{:}^5F_4$ level is populated. The intensity of the pump beam does not appreciably reduce when it passes through the sample, which is 1.6mm long, due to the relatively low absorption at 532nm. For that reason, the intensity of the pump beam can be considered to be approximately constant through the sample. The large energy gap from the $^5S_2{:}^5F_4$ to the next lower energy level prevents multiphonon deexcitation in the fluoride nanophase. Therefore, radiative relaxation of this level is expected. In particular, the radiative transition to the $^5I_7$ metastable level of the Ho^{3+} ions gives rise to an intense emission centered at 750nm (see Figure 1).

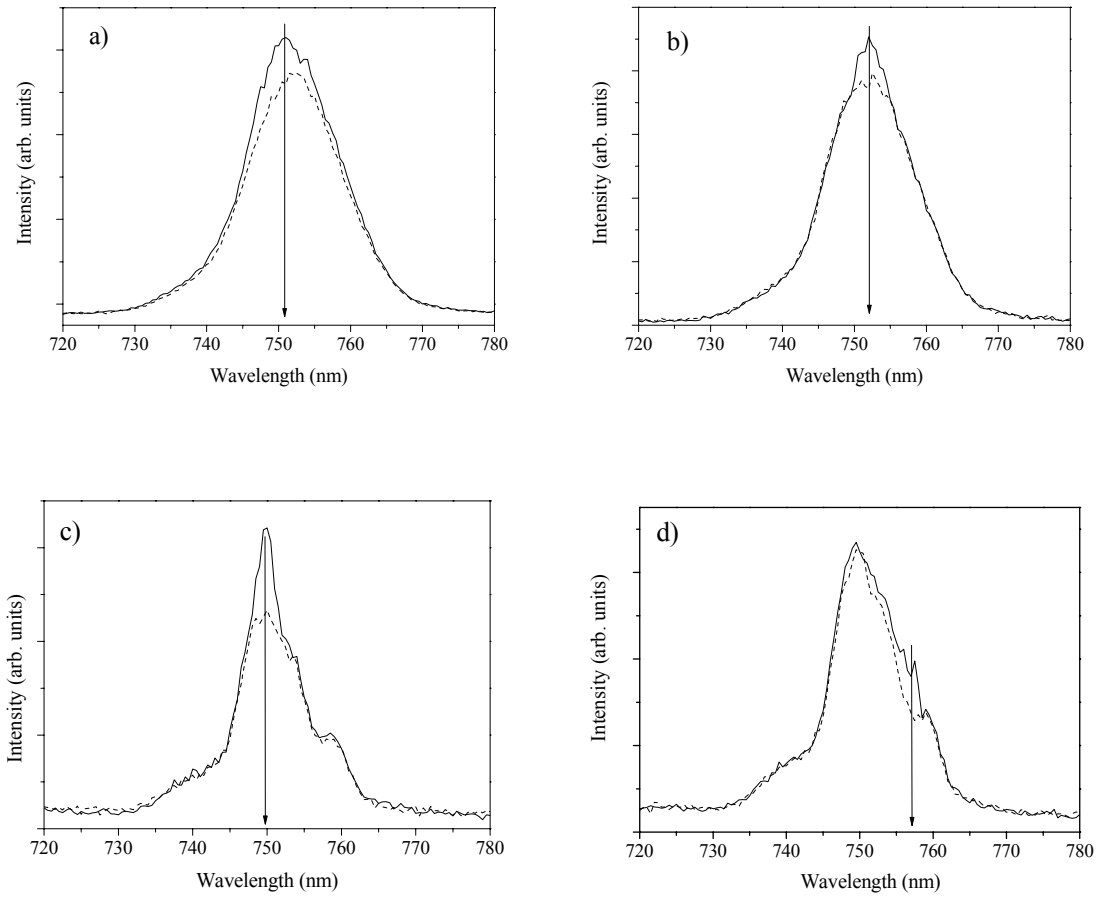

Fig. 2. Emission spectrum associated to the Ho^{3+} $^5S_2{:}^5F_4 \rightarrow {}^5I_7$ transition under pump excitation at 532nm (dashed line); and under simultaneous pump and probe excitation (solid line) for the glass (a and b) and glass-ceramics (c and d). The arrow indicates the probe wavelength in each case.

We have detected evidence of stimulated emission when a pump and probe experiment has been performed. The emission spectra with and without probe are given in Figure 2 for the glass and for the glass-ceramic. The dashed line shows the spontaneous emission spectrum of the sample measured just after the pump pulse when the signal beam is blocked before the sample. The luminescence of the sample was detected by a photomultiplier and analyzed by a digital

oscilloscope. The emission spectra given in the figure are obtained by integrating the first 0.1μs of the luminescence after the pump pulse. The solid line gives the emission measured under the same pump conditions but when the signal or probe beam is present. The wavelength of the signal beam is indicated by an arrow. The continuous background provided by the probe has been subtracted so that the spectrum gives the emission due to the luminescence of the sample. An increase of the detected intensity at the signal wavelength can be clearly appreciated. Moreover, when the wavelength of the signal is shifted from 750nm to the sides of the spectrum, the position of the intensity enhancement is shifted accordingly. The same behaviour is found both in the precursor glass and in the glass-ceramic. In fact, the increment of the luminescence in the pump and probe experiment compared to the pump measurement is due to stimulated emission at the wavelength of the signal.

3.2 Optical gain

We have performed the following calculations in order to determine the net optical gain of the signal due to the stimulated emission of the medium. The signal was fixed at 750nm and its density was as low as 6μW/cm^2 to assure unsaturated low-signal regime. When the probe beam goes through a material medium, its intensity, I_{probe}, decreases according to the exponential law:

$$I_{probe} = I_0 e^{-\alpha L} \tag{1}$$

where I_0 is the probe intensity at he beginning of the medium, α gives the absorption coefficient of the sample at the probe's wavelength, and L means the length of the sample.

In order to estimate the α coefficient, the absorption spectrum of the Ho^{3+} doped glass-ceramic is given in Figure 3. The wavelength of the signal beam, 750nm, matches the $^5I_8 \rightarrow {}^5I_4$ ground state absorption. However, this transition is strongly forbidden. The transitions from the ground state to the different excited levels are indicated in the figure. The position of the absorption band to the $^5I_4$ state at 750nm is indicated by an arrow. No absorption is detected at this wavelength because this transition is extremely weak. For that reason, we can assume that α coefficient at 750nm can be neglected and the intensity of the probe beam is constant through the sample.

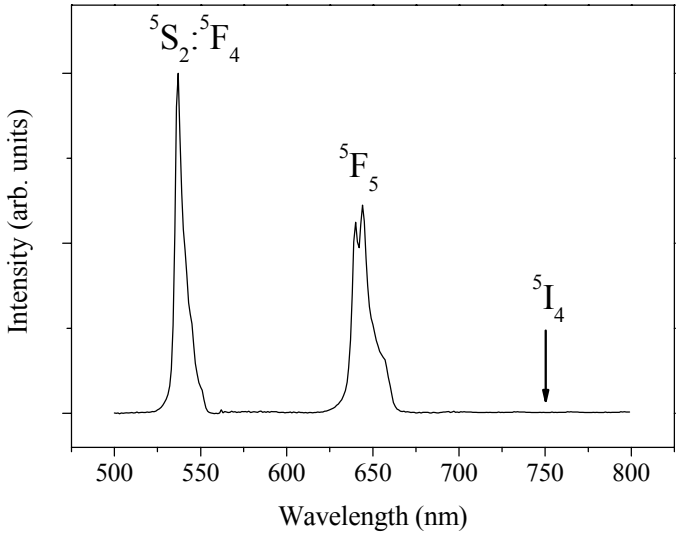

Fig. 3. Ground state absorption of the Ho^{3+} ions. Electronic transitions are indicated. The arrow shows the position that corresponds to the $^5I_8 \rightarrow {}^5I_4$.

If, in addition to the signal beam, the pumping is switched on, the intensity of the pump and probe spectrum at 750nm, I_{pp}, is given by:

$$I_{pp} = I_p + I_0 e^{gL} \tag{2}$$

where I_p represents the spontaneous emission intensity at the same wavelength when the probe is blocked before the sample, and g is the internal gain coefficient which is due to stimulated emission. As there are no other loss mechanisms, g provides the net optical gain coefficient.

We have experimentally measured the so call signal enhancement (*SE*) which is defined as

$$SE = \frac{I_{pp} - I_p}{I_{probe}} \tag{3}$$

This coefficient is related to the net gain coefficient by:

$$SE = exp(gL) \tag{4}$$

We have measured the *SE* parameter just after the pump pulse for a signal power density of 6μW/cm^2. We have calculated the g coefficient as a function of the pump energy density, and the results are given in Figure 4. Positive optical gain is already observed for low pump power excitation. It increases for higher pump energy densities up to a value of about 3.7cm^{-1} (~ 16dB/cm) for a pump energy density of 135mJ/cm^2 per pulse. We wish to remind that the excitation wavelength is non-resonant with the $^5I_8 \rightarrow {}^5S_2{:}{}^5F_4$ GSA. If the excitation could be shifted to the maximum of this transition, around 536nm, a significant reduction of the pump power energy would be required to achieve the same gain values.

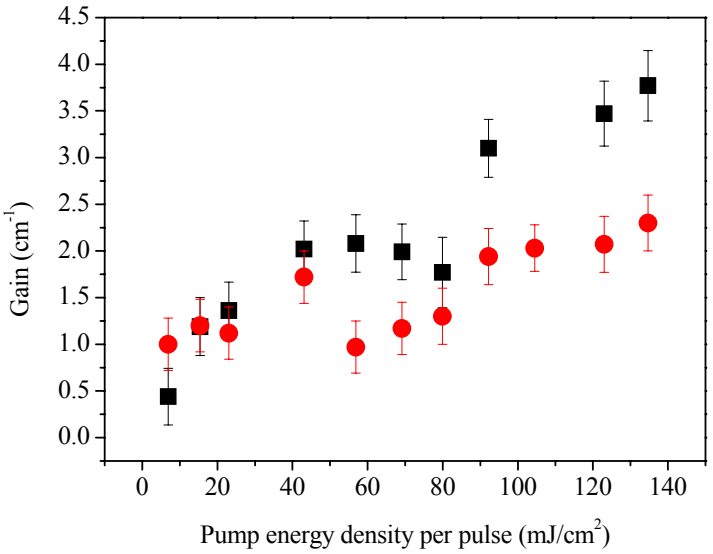

Fig. 4. Optical gain of the Ho^{3+} doped glass (circles) and glass-ceramic (squares) as a function of the pump energy density per pulse when the probe power density is fixed at 6μW/cm^2.

The gain coefficient dependence on the signal power density was also studied and the results are shown in Figure 5 for the glass-ceramic sample. For this experiment, a pump energy density of 80mJ/cm^2 was chosen. The optical gain shows a stable value for signal beams with a power density up to 40μW/cm^2, and drops for higher values, indicating the range of the optimal low-signal regime. As the signal intensity further increases, the gain decreases since the pump can no longer reload the population inversion as fast as the signal depletes it.

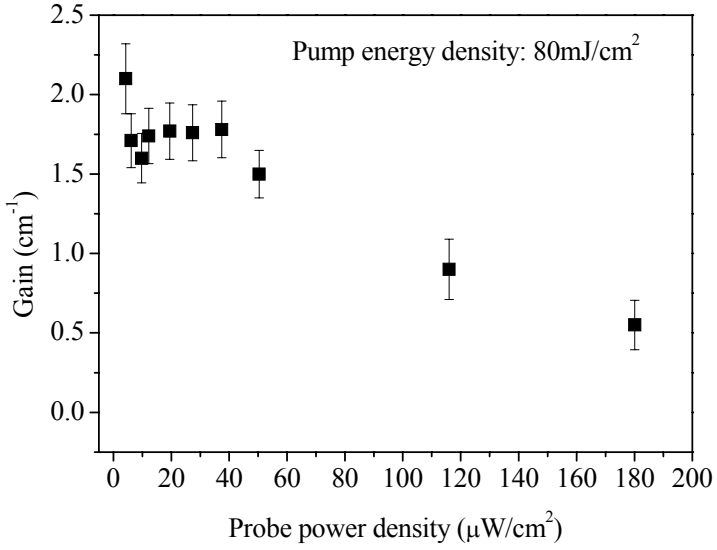

Fig. 5. Optical gain of the Ho^{3+} doped glass-ceramic as a function of the probe power density when the pump energy density per pulse is fixed at 80mJ/cm^2.

A rough estimation of the population inversion that is achieved between the Ho^{3+} $^5S_2$:$^5F_4$ and the $^5I_7$ levels (initial and final estates of the stimulated emission at 750nm, respectively) of the glass-ceramic sample can be made taking into account that the gain coefficient can be expressed as:

$$g = \sigma . N^* \tag{5}$$

where σ is the stimulated emission cross-section of the $^5S_2$:$^5F_4 \rightarrow {}^5I_7$ transition, and N^* represents the population inversion between the initial and the final states of the transition. If we consider, as a first approach, that σ is similar to those found in the literature for different fluoride matrices a value of 7 x 10^{-21} cm^2 can be used.[9] In that case, for a gain coefficient of about 3.7cm^{-1} equation (5) gives a population inversion of about 5 x 10^{20} cm^{-3}. Assuming a homogeneous distribution of the Ho^{3+} ions in the glass-ceramic, the total concentration of the doping ions is about 6 x 10^{20} cm^{-3}. This calculation indicates, firstly that the estimation of the population inversion in the gain medium is consistent with the total Ho^{3+} concentration in the sample, and, secondly, that at the high pumping rates achieved during the excitation pulses, most of the Ho^{3+} ions are promoted to the $^5S_2$:$^5F_4$ emitting level.

3.3 Dynamics of the optical gain

We have studied the dynamics of the optical gain in our pump and probe experiments. For that purpose we have recorded the temporal evolution of the luminescence of the samples under pump and under pump and probe excitations. The luminescence decay curves have been used to calculate the *SE* parameter as a function of time and, using equation (4) the time dependence of the *g* coefficient can be derived. The results are given in Fig. 6.

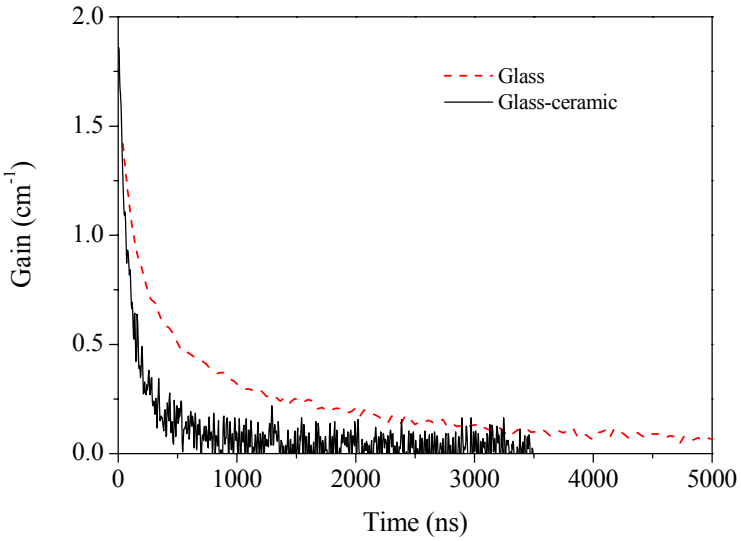

Fig. 6. Temporal evolution of the gain in Ho^{3+} doped glass (dashed line) and glass-ceramics (solid line).

Different results are observed for the glass and for the glass-ceramic. The decay of the gain in the glass-ceramic is much faster than in the glass sample. The gain drops to 1/e its initial value at about 100nm in the glass-ceramic, while it increases to about 450ns in the precursor glass. This is due to the fact that Ho^{3+} ions are much closer in the nanocrystals of the glass-ceramic than in the precursor glass. RE ions partition preferentially in the crystalline nanophase in the glass-ceraming process and, therefore, the local concentration in those samples is very high. This high concentration gives rice to energy transfer and cross-relaxation (CR) processes between the RE ions located in the nanocrystals. In particular, the $(^5S_2{:}^5F_4\ ,\ ^5I_8) \rightarrow (^5I_7,\ ^5I_4)$ CR process is very efficient in the glass-ceramic and is responsible of the shortening of the $^5S_2{:}^5F_4$ decay and, consequently, the fast decay of the gain in the glass-ceramic observed in Fig. 6.

4. CONCLUSIONS

Stimulated emission has been observed in Ho^{3+}-doped transparent oxyfluoride glasses and glass-ceramics. A pump and probe experiment has been designed to show this result. A doubled-frequency Nd-YAG pulsed laser oscillating at 532nm was used as the pump source to strongly populate the Ho^{3+} $^5S_2{:}^5F_4$ level. Low power laser radiation at 750nm was obtained from a tunable Ti:sapphire laser and used as the probe beam to stimulate the Ho^{3+} $^5S_2{:}^5F_4 \rightarrow {}^5I_7$ electronic transition at the same wavelength. When the spontaneous emission of this band is compared to the emission in the pump and probe experiment, an increase of the detected intensity at the signal wavelength can be clearly appreciated, which is due to stimulated emission at the wavelength of the signal.

Light amplification at the wavelength of the probe beam occurs due to the mentioned stimulated emission processes. In fact, net positive optical gain has been observed in Ho^{3+}-doped glasses and glass-ceramics using the pump and probe technique. The high power pump pulses provide population inversion between the Ho^{3+} $^5S_2{:}^5F_4$ and $^5I_7$ electronic levels and a net positive gain in the 750nm signal is observed. The highest optical gain was $3.7cm^{-1}$, corresponding to about 16dB/cm, and was obtained in the glass-ceramic with a pump energy density of $135mJ/cm^2$ per pulse and signal densities of $6\mu W/cm^2$. These results show the ability of the Ho^{3+} ions to produce optical gain at 750nm through stimulated emission of the $^5S_2{:}^5F_4 \rightarrow {}^5I_7$ transition, and also demonstrate that the fluoride nanocrystals of transparent oxyfluoride glass-ceramics can be used as a host of the Ho^{3+} ions to act as an amplifier medium at 750nm.

Concerning the dynamics of the optical gain, a much faster decay of the gain is found in the glass-ceramic as compared to the precursor glass. This is due to the relatively high local concentration of Ho^{3+} ions in the glass-ceramics. The short distance between Ho^{3+} ions gives rice to CR processes that strongly reduce the lifetime of the $^5S_2$:$^5F_4$ level and this is the main reason of the temporal shortening of the optical gain.

REFERENCES

1. F. Lahoz, I.R. Martín, J. Mendez-Ramos, and P. Núñez, "Dopant distribution in a Tm-Yb codoped silica based glass ceramic: An infrared-laser induced upconversion study" *J. Chem. Phys.* **120**, 6180-6190, 2004.
2. W. Höland, and G. Beall, *Glass-Ceramic Technology*, The American Ceramic Society, 2002.
3. P. A. Tick, N. F. Borrelli, and I. M. Reaney, "The relationship between structure and transparency in glass-ceramic materials", *Opt. Mat*. 15, 81-91 , 2000
4. Y. Wang, and H. Ohwaki, "New transparent vitroceramics codoped with Er^{3+} and Yb^{3+} for efficient frequency upconversion" *Appl. Phys. Lett*. 63, 3268-3270, 1993.
5. F. Lahoz, I. R. Martín and J. M. Calvilla-Quintero, "Ultraviolet and white photon avalanche upconversion in Ho3+ doped nanophase glass ceramics" *App. Phys. Lett.* **86**, 051106-1-3, 2005.
6. H. Hayashi, S. Tanabe, T. Hanada, "1.4μm band emisión properties of Tm ions in transparent glass ceramics containing PbF_2 nanocrystals for S-band amplifier" *J. Appl. Phys.* 89, 1041-1045, 2001.
7. V. K. Tikhomirov, D. Furniss, A. B. Seddon, M. Ferrari, and R. Rolli, "Er doped ultra transparent oxy-fluoride glass-ceramics for applications in the 1.54μm telecommunication window" *J. Mat. Sci. Lett*. **21**, 293-295, 2002.
8. R.T.Génova, I.R. Martín, U.R. Rodríguez-Mendoza, F. Lahoz, A.D. Lozano-Gorrin, P. Nuñez, J. González-Platas and V. Lavín, "Optical intensities of Pr ions in transparent oxyfluoride glass and glass ceramics" *J. Alloys and Comp.*, **380**, 167-172, 2004.
9. F. Lahoz, I.R. Martín, and D. Alonso "Theoretical analysis of the photon avalanche dynamics in Ho^{3+}-Yb^{3+} codoped systems under near infrared excitation" *Phys. Rev. B* **71**, art. no. 045115-1-9, 2005.