Optical amplification in Ho^{3+}-doped transparent oxyfluoride glass ceramics at 750 nm

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Positive transient optical gain has been demonstrated in Ho^{3+}-doped transparent oxyfluoride glass-ceramics. A pump and probe experiment has been designed to show this result. High power laser pulses at 532 nm were used as the pump source to strongly populate the Ho^{3+} $^5S_2$:$^5F_4$ level due to nonresonant ground state absorption. Low power cw laser radiation at 750 nm was used as the probe beam. The signal beam stimulates the emission associated with the Ho^{3+} $^5S_2$:$^5F_4 \rightarrow {}^5I_7$ electronic transition at 750 nm. In addition to this, the high power pump pulses provide population inversion between the $^5S_2$:$^5F_4$ and $^5I_7$, initial and final states of the transition, respectively, giving rise to the optical amplification of the signal beam. A gain coefficient of 3.7 cm^{-1} (~16 dB/cm) was obtained for a pump energy density of about 135 mJ/cm^2 and a signal beam power density of 6 $\mu W/cm^2$. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2741146]

Transparent oxyfluoride glass ceramics doped with rare-earth (RE) ions have been widely investigated during the last decade due to the interesting variety of applications that these materials offer. Since Wang and Ohwaki[1] 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, many works have been devoted to the luminescence properties of RE ions in glass ceramics in different spectral ranges. For instance, the mid-infrared emission at about 2.7 μm of Er^{3+}-doped glass ceramics has been reported and its potential application for laser operation discussed;[2] the near-infrared luminescence of Tm^{3+} ions has been measured in nanophase glass ceramics regarding the possibility of optical amplification in the *S*-band telecommunication region;[3,4] efficient emission in the visible range has been observed in Ho^{3+}-doped glass ceramics in the three primary colors, red, green, and blue, via a photon avalanche upconversion process.[5]

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 nanocrystalline phase.[6] 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 and suitability for industrial production of oxide glasses. Moreover, good quality monomode fibers have been obtained from glass-ceramic materials with a composition similar to that used in our laboratory. Moderate propagation looses as low as 1 dB/m were reported,[7,8] and laser operation in Nd^{3+}-doped fibers was achieved.[9] Also, buried waveguide channels have been fabricated in an oxifluoride glass ceramic using a femtosecond laser.[10] However, the practical application of glass ceramics for optical amplification is still an open field of research and reports on experimental demonstrations are seldom.

The continuous improvements in the fabrication techniques of polymer optical fibers have resulted in the reduction of the absorption loss. For example, a transmission loss of about 1 dB/m at 750 nm has been achieved in graded-index microstructured polymer optical fiber.[11] These advances together with the demand of increasing bandwidth for telecommunication applications require the development of optical amplifiers in the spectral range suitable for polymer optical fibers communications.

In this letter, we report on the room temperature (RT) optical amplification of radiation at 750 nm in a Ho^{3+}-doped glass ceramic. We demonstrate a net transient optical gain in a pump and probe experiment in a bulk glass ceramic. Moreover, we show that Ho^{3+} ions can be used to obtain optical amplification at this wavelength region.

The precursor glass was prepared from a homogeneous powder mixture with the following compositions in mol %: 30 SiO_2, 15 Al_2O_3, 29 CdF_2, 22 PbF_2, 1.5 YF_3, and 2.5 HoF_3. The glass was obtained by melting the powder at 1050 °C for 2 h 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 470 °C for 24 h. X-ray diffraction measurements have confirmed the formation of nanocrystals of the β-PbF2 phase.[12]

The Ho^{3+} ground state absorption (GSA) $^5I_8 \rightarrow {}^5S_2$:$^5F_4$ is centered at about 545 nm. When the sample is irradiated at 532 nm, using a frequency-doubled Nd:YAG (yttrium aluminum garnet) pulsed laser, a nonresonant 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 1.6 mm long, due to the relatively low absorption at 532 nm. For that reason, the intensity of the pump beam can be considered to be a 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 fluo-

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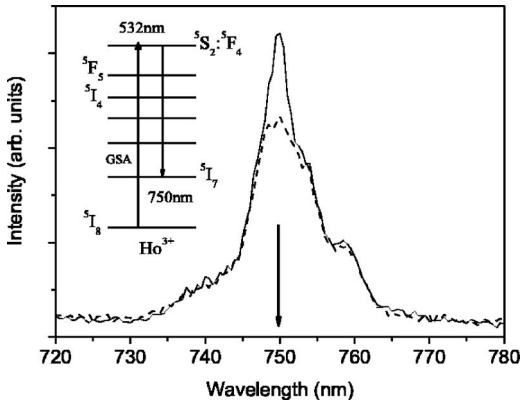

FIG. 1. Emission spectrum associated to the Ho^{3+} $^5S_2$:$^5F_4 \rightarrow {}^5I_7$ transition under pump excitation at 532 nm (dashed line) and under simultaneous pump and probe excitation (solid line). The arrow indicates the probe wavelength. The inset shows a schematic diagram of the pumping.

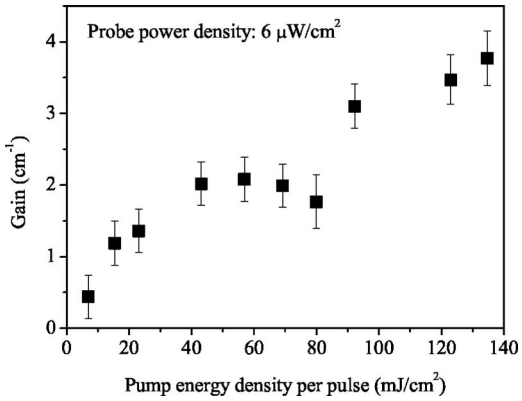

FIG. 2. Optical gain of the Ho^{3+}-doped glass ceramic as a function of the pump energy density per pulse when the probe power density is fixed at 6 μW/cm^2.

ride 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 centred at 750 nm (see the inset of Fig. 1). In order to determine if a net transient optical gain is possible in this material, the following pump and probe experiment has been designed. The end-polished sample was pumped with high energy pulses of about 5 ns of duration at 532 nm and the probe, or signal, was provided by a cw tunable Ti:sapphire laser. Homogeneous pump and signal beams were obtained after a 3 mm 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 the diverging and converging lenses. 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 20° 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 1.6 mm 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.

Evidence of signal amplification is shown in Fig. 1. 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 solid line gives the emission measured under the same pump conditions when the signal beam is present. The wavelength of the signal beam is indicated by an arrow. The steady-state background signal 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 750 nm to the sides of the spectrum, the position of the intensity enhancement is shifted accordingly. In fact, the increment of the luminescence in the pump and probe experiment compared to the pump measurement is due to the stimulated emission at the wavelength of the signal.

In order to determine if a net transient optical gain of the signal is achieved due to the stimulated emission of the medium, the following calculations have been made. The signal was fixed at 750 nm and its density was as low as 6 μW/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,

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

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

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

$$I_{\text{pp}} = I_{\text{p}} + I_0 e^{(g-\alpha)L}, \tag{2}$$

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. The wavelength of the signal beam, 750 nm, matches the $^5I_8 \rightarrow {}^5I_4$ ground state absorption. However, this transition is strongly forbidden. It has been found that it is several orders of magnitude lower than the other electronic transitions and, consequently, the ground state absorption probability at 750 nm is negligible,[13] and α can be disregarded, so that g provides the net optical gain coefficient and Eq. (2) written as

$$I_{\text{pp}} = I_{\text{p}} + I_0 e^{gL}. \tag{3}$$

The signal enhancement (SE) is defined as

$$\text{SE} = \frac{I_{\text{pp}} - I_{\text{p}}}{I_{\text{probe}}}. \tag{4}$$

It can be experimentally measured and is related to the net gain coefficient by

$$\text{SE} = \exp(gL). \tag{5}$$

We have measured the SE parameter just after the pump pulse for a signal power density of 6 μW/cm^2. We have calculated the g coefficient as a function of the pump energy density, and the results are given in Fig. 2. Positive transient optical gain is observed from a pump threshold value of 7 mJ/cm^2. It increases for higher pump energy densities up to a value of above 3.7 cm^{-1} ($\sim$16 dB/cm) for a pump energy density of 135 mJ/cm^2 per pulse. The SE and, conse-

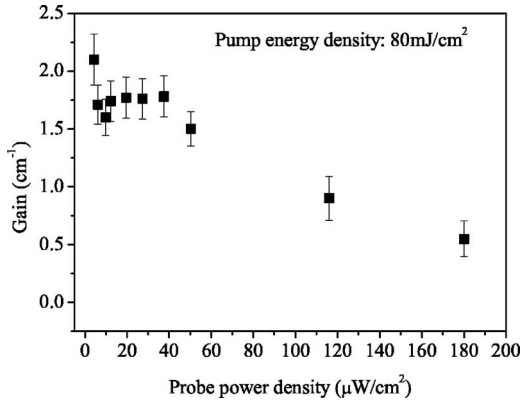

FIG. 3. Optical gain of the Ho^{3+}-doped glass ceramic as a function of the probe power density when the pump energy density per pulse is fixed at 80 mJ/cm^2.

quently, the g coefficient decrease with time after the pump pulse as the $^5S_2:^5F_4$ level population relaxes. 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 Eq. (4) the time dependence of the g coefficient can be derived. It has been observed that the gain drops to $1/e$ times its initial value at about 100 ns due to the quick relaxation of the $^5S_2:^5F_4$ level.

We wish to remind that the excitation wavelength is nonresonant with the $^5I_8 \rightarrow {}^5S_2:{}^5F_4$ GSA. If the excitation could be shifted to the maximum of this transition, around 545 nm, the same gain values would be achieved with a significant reduction in the pump power.

The gain coefficient dependence on the signal power density was also studied and the results are shown in Fig. 3. For this experiment, a pump energy density of 80 mJ/cm^2 was chosen. The transient optical gain shows a stable value for signal beams with a power density up to 40 $\mu W/cm^2$ 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.

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 states of the stimulated emission at 750 nm, respectively) can be made taking into account that the gain coefficient can be expressed as

$$g = \sigma N^*, \tag{6}$$

where σ is the stimulated emission cross section of the $^5S_2:F_45 \rightarrow {}^5I_7$ transition and N^* represents the population inversion between the initial and final states of the transition. If we consider, as an approach, that σ is similar to those found in the literature for different fluoride matrices, a value of 7×10^{-21} cm^2 can be used.[13] In that case, for a gain coefficient of about 3.7 cm^{-1} Eq. (6) gives a population inversion of about 5×10^{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 6×10^{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.

In conclusion, positive transient optical gain has been observed in Ho^{3+}-doped oxyfluoride glass ceramics using the pump and probe technique. A doubled-frequency Nd:YAG pulsed laser oscillating at 532 nm was used as the pump source to strongly populate the Ho^{3+} $^5S_2:^5F_4$ level. Low power laser radiation at 750 nm 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. 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 750 nm signal is observed. A pump energy threshold of about 7 mJ/cm^2 has been estimated to obtain optical amplification. The highest optical gain value was 3.7 cm^{-1}, corresponding to about 16 dB/cm, and was obtained with a pump energy density of 135 mJ/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 transient optical gain at 750 nm 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 750 nm.

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