LETTER TO THE EDITOR

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Letter to the Editor

Red to blue upconversion in Tm-doped sol–gel silicate glasses

Allen P. Otto, Karen S. Brewer, Ann J. Silversmith *

Departments of Physics and Chemistry, Hamilton College, Clinton, NY 13323, USA

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Abstract

In thulium-doped glasses derived from the hydrolysis of orthosilicates we worked with different annealing conditions so as to enhance the fluorescence yield. In addition, we observed blue upconverted fluorescence from both the $^1G_4$ and $^1D_2$ levels of thulium when the glasses were excited with red laser light. Two-step absorption mechanisms with different intermediate levels are responsible for populating the two emitting levels.

Sol–gel chemistry for the synthesis of new materials is becoming increasingly popular because of its relatively simple components and the variety of applications to which it can be applied [1]. The method involves the hydrolysis of a glass precursor – tetraethylorthosilicate (TEOS) or tetramethylorthosilicate (TMOS) for silica glass – in solution, and, therefore, allows for the addition of several additives before the glass is formed. This offers significant advantages over the traditional melt preparation of glass. Silica glasses, doped with trivalent rare earth (RE) ions and prepared by the sol–gel method, are potentially useful in solid state lasers [2]. Recently, sol–gel glasses have gained attention because they can be fabricated at much lower temperatures and they can hold a higher concentration of RE ions without losing the amorphous character of the glass.

Much work has been published on Nd^{3+} and Eu^{3+}-doped sol–gel glasses. Nd^{3+} doped glass is an important laser material so there has been a natural interest in new methods for producing Nd^{3+} doped glass [3]. Sol–gel glass containing Eu^{3+} has proven to be a good probe for investigating the internal character of sol–gel materials with spectroscopic methods [4]. In the present work, we present fluorescence and upconversion measurements in sol–gel glass containing another RE ion, trivalent thulium. Upconversion refers to the emission of photons from energy levels that are higher above the ground state than the energy of the absorbed photons. In order for this to happen, ions absorb two photons – the first absorption populates a metastable intermediate level and the second transition fills the emitting level. This process is called excited state absorption (ESA). Other mechanisms that rely on cooperative energy transfer among RE ions, energy-transfer-upconversion (ETU) and avalanche upconversion, are less common in glasses and we do not observe them in our experiments.

Like several other RE ions (Pr^{3+}, Ho^{3+}, Nd^{3+} and Er^{3+}), Tm^{3+} is known to exhibit upconversion behavior in other host materials. There is much current interest in upconversion in RE based solids because these materials can be used to make

* Corresponding author. Fax: +1-315 859 4696.
E-mail address: asilvers@hamilton.edu (A.J. Silversmith).

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upconversion lasers – lasers that can operate at a higher frequency than their pump sources. Blue upconversion-pumped lasers based on Tm^{3+} in crystals [5] and glass fibers [6–8] have been previously reported in the literature.

Below we describe both the synthesis of the sol–gel materials and the spectroscopic techniques that we use to characterize them. We also present spectra of laser induced fluorescence in a doped sol–gel glass containing Tm^{3+} in which, under red laser excitation, we observe blue emission corresponding to the $^1G_4 \rightarrow {}^3H_6$ and $^1D_2 \rightarrow {}^3F_4$ transitions. We attribute the upconversion to two-step absorption processes involving the $^3F_4$ and $^3H_4$ intermediate levels, respectively.

We have used a modification of the Bray and Lochhead procedure [4] to prepare a variety of RE-doped silica glasses. The thulium-doped sol–gel glasses discussed in this paper were prepared to achieve Tm^{3+} and Al^{3+} dopant levels (by mole) of 0.67% and 1.4%, respectively. In a 50-ml beaker equipped for magnetic stirring, 0.833 g (1.87×10^{-4} mol) of $Tm(NO_3)_3 \cdot 5H_2O$ and 0.144 g (3.83×10^{-4} mol) of $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in 5.16 ml (0.287 mol) deionized water. Propylene oxide (0.24 ml, 3.43×10^{-4} mol), 20 μl concentrated nitric acid, and 4.00 ml of TMOS (99%, 2.71×10^{-2} mol) were then added to the stirred solution. After 10 min, the sol was cast into three tightly capped 12×75 mm polystyrene disposable test tubes and gelled at ambient temperature over 72 h. The gels were heated for 48 h at 60°C after which the temperature was raised from 60°C to 90°C over a period of 7 h and held at 90°C for an additional 48 h. At this point the gels had shrunk to about half of their original volume.

Final densification and formation of the glass was accomplished by heating the gels to 1000°C in air. The heating rate between the soak temperatures of 250°C, 500°C, and 750°C was 1°C/min with 24-h soak times at each of these temperatures. The final heating rate from 750–1000°C was also 1°C/min, but the furnace was turned off and the samples cooled in a closed furnace once 1000°C had been reached. After heating to 1000°C, the monolithic glass samples, measuring approximately 3×15 mm, were clear, colorless, and slightly shrunken from their 90°C size.

Samples of glass were cut and polished for all spectroscopic measurements. For the laser experiments, a cw argon laser was used to excite samples in the blue and also to pump an open cavity dye laser operating with DCM dye. The dye laser linewidth was about 1 cm^{-1} and typical laser powers were 100–200 mW. For the upconversion experiments, a 5 cm focal length lens was used to focus the dye laser beam onto the sample.

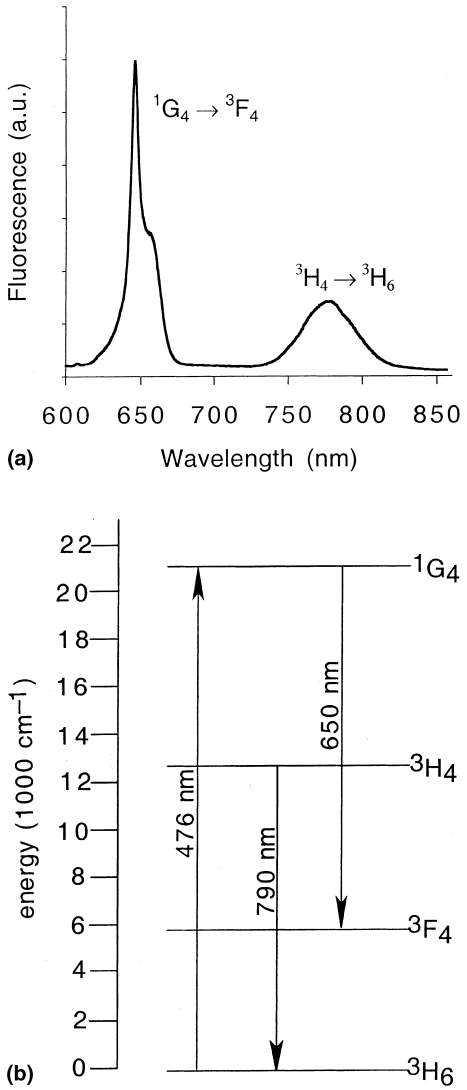

Fig. 1. (a) Emission from Tm^{3+} in sol–gel glass at room temperature under 476 nm excitation; (b) partial energy level diagram of Tm^{3+} showing the absorbing and emitting transitions.

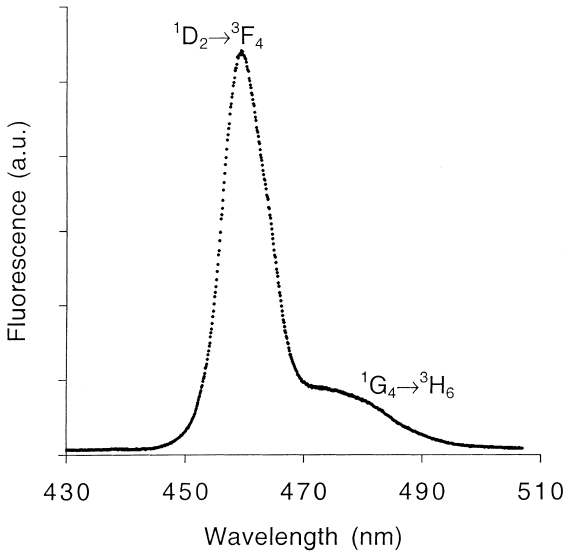

Fig. 2. Room temperature upconversion fluorescence from Tm^{3+} excited at 668 nm. The fluorescence from $^1D_2$ is much stronger than from $^1G_4$.

Fluorescence was collected and sent to a 0.5 m monochromator and then detected by a photomultiplier tube (PMT). The current from the PMT was measured by a pico-ammeter and a voltage signal proportional to the current was sent to a computer through a Vernier analog-to-digital interface. For the transmission spectrum, white light was shone through the sample, and the transmitted light sent to monochromator and detected by the PMT. All measurements were carried out at room temperature.

A significant difference in the fluorescing character of the Tm^{3+} doped glasses was observed between the 800°C samples and the 1000°C samples. Exciting the $^1G_4$ level with an argon laser line – 100 mW at 476 nm – we could not detect fluorescence from glasses that were annealed at a maximum temperature of 800°C. The room temperature spectrum in Fig. 1(a) is from a 1% Tm^{3+} sample ramped to 1000°C and shows red emission corresponding to the $^1G_4 \rightarrow {}^3F_4$ transition. Fig 1(b) has a partial energy level diagram of Tm^{3+} and shows the corresponding excitation and emission transitions. The 476 nm argon line is well matched to the $^3H_6 \rightarrow {}^1G_4$ absorption although the absorption is not very strong – only a few percent through a 1 mm thickness of 1% Tm^{3+} glass.

We have observed a similar marked difference between samples that were annealed at 800°C and samples that were ramped to 1000°C in other RE doped sol–gels [9]. With 1% Pr^{3+} doping, for example, we reported an order of magnitude increase in fluorescence intensity when samples were heated to 1000°C. Similarly, under cw excitation, we were unable to detect emission from Ho^{3+} until the glass was heated past 800°C. It is interesting to note that our samples dwell for 24 h at 800°C but do not dwell at all at 1000°C. (See description of glass preparation above.) Clearly, an important change is occurring in the RE's environment above 800°C that reduces the fluorescence quenching significantly. The presence of residual OH^- is thought to be a primary cause of the quenching and we are currently investigating this further.

Having observed fluorescence from the $^1G_4$ level, we used a red excitation laser to look for upconverted fluorescence from that level. Red excitation of blue fluorescence ($^1G_4 \rightarrow {}^3H_6$) in

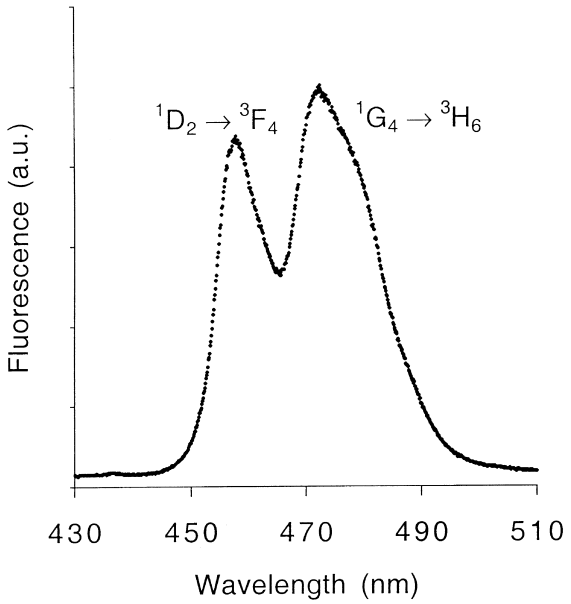

Fig. 3. Upconverted fluorescence from sol–gel produced Tm^{3+}:SiO_2 glass excited at 650 nm. 650 nm is the most effective excitation wavelength for populating the $^1G_4$.

Tm^{3+} has been studied in other materials – crystals [10,11] and glasses [12–14]. Using a red tunable laser as the excitation source, we see two bands of blue fluorescence. The $^1D_2$ and $^1G_4$ levels at 28 000 cm^{-1} and 21 000 cm^{-1} respectively are the emitting levels for the two bands. The emission spectra are shown in Figs. 2 and 3, with the spectrum in Fig. 3 magnified by a factor of two relative to the spectrum shown in Fig. 2. When the samples are cooled to 77 K, the spectral peaks are slightly narrowed, but the overall intensity of the upconverted fluorescence does not change noticeably. We find that as we change the excitation wavelength, the relative amounts of $^1D_2$ and $^1G_4$ fluorescence varies. When the monochromator is set at the peak of the $^1G_4 \rightarrow {}^3H_6$ emission (480 nm), the fluorescence intensity peaks when the excitation wavelength is 650 nm. However, when the $^1D_2$ emission is monitored, the excitation peak shifts; the most effective wavelength for producing upconverted fluorescence from the $^1D_2$ is 668 nm.

We propose two-step absorption as the mechanism for both upconversion excitations, with different intermediate levels. Fig. 4 contains energy level diagrams that illustrate the two-step absorption upconversion mechanisms that populate the two emitting states. These two excitation paths have been seen in other Tm^{3+} hosts – both crystals and glasses – and the photon energies for wavelengths near 650 nm and 668 nm are well matched to the second absorption step transitions: $^3F_4 \rightarrow {}^1G_4$ and $^3H_4 \rightarrow {}^1D_2$ [10,13]. Neither wavelength matches a peak in the ground state absorption spectrum (Fig. 5), so it is clear that ETU is not the upconversion mechanism. As Fig. 5 shows, the $^3H_6 \rightarrow {}^3F_{2,3}$ absorption that peaks at 680 nm is broad enough that the ground state absorption is nonzero at our laser wavelengths. Ions in the ground state absorb laser photons and non-radiative decays populate the intermediate states, both of which have long lifetimes relative to other Tm^{3+} levels. The longer lifetimes allow these levels to accumulate population. Subsequently, ions in these ($^3H_4$ and $^3F_4$) intermediate levels absorb laser photons and become excited to the $^1D_2$ and $^1G_4$ levels that emit the blue fluorescence.

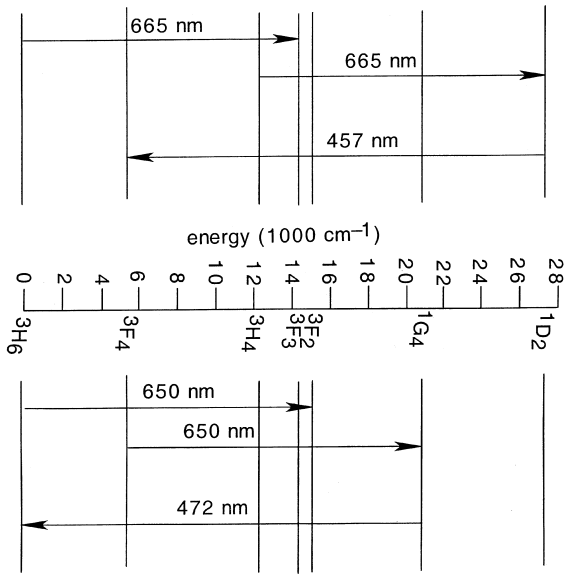

Fig. 4. Energy level diagrams showing the two-step absorption upconversion mechanisms: (a) an excitation laser wavelength of 650 nm favors the excitation of $^1G_4$ while (b) a wavelength of 668 nm favors the excitation of $^1D_2$.

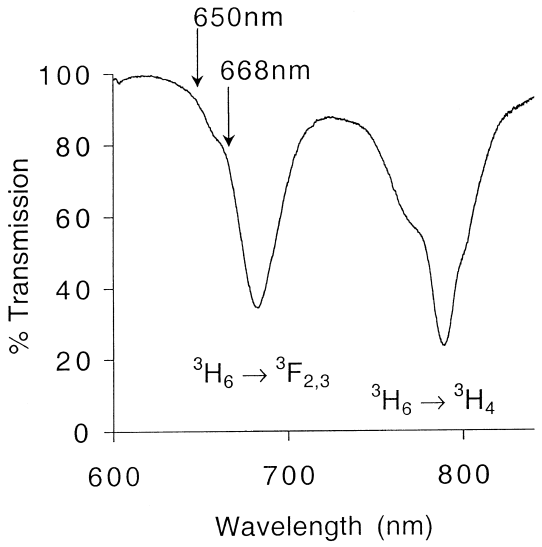

Fig. 5. Transmission spectrum of Tm^{3+} in sol–gel glass generated by monitoring the transmitted light through a 0.5 cm thick sample of 1%Tm doped sol–gel glass. The most effective wavelengths for upconversion excitation are shown.

In summary, we have demonstrated upconversion in a Tm^{3+} doped sol–gel glass. Two-step absorption mechanisms using the $^3H_4$ and $^3F_4$ levels as intermediate levels allow excitation of the $^1D_2$ and $^1G_4$ emitting levels with red laser light. Annealing the glass above 800°C was shown to be essential for the observation of Tm^{3+} fluorescence and we are continuing to investigate the effects of annealing temperatures and conditions. Further investigation will also include the addition of co-dopants for the upconversion experiments.

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