

Upconversion luminescence of transparent Er³⁺-doped chalcohalide glass-ceramics

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ABSTRACT

Upconversion luminescence of Er³⁺ ions in chalcohalide glass and in transparent glass-ceramic samples under continuous wave and pulsed laser excitation in the ⁴I_{9/2} level has been studied. Green and red emissions corresponding to (²H_{11/2}, ⁴S_{3/2}) → ⁴I_{15/2} and ⁴F_{9/2} → ⁴I_{15/2} transitions, respectively, have been observed and attributed to a two photon upconversion process. A significant increase of upconversion luminescence has been observed in the transparent glass-ceramics if compared with the one from the base glass. Moreover, the red emission corresponding to the ⁴F_{9/2} → ⁴I_{15/2} transition is enhanced in the glass-ceramics as compared to the green luminescence from (²H_{11/2}, ⁴S_{3/2}) levels probably due to an increase of the energy transfer processes populating the ⁴F_{9/2} level. The possible excitation mechanisms responsible for this upconversion luminescence are discussed.

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1. Introduction

Rare-earth (RE) doped materials capable of converting infrared radiation into visible light in an efficient way are potential candidates for photonic applications in several areas such as color displays, sensors, detection of infrared radiation, and upconversion lasers [1]. Upconversion luminescence is considered as a promising solution to obtain efficient visible lasers pumped by commercial infrared laser diodes. The upconversion efficiency depends largely on the structure of the energy levels of RE ions and their local environment [2]. To investigate new upconversion materials with high luminescence efficiency, hosts with low phonon energies are required. Chalcogenide glasses based on sulfides, besides low phonon energies (300–400 cm⁻¹) and consequently high quantum efficiencies, show an optical transmission that is blue shifted in the short wavelength side when compared to other chalcogenide glasses. Their suitability to be obtained in fiber form has been demonstrated [3–5] and laser action in neodymium-doped sulfide glass in bulk [6] and fiber [5] has been reported in gallium–lanthanum–sulfide glass. Among many sulfide glasses, the germanium–gallium–sulfide glass system has been studied for its potential as a low phonon energy glass for lasers and fiber optic amplifier appli-

cations [7]. Sulfide glasses, however, usually show a low-energy band gap that causes strong absorption of visible light, which could limit its use in some applications [8]. This drawback is partly circumvented by incorporating ionic compounds like cesium halides, because their strong electronegativity, tends to decrease the delocalization of electrons, which in turn increases the optical band gap. Previous works have demonstrated that chalcogenide glasses can dissolve a large amount of alkali halides such as cesium chloride (CsCl), and still be stable against crystallization [9,10].

Glass-ceramics are a special class of materials in which it is possible to improve mechanical, thermal, or optical properties depending on the glass matrix and the particular crystalline phases. Indeed, photoluminescence efficiency can be greatly improved by generating rare-earth-containing nanocrystals inside the glass-ceramics. As an example oxyfluoride glass-ceramics have generated a great interest because these materials can benefit from the excellent chemical and thermal stability of oxide glasses, and the low phonon energy environment of fluorides [11–14].

In this work we report the infrared to visible upconversion luminescence in glass-ceramics based on chalcohalide glasses in the Ga–Ge–S–CsCl system doped with Er³⁺ ions under excitation in the ⁴I_{9/2} level. We compare the upconversion luminescence obtained from the transparent glass-ceramics with the one obtained from the base glass. Significantly increased green and red upconversion luminescence has been observed from transparent glass-ceramics compared with the base glass. The possible upconversion mechanisms are discussed.

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2. Experimental

The studied samples were prepared with the composition $70\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3\text{-}10\text{CsCl}$ and doped with 0.3% of Er^{3+} ions (3.24×10^{19} ions/cm³). Glass samples were prepared from high purity elements or compounds: Ge (5 N), Ga (6 N), S (5 N), CsCl (3 N) and Er (metallic form) 3 N. Raw materials were weighed and loaded into a silica ampoule which was sealed under vacuum and heated up in a rocking furnace to 850 °C at a rate of 1 °C/min. The mixture was held at this temperature for about 10 h. Then, the ampoule was quenched in water at room temperature and the glass obtained was annealed close to the glass transition temperature to reduce mechanical stress [15]. Glass-ceramic samples were obtained by heating the base glass at 380 °C for 4 h (GC1), 11 h (GC2), 25 h (GC3), and 30 h (GC4). The annealing temperature was between T_g (350 °C) and the crystallization temperature T_x (480 °C).

Glass transition temperature was determined by using a differential scanning calorimeter with a heating rate of 10 °C/min. The DSC curves indicate that the presence of Er^{3+} has a nucleating effect as an intense crystallization peak appears at 480 °C.

Transmission electron microscopy (TEM) was used to demonstrate the presence of nano-crystalline phases in the heated samples. The morphology, size, and quantity of the nanoparticles are similar for the four treated samples. The crystallites are spherical and their average size is around 5 nm. As an example, Fig. 1 shows a dark field image of the GC1 sample. X-ray diffraction patterns of the glass-ceramic samples show that the crystalline phase corresponds to $\alpha\text{-Ga}_2\text{S}_3$.

Conventional absorption spectra were performed with a Cary 5 spectrophotometer. The steady-state emission measurements were made with a Ti-sapphire ring laser (0.4 cm⁻¹ linewidth) as exciting light. The fluorescence was analyzed with a 0.25 m monochromator, and the signal was detected by a Hamamatsu R928 photomultiplier and finally amplified by a standard lock-in technique. The excitation beam was focused on the samples by using a 50 mm focal lens. Lifetime measurements were obtained by exciting the samples with a dye laser pumped by a pulsed nitrogen laser and a Ti-sapphire laser pumped by a pulsed frequency doubled Nd:YAG laser (9 ns pulse width), and detecting the emission with Hamamatsu R928 and R5509-72 photomultipliers. Data were processed by a Tektronix oscilloscope.

3. Results and discussion

The absorption spectra were recorded for all samples at room temperature (RT) in the 400–1700 nm range by using a Cary 5

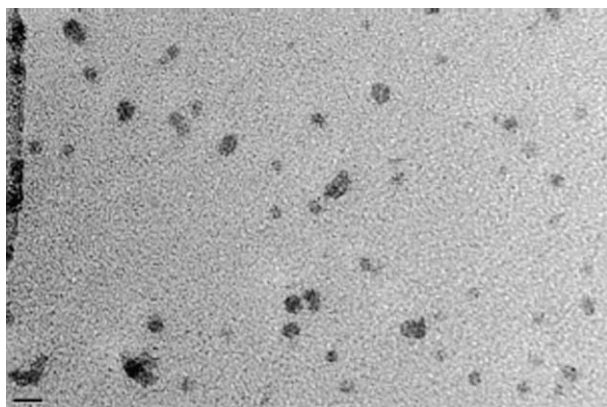


Fig. 1. TEM image in dark field of the sample heat treated at 380 °C for 4 h.

spectrophotometer. As an example, Fig. 2 shows the absorption spectra of the base glass and the GC1 and GC2 samples. The absorption bands are assigned to the transitions from the $^4I_{15/2}$ ground state to the excited states of Er^{3+} ions. As can be seen levels with higher energies than $^2H_{11/2}$ lie in the absorption edge of the samples. The absorption band gap is similar for all samples. Fig. 3 shows a detail of the $^4I_{15/2} \rightarrow ^4I_{13/2}$ absorption band for the glass and glass-ceramic samples after 4 and 11 h treatment. As can be observed, the GC samples show better resolved peaks compared to the glass.

We have observed visible upconversion at room temperature under continuous wave (CW) and pulsed laser excitation in the $^4I_{9/2}$ level. The upconverted emission spectra obtained under CW excitation were measured by using a Ti-sapphire ring laser. Cutoff filters were used to remove the pump radiation. Fig. 4 shows the room temperature emission spectra of the glass and glass ceramic samples after 4, 11, 25, and 30 h heat treatment, respectively. The spectra show the green emissions corresponding to ($^2H_{11/2}$, $^4S_{3/2}$) \rightarrow $^4I_{15/2}$ transitions together with an intense red emission corresponding to the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition. The emission bands become sharper and better resolved in the glass-ceramic if compared to the base glass. Moreover the intensity of the upconversion emission is enhanced by a factor of ≈ 20 in the glass ceramic

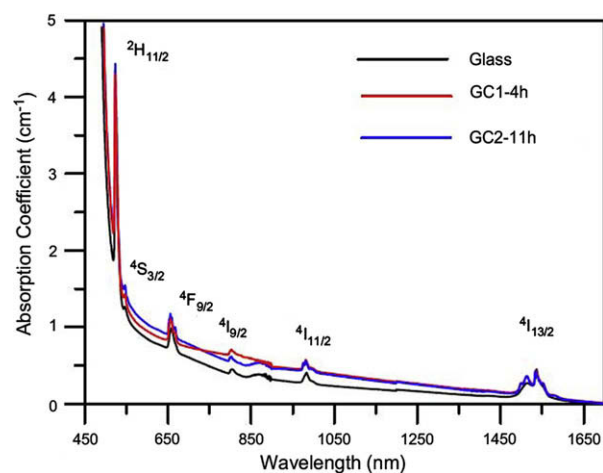


Fig. 2. Room temperature absorption spectra of the base glass and the glass-ceramics heat treated at 380 °C for 4 and 11 h.

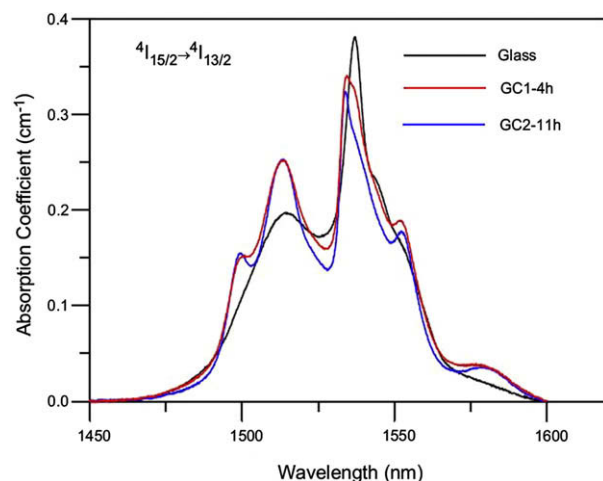


Fig. 3. Room temperature $^4I_{15/2} \rightarrow ^4I_{13/2}$ absorption bands of the base glass and the glass-ceramics heat treated at 380 °C for 4 and 11 h.

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