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1540 nm fiber laser excited upconversion luminescence in erbium-doped lead–fluoride nanocrystals

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ABSTRACT

Upconversion luminescence in erbium-doped $PbGeO_3$–PbF_2–CdF_2-based vitroceramic under 1540 nm infrared excitation is investigated. Luminescence signals around 410, 525, 550, 660 and 850 nm were generated and attributed to the $^2H_{9/2}$, $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ transitions to the $^4I_{15/2}$ ground-state, and $^4S_{3/2}$–$^4I_{13/2}$, respectively. The erbium ions excited-state emitting levels were populated through a combination of stepwise ground-state absorption, phonon-assisted excited-state absorption and cross-relaxation processes. The results also disclosed that all emission signals obtained with vitroceramic samples presented intensities three times higher when compared to the precursor glass samples. In addition, the red emission signal at 660 nm for 1540 nm pumping exhibited an expressively high intensity when compared to the green signal.

1. Introduction

Novel materials suitable for the development of solid-state frequency upconverters based upon rare-earth doped hosts have drawn much scientific and technological interest lately [1–4]. The rare-earth doped solid-state upconverter can find applications in photonic devices including color displays, upconversion lasers, remote sensors, infrared laser viewers and indicators, optical data storage, optical printing, to mention a few. To pursue that objective, it is important to study the frequency upconversion mechanism in alternative hosts and identify the major relaxation and interaction mechanisms of rare-earth ions implanted into the material. Among lanthanide ions which generate efficiently visible and infrared fluorescence, erbium is the most extensively studied. That is because erbium has been used as the active ion for the production of visible upconversion lasers and 3D color displays prototypes [5,6], infrared laser sources around 1.5 μm, in addition to the main application as the gain medium for optical amplifiers in optical telecommunication networks [7–14]. Thus, it is of great deal of interest the development of novel solid-state hosts capable of producing efficient frequency upconversion processes.

Concerning solid-state hosts, vitroceramics have recently emerged as a viable glassy alternative for photonic devices applications [15]. They are produced by means of a suitable heat treatment of samples obtained by standard oxide glass fusion and casting methods [15–18]. Such heat treatment yields the precipitation of nanocrystals in which rare-earth ions are selectively concentrated [16–19]. The crystal sizes are small enough to allow light transmission with no considerable scattering loss. The advantages of the vitroceramics reside in the fact that the rare-earth doping ions are confined in crystalline environments of low phonon-energy, yielding large excited-state lifetimes and optical absorption cross sections as compared to vitreous surroundings. Moreover, the glass host matrices possess the durability and mechanical properties of an oxide glass. In this work upconversion luminescence spectroscopy in Er^{3+}-doped $PbGeO_3$–PbF_2–CdF_2 vitroceramic excited by a laser source around 1540 nm to generate intense blue, green, red, and NIR radiation, is experimentally investigated.

2. Experimental

Erbium-doped vitroceramic samples were obtained after an appropriated heat treatment of the mother-glass with a composition of $60PbGeO_3$–$10PbF_2$–$30CdF_2$ in mol%. The glasses were prepared with reagent grade PbF_2 and CdF_2 and glassy $PbGeO_3$.

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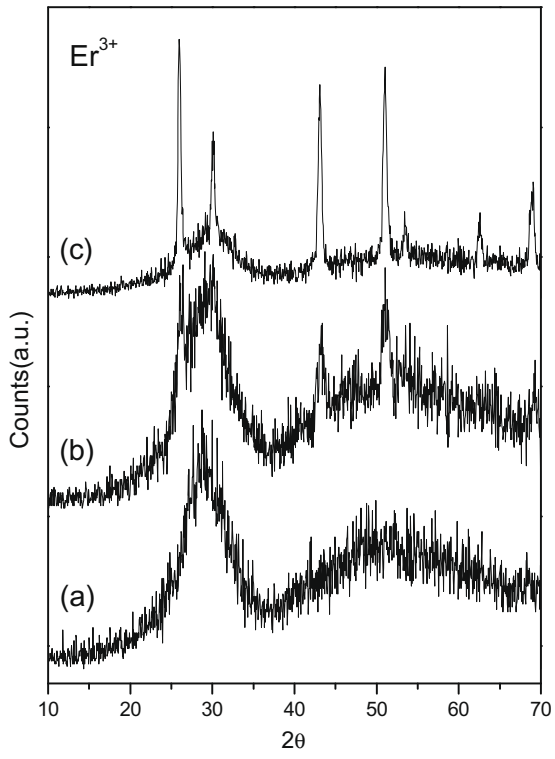

Fig. 1. X-ray diffractograms for an Er^{3+}-doped sample for glass (a), and for vitroceramics treated for 2 h (b), and 60 h (c) at 324 °C .

Starting reagents were mixed in an agate mortar using *n*-heptane as homogenizing medium. After melting in an open Pt–Au crucible at 800 °C for 30 min in air, liquids were quenched at room temperature in graphite molds. Some 30 min annealing treatments at temperatures around the glass transition were performed. Rare-earth ions were introduced in the form of oxides. Starting $PbGeO_3$ glass was obtained using PbO and GeO_2 mixed and melted at 800 °C for 30 min and quenched to room temperature between two copper plaques. Heat treatment was carried out at the temperatures defined by the near T_g exothermic effects given by differential scanning calorimetry (DSC) curves [20,21]. For treatments with time intervals of up to 60 h samples remained transparent and the diffractograms have shown the reflections peaks expected from crystalline particles. Typical samples prepared after 0.1, 0.5, and 1.0 mol% doping of Er^{3+} and treated during 15 h at 360 °C and presenting crystals immersed in the amorphous material, with no observable clustering and a size distribution of 5–10 nm, were obtained. The samples were approximately 1.0 mm thick and the excitation source was a 1064 nm pumped Er^{3+}/Yb^{3+}-codoped optical fiber laser [7] which delivered 1540 nm radiation with a maximum average power of 10 mW. The erbium-doped vitroceramic samples present very good optical quality, stability against atmospheric moisture, and it exhibit low optical attenuation in the spectral region of interest. The material also exhibits good solubility allowing the incorporation of suitable lanthanide concentrations apart from being non-hygroscopic and possess high mechanical and chemical stability. The fluorescence signal was collected and dispersed by a 0.34 m scanning spectrograph with operating resolution of 0.5 nm and detected by a S-20 uncooled photomultiplier tube. Phase detection was used for data acquisition and storage. All measurements throughout our experiment were performed at room temperature. For treatments with time intervals of up to 60 h samples remained fully transparent and side with halo pattern, the X-ray diffractograms depicted in Fig. 1(a)–(c), have shown the reflections peaks expected from crystalline particles. Fig. 2 shows a transmission electronic microscopy

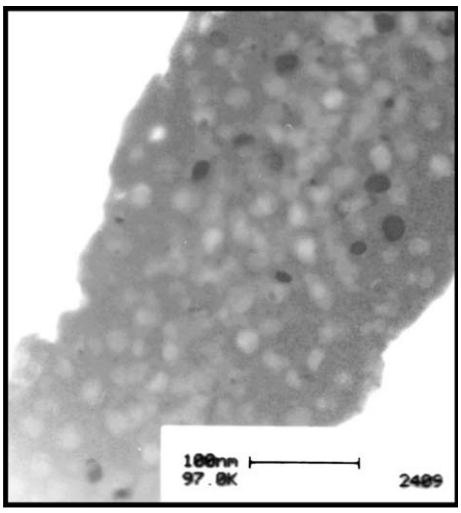

Fig. 2. TEM micrography obtained for the transparent Er^{3+}-doped sample submitted to a 60 h heat treatment 324 °C.

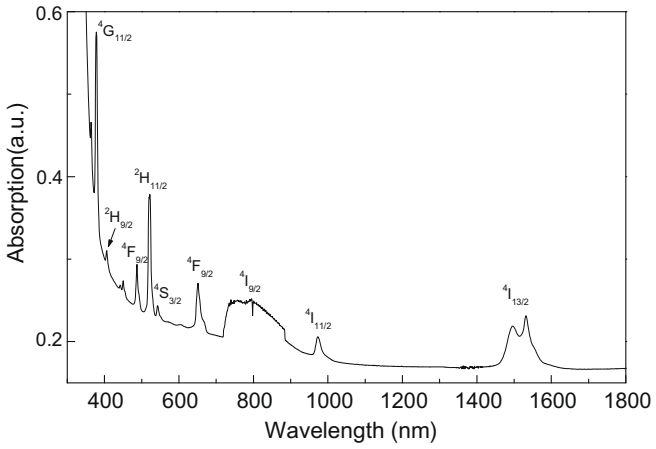

Fig. 3. Absorption spectrum for the erbium-doped vitroceramic sample

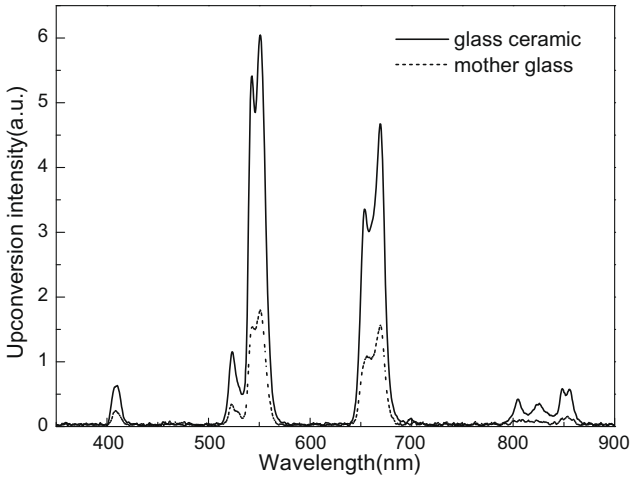

Fig. 4. Spectra of visible–NIR emission emanating from the samples with a fixed excitation power of 10 mW at 1540 nm.

(TEM) micrograph obtained for an Er^{3+}-doped sample treated for 60 h at 324 °C. The low optical attenuation in the spectral region of interest is indicated by the absorption spectrum depicted in Fig. 3.