



Blue–green cooperative upconverted luminescence and radiative energy transfer in Yb³⁺-doped tungsten tellurite glass



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ABSTRACT

Ytterbium-doped tungsten tellurite glasses have been prepared and studied their cooperative upconverted luminescence and radiative energy transfer properties. In a 3.0 mol% Yb₂O₃-doped glass, near-infrared emission band is peaked at around 977 nm with a full width at half maximum of around 15 nm. This glass emits blue–green upconverted emission under 980 nm excitation due to cooperative processes involving two interacting Yb³⁺ ions. The upconverted emission band is centered at around 502 nm with a bandwidth of around 45 nm. Power dependence of cooperative emission intensity and the temporal evolutions of the near-infrared and blue–green emissions confirm the presence of cooperative luminescence. Photoluminescence and lifetimes have been measured by moving the laser excitation from one edge of the sample and found that radiative energy transfer is predominant in 3.0 mol% of Yb₂O₃-doped glass. The absorption coefficient obtained from absorption spectrum is in good agreement with that obtained by fitting the curve of luminescence intensity versus distance from the edge of the sample.

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1. Introduction

Tellurite based glasses are of scientific and technical interest due to their unique properties such as relatively low phonon energy, high refractive index, good infrared transmittivity, low glass transition and melting temperatures and good thermal and chemical stabilities [1]. On the other side, Ytterbium (Yb³⁺)-doped materials have potential technological applications since they may generate tunable lasers in the infrared region from 920 to 1060 nm and visible blue–green emission at about 500 nm by means of cooperative effects [2]. There are only two manifolds in the Yb³⁺ energy level scheme, the ²F_{7/2} ground state and the ²F_{5/2} excited state multiplets. Thus the lack of intermediate levels and the large separation between the excited and the ground state manifolds significantly reduces nonradiative decays.

Cooperative luminescence (CL) is a process in which two interacting Yb³⁺ ions in the ²F_{5/2} excited state decay simultaneously to the ground state, emitting one photon at twice the energy of single ion transition. It is a special type of electronic transition occurring in a spectral region where the individual ions

do not have absorption or emission transitions. It was first observed by Nakazawa and Shionoya in 1970 for Yb³⁺ in YbPO₄ crystalline powder [3]. Since then there were many studies on CL of Yb³⁺ ions in crystals [4–6], glasses [2,7,8], glass-ceramics [9–11] and phosphors [12–14]. The CL depends on phonon energy of the host, Yb³⁺ ions inter-ionic distance, edge of the transmission window in the visible region and laser power employed for excitation. The blue–green CL around 500 nm of Yb³⁺ ions has a considerable advantage over the similar emission of Tm³⁺ ions for 3-D display technology as the Yb³⁺ ions require only one laser pumping beam in the near-infrared (NIR) region [11]. In addition, the CL finds potential applications in scintillators, optical bistability, planar lasers for optical devices in telecommunications and as structural probe in solids [2].

Radiative energy transfer or luminescence self trapping, first observed for Yb³⁺ ions in glasses [15] and theoretically studied by Auzel et al. [16], is a process in which photons that are spontaneously emitted from the metastable level are trapped by reabsorption by other rare earth ions in the ground state. These excited state ions then relax by spontaneously emitting more photons which are again reabsorbed and the entire process is repeated. This leads to increase in fluorescence lifetime, as measured over the volume of the sample, relative to the lifetime of a single

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isolated ion [17,18]. Radiative energy transfer, which occur due to overlapping of absorption and emission bands, can also change the profiles of fluorescence spectrum [19–22].

In the present study, Yb^{3+} -doped tungsten tellurite glasses with two different concentrations (0.1 and 3 mol%) have been prepared and studied their absorption, NIR and cooperative upconversion spectra. The glass with concentration of 3 mol% Yb_2O_3 is found to emit CL under 980 nm excitation. Reabsorption or radiative energy transfer has also been studied in 3 mol% Yb_2O_3 -doped glass by moving the laser excitation from one edge of the sample and measuring photoluminescence (PL) spectra and lifetime of the $^2\text{F}_{5/2}$ excited state, since larger changes are expected in it compared to lower doped glasses.

2. Experiments

Tungsten tellurite glasses of composition (mol%), $70\text{TeO}_2-(25-x)\text{WO}_3-5\text{ZrO}_2-x\text{Yb}_2\text{O}_3$, ($x=0.1$ and 3 ; labeled as TWZYb01 and TWZYb30) were prepared by melt quenching technique. The purity of Yb_2O_3 starting chemical was 99.9%, purchased from Sigma, USA. The batch composition was melted in an electric furnace at a temperature of 1223 K for 45 min and the melt was poured on a preheated brass mould and air quenched. The glasses were annealed at 573 K for 7 h to remove thermal strains and then cut and polished for optical measurements.

Absorption spectrum was measured on UV-visible-NIR Spectrophotometer (Agilent Technologies Cary 5000). Room temperature NIR emission spectrum was measured by exciting at 910 nm using continuum Titanium sapphire laser (Spectra Physics 3900S) pumped by a 532 nm diode-pumped solid state laser (Spectra Physic Millennia 15 W) and detected with cooled CCD (Newton) coupled to a spectrometer (Shamrock 303). Temporal evolution of NIR luminescence was measured by exciting at 915 nm using a 10 ns Optical Parametric Oscillator (OPO, EKSPLA/NT342/3/UVE) and monitoring emission at 980 nm and the signal was registered and averaged using a digital oscilloscope (Tektronix 2430). CL was measured by exciting at 980 nm using the Ti:sapphire laser and its temporal evolution was measured by exciting at 975 nm using the OPO laser.

The Yb^{3+} ions radiative energy transfer or radiative trapping was examined by monitoring the emission spectral profile with increase in path length through the glass. As shown in Fig. 1, the setup was arranged so as to have a 90° angle between the excitation and detection axes with the sample placed on a translation stage that allows its movement along the detection axis. The arrow indicates the direction and orientation of the sample translation. The sample was placed in a waveguide configuration, i.e. with the narrower side facing the detector and wider side facing the excitation. A $20\times$ microscope objective lens (Mitutoyo, M-Plan NIR, NA:0.4) was used to focus the excitation beam. The detection branch consisted of a 60 mm convergent lens that focused the emission at the tip of an optical fiber (Thorlabs M25L02, spectral range: 400–2400 nm, core diameter 200 μm , NA: 0.22) coupled to

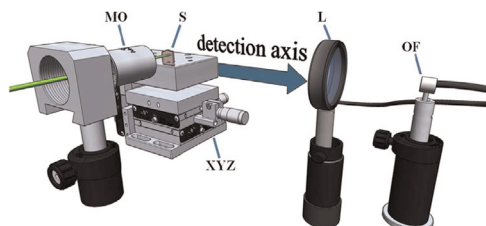


Fig. 1. Experimental setup employed for the determination of the reabsorption processes inside the sample. MO – microscope objective, S – sample, XYZ – translation stage, L – lens and OF – optical fiber.

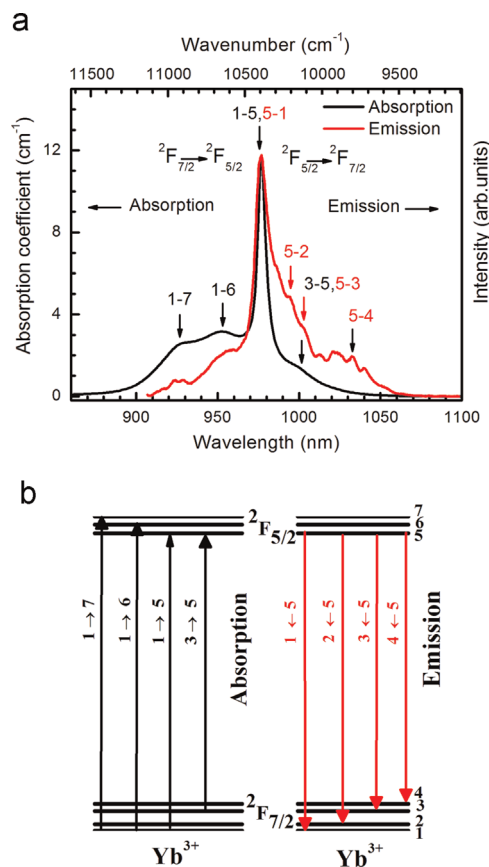


Fig. 2. (a) Absorption and NIR emission spectra of a tungsten tellurite glass doped with 3 mol% of Yb_2O_3 . The Yb^{3+} ions have been excited using a cw 910 nm laser radiation. (b) Energy level diagram of the Yb^{3+} ion showing the fine structure of Stark levels of the ground and the excited states. Electronic transitions in absorption and emission between the Stark levels of both multiplets are also shown.

ANDOR CCD spectrophotometer with a 0.3 nm spectral resolution. Spectra were corrected for instrument response.

3. Results and discussion

The absorption spectrum of the TWZYb30 glass is presented in Fig. 2(a). The spectrum consists of four overlapped bands corresponding to transitions (1–7), (1–6), (1–5) and (3–5) from the lowest Stark levels of the ground state $^2\text{F}_{7/2}$ to the three Stark levels of the excited state $^2\text{F}_{5/2}$. The details of Stark levels of ground and excited states along with possible transitions are shown in Fig. 2(b). Out of these, the band at 977 nm, corresponding to transition (1–5) from the lowest Stark level of ground state to the lowest Stark level of excited state, is the most intense one. Typical NIR luminescence spectrum of TWZYb30 glass, obtained by exciting at 910 nm, is also shown in Fig. 2(a). The peak of the band is at 977 nm with a full width at half maximum (FWHM) of 15 nm. The band is the result of overlap of four transitions from the lowest Stark level of the excited state to the four Stark levels of the ground state multiplet and are assigned as (5–1), (5–2), (5–3) and (5–4). From the splittings of absorption and emission bands, it appears that ground multiplet $^2\text{F}_{7/2}$ splits into four Stark levels and the excited multiplet $^2\text{F}_{5/2}$ into three levels indicating that Yb^{3+} ions in the TWZYb30 glass are in a crystal-field with a symmetry lower than cubic [13].

For the TWZYb30 glass, the temporal evolution of NIR luminescence from the excited $^2\text{F}_{5/2}$ state, obtained by exciting at 915 nm using an OPO laser and monitoring the emission at

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