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Journal of Solid State Chemistry 171 (2003) 278–281

JOURNAL OF SOLID STATE CHEMISTRY

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Red–green–blue upconversion emission and energy-transfer between Tm^{3+} and Er^{3+} ions in tellurite glasses excited at 1.064 μm

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Received 24 April 2002; received in revised form 1 August 2002; accepted 3 August 2002

Abstract

Red, green, and blue emission through frequency upconversion and energy-transfer processes in tellurite glasses doped with Tm^{3+} and Er^{3+} excited at 1.064 μm is investigated. The Tm^{3+}/Er^{3+}-codoped samples produced intense upconversion emission signals at around 480, 530, 550 and 660 nm. The 480 nm blue emission was originated from the $^1G_4 \rightarrow {}^3H_6$ transition of the Tm^{3+} ions excited by a multiphoton stepwise phonon-assisted excited-state absorption process. The 530, 550 nm green and 660 nm red upconversion luminescences were identified as originating from the $^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions of the Er^{3+} ions, respectively, populated via efficient cross-relaxation processes and excited-state absorption. White light generation employing a single infrared excitation source is also examined.

Keywords: Visible; Fluorescence; Upconversion; Rare earth; Glass; Energy-transfer; White light

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1. Introduction

For solid-state color-displays based upon infrared-to-visible frequency upconversion in lanthanide doped materials [1], emission and control of the relative intensities of the three primary red, green and blue (RGB) colors is required. Thus, there exists a need for novel solid-state materials capable of producing multicolor visible light. In addition, it is important to study new routes of the frequency upconversion mechanism in alternative host materials and identify the major relaxation and interaction mechanisms of rare-earth ions implanted into it. In recent reports [2], by triply doping a fluoride glass sample with Tm^{3+}, Er^{3+}, and Pr^{3+}, and exploiting the frequency upconversion process [1] excited by two near-infrared lasers with distinct wavelengths, one has produced blue, green, and red light pursuing the realization of a three-dimensional solid-state display. A new approach has recently been proposed for the generation of either blue [3] or multicolor light [4] taking advantage of both, blue cooperative upconversion from pairs of Yb^{3+} ions [3], and energy-transfer upconversion in Yb^{3+}/Eu^{3+}-codoped multicomponent sol–gel-processed silica glass pumped at 973 nm [4], respectively. The generation and control of the three primary colors through frequency upconversion and white light simulation using double excitation in fluoride glasses codoped with Tm^{3+} and Er^{3+}, has recently been reported [5]. Energy upconversion emission by means of energy-transfer and cross-relaxation processes between Tm^{3+} and Er^{3+} ions implanted into different host materials has been extensively studied by many investigators [5–10]. In reports of Refs. [5–10] no evidence of simultaneous generation of red, green and blue emission was presented, particularly using a single infrared pump laser source. Despite the fact that the multiple pump wavelength configuration produces higher upconversion efficiencies, a single-pump scheme is mostly desirable [11]. In this work we present red, green, and blue light emission through infrared pumped frequency

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doi:10.1016/S0022-4596(02)00176-7

upconversion in a new composition of TeO_2-based glasses codoped with Tm^{3+} and Er^{3+}. The feasibility of additive synthesis of primary colors to compose the visible spectrum and white light production is also examined.

2. Experimental

The tellurite glass samples utilized in the experiment had a composition of $60TeO_2$–$10GeO_2$–$10K_2O$–$10Li_2O$–$10Nb_2O_5$ and the samples were either single doped with Er^{3+} or Tm^{3+} ions or double doped with several combinations of the two dopants. Glasses were prepared with high purity (99.9999%) rare-earth oxides and all special care was taken in the lab during the glass preparation in order to avoid contamination. The tellurite-based glass presents very good optical quality, is stable against atmospheric moisture, it exhibits low optical attenuation from 400 nm to 5.0 μm, and due to the >2.0 refractive index, one expects to obtain significantly high radiative decay rates of rare-earth energy levels. The material also exhibits high solubility allowing the incorporation of high lanthanide concentrations apart from being nonhygroscopic and to present high thermal stability against crystallization. The samples were ~2.5 mm thick and the excitation source was a continuous-wave Nd:YAG laser operated at 1.064 μm. The detection system comprised a 0.34 m scanning spectrograph with operating resolution of 0.5 nm equipped with a S-20 uncooled photomultiplier tube for visible wavelength detection and a 0.64 m spectrometer and a germanium photodetector for the infrared spectral region. A lock-in amplifier in conjunction with a storage-scope coupled to a microcomputer was used for data acquisition and storage.

3. Results and discussion

The recorded upconversion emission spectra in the region of 450–850 nm, for single-doped with Er^{3+}, Tm^{3+} and double-doped with Er^{3+}/Tm^{3+} samples under 1.064 μm excitation is presented in Fig. 1(a), (b) and (c), respectively. As can be observed, the spectrum of Fig. 1(a) exhibits the well-known emission bands centered around 530, 550 and 660 nm associated with the $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ transitions to the $^4I_{15/2}$ ground state of erbium ions [12], and the visible emission signals depicted in Fig. 1(b) 485 and 655 nm were assigned to the $^1G_4 \rightarrow {}^3H_6$, and $^1G_4 \rightarrow {}^3H_4$ transitions of ions, respectively [13]. A small contribution to the red signal around 655 nm owing to the $^3F_{2,3} \rightarrow {}^3H_6$ transition is also identified. The near-infrared 800 nm band is assigned to the $^3F_4 \rightarrow {}^3H_6$ transition of the Tm^{3+} [13]. The effect of the efficient cross-relaxation process between Tm^{3+} and Er^{3+} on the intensity of both green $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, and red emission band due to $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition of erbium ions is very pronounced and is illustrated by the spectrum of Fig. 1(c) for the codoped sample, which also simulates white light (red, green, and blue) emission. We have examined the effect of the Tm^{3+} codoping on the Er^{3+} upconversion luminescence signals and the results indicated that the introduction of Tm^{3+} into the Er^{3+}-doped sample yielded a 50-fold increase in the intensity of the green emission around 530, and 550 nm, and a $\times 10^2$ enhancement in the 660 nm upconversion emission band (for a sample doped with 1%Er^{3+} and 2%Tm^{3+}) associated with the erbium $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition, which is the highest enhancement reported

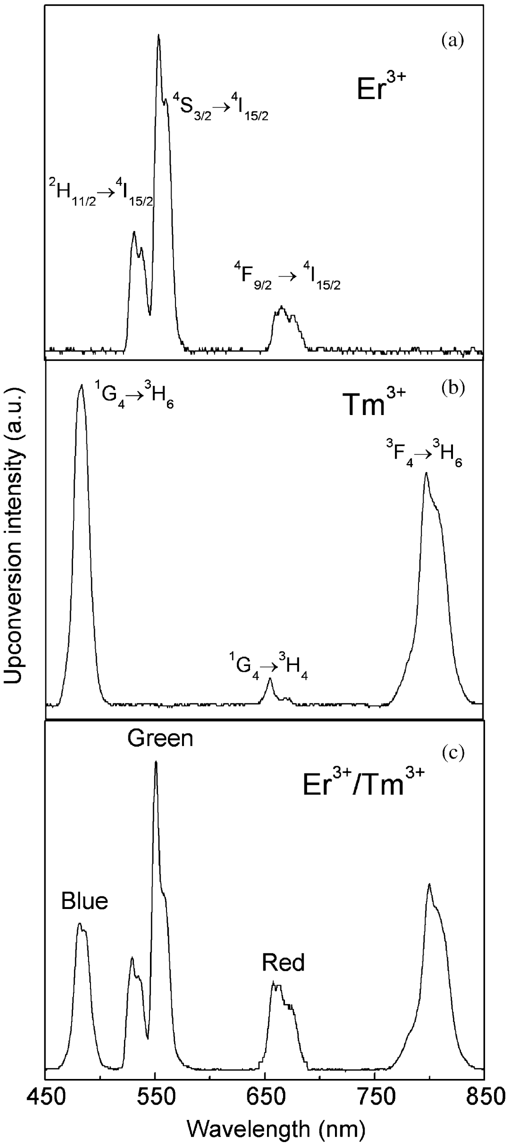

Fig. 1. Room-temperature energy upconversion emission spectra for (a) Er^{3+}-doped, (b)Tm^{3+}-doped and (c) Er^{3+}/Tm^{3+}-codoped samples for an excitation power of 800 mW at 1.064 μm.

to date for this system. The upconversion emission signals due to tullium ions have shown no appreciable changes as the Tm^{3+} concentration increased. The proper choice of the dopant content allows one to obtain upconversion luminescence containing the three fundamental colors with equivalent intensity levels that closely simulates white light. The dependence of the upconversion emission intensities for the red, green, and blue signals upon the excitation power was investigated and a cubic power law behavior was recorded for all samples as shown in the log–log plot of Fig. 2. The results revealed that the upconversion pumping mechanism was accomplished with the participation of at least three pump photons at 1.064 μm in order to populate the excited-state emitting levels of both Tm^{3+} and Er^{3+} active ions.

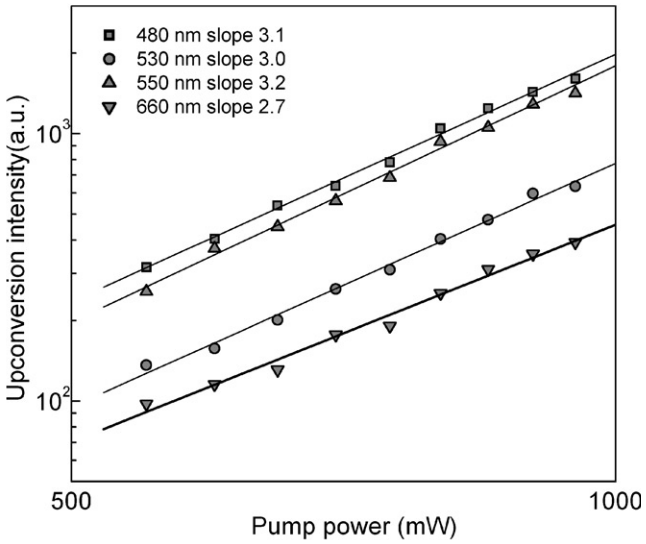

Fig. 2. Log–log plot of the upconversion emission intensity as a function of the excitation intensity.

In order to understand the main upconversion processes involved in the population of the Er^{3+}–Tm^{3+} pair emitting levels, one has to consider the energy-level diagram portrayed in Fig. 3. It is important to mention at this point that either Er^{3+}- or Tm^{3+}-doped samples excited around 1.0 μm generate visible upconversion signals [12,13]. However, the upconversion process for the Er^{3+} single-doped tellurite glass samples pumped around 1.0 μm is quite inefficient demanding massive laser power at 1.064 μm in order to generate detectable visible upconversion emission, as will be shown later in this work. This behavior allow us to discard the contribution of stepwise multiphoton excitation as the upconversion pumping mechanism of the Er^{3+} emitting levels in codoped samples. Despite the relatively weak absorption of thulium ions under excitation around 1.0 μm, efficient upconversion fluorescence bands around 480, 655, and 800 nm in Tm^{3+}-doped tellurite glass samples was recorded as demonstrated in Fig. 1. The population of the excited-states emitting levels in the Tm^{3+} single-doped sample was achieved by means of phonon-assisted sequential multiphoton summation, as pictured in the energy-level

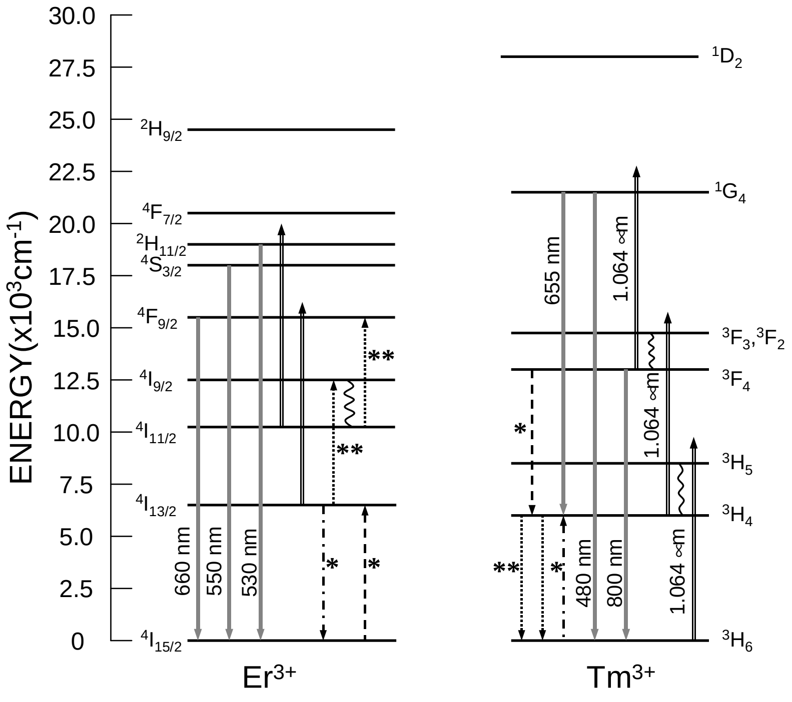

Fig. 3. Simplified energy-level diagram for the Tm^{3+}–Er^{3+} pair pumped at 1.064 μm. The upwards solid double-line arrows indicates pump photons. The asterisks stand for cross-relaxation processes, which enhances the erbium visible emission. The downwards single-line arrows are emitted photons.

diagram of Fig. 3. Pumping at 1.064 μm promotes population from the ground-state $^3H_6$ to $^3H_5$ excited-state, which rapidly nonradiatively decays to the $^3H_4$ level. A phonon-assisted multiphoton stepwise summation process populates the $^3F_4$ and $^1G_4$ levels, which radiatively decay to generate the infrared at 800 nm, and the blue and red signals, respectively [14]. The excitation energy stored in the $^3F_4$ level of Tm^{3+} is transferred nonresonantly to the $^4I_{13/2}$ level of Er^{3+} through the cross-relaxation mechanism $^3F_4(Tm) + {}^4I_{15/2}(Er) \rightarrow {}^3H_4(Tm) + {}^4I_{13/2}(Er)$. As indicated in Fig. 1, a noticeable decrease in the 800 and 480 nm emission intensities takes place as the Er^{3+} content increases in Tm^{3+}-doped samples due to the depopulation of the $^3F_4(Tm)$ caused by cross-relaxation to $^4I_{15/2}(Er)$. From the long-lived $^4I_{13/2}(Er)$ level an efficient excited-state absorption process occurs and promotes the Er^{3+} ions to the $^4F_{9/2}$ excited-state emitting level which radiatively decays to produce the red 660 nm signal. The 660 nm signal can also be generated by an upconversion mechanism which involves a multiphonon relaxation mediated sequential cross-relaxation process $^4I_{13/2}(Er) + {}^3H_4(Tm) \rightarrow {}^4I_{9/2}(Er) + {}^3H_6(Tm)$ and $^4I_{11/2}(Er) + {}^3H_4(Tm) \rightarrow {}^4F_{9/2}(Er) + {}^3H_6(Tm)$. This process has already been attributed to be responsible for the efficient IR-to-red upconversion mechanism in different host materials codoped with Tm^{3+} and Er^{3+} [8–11]. The green emission around 530 and 550 nm, originating from the $(^2H_{11/2}, {}^4S_{3/2}) \rightarrow {}^4I_{15/2}$ transition was accomplished via excited-state absorption from the $^4I_{11/2}$ level. A very important feature of the results herein presented is the 10^2 enhancement of the 660 nm red emission intensity due to Er^{3+} for codoped samples as compared to Er^{3+} single-doped glasses excited around 1.0 μm.

In conclusion, we have demonstrated the simultaneous generation of red, green and blue emission through frequency upconversion in Tm^{3+}/Er^{3+}-codoped tellurite glasses excited by a single infrared laser source at 1.064 μm. Intense fluorescence emission around 480, 550 and 660 nm was recorded. The 480 nm blue signal was attributed to Tm^{3+} ions excited by a stepwise phonon-assisted excited-state absorption process, and the 550 nm green and 660 nm red upconversion luminescences were identified as originating from the Er^{3+} ions populated via efficient cross-relaxation processes and excited-state absorption. A 10^2 enhancement in the 660 nm red emission associated with the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions and sensitized by Tm^{3+} sensitization was also recorded. The three fundamental colors were generated and preliminar results on white light simulation were also presented.

Acknowledgments

The financial support for this research by FINEP, CNPq, PADCT, and PRONEX-NEON (UFPE/UFAL/UFPB), Brazilian agencies, is gratefully acknowledged. Dr. M.V.D. Vermelho was supported by Post-Doctoral studentship from CNPq. The work of F.C. Cassanjes, S.J.L. Ribeiro and Y. Messaddeq is supported by FAPESP-SP—Brazil.

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