Visible light emission under UV and IR excitation of rare earth doped ZrO$_2$ nanophosphor

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Received 8 October 2004; accepted 12 November 2004
Available online 29 January 2005

Abstract

Strong visible emission under UV (320 nm) and IR (967 nm) excitation on ZrO$_2$:Sm$^{3+}$ and ZrO$_2$:Er$^{3+}$ nanophosphors were obtained and the concentration effect on the luminescence and crystalline structure is reported. Experimental results shows that phase composition depend on the ion concentration. The visible emission obtained under UV excitation is produced by the transitions $^4G_{5/2} \rightarrow ^6H_{5/2,7/2,9/2}$ of Sm$^{3+}$ through a non-radiative energy transfer process from the host to the active ion. Energy transfer and quenching effect due to ion concentration was confirmed by measuring the fluorescence decay time. Green (545 nm) and red (680 nm) emissions bands were observed under IR excitation troughs an upconversion process. It was proved that visible emission for both nanophosphor could be tuned by controlling the ion concentration. The nature of this behavior is discussed taking into account the phase composition for ZrO$_2$:Sm$^{3+}$ and two photon absorption and cross-relaxation process was considered for ZrO$_2$:Er$^{3+}$ nanophosphor.

Keywords: Energy transfer; Sol–gel; Zirconium oxide; Nanophosphor; Rare earth; Nanocrystals

1. Introduction

In the field of photonics materials, the demand for high performance systems is increasing everyday. For active applications such as bulk, fiber lasers and planar waveguides the fluorescence quantum efficiency is the key factor controlling the performance of the material. When the number of non-radiative pathways increases, the fluorescence quantum efficiency decreases considerably. One of the most important non-radiative processes that every material shows is the multiphonon relaxation by the vibration bands of the system. When the frequency of this vibration band increases the non-radiative decay rate increases that in turn will reduce the quantum efficiency. The stretching frequency of ZrO$_2$ matrix is about 470 cm$^{-1}$ that is very small compared to that of other hosts. This low phonon energy opens up the possibility of higher efficient luminescence of active ions incorporated into ZrO$_2$ matrix. Furthermore, due to its superior hardness, high refractive index, optical transparency, chemical stability, photothermal stability, high thermal expansion coefficient, low thermal conductivity and high thermomechanical resistance, it can be used in a variety of photonics and industrial applications [1].

Considerable amount of work has been reported on the mechanical and other physical properties of ZrO$_2$, whereas only few research work have been done on the luminescence properties of this material. The reported results on the optical studies include the...
photoluminescence of sol–gel derived amorphous and tetragonal crystalline phase thin films of ZrO2:Eu3+, Tb3+, Sm3+ systems [2,3]. Bulk zirconium oxide has been grown by the Skull method and cubic doped samples have been characterized [4]. More recently, the interest in rare earth doped nanophosphor has been increased. Electrons confinement effect is not expected due the localization of electrons in atomic orbitals of active ions. However, excitation dynamics is influenced by the nanoscopic interaction and has been reported a dependence of the luminescence efficiency with particle size [5,6]. The interest on this new rare earth doped nanophosphor is to produce visible emission for application such as solid state lighting, displays and new generation television screen. In particular, the development of UV LED open up new possibility to obtain visible emission at any wavelength with the proper phosphor that must be developed [7]. Visible emission can also be obtained pumping the nanophosphor with an IR source by upconversion process [8]. This is an interesting approximation considering that IR source is a well developed technology. Using this approximation it is possible to obtain white light for solid state lighting but new nanophosphors with high upconversion efficiency and emission in the basic colors are required. The emission of this kind of nanophosphors is based in two photon absorption process and also finds application in biomedicine [9].

3. Results and discussion

3.1. Visible emission by downconversion in ZrO2:Sm3+

The concentration of the active ion determines the phase composition of the nanocrystals, see Fig. 1. The crystalline structure of ZrO2:Sm3+ nanophosphor annealed at 1000 °C is dominated by the monoclinic structure (98 wt.%) for low ion content (0.2 mol%) and is reduced to 27 wt.% for 2 mol% of active ion being dominant the tetragonal phase; the average crystallite size range from 36 nm to 14 nm for monoclinic and from 54 nm to 42 nm for tetragonal phase. The phase composition and average crystallite size for the crystalline structure was obtained by using the Ritveld method. A full analysis of the crystalline composition and lattice parameter as function of the samarium dopant concentration and annealing temperature has been reported recently [13].

2. Experimental

The samples were prepared by using the sol–gel method. All chemicals were reactive grade and supplied by Aldrich, Inc. Pure ZrO2 was obtained by mixing zirconium n-propoxide (ZP) as precursor in a solution of ethanol (ETOH), nitric and hydrochloric acid at room temperature and vigorous stirring. Doped samples were prepared by adding different molar concentrations (0.2, 1, 1.5 and 2 mol%) and (0.16, 0.98 and 3.46 mol%) of Sm2O3 and Er2O3, respectively. The obtained solution was stirred for 90 min, then CO2-free distilled water in a molar rate of 1/4 was added dropwise to manipulate the gel and oxolation processes. The samples were aged at room temperature, dried at 120 °C for 24 h and annealed at 1000 °C for 10 h.

The crystalline structure of the samples was investigated by X-ray diffraction (XRD), using a Siemens D-500 equipment provided with a Cu tube with Kα radiation at 1.5405 Å. The X-ray spectra were obtained from 20° to 70° with increments of 0.2° and a swept time of 3 s. The optical absorption spectra were measured with a Perkin–Elmer UV–VIS–NIR Lambda 800 by using a 1.5 in. integrating sphere (Labsphere Co.). The fluorescence emission spectra for ZrO2:Sm3+ were obtained with a Perkin–Elmer fluorometer LS50. The upconversion emission of ZrO2:Er3+ was obtained pumping with a diode laser centered at 967 nm and a monochromator (Acton Research) with a resolution of 1 nm with a Hamamatsu Photonics R955 photomultiplier tube connected to a PC was used. All measurements were done at room temperature.

![Fig. 1. XRD for undoped and Sm3+ and Er3+ doped nanocrystalline ZrO2 phosphor annealed at 1000 °C.](image-url)
The absorption spectra of undoped and ZrO₂:Sm³⁺ nanophosphors are shown in Fig. 2. Undoped sample present an absorption band centered at 310 nm and a small shoulder at 375 can be identified. The absorption bands for Sm³⁺ were centered on 405, 420, 468, 477 and 560 nm and were associated to the transition ⁶H₅/₂ → ⁴G₇/₂, ⁴P₅/₂, ⁴I₁₃/₂, ⁴I₁₁/₂ and ⁴G₅/₂, respectively; two absorption bands in the near infrared centered at 942 and 1071 nm corresponding to the transitions ⁶H₅/₂ → ⁴F₁₁/₂,₉/₂ were observed, in addition to the corresponding absorption band of the host. Two important facts must be noted, the blue-shift of the host absorption band from 310 nm to 260 nm as the ion concentration increases and the absence of absorption band of the ion at 320 nm. Fig. 2 also shows the energy levels of the host and the active ion. Here, it is indicated the band gap of the host for monoclinic, ≈4.0 eV (310 nm) and tetragonal ≈4.7 eV (260 nm) structure.

The photoluminescence emission under excitation at 320 nm for both undoped and samarium doped nanophosphor is shown in Fig. 3a. A broad bandwidth signal emitted with the maximum intensity centered at 490 nm was observed for undoped sample. This emission is produced by the non-radiative relaxation of one electron, excited from the valence to the conductive band, to one luminescent recombination site (LRS) and then the luminescent recombination from LRS to the valence band. The broad bandwidth indicates the existence of a recombination band (RB) within the band gap of the host. The signal emitted for ZrO₂:Sm³⁺ nanophosphor is composed by the characteristic emission band of the host and three emission bands corresponding to the transition ⁴G₅/₂ → ⁶H₅/₂ (562, 569, 579 nm), ⁴G₅/₂ → ⁶H₇/₂ (599, 607, 614, 619 nm) and ⁴G₅/₂ → ⁶H₉/₂ (648, 657, 665, 673 nm) characteristic of the Sm³⁺ ion; the splitting of each band is due to the stark effect of the ⁴G₅/₂ state. Considering that no absorption band at the pumping wavelength was observed for samarium ion, these three emission bands were produced.
by energy transfer from the host to the ion. The host emission band overlaps several of the absorption bands of the active ion suggesting the possibility of energy transfer from the host (donor) to the dopant ion (acceptor). Once the host absorbs the pumping energy, part of the electrons decay radiatively producing the emission centered at 490 nm and part decay non-radiatively transferring its energy to the dopant. Electrons from the dopant ion are promoted to different energy levels and/or decay non-radiatively to the lowest sublevels of \( ^4G_{5/2} \) state that in turn decay radiatively to the ground state \( ^6H_{5/2} \) producing the characteristic emission. This explains the reduction of the host emission band intensity and the samarium emission. The relative intensity ratio of the host emission to the acceptor emission \( (I_d/I_a) \) diminishes with the increment of ion concentration as consequence of the little diminishes of the host emission and increment of the ion emission. This effect is reverted after certain concentration due to the quenching effect of the dopant ion. Ion concentration affects the intensity of the signal emitted but not the structure of the signal.

By pumping directly the ion (408 nm) and by changing the ion concentration it is possible to change the structure of the signal emitted by the dopant ion, see Fig. 3b. In this case, electrons were promoted to the \( ^4G_{7/2} \) energy level to decay non-radiatively to \( ^4G_{5/2} \) that in turn decay radiatively to the ground state \( ^6H_{5/2} \) producing the characteristic emission. The emission lines from each band were quenched and only one weak signal was enhanced that become the main line as the ion concentration increases. The main line is centered at 569 nm for the transition \( ^4I_{15/2} \rightarrow ^4I_{11/2} \) of \( \text{Er}^{3+} \). The visible emission was observable at the naked eye and the spectra are shown in Fig. 4a. The proposed upconversion mechanism is described in the energy diagram of Fig. 4b and is as follow. The population in the \( ^4I_{11/2} \) level decays partly non-radiatively to the \( ^4I_{13/2} \) level and then relaxing to the ground state producing the well known signal centered at 1.55 \( \mu \)m; and partly is promoted to the \( ^4F_{7/2} \) level by two-photon absorption (TPA) due to excited state absorption (ESA) and energy transfer (ET) among neighboring \( \text{Er}^{3+} \) ions. Once the

The absorption bands of ZrO\(_2\):Er\(^{3+}\) nanophosphor show the characteristic bands of Er\(^{3+}\) ion in addition to the absorption band of the host. This band is shifted to UV as the concentration increases and is due to the major content of the tetragonal structure. Visible, green and red, emission band by the upconversion mechanism of ZrO\(_2\):Er\(^{3+}\) were observed. In this case, samples were excited at 967 nm for the transition \( ^4I_{15/2} \rightarrow ^4I_{11/2} \) of Er\(^{3+}\). The visible emission was observable at the naked eye and the spectra are shown in Fig. 4a. The proposed upconversion mechanism is described in the energy diagram of Fig. 4b and is as follow. The population in the \( ^4I_{11/2} \) level decays partly non-radiatively to the \( ^4I_{13/2} \) level and then relaxing to the ground state producing the well known signal centered at 1.55 \( \mu \)m; and partly is promoted to the \( ^4F_{7/2} \) level by two-photon absorption (TPA) due to excited state absorption (ESA) and energy transfer (ET) among neighboring \( \text{Er}^{3+} \) ions. Once the

3.2 Visible emission by upconversion in ZrO\(_2\):Er\(^{3+}\)

As is expected, the presence of erbium ion determines the phase composition, see Fig. 1. For low concentration of dopant the dominant structure is the monoclinic phase. But, as the Er\(^{3+}\) ions concentration increases the monoclinic content diminishes while the tetragonal content increases obtaining a mixture of both crystalline phases. The tetragonal content is 4.3 wt.% for 0.16 mol%, 6.5 wt.% for 0.98 mol% and 59.6 wt.% for 3.46 mol% of dopant. No evidence of any other crystalline phase was observed. The average crystallite size range from 17.5 to 67.5 nm for tetragonal and from 46.3 to 28.7 nm for monoclinic from lowest to highest dopant concentration, respectively.

![Fig. 4. (a) Fluorescence emission of ZrO\(_2\):Er\(^{3+}\) nanophosphor excited at 967 nm. (b) Energy diagram for Er\(^{3+}\) ion showing the proposed mechanism for upconversion process.](image-url)
$^4F_{7/2}$ is populated, multiphonon relaxation processes populate the mixed $^2H_{11/2} + ^4S_{3/2}$ and the $^4F_{9/2}$ levels that in turn decay radiatively to the ground state producing the green and red emission band, respectively. The change in the intensity of the green and red emission band, as the ion concentration increases, could be explained in terms of the cross-relaxation process (CR). Cross-relaxation ($^2H_{11/2} + ^4S_{3/2} \rightarrow ^4I_{13/2}$) becomes important at higher concentration, in this case levels $^4I_{9/2}$ and $^4I_{13/2}$ become populated, see Fig. 4b. Level $^4I_{9/2}$ is partly depopulated by decaying to the ground level producing the band centered at 780 nm, and partly relaxed non-radiatively, via multiphonon relaxation, to the lower levels $^4I_{11/2}$ and $^4I_{13/2}$. For the population on the $^4I_{13/2}$ level, the electrons could decay radiatively to the ground state or could follow an upconversion promotion above the $^4F_{9/2}$ level via the ET process ($^4I_{13/2} + ^4I_{11/2} \rightarrow ^4F_{9/2} + ^4I_{15/2}$) among neighboring ions. Assuming the later process takes place the overall result will be an enhanced red emission from the $^4F_{9/2}$ and an increased quenching of the green luminescence from the mixed $^2H_{11/2} + ^4S_{3/2}$ level. As can be observed, for higher Er$^{3+}$ concentration it is clear the strong quenching of the green band whereas the red one still as an increasing emission. Thus, the behavior of the spectra shown in Fig. 4 suggests that the enhanced emission from the red band in fact follow the CR + ET mechanism described above. This is a remarkable result since implies that in ZrO$_2$:Er$^{3+}$ we can control the red or green upconversion emission by controlling the Er$^{3+}$ concentration.

The dependence of the signal emitted as function of the pump power is analyzed in order to verify our hypothesis described above. Experimental results, see Fig. 5, were fitted by the equation $I_{upc} = kI^n_p$, where $I_{upc}$ and $I_p$ stand for the upconverted and pumping signal, respectively, and $n$ is an integer denoting the number of photons required to excite the corresponding emitting level. It is clear for all samples and for both bands the existence of two regimes in the dependence of the upconverted signal. The change indicates that equilibrium situation has been reached. Notice that for 0.16 and 0.98 mol% of dopant the equilibrium was reached at 580 mW, but the equilibrium for 3.46 mol% was obtained at 380 mW. By the way, for pumping intensity lower than 580 mW and 380 mW for the corresponding sample, the slope of each curve denote the number of photons required to produce such emission. The best fit for green emission band range was $n = 2.0$, $n = 1.9$ and $n = 1.7$ from lower to higher concentration, respectively, indicating a two photon absorption process that is in agreement with the discussion above. For the red band, the slope change with ion concentration, $n = 1.9$ for 0.16 mol%, $n = 1.7$ for 0.98 mol% and $n = 1.3$ for 3.46 mol% of dopant, that also agree with the discussion above. It means, for low ion concentration $^4F_{9/2}$ energy level is fed non-radiatively by the mixed level $^2H_{11/2} + ^4S_{3/2}$ that require two photons absorption to be populated. However, for higher ion concentration CR become much more important to feed the $^4F_{9/2}$ level and by this process only one photon is required to populate such level. The slope value higher than one indicate that such level still receiving electrons from the mixed levels $^2H_{11/2} + ^4S_{3/2}$.

4. Conclusion

Visible emission pumping with UV light (320 nm) by non-radiative energy transfer from the luminescent sites of the host to the samarium ion and by upconversion process pumping at (967 nm) were obtained. It was also shown that the ion concentration stabilize the tetragonal structure of ZrO$_2$ at 1000 °C. Tetragonal structure prove to be important to tune the visible emission by pumping directly the active ion at 408 nm. In the upconversion process, visible emission can be tuned controlling the Er$^{3+}$ concentrations. These results suggest the possibility of tuning the visible emission by controlling the ion concentration opening a lot of possibilities for photonic applications under UV and NIR excitation source. Because of its superior luminescence characteristics rare
earth doped ZrO$_2$ can be considered as a good candidate for photonics applications.

Acknowledgments

This work was partially supported by CONACyT, México through Grant 43168-F and G34629-E.

References