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Upconversion luminescence of Er^{3+}-doped YSZ single crystals

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Abstract

The upconversion luminescence of erbium-doped yttria stabilized zirconia single crystals was studied upon excitation in the near-infrared region inside the $^4I_{9/2}$ level. Direct excitation in the visible region was also carried out. A strong green luminescence from the $^4S_{3/2}$ level, and a less intense red emission from the $^4F_{9/2}$ level, were observed for both visible and upconversion excitations. Absorption measurements and direct site-selective emission measurements revealed the presence of different types of optical Er^{3+} centers. Pulsed and continuous IR excitation experiments show that different optical centers undergo upconversion processes. Cw infrared excitation, compared with both pulsed infrared excitation and direct visible excitation, seems to be a more sensitive site-selective technique. High power continuous excitation 'saturates' the upconverted emission, while high power pulsed excitation increases the rate of the upconversion luminescence. It is concluded that the upconversion mechanisms are not the same for high power pulsed and continuous excitation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Optical properties; Luminescence

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1. Introduction

Infrared-to-visible upconversion luminescence is of great interest for a wide range of applications, including sensors, infrared quantum counters, and the development of visible lasers. Conversely, in applications where a high excited state population is required, upconversion processes are undesirable.

Because of the rich energy level scheme of Er^{3+}, multiphoton processes leading to upconversion emission have been observed, under different excitation wavelengths, in many Er^{3+}-doped hosts such as fluorides [1], silicates [2], chlorides [3], oxides [4,5], and others. Upconversion laser emission was observed in several hosts such as $LiYF_4$ [6] and ZBLA fibers [7]. The most common upconversion mechanisms are excited-state absorption (ESA) and energy transfer (ETU).

Yttria stabilized zirconia (YSZ) is a cubic solid oxide with remarkable mechanical, thermal, electrical, and optical properties. Most of its properties are related to the presence of structural oxygen vacancies, induced when yttrium cations are added to zirconia oxide to stabilize the cubic fluorite phase. Single crystals doped with rare-earth ions have been studied in recent years because of their useful optical properties [8,9]. Laser action has been reported when several rare-earth ions (Er^{3+}, Nd^{3+}, Tm^{3+} or Ho^{3+}) were incorporated in this matrix [10]. Due to the presence of oxygen vacancies, the impurity ions can be located in a large number of sites with different oxygen coordination and/or symmetry. In Er^{3+}-doped YSZ single crystals, three environments (eight-fold, seven-fold and six-fold coordinations) have been reported [11,12], with the amount of ions in each site depending on the crystal composition.

In this paper, we present a study of the visible (red and green) upconversion luminescence in YSZ:Er^{3+} single crystals, in the temperature range 15 to 300 K, under excitation in the near-infrared region (776 to 813 nm). The samples were pumped with either a continuous or a pulsed Ti:sapphire laser. The luminescence spectra were compared with those obtained under excitation with either a continuous Ar^+ laser or a dye pulsed laser. Pumping-power dependence measurements were also carried out. The possible excitation mechanisms responsible for the upconversion processes are discussed.

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2. Experimental procedures

Cubic single crystals of ZrO_2 stabilized with 16 wt.% of Y_2O_3 and doped with 7360 ppm of erbium were purchased from CERES (USA). The crystals were grown by the skull technique.

Optical absorption measurements in the UV–VIS–IR were performed with a Perkin-Elmer Lambda 19 spectrophotometer. For luminescence experiments, one of the following four lasers was used: (1) as visible-excitation sources, either an LSI pulsed dye laser with a pulse width of about 3 ns, or a cw Spectra Physics Ar^+ laser; and (2) as infrared-excitation sources, either a pulsed Spectra Physics (Tsunami) Ti:sapphire laser with a pulse width of 1.2 ps, or a cw Lexel 710 Ti:sapphire laser. The emitted light was focused onto the entrance slit of a SPEX 1000M monochromator, detected with a Hamamatsu R943-02 cooled photomultiplier tube, and recorded with a Stanford SR400 gated photocounter. For low temperature measurements, the samples were cooled in a He closed-cycle Leybold cryostat.

3. Results and discussion

3.1. Optical absorption measurements

Fig. 1 shows the room-temperature absorption spectrum of a YSZ:Er^{3+} single crystal. The absorption bands were labeled by comparison with previous data [11]. The structure of the bands reveals the presence of several optical centers. This is particularly clear for the $^4I_{15/2}$→$^4S_{3/2}$ transition, at about 542 nm, since this level does not split in a cubic crystal field, and the observed band is formed by at least three contributions. The energy-level diagram derived from the absorption spectrum reveals a series of energetic equally spaced multiplets, which allows for either efficient ETU or ESA processes to take place.

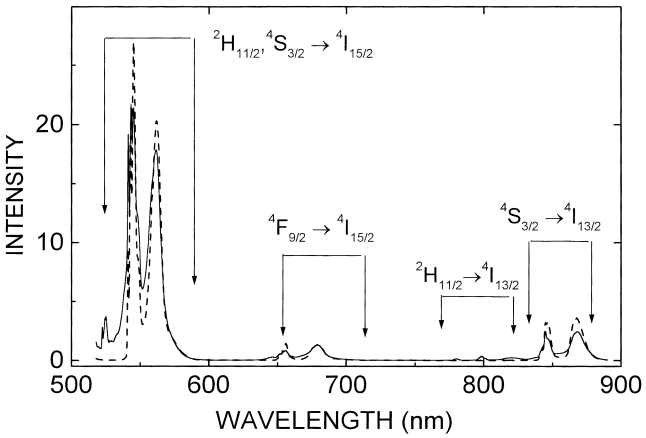

Fig. 2. Luminescence spectra excited with a continuous Ar^+ laser (λ_{exc} = 515 nm) at 300 K (———) and 20 K (- - -). Levels involved in the transitions are indicated.

3.2. Direct luminescence

The emission spectra measured under excitation in the $^2H_{11/2}$ multiplet with the 515 nm line of a cw Ar^+ laser at $T = 20$ and 300 K are shown in Fig. 2. The three groups of lines correspond to $^2H_{11/2}$, $^4S_{3/2}$→$^4I_{15/2}$ (≈520–600 nm), $^4F_{9/2}$→$^4I_{15/2}$ (≈640–690 nm) and $^2H_{11/2}$, $^4S_{3/2}$→$^4I_{13/2}$ (≈760–890 nm). At low temperature, the transitions starting at the $^2H_{11/2}$ level disappear and the relative intensity of the transitions from the $^4F_{9/2}$ level decreases. The former indicates that the $^2H_{11/2}$ level is thermally populated, and the latter indicates thermally assisted relaxation from the $^4S_{3/2}$ to the $^4F_{9/2}$ level. No emission associated with the $^4I_{9/2}$→$^4I_{15/2}$ transition was observed. Similar emission spectra, with small changes in the relative

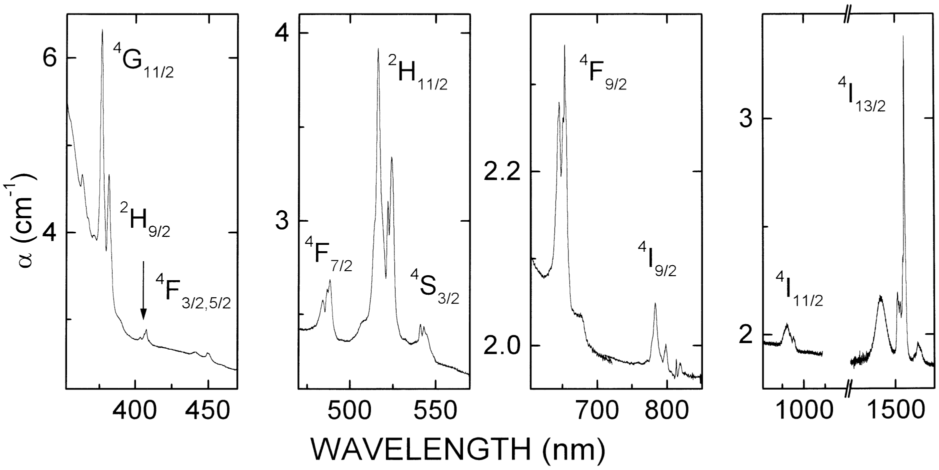

Fig. 1. Room-temperature absorption spectrum of a YSZ:Er^{3+} single crystal. The starting level is $^4I_{15/2}$. Final levels are labeled.

intensity of some peaks, were obtained by excitation with the 477 and 488 nm Ar^+ laser lines.

Emission from the $^4I_{9/2}$ level is only present in host materials with low phonon energy [13]. The energy gap between the lower crystal field level of $^4I_{9/2}$ and the highest crystal field level of $^4I_{11/2}$ is $\approx$1900 cm^{-1}. Since the average phonon energy for YSZ crystals is $\approx$520 cm^{-1} [11], only four phonons are needed to bridge this gap. Thus, the $^4I_{9/2}\rightarrow{}^4I_{11/2}$ multiphonon relaxation is the main deexcitation mechanism of the $^4I_{9/2}$ level.

In order to identify the contribution of different optical centers, emission measurements were performed by pumping the sample with a tunable dye laser. Emission spectra were recorded with the excitation wavelength ranging from 505 to 520 nm (inside the $^2H_{11/2}$ absorption band), and from 530 to 550 nm (inside the $^4S_{3/2}$ absorption band). Two different emission spectra were observed (Fig. 3) for excitation with either 519 and 549.5 nm or 516 and 545.5 nm, indicating the presence of two different centers. The emission spectra, obtained upon excitation with either the Ar^+ laser or other dye laser wavelengths, are due to the contribution of both types of centers.

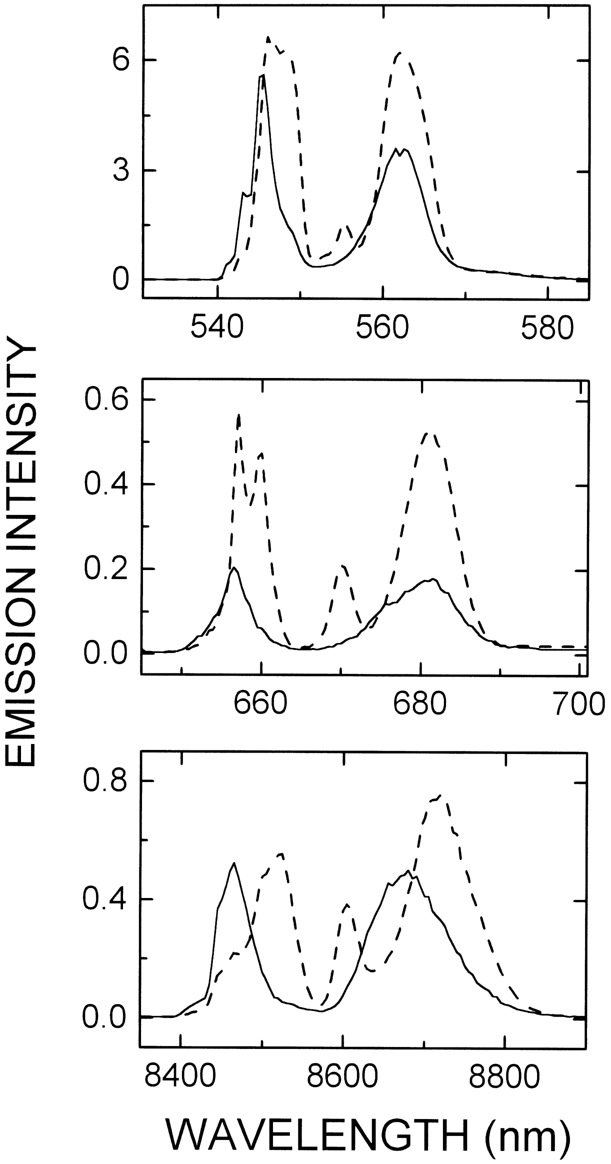

Fig. 3. Luminescence spectra under excitation with a pulsed dye laser at $T = 20$ K for two selected excitation wavelengths: $\lambda_{exc} = 516$ nm (——) and $\lambda_{exc} = 519$ nm (- - -).

3.3. Upconversion luminescence

Upconversion luminescence measurements in the visible region were performed under excitation inside the $^4I_{9/2}$ absorption band for selected wavelengths ranging from 776 to 813 nm. Either a pulsed or a continuous Ti:sapphire laser was used as pumping source. A strong green emission and a less intense red emission, associated with the $^2H_{11/2}$, $^4S_{3/2}\rightarrow{}^4I_{15/2}$ and with the $^4F_{9/2}\rightarrow{}^4I_{15/2}$ transitions, respectively, were observed.

3.3.1. Pulsed infrared excitation measurements

The upconversion luminescence was studied for the excitation wavelengths 777, 780, 801 and 814 nm. With the exception of 801 nm wavelength, there were no significant differences between the upconversion and the direct luminescence. A typical spectrum ($\lambda_{exc} = 780$ nm) at $T = 20$ K is shown in Fig. 4a. In addition, the temperature dependence of the upconverted emission intensity was similar to that observed by direct excitation in the visible region.

Under excitation with 801 nm light, the upconverted and the direct spectra differ strongly (Fig. 4b). There are two main differences: (1) the shape of the spectrum in the green region (540–570 nm) is similar to that observed under visible excitation with 519 nm (see Fig. 3), and (2) the red emission intensity increases relative to the green luminescence.

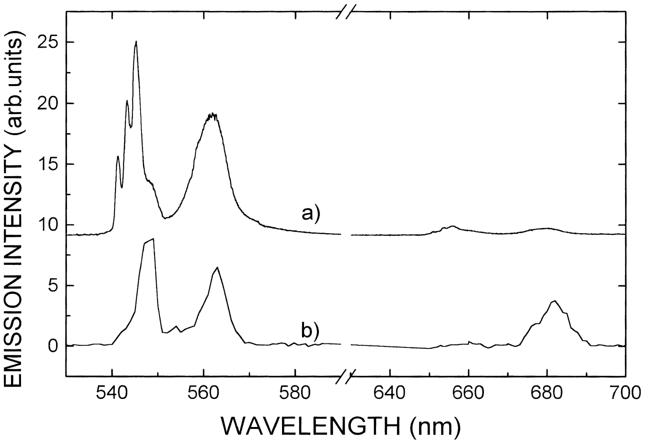

Fig. 4. Upconverted luminescence spectra at $T = 20$ K in the green and red regions, under excitation with a pulsed Ti:sapphire laser for two excitation wavelengths: (a) $\lambda_{exc} = 780$ nm and (b) $\lambda_{exc} = 801$ nm.

3.3.2. Cw infrared excitation measurements

Under continuous IR excitation, both green and red upconverted emissions were observed. The green upconversion was studied upon cw excitation with 780.2, 786.2 and 800.4 nm. The low temperature luminescence spectra are shown in Fig. 5. A strong dependence of the upconverted emission on the pumping wavelength was observed. The existence of different types of Er^{3+} centers was demonstrated in Section 3.2 under dye laser excitation; here, cw infrared excitation induces a site-selective upconversion.

The emission spectrum under 786.2 nm excitation (Fig. 5b) is quite similar to that obtained on excitation with 519 nm light (see Fig. 3). In contrast, direct excitation inside the $^4S_{3/2}$ or $^2H_{11/2}$ absorption bands does not produce an emission band similar to that obtained under cw 800.4 nm excitation (see Fig. 5c).

Pulsed or cw excitation with 780 nm wavelength produces the same green emission (Figs. 4a and 5a). On the contrary, pulsed or cw excitation under 800 nm wavelength yields different emission shapes (Figs. 4b and 5c). These results suggest that the upconversion mechanisms are different for pulsed and for cw excitation. In addition, cw infrared excitation seems to be a more sensitive site-selective technique.

The dependence of the emission intensity on the excitation power was measured for both green and red upconverted luminescences at $T = 20$ K under either continuous or pulsed excitation with 780 nm. The results are depicted in Fig. 6. For low excitation powers, the emission intensities show the same dependence for both continuous and pulsed excitation. At excitation powers greater than ≈ 1 W, the dependence of the emission intensity varies with the excitation source. For continuous excitation, a 'saturation' is observed, i.e. the dependence of the upconverted luminescence on pump power decreases in slope with increasing power excitation [14]. On the contrary, upon pulsed excitation the emission intensity increases with pump power. This behavior is more marked for the green than for the red emissions. The slope of the luminescence intensity versus pump power in a double logarithmic plot provides information on the number of pump photons required to excite the emitting levels. For low power excitation, the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ emissions exhibit slope values of 1.4 and 1.2, respectively, suggesting that a cross-relaxation process and more than one photon are responsible for the population of the $^4S_{3/2}$ and $^4F_{9/2}$ levels. For high power continuous excitation, the competition between upconversion and linear decay for depletion of the intermediate excited states results in a decreasing slope [14], and in a 'saturation' effect. High power pulsed excitation measurements indicate that, under these pumping conditions, the upconversion mechanisms must be different, involving different upconversion processes and/or different kinds of centers, only excited at high power.

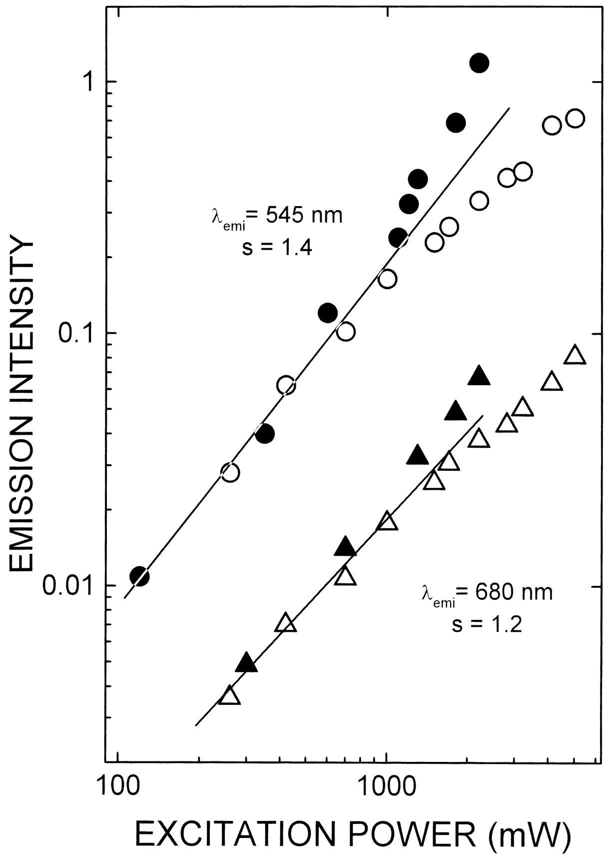

Fig. 6. Power dependence of the intensity of some upconverted luminescence transitions: $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (circle) and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (triangle). Solid symbols, pulsed excitation; open symbols, cw excitation. Excitation wavelength: 780 nm. The slope values of the linear fits are also shown.

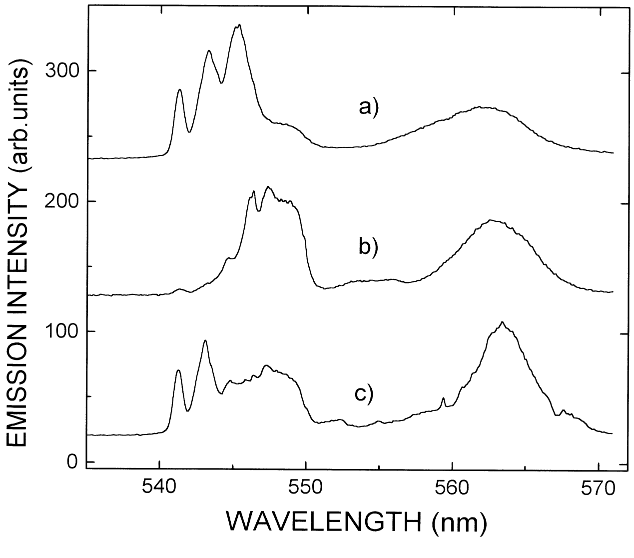

Fig. 5. Upconverted luminescence spectra in the green region (20 K), under excitation with a cw Ti:sapphire laser: (a) $\lambda_{exc} = 780.2$ nm, (b) $\lambda_{exc} = 786.2$ nm, and (c) $\lambda_{exc} = 800.4$ nm.

4. Conclusions

Erbium-doped YSZ single crystals exhibit a green ($^4S_{3/2}\rightarrow{}^4I_{15/2}$) and a red ($^4F_{9/2}\rightarrow{}^4I_{15/2}$) emission bands when excited in the visible region. Optical absorption and direct site-selective emission measurements reveal the presence of different types of optical Er^{3+} centers. Under excitation in the near-infrared region inside the $^4I_{9/2}$ level, upconversion luminescence is observed. Pulsed and continuous IR excitation measurements with different wavelengths and pumping powers were performed. The dependence of the emission spectra on the excitation wavelength reveals that upconversion processes occur in different optical centers. Cw infrared excitation, compared with both pulsed IR excitation and direct visible excitation, seems to be a more sensitive site-selective technique. For low power excitations, the dependence of the upconversion emission intensity on the pumping power is the same for both types of excitation sources. The resulting slopes are 1.4 and 1.2 for the green and red emissions, respectively, indicating that the upconversion mechanism is the same for both excitation sources. On the contrary, in the high power excitation range, cw excitation 'saturates' the upconverted luminescence, and pulsed excitation increases the slope of the log–log plot. These results indicate that, for pulsed infrared excitation, different mechanisms of upconverted luminescence operate for each power range.

Acknowledgements

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