

# Upconversion luminescence of an insulator involving a band to band multiphoton excitation process

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**Abstract:** A multiphoton process to the conduction band of the insulator Er<sub>2</sub>O<sub>3</sub> is reported, which occurs in vacuum under near infrared excitation. The enormous upconversion intensity is two orders of magnitude greater than that in air, and also the intensity ratio for green and red emission bands is inverted. The mechanism is probed by experiments of laser power dependence, cathodoluminescence, photoconductivity dependence and chemical dilution, and it involves cross-relaxation energy transfer upconversion of erbium ions to reach the conduction band. The upconversion color is tunable by changes in pressure, laser diode intensity and wavelength, or dopant ion concentration.

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## References and links

1. E. Desurvire, *Erbium-Doped Fiber Amplifiers: Principles and Applications* (John Wiley & Sons, 1994).
2. F. Auzel, "Upconversion and anti-Stokes processes with f and d ions in solids," *Chem. Rev.* **104**(1), 139–174 (2004).
3. D. Casanova, C. Bouzigues, T.-L. Nguyen, R. O. Ramodiharilafy, L. Bouzahir-Sima, T. Gacoin, J. P. Boilot, P.-L. Tharaux, and A. Alexandrou, "Single europium-doped nanoparticles measure temporal pattern of reactive oxygen species production inside cells," *Nat. Nanotechnol.* **4**(9), 581–585 (2009).
4. D. R. Gamelin and H. U. Gudel, "Upconversion processes in transition metal and rare earth metal systems," *Top. Curr. Chem.* **214**, 1–56 (2001).
5. S. Sivakumar, F. C. van Veggel, and M. Raudsepp, "Bright white-light through up-conversion of a single NIR source from sol-gel-derived thin film made with Ln<sup>3+</sup>-doped LaF<sub>3</sub> nanoparticles," *J. Am. Chem. Soc.* **127**(36), 12464–12465 (2005).
6. F. Wang, Y. Han, C. S. Lim, Y. Lu, J. Wang, J. Xu, H. Chen, C. Zhang, M. Hong, and X. Liu, "Simultaneous phase and size control of upconversion nanocrystals through lanthanide doping," *Nature* **463**(7284), 1061–1065 (2010).
7. E. Beurer, J. Grimm, P. Gerner, and H. U. Gudel, "New type of near infrared to visible photon upconversion of Tm<sup>2+</sup>-doped CsCaF<sub>3</sub>," *J. Am. Chem. Soc.* **128**(10), 3110–3111 (2006).
8. C. Cao, W. Qin, J. Zhang, Y. Wang, P. Zhu, G. Wei, G. Wang, R. Kim, and L. Wang, "Ultraviolet upconversion emissions of Gd<sup>3+</sup>," *Opt. Lett.* **33**(8), 857–859 (2008).
9. S. Schietinger, L. S. Menezes, B. Lauritzen, and O. Benson, "Observation of size dependence in multicolor upconversion in single Yb<sup>3+</sup>, Er<sup>3+</sup> codoped NaYF<sub>4</sub> nanocrystals," *Nano Lett.* **9**(6), 2477–2481 (2009).
10. W. Kaiser and C. B. Garrett, "Two-photon excitation CaF<sub>2</sub>: Eu<sup>2+</sup>," *Phys. Rev. Lett.* **7**(6), 229–231 (1961).
11. D. Jia, L. Liu, and W. M. Yen, "Erbium energy levels relative to the band gap of gadolinium oxide," *Opt. Commun.* **212**(1-3), 97–100 (2002).
12. W. S. Mallory, "The distribution of energy in the spectrum of erbium oxide," *Phys. Rev.* **14**(1), 54–66 (1919).
13. Z. L. Wang, H. L. W. Chan, H.-L. Li, and J. H. Hao, "Highly efficient low-voltage cathodoluminescence of LaF<sub>3</sub>:Ln (Ln=Eu<sup>3+</sup>, Ce<sup>3+</sup>, Tb<sup>3+</sup>) spherical particles," *Appl. Phys. Lett.* **93**(14), 141106 (2008).
14. H. L. Li, Z. L. Wang, S. J. Xu, and J. H. Hao, "Improved performance of spherical BaWO<sub>4</sub>: Tb<sup>3+</sup> phosphors for field-emission displays," *J. Electrochem. Soc.* **156**(5), J112–J116 (2009).

15. P. A. Tanner and K. L. Wong, "Synthesis and spectroscopy of lanthanide ion-doped  $\text{Y}_2\text{O}_3$ ," *J. Phys. Chem. B* **108**(1), 136–142 (2004).
  16. C. K. Jørgensen, H. Bill, and R. Reisfeld, "Cathodoluminescence of rare earth," *J. Lumin.* **24-25**, 91–94 (1981).
  17. J. Wang and P. A. Tanner, "Upconversion for white light generation by a single compound," *J. Am. Chem. Soc.* **132**(3), 947–949 (2010).
  18. C. Brandt, S. T. Fredrich-Thornton, K. Petermann, and G. Huber, "Photoconductivity in Yb-doped oxides at high excitation densities," *Appl. Phys. B* **102**(4), 765–768 (2011).
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## 1. Introduction

The lanthanide ion erbium,  $\text{Er}^{3+}$ , is well known for its optical communication applications [1] and two-photon upconversion processes [2] with a quantum efficiency surpassing values for other  $\text{Ln}^{3+}$  ions [3]. The mechanisms are mainly based upon excited state absorption (ESA), energy transfer upconversion (ETU) and photon avalanche (PA) for  $\text{Er}^{3+}$  or  $\text{Er}^{3+}$ ,  $\text{Yb}^{3+}$  ion co-doped systems [2,4]. Efforts to improve the quantum efficiency of upconversion have largely focused upon the selection of a suitable host for this activator ion. Oxide and fluoride host lattices, such as  $\text{LaF}_3$ ,  $\text{Y}_2\text{O}_3$  and  $\text{NaYF}_4$  are well studied since their relatively low phonon frequencies inhibit nonradiative pathways [5]. Here, we report a novel multiphoton upconversion to the conduction band of  $\text{Er}_2\text{O}_3$  which occurs in vacuum under near infrared (NIR) excitation and which results in an enormous increase in intensity and obvious change in emission spectra. The upconversion emission color can be tuned by pressure, laser diode intensity, excitation wavelength, or chemical modification.

The lanthanides are long known as the *lighting elements* and the present article illuminates their burgeoning importance. Concerning their upconversion investigations, the following topics have been of wide interest in recent years: tuning upconversion nanoparticles by lanthanide doping to access a wide emission range from the visible to near infrared regions [6], utilizing the transitions of highly excited 5d [7] or  $4f^N$  [8] energy levels; and producing white light upconversion by the combination of several  $4f^N$ - $4f^N$  transitions of lanthanide ions [5]. Most importantly, the improvement in upconversion efficiency has been enthusiastically pursued by different means, such as by using noble metal surface plasmon-enhancement [9]. The three basic upconversion mechanisms have not previously been utilized to excite lanthanide ion electrons to the conduction band *via* a multiphoton process. Part of the reason for this is that the multiphoton upconversion efficiency decreases dramatically when compared with a two photon process [10]. As a move in these directions, we present in this work the upconversion luminescence of  $\text{Er}_2\text{O}_3$  involving a band to band multiphoton excitation process. In vacuum, the green and red upconversion and near infrared (NIR) emission were observed to be more than two orders of magnitude stronger than in air. The upconversion mechanism involves excitation from within the valence band (VB) to the conduction band (CB) with the simultaneous production of photoconductivity, as also shown by the dependence of upconversion emission intensity upon incident laser power. This mechanism is expected to be applicable to other lanthanide sesquioxides with interband metastable states of the  $4f^N$  configuration.

## 2. Experiments

The purity of crude lanthanide oxide powders obtained from American Elements (USA), International laboratory (USA) and Sigma-Aldrich (Germany) was from 99.99% to 99.999%. The samples were mounted in a closed chamber pumped by a vacuum pump (BOC Edwards), whose maximum vacuum is 0.02 mbar. The upconversion and NIR emissions as well as the time-resolved intensity evolution of the spectra were measured by an Edinburgh 920 instrument using 975 nm laser diode excitation. The beam diameter was 1 mm and the maximum power of 1 W represents  $50 \text{ W cm}^{-2}$ . Cathodoluminescence was measured under a pressure of  $\sim 0.1$  mbar and recorded by Ocean Optic USB 4000 fiber optic spectrometer. The luminance for  $\text{Er}_2\text{O}_3$  excitation in vacuum and the Commission Internationale de L'éclairage (CIE) coordinates were measured by PR-670 SpectraScan Spectroradiometer. The powder was pressed into thin slab (0.2 mm thickness) for the photoconductivity measurements, and then mounted between two copper alloy electrodes in vacuum. The laser beam irradiated the

edge of slab through the window of the chamber. A Keithley 6517A electrometer was used as the voltage supply and resistance detector.

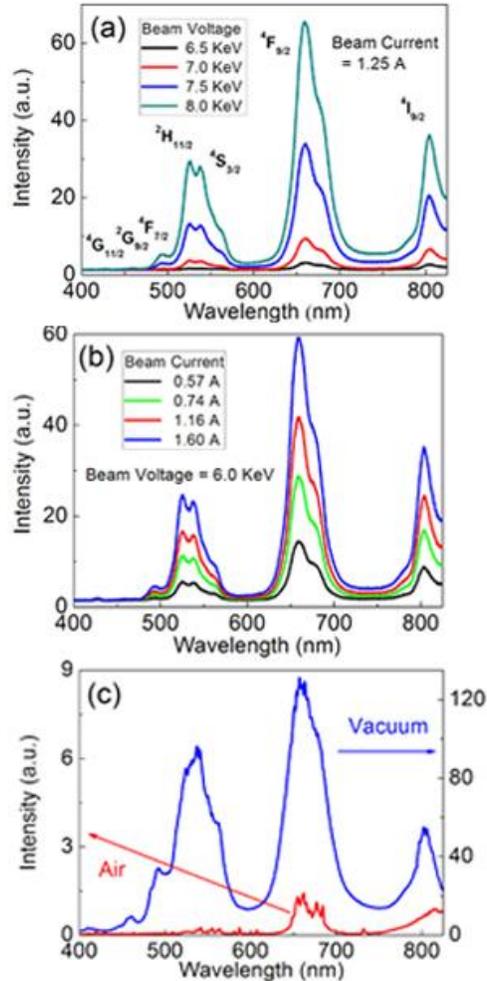


Fig. 1. Luminescence of  $\text{Er}_2\text{O}_3$  powders between 400 and 825 nm. (a) Cathodoluminescence (CL) intensity versus beam voltage under 1.25 A beam current. (b) CL intensity versus beam current under 6.0 keV beam voltage. (c) 975 nm excited upconversion luminescence in air or vacuum under 750 mW irradiation.

### 3. Results and discussion

#### 3.1 Comparison of luminescence under cathode-ray and near infrared excitation

Electron-beam excitation may produce orders-of-magnitude greater carrier generation rates than optical excitation, and it is advantageous in studies of wide band-gap materials. The band gap of  $\text{Er}_2\text{O}_3$  is located at  $5.0 \pm 0.6$  eV ( $35490\text{-}45170$   $\text{cm}^{-1}$ ) [11]. The cathodoluminescence (CL) spectra of  $\text{Er}_2\text{O}_3$  in vacuum under various beam voltage and beam current values are shown in Figs. 1(a) and 1(b). As previously published [12], it is thus demonstrated that above-band gap excitation leads to visible emission from electronic energy levels of  $\text{Er}^{3+}$ . These extensive spectral bands are assigned to emissions from the  $^4\text{G}_{11/2}$  /  $^2\text{G}_{9/2}$  (ultraviolet),  $^4\text{F}_{7/2}$  (blue),  $^2\text{H}_{11/2}$ ,  $^4\text{S}_{3/2}$  (green),  $^4\text{F}_{9/2}$  (red) and  $^4\text{I}_{9/2}$  (NIR)  $J$ -multiplets to the  $^4\text{I}_{15/2}$  electronic ground state, as marked in Fig. 1(a). These levels are therefore populated by various nonradiative processes from the conduction band (CB) and from interband trap levels. The total  $\text{Er}^{3+}$

emission intensity increases with both excitation voltage and current, similar to the studies of other systems [13,14]. but the red/green emission intensity ratio decreases with increase of each of these parameters. Emission from higher multiplet terms of  $\text{Er}^{3+}$  is quenched by cross-relaxation processes in this concentrated material. Figure 1(c) compares the  $4f^{11}$  upconversion luminescence from the same high purity  $\text{Er}_2\text{O}_3$  powder in air (left hand ordinate scale) and vacuum (right hand ordinate) environments when employing a 975 nm ( $10256\text{ cm}^{-1}$ ; 1.27 eV) laser diode with excitation power of 750 mW. Red emission,  $\lambda_{\text{max}} 660\text{ nm}$ :  ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ , is dominant in air and the green emission,  $\lambda_{\text{max}} 564\text{ nm}$ :  ${}^2H_{11/2}, {}^4S_{3/2} \rightarrow {}^4I_{15/2}$ , is very weak. However in a modest vacuum of up to  $2 \times 10^{-2}$  mbar, the intensity of red emission increases by two orders of magnitude, and the intensity ratio of green to red emission increases considerably so that the intensities of these emissions now become comparable.

The sample temperature may be readily calculated from the comparison of the relative intensities of the emission transitions from  ${}^2H_{11/2}$  and  ${}^4S_{3/2}$ . The comparison of the “air” spectrum [Fig. 1(c)] with the literature spectrum [15] shows that the sample temperature under 750 mW laser diode excitation in air is  $\sim 500\text{ K}$ , and in “vacuum” it is  $\sim 800\text{ K}$ . This elevated temperature partly accounts for the differences in the “air” and “vacuum” spectra in Fig. 1(c), where the former are more clearly resolved and the latter include more transitions from thermally-excited luminescent states. The most important point, however, concerns the similarity between Figs. 1(a) and 1(b) on the one hand, and 1(c) “vacuum”, although the former are excited by radiation above, and the latter below, the band gap. Following this observation, we now show that just as for the spectra in Figs. 1(a) and 1(b), that in Fig. 1(c) also results from initial excitation into the conduction band. Note that candoluminescence is negligible at 800 K [12,16].

### 3.2 Dependence of laser power, photoconductivity and chemical dilution

The log-log plots of integrated emission intensity for the wavelength range between 400 and 850 nm, versus laser diode power, for the sample in air or vacuum are shown in Fig. 2(a). The slopes of the plots are an indication of the number of photons involved in the upconversion processes, given certain conditions described by Gamelin and Güdel [4]. The laser diode radiation is absorbed by a  $4f^{11} \rightarrow 4f^{11}$  intraconfigurational transition, and in the present case it is the  ${}^4I_{15/2} \rightarrow {}^4I_{11/2}$  transition of  $\text{Er}^{3+}$ . The “vacuum” plot in Fig. 2(a) is consistent with ground state absorption to the CB involving 6 ( $1.27\text{ eV}$ ,  $10256\text{ cm}^{-1}$ ) photons.

Excitation to the conduction band is accompanied by the production of free charge carriers. The measurement of electrical conduction by the insulator  $\text{Er}_2\text{O}_3$  under NIR irradiation was performed by inserting an electrode at each side of a lightly-compressed disc of the powder. In fact, as shown in Fig. 2(b) for three different ambient pressures, there is a large increase in the current detected when irradiating  $\text{Er}_2\text{O}_3$  with increasing laser diode powers, with a variable slope which depends upon the laser power. For 0.05 mbar pressure an avalanche increase to a slope value near 20 occurs for laser diode powers above 750 mW. The photocurrent is very sensitive to ambient pressure, as shown in Fig. 2(c), which may indicate that charge carriers are at the surface, rather than the bulk, of the material. Figure 2(c) also demonstrates that the upconversion emission intensity and photoconductivity are inter-related, although the emission slope has no “bend”.

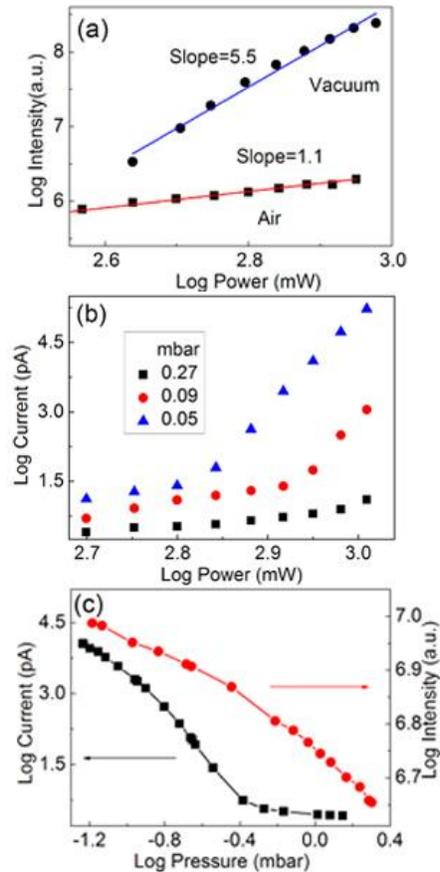


Fig. 2. Log-log plots of various experimental variables for  $\text{Er}_2\text{O}_3$  powders: (a) integrated emission intensity versus 975 nm laser diode power in the region between 400 and 850 nm in ambient air or vacuum of  $2 \times 10^{-2}$  mbar; (b) photocurrent versus laser power for three pressures; c) photocurrent and upconversion intensity versus pressure using 950 mW NIR laser excitation power: these results are not simultaneous.

The upconversion enhancement under 975 nm excitation does not occur for  $(\text{Y}_{0.95}\text{Er}_{0.05})_2\text{O}_3$  so that a cross-relaxation process is implied to be responsible for upconversion to the conduction band in the neat  $\text{Er}_2\text{O}_3$  powder. Also, we have conducted further experiments in “air” at elevated temperatures to show that the higher sample temperature in “vacuum”, mentioned above, is not responsible for the enhancement of upconversion. Figure 1(a) shows that the highest metastable states in  $\text{Er}_2\text{O}_3$  are  ${}^2\text{H}_{11/2}$ ,  ${}^4\text{S}_{3/2}$ , which may be reached by a 2-photon process from  ${}^4\text{I}_{15/2}$ . A collective energy transfer from three  $\text{Er}^{3+}$  ions excited in these states (i.e. a 6-photon process) could raise an electron from the valence band into the conduction band. The observation of  $\text{Er}^{3+}$  emission demonstrates that nonradiative population of interband states follows the excitation.

It has been demonstrated [17] that quenching of  $\text{Yb}_2\text{O}_3$  broad band emission by gas molecules can be interpreted under a model focusing upon the number of collisions by gas molecules irrespective of the nature of the gas. The emission was characterized by a characteristic pressure ( $P_0$ ) which was linearly dependent upon the laser power and the square root of the mass of the ambient gas molecules. The additional results from the present work suggest that the most important action of these gas molecules is surface charge neutralization, thus depleting the occupation of the CB.

### 3.3 Measured luminance and calculated CIE coordinates

Luminance measurements were performed for the same powder sample of  $\text{Er}_2\text{O}_3$  under various excitation regimes. For CL under 6.0 kV with 1.5 A beam current, the luminance was  $6000 \text{ cd m}^{-2}$ ; whereas under NIR 1 W excitation power, the luminance was  $30000 \text{ cd m}^{-2}$  for 975 nm upconversion and  $70000 \text{ cd m}^{-2}$  for 808 nm upconversion, as displayed in Fig. 3. Considering that the luminance of a commercial fluorescent lamp or white LED is around  $30000 \text{ cd m}^{-2}$ , the luminance of upconversion is extraordinary. Employing 975 nm laser excitation with 950 mW power, the luminous efficacy is  $\sim 4 \text{ lm W}^{-1}$ . The corresponding value is  $14 \text{ lm W}^{-1}$  using 808 nm laser excitation and the color coordinate is closer to white emission compared with that of 975 nm upconversion.

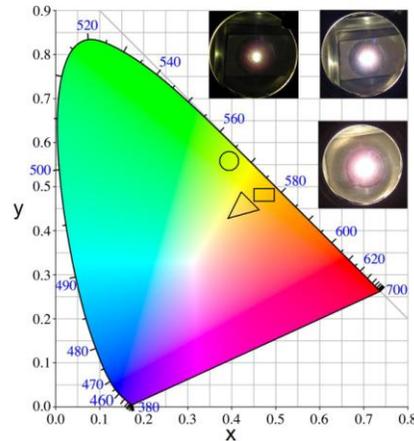


Fig. 3. Calculated Commission Internationale de L'éclairage (CIE) coordinate ranges of  $\text{Er}_2\text{O}_3$  powder sample under electron gun (CL) and NIR excitation. The circle is for CL; the triangle region for 808 nm excitation and the rectangle for 975 nm excitation. The insets are photographs of  $\text{Er}_2\text{O}_3$  powder in a circular metal holder behind a glass window of the vacuum chamber: (top) of the upconversion under 975 nm excitation, (bottom) of the upconversion under 808 nm excitation and (left) of CL.

## 4. Conclusions

In summary, the use of vacuum leads to much more intense upconversion emission in  $\text{Er}_2\text{O}_3$  than in air. This behavior is not followed in the diluted  $\text{Er}^{3+}$  system  $\text{Y}_2\text{O}_3:\text{Er}^{3+}$ . The similarity of the emission with that obtained using above band gap excitation, as well as the power dependence of emission intensity and the production of photocurrent, show that upconversion to the conduction band has been achieved. The luminance under NIR excitation is spectacular and the emission color can be tuned by various means. A reviewer has drawn our attention to a recent paper by Brandt et al. [18] which reports photoconductivity under NIR excitation for oxides which are heavily-doped in  $\text{Yb}^{3+}$ . Our analogous results support electron transport in the CB, rather than hole transport in the VB.

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