

## Upconversion for White Light Generation by a Single Compound

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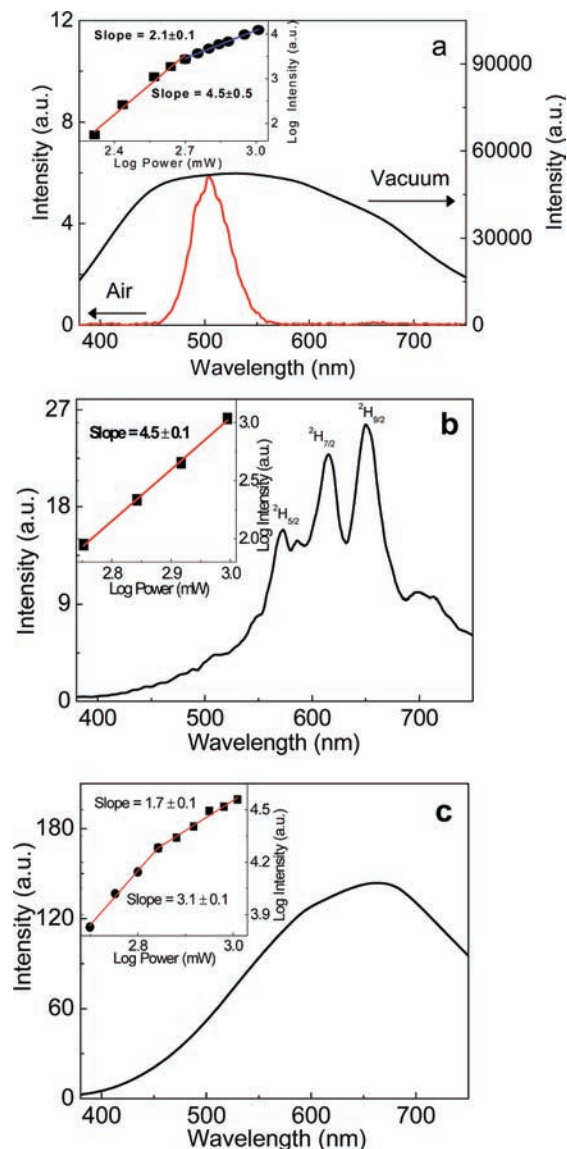
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Photon upconversion involves the absorption of several photons of low energy with subsequent emission of a higher energy photon. Various processes can lead to upconversion, including second harmonic generation, two-photon absorption, ground state followed by excited state absorption, energy transfer upconversion, and photon avalanche. These processes have been extensively reviewed,<sup>1</sup> and the distinction of the appropriate mechanism for a particular scenario can be made, for example, by the power dependence of emission, the activator concentration dependence of emission intensity, the upconversion excitation spectrum, or the emission lifetime measurement. In 2002, He et al. observed stimulated emission by direct three-photon excitation.<sup>2</sup> More recent reports of upconversion have utilized the forced electric dipole  $4f-4f$  luminescence of lanthanide ions ( $\text{Ln}^{3+}$ ), which comprises sharp emission lines.<sup>3</sup> Two new types of upconversion processes involve  $5d-4f$  emission<sup>4</sup> and a heterolooping-enhanced energy transfer process (Hetero-LEET).<sup>5</sup> However, the efficiency of these processes has seldom been measured and has been estimated to be too low for commercial applications.<sup>1</sup> Much of the lighting which is employed at present utilizes the excitation of a mixture of several phosphors in an atmosphere containing mercury. The trend to other more environmentally friendly types of lighting necessitates a search for alternative mechanisms and new phosphors. With the advent of cheap laser diodes, the upconversion of infrared radiation by suitable  $\text{Ln}^{3+}$  combinations is of current interest. Recently, the production of white light by upconversion employing several lanthanide ion phosphors has been exploited in sol-gel derived thin films,<sup>6</sup> although the three color, solid-state display principle was introduced 13 years ago.<sup>7</sup>

In this study we present a new upconversion process in vacuum which generates intense, pure white light. The mechanism differs from previous reports in that the white light is produced by broadband emission from a single material, rather than a composite addition of individual sharp emission bands.

We have employed crude lanthanide oxide powders obtained from American Elements (USA), International laboratory (USA) and Sigma-Aldrich (Germany) of 99.99% to 99.999% purity. The powders were employed as received, after heating at 900 °C for several hours to remove traces of carbonates or organic material, or by precipitation as oxalates followed by calcination. FT-IR spectra showed the absence of carbon species, and no other impurities were detected. Under 975 nm excitation by a laser diode in air, no emission signals were recorded for  $\text{CeO}_2$  and  $\text{Sm}_2\text{O}_3$  powders at up to, and including, the maximum power employed (950 mW). In the case of  $\text{Yb}_2\text{O}_3$  in air (Figure 1a: left-hand ordinate) the  $\text{Yb}^{3+}$  cooperative emission was observed, as previously reported.<sup>8</sup> However, when the samples were mounted in a closed chamber connected to a vacuum pump (BOC Edwards), whose ultimate maximum vacuum is  $2 \times 10^{-2}$  mbar, bright luminescence was detected by a photomultiplier tube (Hamamatsu, R928). Figure 1a (right-hand ordinate) and b,c depict the upconversion emission



**Figure 1.** 975 nm upconversion of lanthanide oxide powders between 380–750 nm with 890 mW irradiation power under  $2 \times 10^{-2}$  mbar: (a)  $\text{Yb}_2\text{O}_3$ ; (b)  $\text{Sm}_2\text{O}_3$ ; (c)  $\text{CeO}_2$ . The figure insets are log–log plots of integrated upconversion emission intensity versus laser power with the slopes marked. The terminal  $4f^2$  states are marked in (b), where the initial state is  $^4G_{5/2}$ . The relative intensities are arbitrary for different figures.

spectra of several oxide powders in the visible spectral region. In each case there is a broad band covering the entire region. In the case of  $\text{Sm}_2\text{O}_3$ , the  $4f^2$  intraconfigurational transitions from  $^4G_{5/2}$  are superimposed upon the broad emission band. By contrast, there are no  $4f^N-4f^N$  transitions within this region for  $\text{Ce}^{4+}$  in  $\text{CeO}_2$  and

$\text{Yb}^{3+}$  in  $\text{Yb}_2\text{O}_3$ . The upconversion process was only observed for powder samples and for dopant ion concentrations of  $\sim 20$  at.%  $\text{Ln}^{3+}$  or higher in  $\text{Y}_2\text{O}_3$ . White light downconversion has previously been reported for  $\text{Y}_2\text{O}_3$  due to carbon impurities,<sup>9</sup> but in our experiments no upconversion luminescence was obtained from this compound.

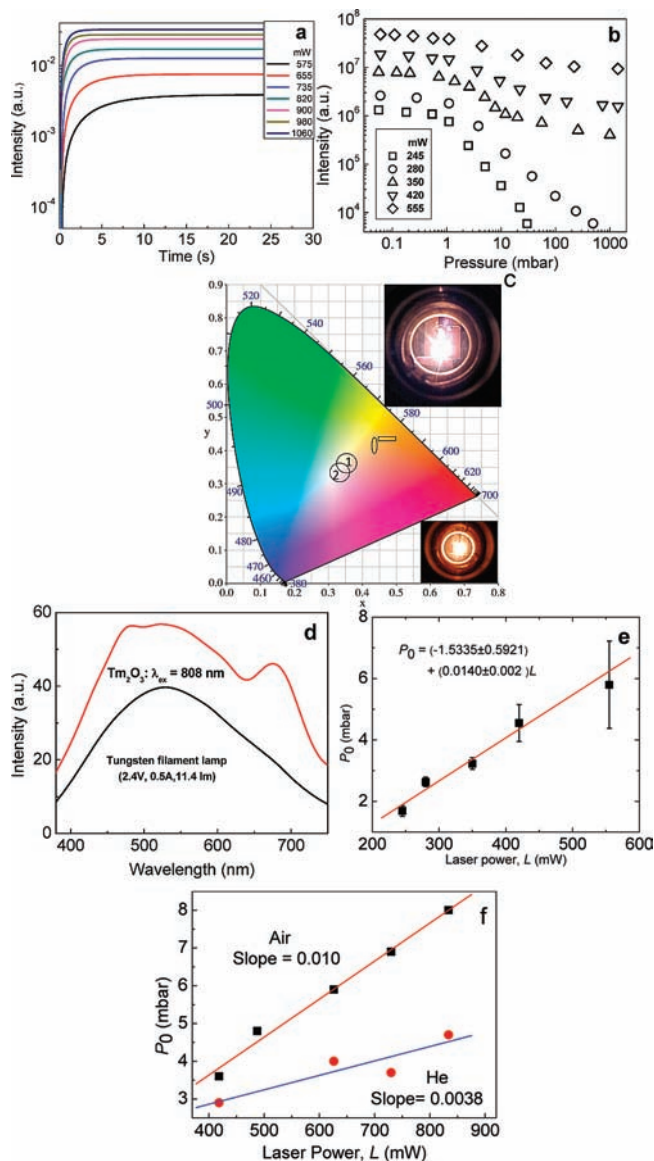
Unlike the upconversion spectra of lanthanide ions diluted into  $\text{Y}_2\text{O}_3$ ,<sup>10</sup> the present emission spectra not only are broad band in nature but also present significant rise times for the emission to build up in intensity. The time-resolved spectra were recorded by a Tektronix TDS5054B 500 MHz digital oscilloscope. Thus several seconds were required for the emission intensity of  $\text{Tm}_2\text{O}_3$  to build up to the maximum, depending upon the excitation power (Figure 2a). The intensity buildup was quicker for higher laser powers. Figure 2b shows that there is a considerable decrease of the emission intensity of  $\text{Tm}_2\text{O}_3$  when increasing the pressure in the container.

The color purity is excellent for the oxides that we have investigated. Figure 2c shows the ranges of the International Commission on Illumination (CIE) coordinates for  $\text{Ln}_2\text{O}_3$  ( $\text{Ln} = \text{Sm}, \text{Tm}, \text{Yb}$ ) and  $\text{CeO}_2$  under excitation in vacuum. The coordinates for neat  $\text{Tm}_2\text{O}_3$  and  $\text{Yb}_2\text{O}_3$  are close to those for pure white light, and we have noticed that the coordinates can be fine-tuned by codoping with other  $\text{Ln}^{3+}$ . The inset photographs in Figure 2c show the upconversion emissions from  $\text{Tm}_2\text{O}_3$  and  $\text{Sm}_2\text{O}_3$ .

We give an estimate of the power efficiency of the upconversion process by comparison of the known radiant output from a tungsten filament lamp with the upconversion emission from  $\text{Tm}_2\text{O}_3$  under the same experimental conditions and geometry. The power efficiency of the bulb was known to be 6.8%. From the spectra in Figure 2d, the luminescence upconversion efficiency of  $\text{Tm}_2\text{O}_3$  is 13% using 1 W laser diode power. Taking into account that the efficiency of the laser diode is 60%, the power efficiency of the entire upconversion process is nearly 8%.

The mechanism of the upconversion is of particular interest. The insets in Figures 1a–c show the log–log plots of upconversion emission intensity versus laser diode power. If a multiphoton process is involved, the number of photons involved may be inferred from the slopes of the plots.<sup>1</sup> For  $\text{CeO}_2$ , for example, the initial slope ( $3.1 \pm 0.1$ ) would show that three photons are involved in the upconversion process. This is consistent with excitation from the valence band to the conduction band since the band gap is 3.19 eV<sup>11</sup> and three 975 nm (1.27 eV) photons are required. The band gaps of  $\text{Sm}_2\text{O}_3$  and  $\text{Yb}_2\text{O}_3$  are  $4.9 \pm 0.2$  eV and  $5.1 \pm 0.3$  eV, respectively,<sup>12</sup> which would require at least a four-photon upconversion. The relative energies of the  $\text{Yb}^{3+} 4f^{13}$  levels are compared with those of the host lattice,  $\text{Yb}^{2+}$ , and the dimer system  $\text{Yb}^{3+}-\text{Yb}^{3+}$  in Figure S3. It is evident that four-photon (from the dimer) or two-photon (from  $\text{Yb}^{2+}$ ) processes are capable of producing excitation up to the conduction band. However, such models cannot explain the pressure dependence of the upconversion luminescence intensity.

We estimate that an excitation density of  $\sim 10$  MW  $\text{cm}^{-2}$  is required to produce the broad-band emission from our powder samples. The melting point of  $\text{Yb}_2\text{O}_3$  is  $\sim 3000$  K, and no evidence of melting was found in our experiments. Some other authors have remarked upon unusual phenomena when irradiating lanthanide sesquioxides at high laser powers. Redmond et al.<sup>13</sup> reported that when using radiation tuned to an absorption band of  $\text{Yb}^{3+}$  in  $\text{Y}_2\text{O}_3$  nanopowder, the onset of blackbody emission was observed above a well-defined threshold. Local melting occurred above this threshold. Bisson et al.<sup>14</sup> studied the emissivity and photoconductivity of highly  $\text{Yb}^{3+}$ -doped  $\text{Y}_2\text{O}_3$  and  $\text{Lu}_2\text{O}_3$  bulk ceramics. When the latter sample was pumped at 940 nm using low excitation



**Figure 2.** (a) Time dependence of the upconversion emission intensity for  $\text{Tm}_2\text{O}_3$  excited by a 808 nm laser diode into an absorption band at various laser powers. (b) Effect of pressure on the upconversion intensity of  $\text{Tm}_2\text{O}_3$  at various incident laser powers. (c) Calculated color coordinate ranges for upconversion emission of powders under different power conditions of 400–1000 mW. The circles 1 and 2 represent the coordinate range for  $\text{Tm}_2\text{O}_3$  (808 nm excitation) and  $\text{Yb}_2\text{O}_3$  (975 nm excitation), respectively, the ellipse region for  $\text{Sm}_2\text{O}_3$  and the rectangle for  $\text{CeO}_2$  (both under 975 nm excitation). The insets are photographs of the upconversion emission of  $\text{Tm}_2\text{O}_3$  under 808 nm excitation (top) and  $\text{Sm}_2\text{O}_3$  under 975 nm excitation (bottom) powder samples in the groove of a copper holder behind the sapphire window of the closed chamber respectively. (d) Comparison of emission from  $\text{Tm}_2\text{O}_3$  under 808 nm diode laser excitation with that from a tungsten filament lamp under the same measurement conditions. (e) Plot of the characteristic pressure,  $P_0$ , against laser power,  $L$ , for  $\text{Tm}_2\text{O}_3$  in air. (f) Comparison of slopes of  $P_0$  vs  $L$  plots for  $\text{Tm}_2\text{O}_3$  upconversion in air and helium atmospheres under different excitation powers.

densities, neither blackbody emission nor photocurrent was detected. However, when more than 6 W of pump power was focused upon the sample, the luminescence signal at 1100 nm showed a decrease over  $\sim 0.5$  s and then a sharp jump. The detection of photocurrent was coincident with this sharp increase. The experiment was repeatable over 1000 laser shots. These experiments demonstrate that the effects of high intensity laser irradiation not only results

in sample heating but also can lead to broad-band emission following the recombination of charge carriers.

In our present experiments, the pressure-dependence of upconversion and the slow rise (and descent) times demonstrate that thermal effects are again important in producing the broad-band emission. We estimate (from the hot bands in 4f–4f transitions) that the temperature of our samples is 500–1000 °C, and this is considerably smaller than the blackbody temperature necessary to produce white light. However, the supralinear dependence of emission intensity against laser power can be predicted by a model where in vacuum the powder can only dissipate the incident laser energy as radiation. Under this model, the emission intensity follows an exponential decrease with pressure. From Figure 2b the quenching of emission intensity,  $I_{em}$ , follows an exponential dependence upon pressure,  $P$ , except for the saturation at higher laser powers:

$$I_{em} = I_0 \exp(-P/P_0) \quad (1)$$

The values of  $P_0$  deduced from the fittings of Figure 2b amount to several mbar, and these are plotted against the incident laser powers,  $L$ , for  $\text{Tm}_2\text{O}_3$  powder in air in Figure 2e. The thermal dissipation model has the relationship

$$P_0 \approx Lm^{1/2} \quad (2)$$

where  $m$  is the average relative molecular mass of the gas mixture ( $m = 28.8$ ). The relation  $P_0 \propto L$  is obeyed in Figure 2e. The quenching was determined to be less efficient in a helium ( $m = 4$ ) atmosphere (Figure S2) than in air. In the repeated experiment, Figure 2f, the ratio of the  $P_0$  values for helium and air was determined from the slopes to be 0.38. This value is in good agreement with the ratio of the values of  $m^{1/2} = (4/28.8 = 0.37)$  and shows that the diatomic molecule of higher mass can dissipate more energy by collision with the particles in the  $\text{Tm}_2\text{O}_3$  powder. In summary, the upconversion process is a thermal avalanche process which leads to photoconductivity.

It is constructive to compare the present thermal emission with previous literature. Studies of  $\text{LaF}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ ,<sup>15</sup>  $\text{Gd}_2\text{O}_3:\text{Er}^{3+}, \text{Yb}^{3+}$ ,<sup>16</sup> and  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Yb}^{3+}, \text{Nd}^{3+}$ <sup>17</sup> have reported a considerable temperature increase of the samples under high laser power irradiation. Supralinear emission intensity versus laser power dependence was reported for the former system by Sivakumar et al.,<sup>5</sup> where the Hetero-LEET upconversion process was proposed. In fact, the mechanism proposed in Figure 7 of ref 5 is not possible at room temperature, since the detailed energy level schemes of  $\text{LaF}_3:\text{Er}^{3+}$ <sup>18</sup> and  $\text{LaF}_3:\text{Yb}^{3+}$ <sup>19</sup> (which are similar for both bulk and nanocrystalline systems) show that considerably endothermic cross-relaxation processes are involved. However, with laser heating under high power densities, the populations of excited states, such as those of  $\text{Er}^{3+} \text{ } ^2\text{H}_{11/2}$ , enable the proposed cross-relaxation processes to be realized by a thermal avalanche process.

In summary, the use of laser diode infrared excitation has been shown to provide intense white light from several rare earth oxides,

with a power efficiency approaching 10%. A slow rise time of several seconds is observed. The mechanism involves a thermally induced production of free carriers.

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**Supporting Information Available:** Materials employed; instrumental details; measurement of power efficiency; Figures S1–S3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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