Luminous and tunable white-light upconversion for YAG ($Yb_3Al_5O_{12}$) and $(Yb, Y)_2O_3$ nanopowders

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We report on multiphoton white-light upconversion in vacuum for Pechini synthesis $Yb_3Al_5O_{12}$ (YbAG) and combustion synthesis $(Yb, Y_2)O_3$ nanopowders under IR excitation. Their intense white-light upconversion is attributed to charge transfer luminescence superimposed upon a broadband emission. Unlike common nanoscale phosphors, which show low luminescence efficiency, the intensity of white-light upconversion for nanopowders is similar to that of their bulk counterparts. The luminary efficacy of the upconversion is estimated to be 10–15 lm W^{-1}, and the Commission Internationale d'Eclairage (CIE) coordinates can be widely tuned by the excitation power, pressure, and codoping ratio. The nano-YbAG sample exhibits a longer buildup time for emission, a higher excitation threshold, and a wider CIE range than the oxide nanopowders.

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Most of the methods for producing white light, based on upconversion of rare earths, utilize a combination of several $4f^N$–$4f^N$ transitions of lanthanide (Ln^{3+}) ions, such as Er^{3+}, Tb^{3+}, Tm^{3+}, and Ho^{3+}. The quantum efficiency depends upon the phonon frequency of the host lattice, and it dramatically decreases with the increasing order of the multiphoton process [1,2]. The background of the present study is our previous report of intense white-light upconversion generated by a single compound, in which case the broadband emission was not related to lanthanide ion $4f^N$–$4f^N$ transitions [3]. Herein, we investigate the comparative upconversion properties of nanosize systems for white-light generation. The properties of YbAG synthesized by the Pechini method [4] have been compared with those of Yb_2O_3 and $(Yb_{0.3}Y_{0.7})_2O_3$ (hereafter $(Yb, Y)_2O_3$: in which Yb is at similar content as in YbAG), both prepared by combustion synthesis [5].

The different morphological characteristics of our studied materials were illustrated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The TEM micrograph of nano-Yb_2O_3 prepared by combustion synthesis exhibited distinct boundaries between irregularly shaped nanoparticles with individual sizes of about 50 nm. The selected area diffraction and the lattice fringes presented clear crystal planes and long-range crystallinity. The nano-YbAG sample prepared by the Pechini method displayed particles with dimensions of hundreds of nanometers whose spherical surfaces include fragmented crystals (of about 30 nm dimension) with disordered crystal planes. The selected area diffraction did not present identical crystal planes, but the lattice fringe was found within a range of 5 nm, indicating short-distance order in the fragmented constituent crystals. The SEM micrograph of nano-$(Yb, Y)_2O_3$ synthesized by combustion synthesis comprised a porous continuous block, like a sponge, with hollows of hundreds of nanometers. By contrast, the Pechini-synthesized nano-YbAG sample consisted of globular aggregates measuring hundreds of nanometers, which were stacked together.

As shown in Fig. 1(a), under excitation using a 975 nm (10,256 cm^{-1}, 1.27 eV) laser diode in a modest vacuum, the upconversion of YbAG nanopowder presents two bands with a separation of ~10,000 cm^{-1}, which matches the energy difference between the $^2F_{5/2}$ (band A) and $^2F_{7/2}$ (band B) multiplet terms of Yb^{3+}. These two bands are attributed to charge transfer (CT) luminescence, and they are superposed upon the broadband emission. When the excitation power increased from 630 to 965 mW, band A blueshifted, while band B redshifted, and thus their apparent separation decreased from 10,000 cm^{-1} to 6800 cm^{-1} and was interpreted as the increased intensity of the broadband overlapping emission. This overlapping band could arise from emission from a trap below the conduction band, but it is similar to that observed by Redmond *et al.* [6] and attributed to blackbody emission.

The similarity with blackbody radiation for wavelengths longer than 500 nm can be demonstrated by the comparison of the emission spectra of Yb_2O_3, $(Yb, Y)_2O_3$, and YbAG nanopowders with the emission spectrum of the incandescent tungsten flashlight bulb (2.4 V, 0.5 A: 9.5 lm W^{-1}), as shown in Fig. 1(b). Taking the ratios of the integrated areas of emission for the lamp and the powders, and assuming the energy efficiency of the laser diode to be ~60%, then the deduced luminary efficacies for upconversion are in the range from 10 to 15 lm W^{-1}.

To more clearly confirm the occurrence of CT luminescence, a trace amount of the YbAG or Yb_2O_3 nanopowder sample was attached to the copper holder in a closed cycle cryostat and the temperature was lowered to a sensor reading of 10 K [Fig. 1(c)]. However, the actual temperature of the irradiated powder sample was unknown but was expected to be much higher, because the thermal conductivity is low. The major finding was that when using 300 mW of laser excitation power at the sensor temperature of 10 K, the underlying broad emission was less prominent and two bands were observed in each case for the Yb_2O_3 and YbAG powders, with separations of 10,700 ±700 cm^{-1}. The bands are displaced to a lower

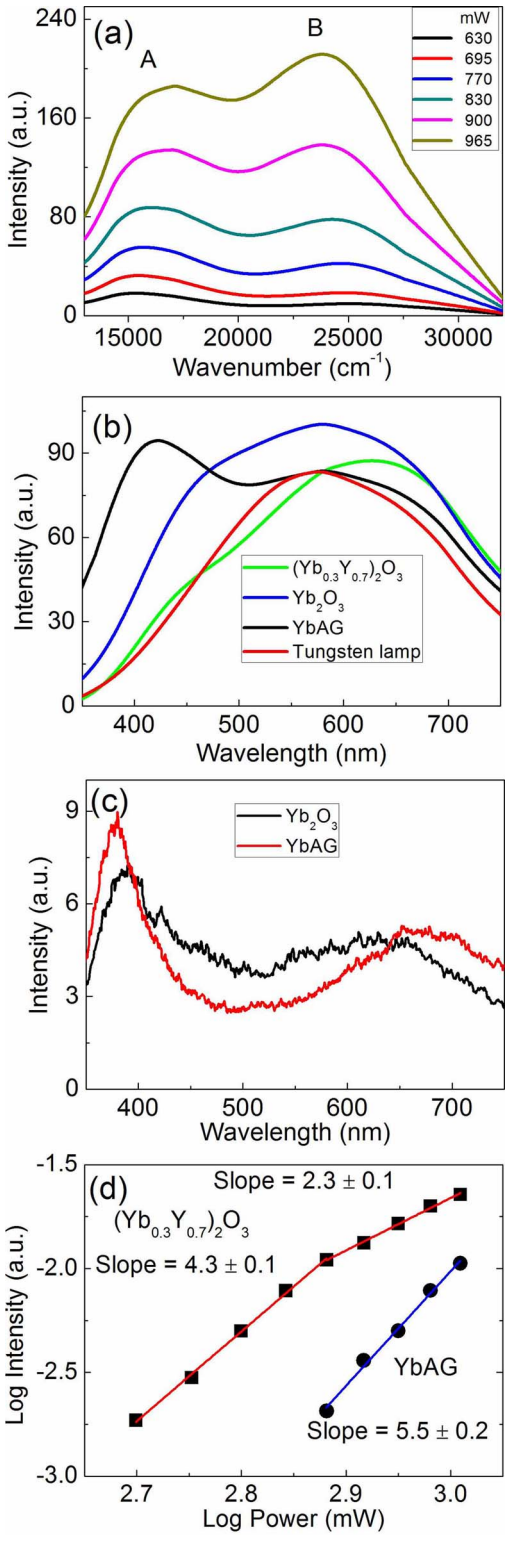

Fig. 1. (Color online) Upconversion emission spectra of nanoscale powders under 2×10^{-2} mbar pressure. (a) $Yb_3Al_5O_{12}$ (YbAG) nanopowder under different excitation powers. (b) Comparison of white-light upconversion as indicated (under 1 W irradiation power) with that from a tungsten filament lamp (9.5 lm W^{-1}) under similar measurement conditions. (c) Trace YbAG or Yb_2O_3 nanopowder sample attached to a 10 K copper sample holder in a closed-cycle cryostat using 300 mW excitation power. (d) Log–log plot of upconversion intensity for YbAG and $(Yb_{0.3}Y_{0.7})_2O_3$ versus laser diode power.

energy than in the previously reported CT luminescence of Yb_2O_3:Yb^{3+} (concentration of Yb^{3+} not stated) and YAG:Yb^{3+} (15 at.%) [7–9].

Figure 1(d) shows a log–log plot of emission intensity versus the incident laser power for YbAG and the slope indicates that five or six photons of 1.27 eV are involved in the upconversion process. It is clear that the initial step is the absorption of the laser diode radiation by $^2F_{7/2}Yb^{3+}$, which has the $4f^{13}$ electron configuration, leading to the population of the $^2F_{5/2}$ excited state. No upconversion emission was observed in vacuum for Y_2O_3 or Lu_2O_3 (which have closed shell Ln^{3+} configurations), so that the process is not purely thermal in origin. These compounds do not possess metastable initial or intermediate levels in the IR or visible spectral regions to act as upconversion steps. Although, in principle, five-photon upconversion to the conduction band is possible from the Yb^{3+} $^2F_{7/2}$ state, the mechanism more likely involves a cooperative interaction between two (or more) Yb^{3+}, where the dimer energy level is at ~0.5 eV above the valence band. In the case of Yb_2O_3, the conduction band is at 5.1 eV above the valence band, so that at least a four-photon excitation process is required from the dimer state to the conduction band. From the consideration of the relevant energy levels, a two-photon excitation process from the CT state to the conduction band is also possible.

The calculated Commission Internationale d'Eclairage (CIE) color coordinates under different laser excitation powers of nano-YbAG exhibit a wide range, as shown by the outer ellipse in Fig. 2. The CIE ranges for the nano-oxides are also shown in the figure. The values are tunable by changing the laser power or ambient pressure, as

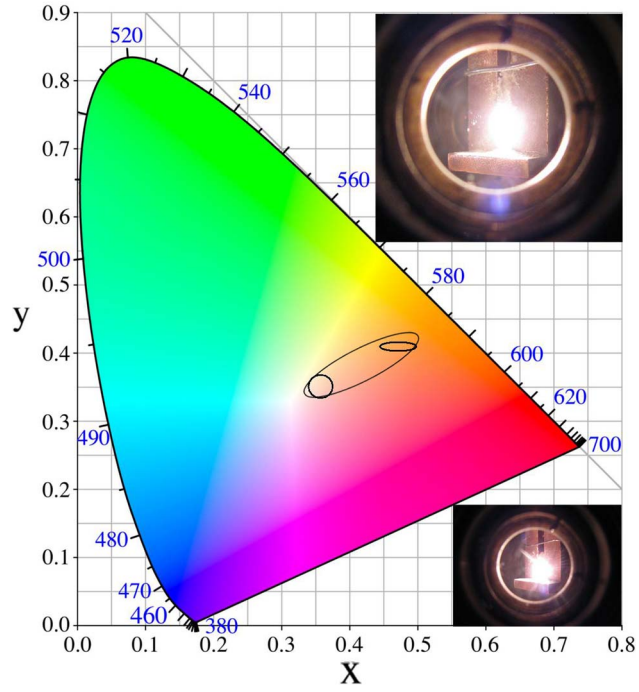

Fig. 2. (Color online) Color coordinate ranges for upconversion emission of nanopowders under different laser powers: circle, Yb_2O_3; outer ellipse, YbAG; and inner ellipse, $(Yb_{0.3}Y_{0.7})_2O_3$. The insets are photographs of the upconversion emission of YbAG (top) and Yb_2O_3 (bottom) nanopowders in the groove of a copper sample holder behind the sapphire window of the closed chamber, respectively.

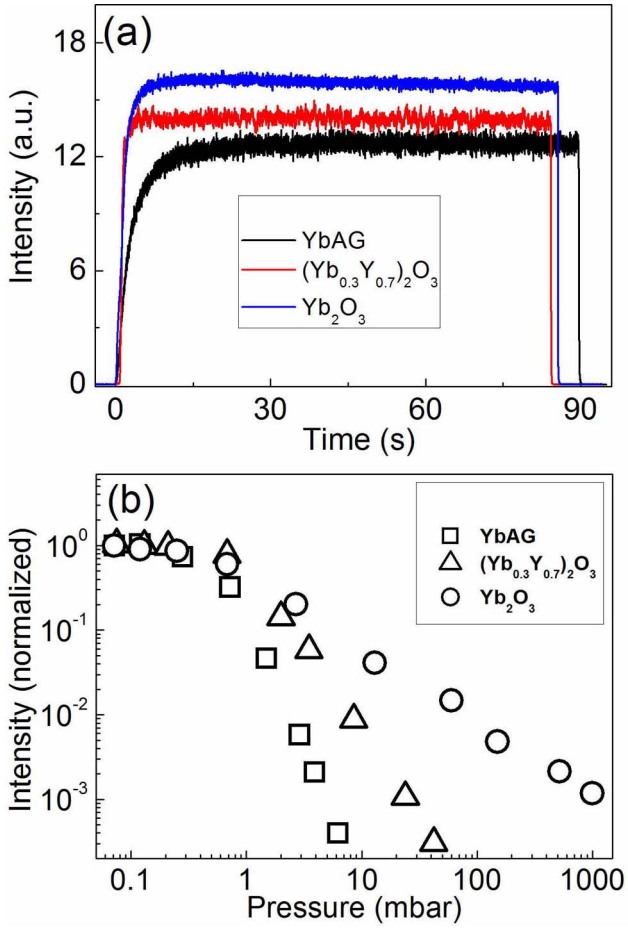

Fig. 3. (Color online) (a) Temporal and (b) pressure dependences of the nanopowder upconversion processes under 500 mW of 975 nm laser diode excitation in vacuum.

well as by changing the dopant ratio Yb:Y in the $(Yb, Y)_2O_3$ nanopowder.

Figure 3(a) shows that the upconversion luminescence intensity undergoes a buildup over several seconds, and a distinguishing feature is that the rise times are shorter for nanopowders of Yb_2O_3 and $(Yb_{0.3}Y_{0.7})_2O_3$ than for the YbAG nanopowder. Figure 3(b) shows the integrated intensity of the upconversion emission as a function of ambient air pressure for different nanopowders under the same excitation power. The emission intensity decreases by orders of magnitude with the introduction of air, and similar results were obtained using nitrogen or helium atmospheres. Under the same pressure, the threshold intensity of the nano-YbAG is lower than that of the oxide nanopowders. The different rise times and intensity-pressure dependences of the powders may possibly be related to their different morphologies, and this is under more detailed study.

In summary, large luminosity and tunable white light upconversion have been observed for YbAG and $(Yb, Y)_2O_3$ nanopowders. CT emission has been identified at the high-energy side of broadband emission. Together, these emissions produce white light upconversion under IR excitation. Unlike common nanoscale phosphors, which show low luminescence efficiency due to the presence of surface defects, the intensity of white-light upconversion in vacuum for the nanopowders is no less than their bulk counterparts. The YbAG produced by the Pechini method presents a longer buildup time for emission and a higher excitation threshold and its CIE values cover a wider range.

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