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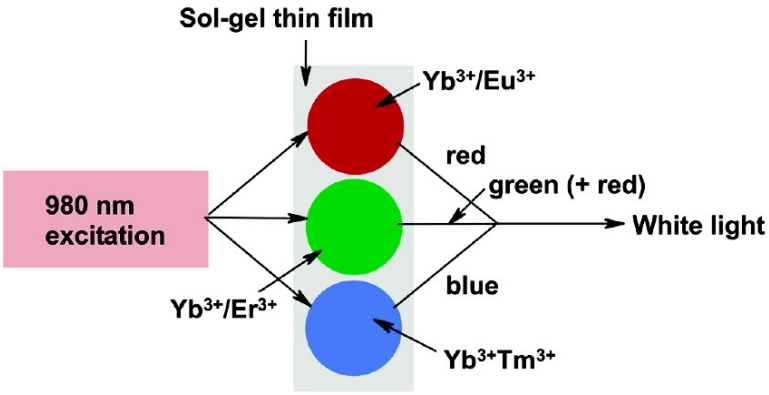

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Bright White Light through Up-Conversion of a Single NIR Source from Sol−Gel-Derived Thin Film Made with Ln^{3+}-Doped LaF_3 Nanoparticles

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There is a large interest in cheap, efficient generation of (white) light sources for a variety of purposes, such as displays, liquid crystal display, back light, and alternatives to general lighting (incandescent light bulb).[1−3] Approaches are (i) the conversion of electricity, (ii) the conversion of light, either by down-conversion or up-conversion, and (iii) thermal radiation in the incandescent lamp. Electricity is exploited in light-emitting diodes with some major recent advances in OLEDs[4−7] and PLEDs.[8−10] White light sources are challenging because (1) blue and white light emitters are not as efficient as green and red emitters,[11,12] (2) energy down-conversion in the case of multilayer devices, by reabsorption and subsequent emission of lower-energy photons, (3) bias dependent color variation,[13] (4) multilayer devices lead to high manufacturing cost,[14] and (5) long-term stability of emitters remains an issue.[15] Down-conversion is the conversion of UV into visible light and is widely exploited in phosphors.[16] The up-conversion process converts near-infrared photons via multiphoton processes into visible photons (details below).[17] The incandescent light bulb produces light by heating and is one of the oldest devices, but the efficiency is still very low (10−12%).[18]

The up-conversion process is based on sequential absorption and energy transfer steps. This event is different from multiphoton absorption processes, requiring high excitation densities. Lanthanide ions are suitable candidates for up-conversion processes because of their energy levels.[17,19,20] To achieve an efficient, cost-effective and durable white light source we need (i) stable photocycle, (ii) cheap excitation (e.g., 980 nm CW laser) and efficient absorption, (iii) control over the intensity of red, green, and blue emission, and (iv) easy and cost-effective device fabrication.

Here, we report a simple method to produce white light from sol−gel matrices, such as SiO_2 and ZrO_2, made with Ln^{3+}-doped LaF_3 nanoparticles co-doped with Yb^{3+} ions. Up-conversion with lanthanide ions in Y_2O_3,[21,22] Gd_2O_3,[23] ZrO_2,[24,25] and SiO_2[26] is known; however, white light generation has not been reported. The co-doping with Yb^{3+} ions makes it possible to excite with 980 nm light only. Red, green, and blue emission was generated from three different lanthanide ions, that is, Er^{3+} (red as well as green), Eu^{3+} (red), and Tm^{3+} (blue) ions. We have achieved the following: (1) the CIE coordinates of the resulting light can easily be adjusted by controlling the concentration of lanthanide ions in the nanoparticles[27−31] as well as the concentration of nanoparticles (Ln^{3+} doped) in the sol−gel thin layer; (2) internal energy transfer between Eu^{3+}, Er^{3+}, and Tm^{3+} ions is avoided by their spatial isolation. The sol−gel process is simple, gives robust layers, and allows tuning of the properties.[32] These films are potential candidates for making planar waveguides, flat panel display, and fiber amplifiers.

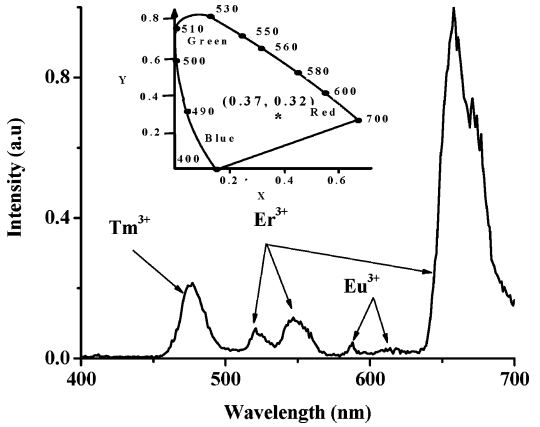

Figure 1. Up-conversion emission spectrum of silica thin film prepared at 800 °C made with $La_{0.45}Yb_{0.5}Er_{0.05}F_3$, $La_{0.75}Yb_{0.2}Tm_{0.05}F_3$, and $Yb_{0.75}La_{0.2}Eu_{0.05}F_3$ nanoparticles under 300 mW 980 nm CW laser excitation (the insets show the CIE color coordinates of the resulting white light).

This work profits from our route to improve the NIR emission of Ln^{3+} ions in sol−gel-derived thin films.[33,34]

$La_{0.45}Yb_{0.5}Er_{0.05}F_3$, $La_{0.75}Yb_{0.2}Tm_{0.05}F_3$, and $Yb_{0.75}La_{0.2}Eu_{0.05}F_3$ nanoparticles were prepared by the co-precipitation technique. The sol−gel made with nanoparticles was prepared by acid hydrolysis, and the sol was spin coated on a quartz plate (see Supporting Information for details). Figure 1 shows the up-conversion emission spectra of silica films made with three different nanoparticles. Emission peaks at red, green, and blue region can clearly be seen. The calculated color coordinates are 0.37 and 0.32.[35,36] These fall within the white region of the 1931 CIE diagram.[37] This white light was bright and can been seen by our naked eye even at a laser pump power of only 200 mW. There is no change in the color coordinates of the white light with a change in excitation power. The weak emissions from the Eu^{3+} ions are necessary because, otherwise, the color coordinates move toward the green region (0.30, 0.41).

A control silica thin film with the same concentrations of La^{3+}, Er^{3+}, Tm^{3+}, Eu^{3+}, and Yb^{3+} ions by direct incorporation only showed green and red emission from Er^{3+} ions (Figure 2). This clearly demonstrates that a single silica thin film prepared with three different Ln^{3+}/Yb^{3+}-doped nanoparticles is necessary to produce white light. An emission band of Tm^{3+} ions at 790 nm was also observed (Figure S1). The intensity ratio of red to green emission from Er^{3+} ions can be tuned by changing the concentration of Yb^{3+} ions in the Gd_2O_3 nanoparticle.[23] We also found similar green-to-red ratio dependence by changing the Yb^{3+} concentration in the nanoparticle. We also observed very weak blue emission at 490 nm, compared that of Tm^{3+}, from a silica film made only with $Yb_{0.8}La_{0.15}Eu_{0.05}F_3$ nanoparticles, which results from cooperative up-conversion of two Yb^{3+} ions. The blue emission is not from

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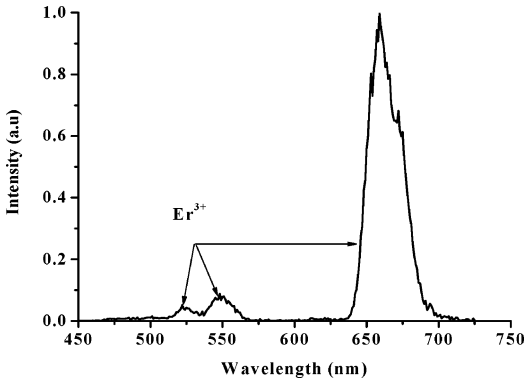

Figure 2. Up-conversion emission spectrum of Ln^{3+} (Er^{3+}, Tm^{3+}, and Eu^{3+}) and Yb^{3+} ions directly incorporated in one silica film prepared at 800 °C as control sample under 300 mW 980 nm CW laser excitation.

Eu^{3+} ions because no blue emission at 490 nm was observed when the Eu^{3+} was excited directly at 418 or 464 nm. Maciel et al.[26] have reported this cooperative up-converted emission mechanism in silica glasses. There was no blue emission from Er^{3+} ions, due to a three-photon process, and no UV emission from Tm^{3+} ions, either. It is obvious that blue, green, and red emission can be produced separately as well.

Control films with Tm^{3+} and Eu^{3+} each co-doped with Yb^{3+} ions did not show any up-conversion. The up-conversion luminescence can likely be improved by using LaF_3:Ln^{3+} core−shell nanoparticles (the doped LaF_3 core is surrounded by an undoped shell of LaF_3).[33] Possible mechanisms for the up-conversion processes are photoavalanche (PA), excited-state absorption (ESA), and energy transfer (ET).[17] Figure S2 shows the dependence of the up-conversion emission intensity on the excitation power, showing the blue emission from Tm^{3+} ions is a three-photon process, the green and red emission from Er^{3+} and Ho^{3+} ions are two-photon processes. All of the three up-conversion processes are not due to photoavalanche process because there is no appearance of threshold in the power dependence graph, and no s-shaped curves are observed. Up-conversion from Tm^{3+} and Eu^{3+} ions is due to energy transfer processes because both ions have no ground or excited-state absorption that matches the 980 nm photon. Green and red emission from Er^{3+} ions is predominantly due to energy transfer processes, and little contribution is from Er^{3+} excited-state absorption, as can be seen from a silica thin film made with $La_{0.45}Yb_{0.5}Er_{0.05}F_3$ nanoparticles that showed intense luminescence when compared to a silica thin film made with $La_{0.95}Er_{0.05}F_3$ nanoparticles (Figure S3).

Similar to SiO_2 matrix, white light was observed with CIE coordinates of 0.37 and 0.31 when ZrO_2 films were made with the above Yb^{3+}/Eu^{3+}, Yb^{3+}/Er^{3+}, and Yb^{3+}/Tm^{3+} nanoparticles (Figure S4). A ZrO_2 thin film prepared with the same concentrations of La^{3+}, Er^{3+}, Tm^{3+}, and Eu^{3+} ions with Yb^{3+} ions by direct incorporation only showed green and red emission from Er^{3+} ions, which substantiates the importance of the role of three different nanoparticles. A lanthanum silicate phase ($La_{9.31}Si_{6.24}O_{26}$) along with the expected LaF_3 phase was observed by X-ray diffraction (XRD) on a silica thin film sample. XRD studies on ZrO_2 thin films made with nanoparticles showed the presence of lanthanum zirconate ($La_2Zr_2O_7$), but no LaF_3 (Figure S5). We conclude that the nanoparticles have reacted with OH groups present in the ZrO_2 sol−gel to form Ln^{3+}-doped lanthanum zirconate. Despite the formation of lanthanum zirconate, the three pairs of Ln^{3+} ions are spatially isolated in the sol−gel layer made with nanoparticles, which is unlikely in the case of direct incorporation of Ln^{3+} ions. So, effectively, the pairs of Ln^{3+} ions are still in a nanoparticle that has very low phonon energy (~300 cm^{-1}).

In conclusion, white light can easily be generated from SiO_2, ZrO_2 sol−gel thin film made with Ln^{3+}-doped nanoparticles co-doped with Yb^{3+} ions. Our control experiments prove the need for Ln^{3+}-doped nanoparticles rather than Ln^{3+} ion directly incorporated in SiO_2 and ZrO_2 thin films.

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Supporting Information Available: Emission spectra, decay curve, energy transfer diagrams, power dependence upconversion graph, and XRD of the prepared thin films. This material is available free of charge via the Internet at http://pubs.acs.org.

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