

## Efficient fluorescence emission and photon conversion of LaOF:Eu<sup>3+</sup> nanocrystals

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Efficient spectral conversion of 325–550 nm light to 570–710 nm light has been demonstrated in LaOF:Eu<sup>3+</sup> nanocrystals. When levels above the <sup>5</sup>D<sub>0</sub> level of Eu<sup>3+</sup> are optically excited, strong emission arising from the <sup>5</sup>D<sub>0</sub> level is obtained in the range of 570–710 nm, a highly efficient working range for organic solar cells. The influences of ambient temperature, particle size, dopant concentration, and codoped ions on the fluorescence intensity of Eu<sup>3+</sup> are discussed in detail. The photon conversion efficiency can reach 3.91% in LaOF:Eu<sup>3+</sup> codoped with Tm<sup>3+</sup>, if light reflection and scattering effects are ignored © 2011 American Institute of Physics. [doi:10.1063/1.3535983]

Organic solar cells have the most efficient photon conversion with light in the range of 550–1000 nm. Light in the 300–550 nm range that is incident upon organic solar cells does not participate in photon to electron conversion.<sup>1,2</sup> Greater overall photon conversion efficiency (PCE) would occur if photons in the range of 300–550 nm could be downconverted. Much of the early work in downconversion searched for phosphors that efficiently converted the vacuum ultraviolet and uv light emitted from a mercury lamp into visible light.<sup>3</sup> Since the solar spectrum is broad and continuous up into the uv, it would be advantageous to have a downconverting system with a strong, broadband absorption at short wavelength with efficient emission in the appropriate long wavelength region. Fluoride host matrices are commonly studied due to their low phonon energy and relatively high chemical stability.<sup>4</sup> In contrast to the LaF<sub>3</sub> host matrix, our previous studies indicate that LaOF not only offers a much higher emission intensity, but also generates different emission wavelengths.<sup>5,6</sup> Thus, LaOF nanocrystals (NCs) provide a complementary host matrix to LaF<sub>3</sub> for technical applications in organic solar cell, scintillation, and tunable multicolor emission devices.

In the current work, efficient spectral conversion is obtained from Eu<sup>3+</sup> doped LaOF NCs. When levels above the <sup>5</sup>D<sub>0</sub> level of Eu<sup>3+</sup> are optically excited, downconversion emission is observed in the range of 550–710 nm. The effects of temperature, particle size, dopant concentration, and codoped ions (Tm<sup>3+</sup>, Pr<sup>3+</sup>, Yb<sup>3+</sup>, Tb<sup>3+</sup>, and Gd<sup>3+</sup>) on the fluorescence efficiency of Eu<sup>3+</sup> doped LaOF NCs have been investigated systematically and are presented here.

Samples used in this study are lanthanide-doped tetragonal LaOF NCs obtained through a postheating treatment of prepared LaF<sub>3</sub> NCs. The process for synthesizing the NCs is given in Refs. 6 and 7. The grain size of the NCs is 20–30 nm (Fig. S1, supporting information).<sup>16</sup> Additional experimental details are provided in the supporting information.

The energy level diagram of Eu<sup>3+</sup> and associated transitions<sup>8</sup> are presented in Fig. 1(a). Figure 1(b) shows the fluorescence spectra of LaOF:Eu<sup>3+</sup> NCs. When the sample is excited with 532 nm laser light, both <sup>5</sup>D<sub>0</sub> and <sup>5</sup>D<sub>1</sub> levels are populated and strong fluorescence is observed in the range of 570–710 nm. According to the energy structure of Eu<sup>3+</sup> and the temporal characteristics of fluorescence emission (Fig. S2, supporting information),<sup>16</sup> transitions corresponding to the fluorescence are labeled in Fig. 1(b).

The fluorescence intensity decreases with decreasing temperature even under selective excitation conditions [Fig. 1(b)]. This indicates that not all of the dopant ions sit in equivalent sites. This view is further supported by the observation of nonexponential fluorescence decay curves (Fig. S2, supporting information).<sup>16</sup>

Figure 2 shows the emission spectra obtained from LaOF:Eu<sup>3+</sup> under resonant and nonresonant excitations at room temperature. It can be seen that the spectral features remain as the excitation wavelength is tuned from 325 to 532 nm. The <sup>5</sup>D<sub>0</sub> level becomes populated through rapid nonra-

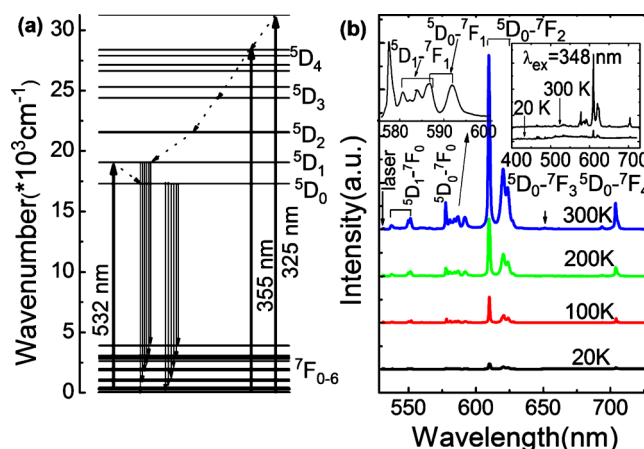


FIG. 1. (Color online) (a) Energy level diagram and corresponding transitions for Eu<sup>3+</sup> doped NCs. (b) Emission spectra of LaOF: 1.0 mol % Eu<sup>3+</sup> NCs with 532 nm excitation at different temperatures. Inset: emission spectra of LaOF: 1.0 mol % Eu<sup>3+</sup> NCs with 348 nm excitation.

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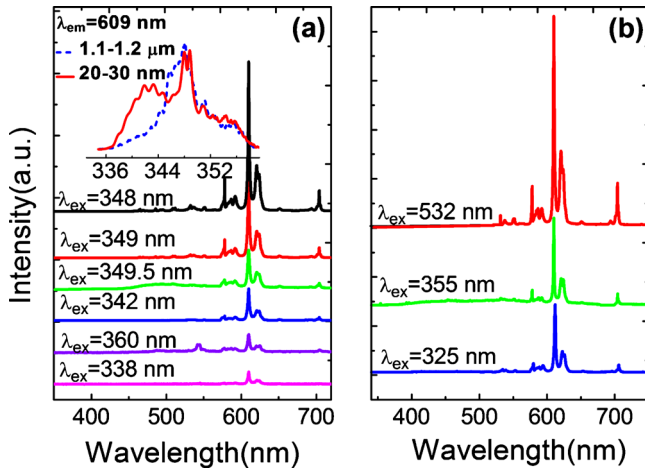


FIG. 2. (Color online) Room temperature emission spectra of LaOF: 1.0 mol %  $\text{Eu}^{3+}$  NCs with different excitation wavelengths. Inset: excitation spectra of different size samples monitoring at 609 nm.

diative relaxation when any level above  $^5D_0$  (such as  $^5D_1$ ,  $^5D_2$ ,  $^5D_3$ ,  $^5L_6$ ,  $^5L_7$ ,  $^5D_4$ , and  $^5G_2$ ) [Fig. 2(a)] is optically excited, leading to a strong emission in the region of 570–710 nm through radiative transitions  $^5D_0 \rightarrow ^7F_x$  ( $x=0-6$ ). By comparing the excitation spectra of different particle sizes [the inset of Fig. 2(a)], we have found that new absorption peaks appeared on the shorter wavelength side for the smaller NC particles.  $\text{Eu}^{3+}$  ions at or near the surface of a NC experience lower local symmetry due to surface defects. This and other surface effects are more significant for smaller particles and can offer the proper conditions for broader absorption and stronger fluorescence.<sup>9</sup>

Concentration quenching is a common energy loss mechanisms for dopant ions.<sup>10</sup> Previous studies have shown that the quenching concentration of  $\text{Eu}^{3+}$  is less than 2.0 mol % in bulk material.<sup>11</sup> To investigate the concentration quenching effect in our nanoparticle system, we have prepared LaOF NCs doped with different concentrations (0.1–15.0 mol %) of  $\text{Eu}^{3+}$ . It is found that the total fluorescence intensity initially increased with  $\text{Eu}^{3+}$  concentration and then decreased above 9.0 mol %. This phenomenon indicates that the quenching concentration is about 9.0 mol % for  $\text{Eu}^{3+}$ :LaOF NCs, much higher than that observed in the bulk samples.<sup>10,11</sup> Therefore, fluorescent  $\text{Eu}^{3+}$  ions in NCs have

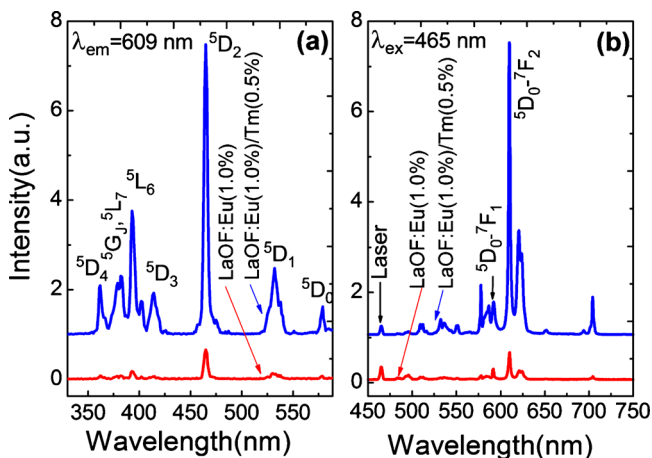


FIG. 3. (Color online) (a) Excitation and (b) emission spectra of doped LaOF NCs at 300 K.

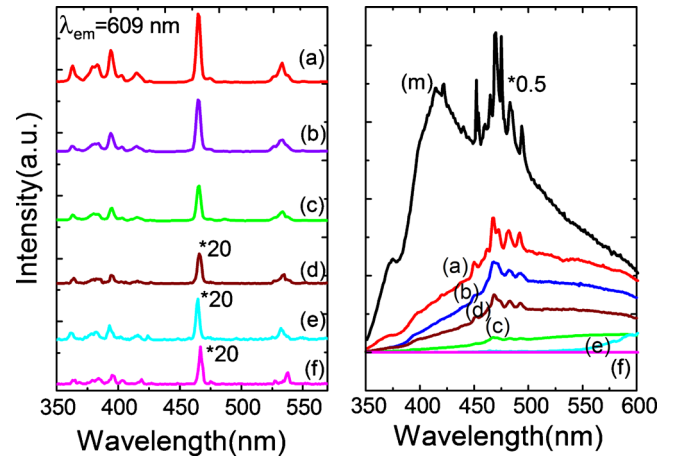


FIG. 4. (Color online) Excitation (left) and transmission (right) spectra of doped LaOF NCs at 300 K. (a) LaOF: $\text{Eu}^{3+}$  (1.0 mol %)/ $\text{Tm}^{3+}$  (0.5 mol %); (b) LaOF: $\text{Eu}^{3+}$  (1.0 mol %)/ $\text{Gd}^{3+}$  (1.0 mol %); (c) LaOF: $\text{Eu}^{3+}$  (1.0 mol %)/ $\text{Tb}^{3+}$  (1.0 mol %); (d) LaOF: $\text{Eu}^{3+}$  (1.0 mol %); (e) LaOF: $\text{Eu}^{3+}$  (1.0 mol %)/ $\text{Pr}^{3+}$  (1.0 mol %); (f) LaOF: $\text{Eu}^{3+}$  (1.0 mol %)/ $\text{Yb}^{3+}$  (1.0 mol %), and (m) the spectra profile of the light source. The spectra multiplied by the factors are shown in the figure.

elevated thresholds for concentration quenching due to the hindrance of the particle boundary beneficial effects on the absorption and emission.<sup>12</sup>

The fluorescence emission of  $\text{Eu}^{3+}$ :LaOF NCs can be affected by codoping with other  $\text{Ln}^{3+}$  ions due to the fact that the uneven components increase of hosts can enhance the 4f–4f transition probabilities of the dopant ions.<sup>13</sup> Figure 3 shows the excitation and emission spectra of LaOF: $\text{Eu}^{3+}$  (1.0 mol %) and LaOF: $\text{Eu}^{3+}$  (1.0 mol %)/ $\text{Tm}^{3+}$  (0.5 mol %). It is seen that the fluorescence is enhanced by a factor of 10 when codoping  $\text{Tm}^{3+}$  ions. We have noted that all of the peaks in the excitation spectra presented in Fig. 3(a) are from  $\text{Eu}^{3+}$ , which suggests that no energy transfer from  $\text{Tm}^{3+}$  to  $\text{Eu}^{3+}$  occurs. However, the  $\text{Tm}^{3+}$  concentration has a positive effect on the fluorescence intensity and lifetime of  $\text{Eu}^{3+}$ . The fluorescence intensity of  $\text{Eu}^{3+}$  reaches its maximum value in LaOF: $\text{Eu}^{3+}$  (1.0 mol %) codoped with 0.5 mol %  $\text{Tm}^{3+}$  ions.

It is also found that the x-ray diffraction peaks shift to larger angles when  $\text{Tm}^{3+}$  or  $\text{Yb}^{3+}$  are codoped into  $\text{Eu}^{3+}$ :LaOF NCs (Fig. S3, supporting information),<sup>16</sup> indicating that codoped ions induce a decrease in lattice dimension and an adjustment of the local symmetry for  $\text{Eu}^{3+}$ . Small variations in the local symmetry for  $\text{Eu}^{3+}$  could result in a significant change in the fluorescence yield.<sup>13,14</sup>

Local symmetry adjustment through codopant ions can also be verified by examining the intensity ratio of the  $^5D_0-^7F_1$  and  $^5D_0-^7F_2$  transitions for  $\text{Eu}^{3+}/\text{Tm}^{3+}$ :LaOF NCs and  $\text{Eu}^{3+}$ :LaOF NCs as shown in Fig. 3(b). Since the  $^5D_0-^7F_2$  transition is sensitive to the local symmetry while the  $^5D_0-^7F_1$  is not, the difference in the ratio for the above two samples correlates with the variation in the local crystal symmetry.<sup>15</sup>

The reduction of the fluorescence lifetime was obtained in different codoped samples (Fig. S4, supporting information),<sup>16</sup> which show nonradiative relaxation probability that was induced by codopant ions cannot be removed.

Two modifications occur when codoping with other  $\text{Ln}^{3+}$  ions in LaOF: $\text{Eu}^{3+}$  NCs.<sup>16</sup> First, modifications of the bond lengths and bonding states associated with  $\text{Eu}^{3+}$  ions result in

TABLE I. PCE ( $\eta$ ) of 20–30 nm LaOF NCs.

Sample	1.0%Eu	1.0%Eu:1.0%Gd	1.0%Eu:0.5%Tm	1.0%Eu:1.0%Pr	1.0%Eu:1.0%Yb	1.0%Eu:1.0%Tb
$\eta$	0.16%	2.90%	3.91%	0.22%	0.15%	1.87%

changes in the local symmetry. Second, nonradiative decay can be increased by impurity defects and cross-relaxation processes that are induced by codopant ions. Thus the introduction of properly selected codopant ions can enhance the absorption and emission, with a subsequent positive effect on spectral conversion.

In the solar cell industry, PCE is a common measure for comparison. In order to describe the photon conversion capabilities of the samples, we assume that the scattering light from the samples is negligible. Then, the PCE( $\eta$ ) from 350–550 to 550–750 nm is defined as

$$\eta = \left( \frac{I_{\text{total}}}{I_{609}} \right) * [I_{\text{ex}} / (I_{\text{xenon}} - I_{\text{tr}})], \quad (1)$$

where  $I_{\text{total}}$  and  $I_{609}$  are integral intensities of the fluorescence emissions at 550–750 nm and around 609 nm, respectively.  $I_{\text{ex}}$  is the intensity of the excitation band at 300–550 nm when the emission at 609 nm is monitored.  $I_{\text{xenon}}$  and  $I_{\text{tr}}$  represent the integral spectral intensities of the light source and transmission measurement in the range of 350–550 nm.

From the data in Fig. 4, values of the PCE( $\eta$ ) from different samples are calculated and listed in the Table I. Values of up to 3.91% PCE is obtained for LaOF:1.0 mol % Eu<sup>3+</sup>/0.5 mol % Tm<sup>3+</sup>, while it is only 0.16% for LaOF:1.0 mol % Eu<sup>3+</sup>. This indicates that the introduction of codopant ions can improve the PCE of the NCs.

In conclusion, broadband conversion from 325–550 to 570–710 nm is achieved in Eu<sup>3+</sup> doped LaOF NCs. Factors that might influence the spectral properties and conversion efficiencies, which include ambient temperature, particle size, dopant concentration and codoped ions, were investigated systematically. The results indicate that smaller NCs are beneficial for improving fluorescence emission and conversion efficiency under the broadband excitation. The introduction of codopant ions to LaOF:Eu<sup>3+</sup> NCs has a signifi-

cant and positive effect on the spectral conversion efficiency through local symmetry adjustment and additional nonradiative relaxation channels.

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