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Facile synthesis of intense green-emitting LiGdF$_4$:Yb,Er-based upconversion bipyramidal nanocrystals and their polymer composites

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ABSTRACT

A pathway for achieving intense green-emitting LiGdF$_4$:Yb,Er upconversion nanophosphors (UCNPs) via Y$^{3+}$ doping was demonstrated. It was revealed that Y$^{3+}$ doping initiated the formation of a tetragonal phase and affected the particle size. Single tetragonal-phase LiGd$_{0.4}$Y$_{0.4}$F$_4$:Yb(18%),Er(2%) (LGY$_{0.4}$F:Yb,Er) UCNPs exhibited strong upconversion (UC) green luminescence and tetragonal bipyramidal morphologies. They showed 1325 and 325-fold higher photoluminescence intensity than the 0 and 80 mol% Y$^{3+}$-doped LiGdF$_4$:Yb,Er UCNPs, respectively. Additionally particle size (edge length) of LiGdF$_4$:Yb,Er-based upconversion tetrahedral bipyramids (UCTBs) was controlled from 60.5 nm to ultrasmall size of 9.3 nm with varying Y$^{3+}$ doping concentration. In an LGY$_{0.4}$F:Yb,Er UCTB, uniform distribution of all constituent elements was directly confirmed by using a high-angle annular dark-field scanning transmission electron microscopy and energy-filtered transmission electron microscopy (EFTEM) image analyses. In particular, existence of activator Er$^{3+}$ ions with
extremely small quantity was clearly seen over a particle on the EFTEM image. Moreover, the

$\text{LGY}_{0.4}\text{F:Yb,Er UCTBs}$ were successfully incorporated into polydimethylsiloxane (PDMS) polymer
and the highly transparent UCTB-PDMS composites showed bright green light under the excitation of

980 nm infrared light.
1. Introduction

Lanthanide doping into inorganic crystals gives these materials new functionalities such as upconversion (UC),\(^1\)\(^-\)\(^3\) downconversion/downshifting,\(^4\)\(^-\)\(^7\) dual-mode luminescence,\(^8\)\(^-\)\(^10\) enhanced computed tomography (CT) contrast\(^11\) and magnetism.\(^12\)\(^-\)\(^13\) In particular, lanthanide ion-doped (Ln\(^{3+}\)-doped) upconversion nanophosphors (UCNPs) have been in spotlight due to their excellent chemical and optical properties. The UCNPs have many advantages over conventional fluorescent organic dyes and quantum dots, such as high photostability (without photobleaching), long life time (from µs to ms) due to the luminescence attributed to parity-forbidden f-f transition, large anti-Stokes shifts, non-toxicity (no Cd or Pb), and a lack of photoblinking.\(^14\) Moreover, the UCNPs exhibit an infrared (IR) to visible light conversion efficiency an order of magnitude higher than the two-photon absorption process. This high conversion efficiency of the UCNPs is due to the existence of a real, intermediate energy level between the ground and excited states.\(^14\)\(^,\)\(^15\) Given this high UC efficiency, commercially available, inexpensive continuous-wave diode lasers can be used as an excitation light source. Recently, sub-10 nm, ultrasmall UCNPs were successfully synthesized with excellent luminescent properties that could allow further bioimaging applications.\(^16\)\(^,\)\(^17\)

Until now, Ln\(^{3+}\)-doped fluoride-based UCNPs have been extensively studied, because fluoride materials have low phonon energies and show high optical transparency in the visible region due to their large band-gap energy.\(^18\)\(^,\)\(^19\) In particular, NaLnF\(_4\) (Ln = Gd, La, Lu, and Y)-based UCNPs have attracted great attention.\(^17\)\(^,\)\(^20\)\(^-\)\(^25\) For example, β-NaYF\(_4\) is known as the most efficient host material for blue and green upconversion luminescence.\(^26\) On the other hand, LiGdF\(_4\) is an outstanding host for downconversion luminescence with a visible quantum efficiency approaching 190%.\(^27\) However, although LiYF\(_4\):Yb,Tm/Er and LiYF\(_4\):Er UCNPs have been reported,\(^28\)\(^-\)\(^31\) few reports describe LiGdF\(_4\)-based UCNPs possibly due to the difficulty in synthesizing LiGdF\(_4\) nanocrystals with a single tetragonal phase.\(^32\) Because lanthanide doping simultaneously affects both the size and phase of the UCNPs,\(^33\) we used Y doping as a synthetic pathway to single-phase LiGdF\(_4\) UCNPs. In this article, we report on the facile synthesis of highly bright Y\(^{3+}\)-doped LiGdF\(_4\):Yb,Er UCNPs with a single...
tetragonal phase. The Li(Gd,Y)F$_4$:Yb,Er showed intense green UC luminescence with higher efficiency than β-NaYF$_4$:Yb,Er UCNPs at 150 W/cm$^2$ power density and tunable size from several tens of nanometers to sub-10 nm via Y$^{3+}$ doping. In addition, the applicability of the Li(Gd,Y)F$_4$:Yb,Er UCNPs to transparent display devices was examined through fabrication of transparent polymer composites.

On the other hand, one must establish a compositional map of these UCNPs and the locations of the activator Ln$^{3+}$ ions within the particles because the luminescence of the UCNPs is strongly affected by surface defects.$^{34,35}$ Although the dopant distribution in the Ln$^{3+}$-doped NaGdF$_4$ has been analyzed via synchrotron X-ray photoelectron spectroscopy (XPS), determining the precise elemental distribution at the single-nanoparticle level remains difficult because XPS technique is an ensemble measurement.$^{36}$ Thus, transmission electron microscopy (TEM) combined with energy dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS) analysis is necessary to identify the compositional distributions within a nanoparticle. Here, for the first time, we successfully synthesized highly bright, single-phase LiGdF$_4$-based UC tetragonal bipyramids (UCTBs) via Y doping. We also provide direct identification of the elemental distribution of each constituent in the UCTBs by applying energy-filtered TEM (EFTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF STEM).

2. Experimental

2.1. Materials

LiOH·H$_2$O (99.995%), GdCl$_3$·6H$_2$O (99%), YCl$_3$·6H$_2$O (99.99%), YbCl$_3$·6H$_2$O (99.9%), ErCl$_3$·6H$_2$O (99.9%), NH$_4$F (99.99%), oleic acid (OA, technical grade 90%), and 1-octadecene (ODE, technical grade 90%) were purchased from Aldrich and they were used without further purification. Sodium oleate (> 97%) was obtained from TCI.

2.2. Synthesis of the Li(Gd,Y)F$_4$:Yb,Er upconversion nanophosphors
First, the lanthanide oleates \([\text{Ln(oleate)}_3], \text{Ln} = \text{Gd}, \text{Y}, \text{Yb}, \text{and Er}\) were prepared by adapting the synthesis reported by Hyeon’s group. Then, 1 mmol of \(\text{Ln(oleate)}_3\) complexes, in which the quantities of Yb and Er were fixed at 0.18 and 0.02 mmol, respectively, were loaded into a three-necked flask containing a solvent mixture of 10.5 ml OA and 10.5 ml ODE. The mixture was heated to 150 °C for 40 min to yield a transparent solution. After the reaction mixture cooled to 50 °C, a methanol (MeOH) solution (10 ml) containing LiOH·H\(_2\)O (2.5 mmol) and NH\(_4\)F (4 mmol) was added to the reaction flask and then stirred for 40 min. After the MeOH was removed, the solution was heated to 320 °C for 90 min under an Ar atmosphere. The as-synthesized nanophosphors were washed several times with ethanol and dispersed in chloroform.

### 2.3. Preparation of the UCTB-PDMS composites

To prepare the UCTB-polydimethylsiloxane (PDMS) composites, 0.4 ml of the UCTB solution (approximately 1 wt\%) was thoroughly mixed with 10 ml of SYLGARD silicone elastomer 184 followed by the addition of a curing agent (1 ml). Finally, the UCTB-PDMS composites (approximately 0.04 wt\% UCTB) were aged overnight and then heat-treated at 80 °C for 1 h.

### 2.4. Characterization

The absorption and transmittance spectra were obtained using a Perkin-Elmer Lambda25 UV/VIS spectrophotometer. The absorption spectrum of the UCNP chloroform solution (~ 1wt\%) in quartz cuvette (1 cm × 1 cm, Hellma QS cell) was obtained under the condition of 240 nm/min of scan speed and 1 nm of slit width. The crystal structures of the as-synthesized nanophosphors were determined using a Bruker D8 ADVANCE diffractometer with Cu K\(_\alpha\) radiation at 40 kV and 40 mA. The Photoluminescence (PL) spectra were collected using a Hitachi F-7000 spectrophotometer. The scanning electron microscopy (SEM) and TEM images were obtained on an FEI Nova nanoSEM operated at 10 kV and a Tecnai G2 F20 operated at 200 kV, respectively. The EFTEM images were obtained on an FEI Titan 80/300 operated at 300 kV equipped with a GIF Quantum® ERS (Gatan, Inc.,
USA). The high-resolution STEM (HR-STEM) images were obtained using an FEI Tecnai G2 F30 S-TEM operated at 300 kV.

2.5. Density functional theory (DFT) calculation

We performed spin-polarized density functional theory (DFT) calculation in a plane-wave basis with the Vienna Ab-initio Simulation Package (VASP) code\textsuperscript{38} and the Perdew-Burke-Ernzerhof (PBE)sol\textsuperscript{39} GGA functional. Valence electrons were described by plane waves up to an energy cutoff of 400 eV and the core electrons were described within the projector augmented wave framework.\textsuperscript{40} We used a 6×6×3 k-points grid sampling of the Brillouin zone for unit cell calculations. Final convergence criteria for the electronic wave function and geometry were 10$^{-4}$ eV and 0.01 eV/Å, respectively. The Gaussian smearing method with a width of 0.05 eV was used to improve convergence with respect to states near the Fermi level.

3. Results and discussion

All UCNP solutions, which are highly transparent, exhibited green luminescence under IR illumination (Figure S1). Figure 1a presents the PL spectra of the Li(Gd,Y)F$_4$:Yb,Er UCNP under 980 nm IR excitation (the Yb and Er concentrations were 18 and 2 mol%, respectively). The PL peaks are ascribed to the 4f-4f electronic transitions of the Er$^{3+}$ ions via an Yb$^{3+}$ → Er$^{3+}$ energy transfer following the IR light absorption by the Yb$^{3+}$ which has an absorption band at approximately 960 nm (Figure S2). The emission peaks in the green and red spectral regions result from two-photon upconversion process, as evidenced by the light power-dependent PL intensity (See Figure S3). As the Y$^{3+}$ concentration increased to 40 mol% in the host lattice, the PL intensity increased. At higher Y$^{3+}$ concentrations, however, the PL intensity decreased significantly. For example, 40 mol% Y$^{3+}$-doped LiGdF$_4$:Yb,Er (LGY$_{0.4}$F:Yb,Er) exhibited an approximately 1325 and 325-fold higher PL intensity than the 0 and 80 mol% Y$^{3+}$-doped LiGdF$_4$:Yb,Er UCNP, respectively. Given the strong PL intensity ascribed to the $^4$S$_{3/2}$ → $^4$I$_{15/2}$ transition, which peaks at 550 nm, the LGY$_{0.4}$F:Yb,Er UCNP emit a
bright green light, as depicted in Figure 1b inset. Previously, Chen et al. obtained the quantum yield (QY) of LiYF₄:Er UCNPs by comparing with β-NaYF₄:Yb,Er UCNPs.³⁰ When the PL intensity of the LGY₀.₄F:Yb,Er UCNPs was compared with that of β-NaYF₄:Yb,Er UCNPs, the LGY₀.₄F:Yb,Er showed higher PL intensity (Figure S5). Its QY was calculated to be 0.16% by using the QY (0.1%) of β-NaYF₄:Yb,Er with 30 nm size.⁴¹ Although the relative QY of the LGY₀.₄F:Yb,Er UCNPs was obtained at current study, absolute QY of the LGY₀.₄F:Yb,Er UCNPs will be further studied by using an integrating sphere. When we calculated intensity ratio of green to red emission \( R_{g/r} \) of the Li(Gd,Y)F₄:Yb,Er UCNPs, the \( R_{g/r} \) value increased with increasing Y³⁺ concentration under the condition of 0 and 20 mol% Y³⁺ doping. In that case, particle size increased with increasing Y³⁺ concentration. On the other hand, the \( R_{g/r} \) value decreased when the particle size was decreased with increasing Y³⁺ concentration (Y³⁺ concentration = 40, 60, and 80 mol%). As shown in Figure S6, LGY₀.₄F:Yb,Er showed the highest \( R_{g/r} \) value of 2.85. As a consequence, the \( R_{g/r} \) value was dependent on the particle size and it decreased with decreasing particle size. When particle size decreases, quenching of UC luminescence induced by surface defects and ligands becomes more important and it modifies the relative population among various excited states through phonon-assisted nonradiative relaxations.⁴²,⁴³ However, although edge size of the 20 mol% Y³⁺-doped Li(Gd,Y)F₄:Yb,Er was larger than that of 60 mol% Y³⁺-doped Li(Gd,Y)₄:Yb,Er, its \( R_{g/r} \) value was smaller than that of the 60 mol% Y³⁺-doped Li(Gd,Y)F₄:Yb,Er due to different crystal structure (see Figure S6). The Commission Internationale de l’Eclairage (CIE) color coordinates of the LGY₀.₄F:Yb,Er UCNPs are (0.2929, 0.6917). The LGY₀.₄F:Yb,Er UCNPs exhibit very high color purity of 98.9%, which is approaching that of monochromatic light due to the sharp emission peak and high green-to-red ratio in the PL intensity.

As indicated in Figure 1c, the LGY₀.₄F:Yb,Er UCNPs are much larger than the other Li(Gd,Y)F₄:Yb,Er UCNPs. In addition, the X-ray diffraction (XRD) patterns presented in Figure S7 reveal the formation of an orthorhombic GdF₃ phase at doping conditions between 0 and 20 mol% Y³⁺. The crystal structures were also verified from the UCNP lattice spacings measured via high-resolution
TEM (HR-TEM) (Figure S8). A tetragonal LiGdF$_4$ phase (the LiYF$_4$ phase for 80 mol% Y$^{3+}$ doping) was formed at doping conditions between 40 and 80 mol% Y$^{3+}$. It was reported that single LiGdF$_4$ tetragonal phase is hardly synthesized and instead, GdF$_3$ orthorhombic phase is apt to be formed. However, as the Gd$^{3+}$ ions were replaced by Y$^{3+}$ ions (> 20 mol%), a tetragonal phase was formed without changing the reaction temperature and/or time, which may be attributed to a decrease in the energetic barrier for the formation of a LiGdF$_4$ phase due to lanthanide doping. Large size and formation of single tetragonal phase may attribute to strong UC luminescence of LGY$_{0.4}$F:Yb,Er UCNPs. It is believed that size effect is more dominant than phase effect on the luminescence, judging from similar brightness of small UCNPs corresponding to Figures 1c-i, ii, iv, and v, as shown in Figures 1 and S1b. However, further study is necessary to reveal exact origin of strong UC luminescence from LGY$_{0.4}$F:Yb,Er UCNPs. It is noted that particle size could be controlled via Ln$^{3+}$ ion doping for the case of LiGdF$_4$ tetragonal phase, whereas it was hardly controlled for the GdF$_3$ orthorhombic phase. Thus, we can achieve intense UC luminescence by simply controlling the particle size when we synthesize single tetragonal LiGdF$_4$ phase. In addition, morphologies of the Li(Gd,Y)F$_4$:Yb,Er UCNPs are affected by their phases. Minute differences may be noted in the TEM images in Figure 1c. The UCNP morphologies in Figures 1c-i and 1c-ii exhibit rhombic plate-like shapes, while plate shape was not observed in Figures 1c-iii–1c-v. The particle shapes in Figures 1c-iv and 1c-v appear octahedral or truncated octahedral. This morphological difference is believed to result from their different crystal structures. The rhombic plates depicted in Figure 1c-i have edge lengths of 12.1 ± 1.0 nm and thicknesses of 4.0 ± 0.5 nm. The nanoplates are easily aligned into two-dimensional aggregates as shown in Figures 1c-i and S9 because this alignment minimizes the free energy by hydrophobic interactions of the surface ligands of the nanoplates at their largest faces. As the quantity of Y$^{3+}$ ions increased in the host lattice, the particle size decreased from 60.5 nm (edge length) for the 40 mol% Y$^{3+}$ doping to 9.3 nm (edge length) for the 80 mol% Y$^{3+}$ doping, which resulted in weak PL intensities for the Li(Gd,Y)F$_4$:Yb,Er. As observed in Figures 1c-iv and 1c-v, the
small Li(Gd,Y)F$_4$:Yb,Er UCNPs appear somewhat spherical with slight faceting, while the large LGY$_{0.4}$F:Yb,Er UCNPs exhibit sharp facets.

We studied the trend in the change of the particle sizes of the Li(Gd,Y)F$_4$:Yb,Er UCNPs with tetragonal structure as a function of Y$^{3+}$ concentration from 40 mol% to 80 mol%. In the high concentration regime, 60 and 80 mol% Y$^{3+}$, the difference in the particle size was marginally small (see Table S1 and Figure S10). However, there was significant increase in the particle size between 60 and 40 mol% Y$^{3+}$-doped Li(Gd,Y)F$_4$:Yb,Er UCNPs; the LGY$_{0.4}$F:Yb,Er UCNPs was approximately 6 times larger than the 60 mol% Y$^{3+}$-doped Li(Gd,Y)F$_4$:Yb,Er UCNPs. Previously, Wang et al. studied the size change of NaYF$_4$:Yb,Er UCNPs by Gd$^{3+}$ doping by using density functional theory (DFT) calculation. They found that the Gd$^{3+}$ ions donate more electron density to adjacent F$^-$ ions than Y$^{3+}$ ions do leading to the increased electron polarization between cations and F$^-$ ions. Increased electrostatic repulsive force between the electron rich F$^-$ ions at the surface layer of NaYF$_4$ and F$^-$ ions in the solution can substantially slow down the diffusion of F$^-$ ions from solution to the nanocrystal surface. They associated this with the reduced nanocrystal size. In contrast to the case of NaYF$_4$, the Bader charge analysis$^{45,46}$ on a unit-cell of LiYF$_4$, LiGdF$_4$, and Li(Gd$_{0.5}$,Y$_{0.5}$)F$_4$ (LiGdYF$_4$) shows that there is no significant charge redistribution upon Y$^{3+}$ doping in bulk level as shown in Table S2. It may attribute to experimentally observed small change in size of the nanocrystals for 60 and 80 mol% Y$^{3+}$ doping. However, in the case of similar concentrations of Y$^{3+}$ to Gd$^{3+}$, upon the surface formation, some of the surface-exposed F$^-$ ions adjacent to Y$^{3+}$ dopants of the most stable LiGdYF$_4$(101) surface, which is experimentally and theoretically confirmed (see below), were less-negatively charged compared to the F$^-$ ions in a bulk phase ($\Delta e = 0.06$). According to the discussion in Ref. 33, we postulate that these less-negatively charged F$^-$ ions will reduce the electrostatic repulsive force upon the approach of F$^-$ ions in solution to the LiGdYF$_4$(101) surface and thus can accelerate the formation of LiGdYF$_4$ with large size.

Previous reports indicate that LiYF$_4$-based nanocrystals are plate shaped.$^{28,32}$ Although a TEM image of the LGY$_{0.4}$F:Yb,Er observed along a particular crystallographic orientation (Figure 1c-iii)
demonstrates a plate-like shape, the actual morphology of the LGY\(_{0.4}\)F:Yb,Er is octahedral as indicated in Figure 2. Figure 2a presents a TEM image of the LGY\(_{0.4}\)F:Yb,Er particles that were not aligned parallel to the TEM grid. No plate-shaped particles were observed in our TEM images of the Li(Gd,Y)\(_4\)F\(_4\):Yb,Er UCNPs for 40, 60, and 80 mol% Y\(^{3+}\) doping. As demonstrated in the TEM images in Figure 2a, the central portions of the LGY\(_{0.4}\)F:Yb,Er UCNPs are much darker than their edges (vice versa in the HAADF STEM images, Figure S11). This severe contrast in the UCNPs indicates that the UCNPs are thicker in their centers than at the edges. The STEM and SEM studies also revealed that LGY\(_{0.4}\)F:Yb,Er exhibits a tetragonal bipyramidal morphology (Figures S11 and S12). The HR-TEM and HAADF HR-STEM analyses of the LGY\(_{0.4}\)F:Yb,Er UCTBs shown in Figure 2 proved the particles were bounded by \{101\} planes. The angles between two adjacent planes were measured to be 50.7 and 129.3° which are in agreement with the angles between the (101) and (10\(\overline{1}\)) planes of tetragonal LiGdF\(_4\). The fast Fourier transform (FFT) pattern presented in the inset of Figure 2b can be indexed to be the zone axis along the [010] direction of the tetragonal LiGdF\(_4\) structure. The results indicate that LGY\(_{0.4}\)F:Yb,Er UCTBs have a single crystalline phase with high crystallinity. To investigate the origin of the formation of tetragonal bipyramidal morphology, the surface energies of the low-index planes of Li(Gd,Y)\(_4\)F\(_4\)–(100), (101) and (111)– were calculated using density functional theory. The unit cell of LiGdF\(_4\) was initially optimized and two of total for Gd\(^{3+}\) ions were substituted with Y\(^{3+}\) ions. The unit cell of Li(Gd\(_{0.5}\),Y\(_{0.5}\))F\(_4\) with energetically most stable configuration of Gd\(^{3+}\) and Y\(^{3+}\) ions is presented in Figure 3a. The morphology of each plane and their surface energies are presented in Figures 3b-d and Table 1, respectively. The calculations confirm that the (101) surface is thermodynamically favored. The LGY\(_{0.4}\)F:Yb,Er UCTBs are faceted by eight equivalent \{101\} planes in a tetragonal structure, which induces a tetragonal bipyramidal morphology due to longer lattice parameter along c-axis. The lattice parameters, \(a = b = 5.177\ \text{Å}\) and \(c = 10.773\ \text{Å}\), were calculated from the high resolution XRD pattern. All facets are atomically flat, and the two apexes along the c-axis are blunt (Figure S13). The tips are blunted in the cross-sectional region of approximately \(20 \times 20\ \text{unit cell (uc)}^2\) in the \(ab\) plane (Figure S13).
The Z-contrast of the atomic columns was examined in the HAADF STEM images (Figure 2e). The potential contrast variation by electron beam damage, which was observed in highly exposed areas (Figures 2c, S14, and S15), can largely be prevented by acquiring fresh STEM images. The intensity profile across XY indicates considerable variation: a higher intensity can support the existence of dopants such as Er and Yb in the Gd sites, and a lower intensity can indicate Y in Gd sites as designated by the arrows (see also Figure S14). The lanthanide elements are clearly observed in the low-pass filtered HAADF HR-STEM image (Figure 2f), and their arrangement is consistent with a projection of LiGdF$_4$ unit cell in the [010] direction. The LiGdF$_4$ has a scheelite structure ($I4_1/a$, $Z = 4$), and the Li$^+$ and Gd$^{3+}$ ions are four-fold and eight-fold coordinated by the F$^-$ ions, respectively (Figure 2d).$^{47,48}$ It should be noted that the Li and F atoms are not visible in the HAADF STEM image in Figure 2f because they are very light in comparison with the Y$^{3+}$ and Ln$^{3+}$ ions.

The elemental distribution within a nanoparticle was examined using an EELS-based EFTEM technique. For the materials containing Li, such as our LGY$_{0.4}$F:Yb,Er UCTBs, EELS analysis is a powerful tool because, unlike EDS, it can detect light elements such as Li. Additionally, EFTEM provides rapid elemental mapping for electron-beam-sensitive materials. Figure 4 presents an elastic TEM image and thickness map of the LGY$_{0.4}$F:Yb,Er UCTBs and the corresponding elemental maps. The core-loss EELS spectra of the Li-K, Gd-M$_{4,5}$, Y-L$_{2,3}$, F-K, Yb-M$_{4,5}$, and Er-M$_{4,5}$ maps obtained from the LGY$_{0.4}$F:Yb,Er UCTBs are presented in Figure S16. Acquiring the high energy-loss spectra in TEM (above approximately 1500 eV) is challenging due to the small signal-to-noise ratio. Surprisingly, however, the core-loss edges such as the Gd-M$_{4,5}$ (1185 eV), Er-M$_{4,5}$ (1409 eV), Yb-M$_{4,5}$ (1528 eV) and even the Y-L$_{2,3}$ (2080 eV) edges were successfully acquired with the enhanced signal-to-noise ratio and collection efficiency of the GIF Quantum® ERS (Gatan, Inc., Pleasanton, CA, USA). As a result, EFTEM maps from all elements including lanthanide elements could be successfully obtained as shown in Figure 4. One thing to note is that the sharp features observed in the image of Figure 4a are not observed in the Gd, Y, and Yb EFTEM images of Figure 4c which appear more rounded due to low signal intensity at thin regions such as the apex and the edge of this bipyramidal
nanocrystal (see thickness map of Figure 4b), particularly for high energy-loss peaks (above 1000 eV). Excepting this smoothing effect, however, one can notice that all elements are uniformly distributed over a single UCTB. Even the quantity of the activator Er$^{3+}$ ion is very small, existence of Er$^{3+}$ ions over a particle is clearly seen.

The as-synthesized LGY$_{0.4}$F:Yb,Er UCTBs were highly uniform in size and shape (60.5 ± 1.6 nm × 55.3 ± 1.4 nm), which allows for two-dimensional (2D) ordered arrangement of LGY$_{0.4}$F:Yb,Er UCTBs (Figures 5a and S11b). When the size of the UCTBs decreased due to slight increase of Y$^{3+}$ concentration in the host lattice, an even higher ordered 2D superlattice could be obtained (Figures 5b-d).

The Li(Gd$_{0.35}$Y$_{0.45}$)F$_{4}$:Yb,Er (LGY$_{0.45}$F:Yb,Er) also exhibits a single tetragonal phase with high crystallinity (Figure S17). The slow evaporation of the solvent allows the LGY$_{0.45}$F:Yb,Er UCTBs to assemble into 2D monolayers in which the {101} planes of the UCTBs are parallel to the TEM grid. The spotty selected area electron diffraction (SAED) pattern supports a highly ordered UCTB assembly. The HAADF STEM image of Figure 5d confirms that the smaller LGY$_{0.45}$F:Yb,Er constituting the 2D superlattice also has a bipyramidal shape. The bright contrast at the apexes results from the overlap of apexes of adjacent particles.

The feasibility of applying LGY$_{0.4}$F:Yb,Er UCTBs to transparent volumetric three-dimensional (3D) displays was investigated by incorporating UCTBs into a polydimethylsiloxane (PDMS) polymer. Although these UCTBs have an anisotropic morphology and are larger than the previously reported NPs that were successfully incorporated into a PDMS polymer, they were well-dispersed in the PDMS polymer, which allowed for the fabrication of highly transparent UCTB-PDMS composites (Figure 6). The transmittance of the UCTB-PDMS composites was found to exceed 90% in the visible spectral region (Figure 6a). As indicated in photographs of the LGY$_{0.4}$F:Yb,Er UCTB-PDMS bar and disk in Figure 6c, the luminescence is homogenous, bright green and sufficiently intense to render characters on the background paper legible. The high transparency and brightness of the UCTB-PDMS composites can be attributed to the strong UC luminescence from the LGY$_{0.4}$F:Yb,Er UCTBs which
allows small quantities of the UCTBs to mix with PDMS. These results also indicate that the UCTBs have the potential for applications in volumetric 3D displays.\textsuperscript{1,33}

4. Conclusions

In summary, we demonstrated a pathway for achieving highly bright LiGdF\textsubscript{4}:Yb,Er UCNPs via Y\textsuperscript{3+} doping. We found that Y\textsuperscript{3+} doping initiated the formation of a tetragonal phase and affected the particle size. Single tetragonal-phase Li(Gd,Y)F\textsubscript{4}:Yb,Er UCNPs with Y\textsuperscript{3+} concentrations similar to the Gd\textsuperscript{3+} concentration exhibited intense UC green luminescence and tetragonal bipyramid morphologies. Additionally, sub-10 nm ultrasmall UCTBs could be obtained via Y\textsuperscript{3+} doping. Uniform distribution of all constituent elements of LGY\textsubscript{0.4}F:Yb,Er UCTBs was directly seen via EFTEM mapping. These LGY\textsubscript{0.4}F:Yb,Er UCTBs were also successfully incorporated into and uniformly distributed throughout PDMS polymer composites. The strong UC luminescence of the LGY\textsubscript{0.4}F:Yb,Er allowed the fabrication of highly transparent and bright green-emitting PDMS composites. These Li(Gd,Y)F\textsubscript{4}:Yb,Er materials are potentially applicable in the highly desired transparent volumetric 3D displays.

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References


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Figure Captions

Fig. 1 (a) PL spectra, (b) CIE color coordinates, and (c) TEM images of Li(Gd,Y)F₄:Yb,Er UCNPs. [i: Y = 0 mol%, ii: Y = 20 mol%, iii: Y = 40 mol%, iv: Y = 60 mol%, v: Y = 80 mol%] Inset in (a) shows magnified PL spectra of low PL intensity region. Inset in (b) shows luminescent LGY₀.₄F:Yb,Er UCNPs solutions (~ 1 wt%) under the irradiation of 980 nm IR diode laser. [I: ⁴G₁₁/₂→⁴I₁₅/₂, II: ²H₉/₂→⁴I₁₅/₂, III: ⁴F₇/₂→⁴I₁₅/₂, IV: ²H₁₁/₂→⁴I₁₅/₂, V: ⁴F₃/₂→⁴I₁₅/₂, VI: ⁴F₉/₂→⁴I₁₅/₂, VII: ⁴I₉/₂→⁴I₁₅/₂, VIII: ⁴S₃/₂→⁴I₉/₂]

Fig. 2 (a) Bright-field TEM, (b) HR-TEM, and (c) HAADF STEM images, (d) perspective view of LGY₀.₄F:Yb,Er unit cell structure, (e) HAADF HR-STEM and (f) filtered HAADF HR-STEM images of LGY₀.₄F:Yb,Er UCTBs. Inset in (a) shows a schematic diagram of the crystal morphology and inset of (b) indicates FFT diffractogram for the HR-TEM image. Inset in (e) indicates ZW-contrast intensity profile across line XY. [010]-projection of the unit cell was superimposed in (f) filtered HAADF HR-STEM image of LGY₀.₄F:Yb,Er UCTBs.

Fig. 3 Morphology of Li(Gd₀.₅Y₀.₅)F₄ host crystal: (a) a single unit cell, (b) a 3×2×1 supercell of the (100) plane, (c) a 2×3×1 supercell of the (101) plane, and (d) a 3×2×1 supercell of the (111) plane.

Fig. 4 (a) Elastic TEM image and (b) thickness map of LGY₀.₄F:Yb,Er UCTBs. (c) EFTEM elemental maps for (i) Li, (ii) Gd, (iii) Y, (iv) F, (v) Yb, and (vi) Er are shown.

Fig. 5 (a) TEM image of LGY₀.₄F:Yb,Er, (b, c) TEM and (d) STEM images of LGY₀.₄₅F:Yb,Er UCTBs. Inset in (c) shows a corresponding SAED pattern showing diffraction spots resulting from superlattice of the LGY₀.₄₅F:Yb,Er UCTBs.

Fig. 6 (a) Transmittance spectrum of LGY₀.₄F:Yb,Er UCTB-PDMS bar and digital camera images of LGY₀.₄F:Yb,Er UCTB-PDMS bar (left) and disk (right) under (b) ambient conditions and (c) IR light irradiation.

Table list

Table 1. DFT calculated surface energies of (100), (101), and (111) planes of Li(Gd₀.₅Y₀.₅)F₄ host crystal.
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<th>Surface index</th>
<th>(100)</th>
<th>(101)</th>
<th>(111)</th>
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<td>Surface energy (eV/Å$^2$)</td>
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<td>0.051</td>
<td>0.098</td>
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<td>Surface energy (J/m$^2$)</td>
<td>6.67</td>
<td>0.82</td>
<td>1.57</td>
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Intense upconversion green-emitting LiGdF$_4$:Yb,Er-based tetragonal bipyramidal nanophosphors are synthesized via Y$^{3+}$ doping. Crystal phase and particle size of LiGdF$_4$:Yb,Er are simultaneously controlled via Y$^{3+}$ doping. The highly transparent Li(Gd,Y)F$_4$:Yb,Er upconversion bipyramid-polydimethylsiloxane composites are prepared and they emit bright green light under infrared irradiation.