Thermally Induced Disorder–Order Phase Transition of Gd$_2$Hf$_2$O$_7$:Eu$^{3+}$ Nanoparticles and Its Implication on Photo- and Radioluminescence

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Supporting Information

ABSTRACT: Crystal structure has a strong influence on the luminescence properties of lanthanide-doped materials. In this work, we have investigated the thermally induced structural transition in Gd$_2$Hf$_2$O$_7$ (GHO) using Eu$^{3+}$ ions as the spectroscopic probe. It was found that complete phase transition from the disordered fluorite phase (DFP) to the ordered pyrochlore phase (OPP) can be achieved in GHO with the increase of annealing temperature from 650 → 1100 → 1300 °C. OPP is the more stable structural form for the GHOE nanoparticles (NPs) annealed at a higher temperature based on the energy calculation by density functional theory (DFT). The asymmetry ratio of the GHOE-650 NPs was the highest, whereas the quantum yield, luminescence intensity, and lifetime values of the GHOE-1300 NPs were the highest. Emission intensity of Eu$^{3+}$ ions increases significantly with the phase transition from the DFP to OPP phase and is attributed to the higher radiative transition rate (281 s$^{-1}$) of the $^5D_0$ level of the Eu$^{3+}$ ion in the environment with relatively lower symmetry ($C_{2v}$) because of the increase of crystal size. As the structure changes from DFP to OPP, radioluminescence showed tunable color change from red to orange. The Eu$^{3+}$ local structure obtained from DFT calculation confirmed the absence of inversion symmetry in the DFP structure, which is consistent with the experimental emission spectra and Stark components. We also elucidated the host to dopant optical energy transfer through density of states calculations. Overall, our current studies present important observations for the GHOE NPs: (i) thermally induced order–disorder phase transition, (ii) change of point group symmetry around Eu$^{3+}$ ions in the two phases, (iii) high thermal stability, and (iv) tunability of radioluminescent color. This work provides fundamental understanding of the relationship between the crystal structure and photophysical properties of lanthanide-doped materials and helps design a strategy for advanced optoelectronic materials.

1. INTRODUCTION

Materials with A$_2$B$_2$O$_7$ composition belonging to the pyrochlore group have been the focal point of research in the scientific community for the past few decades owing to their various interesting properties such as low thermal conductivity, high dielectric constant, suitable refractive index, high structural stability, high radiation stability, and so forth. These properties enable them to be suitable for many applications such as catalysis,1 phosphor,2 nuclear waste host,3 scintillator,4 defect fluorescence,5 magnetism,6 thermal barrier coatings,7 and sensors.8 They are known to exist in two structural variants: ordered pyrochlore (OP, Fd$ar{3}$m) and disordered fluorite (DF, Fm$ar{3}m$). OP is structurally very close to DF, except it has two cationic sites, three anionic sites located at 48f (O$_x$), 8a (O$_y$), and 8b (O$_z$) Wyckoff positions, and 1/8th of oxygen ions at the 8b site are missing. Hence, they are considered as similar phases but with different degrees of anion and cation ordering. The phase transition is normally induced by chemical doping,9 pressure,10 temperature,11 irradiation,12 and so forth. The ionic radius ratio (IRR) plays an important role in the structural phase transition of DF ⇄ OP. It is reported that the OP phase is stable when the IRR value is greater than 1.46, while the DF phase is the more stable phase when the IRR value is below 1.46.13 Some of the complex A$_2$B$_2$O$_7$ oxides fall in the “boundary” region with IRR ~1.46, where they can have the DF structure or the OP structure depending on the synthesis conditions adopted. Among various A$_2$B$_2$O$_7$ compounds, Gd$_2$Hf$_2$O$_7$ (GHO) stands out owing to its interesting properties such as high dielectric constant, wide temperature range of phase stability, and high melting point, which gives GHO broad application.

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potentials as magnetic materials,\textsuperscript{14,15} high dielectric constant materials,\textsuperscript{16} high-temperature ceramics, solid electrolyte in solid oxide fuel cells,\textsuperscript{17} and thermal barrier coatings.\textsuperscript{18} GHO has a cubic structure as well as high $Z_{\text{eff}}$ making it a potential host lattice for scintillators.\textsuperscript{19,20} Moreover, given its high melting point and high structural and thermal stabilities, it can be a potential host for lanthanide ion-doped phosphor. The IRR of GHO is approximately around 1.48 (close to 1.46),\textsuperscript{21,22} so it is expected that the DF and OP phases can coexist in GHO depending on the synthesis conditions.

Recently, many studies have revealed that precise architectural manipulation of nanomaterials have fetched lots of scientific attention because the properties of nanocrystals depend strongly on shape, size, and structure.\textsuperscript{22} It is reported that when GHO is synthesized at a nanodomain, it can undergo DF to OP phase transition at temperatures above 1300 °C.\textsuperscript{23} The phase transition proceeds via formation of the pyrochlore nanoparticles (NPs) in the matrix of well-crystallized fluorite. Therefore, it becomes imperative to probe the structural phase transition and its influence on the luminescence properties of GHO from the perspective of using it as a host for other lanthanide-based phosphors and scintillators. Recently, it was found that the crystal structure plays a very important role in designing efficient luminescent materials. The hexagonal structure of GdF$_3$:Eu$^{3+}$ was found to be more efficient phosphor than its orthorhombic counterpart.\textsuperscript{22} Similarly, hexagonal EuF$_3$ is more efficient luminescent material compared to orthorhombic EuF$_3$.\textsuperscript{23} There is very scarce literature collection on the optical properties of GHO pyrochlore. Previously, Papan et al. have carried out luminescence spectroscopy and Judd–Ofelt analysis on the combustion-synthesized europium-doped Y$_2$Hf$_2$O$_7$, GHO, and Lu$_2$Hf$_2$O$_7$.\textsuperscript{24} Our group has also investigated the effect of A-site ions on the structural and optical properties of a series of europium-doped rare-earth hafnate RE$_2$Hf$_2$O$_7$ NPs (RE = Y, La, Pr, Gd, Er, Lu).\textsuperscript{25} There have been few work on luminescence properties of europium ion-doped gadolinium-based pyrochlores, such as zirconate, titanate, and stannate, wherein fundamental photophysical properties of Eu$^{3+}$, its symmetry, and red-emitting phosphor applications have been discussed.\textsuperscript{26–29} Zhang et al. observed high intensity of $^5D_0 \rightarrow ^7F_1$ transition than that of $^5D_0 \rightarrow ^7F_2$ transition.\textsuperscript{30} Their group has also investigated the effect of codoping V$^{5+}$ ions on an orange/red emission ratio of Gd$_2$Ti$_3$O$_7$:Eu$^{3+}$ phosphor. Liao et al. have investigated a similar trend which indicated a local symmetry of the Eu$^{3+}$ ion in the GSO crystal lattice with an inversion center of the Gd$^{8+}$ ion with the $D_{4d}$ point group.\textsuperscript{31} None of the reported work investigated the thermally induced disorder–order phase transition and its effect on photo- and radioluminescence properties of lanthanide-doped GHO NPs for possible applications in UV-based phosphors and scintillators.

Temperature is an important physical parameter that can alter lattice spacing and modify the band and therefore the electronic properties of various materials. By executing high-temperature annealing, one can modulate the structures, create novel properties, and bring out the phenomena not observed at ambient conditions.\textsuperscript{32–34} Thermally induced structural phase transition of pyrochlore NPs would be expected to unravel various interesting optical properties. Therefore, it is of great interest to explore the disorder–order phase transition and luminescence properties of nanosized GHOE under various annealing temperatures. Up until now, there has been no report about the thermally induced structural transition and its implication on photo- and radioluminescence (RL) properties of nanosized GHOE. The studies on the high-temperature annealing of nanosized GHOE would be of great significance not only to fundamental and applied research but also would give new insights into the nature of the A$_2$B$_2$O$_7$ system.

In this study, we have first synthesized GHO NPs using a molten-salt synthesis (MSS) method at a relatively low temperature of 650 °C. We have doped 5.0% of trivalent europium ions into GHO (GHOE) with the aim of exploring GHO as a host for phosphors and scintillators, which has never been reported before. A europium ion is selected because its electronic transitions are strongly affected by the structural change, coordination number, crystal field, and so forth. We correlated the change of its photoluminescence (PL) properties as GHO undergoes the DF phase (DFP) $\rightarrow$ OP phase (OPP) phase transition using europium ions as a spectroscopic probe.\textsuperscript{35} Because DFP has a disordered array of cations/anions, whereas the opposite prevails in OPP, structural changes could be easily identified based on PL properties such as asymmetry ratio, Stark splitting, and lifetime of europium ions. The goals of this work include the synthesis of GHOE with the DFP structure at low temperature using our MSS procedure, the investigation of thermally induced structural phase transition and its implication on the photo- and radioluminescence properties of GHOE, and the determination of various optical parameters for the GHOE samples. Therefore, our work does not only exploit the potential of this interesting material as light-emitting phosphor and scintillator but also unveils a phase-dependent design strategy to develop materials with desirable properties. We have also explored the thermal stability of GHOE NPs for possible application in thermal sensors and high-temperature luminescence.

The phase transition from DF to OP at high temperature is further supported by density functional theory (DFT)-calculated cohesive energies of both GHO and GHOE. DFT calculations were performed to study the relative phase stability of DF and OP phases of both GHO and GHOE. DFT calculation results were used to bring out the structure–PL correlation by explaining the origin of intense hypersensitive electric dipole transition (EDT) and large spectral splitting. The complete host to europium energy transfer is also explained using density of state (DOS) calculations for both GHO and GHOE.

## 2. RESULTS AND DISCUSSION

### 2.1. Structural Characterization by X-ray Diffraction, Raman Spectroscopy, and Scanning Electron Microscopy

Figure S1 shows the X-ray diffraction (XRD) patterns of the GHO-650, GHOE-650, GHOE-1100, and GHOE-1300 NPs to see any kind of phase transition or structural evolution. All patterns and the corresponding 2θ values are in agreement with DFP,\textsuperscript{36} which reveals that all of the GHO and GHOE NPs are single phased with the $Fm\overline{3}$m space group. There is no evidence of the di...
numbers of gadolinium \((Z = 64)\) and hafnium \((Z = 72)\), the superstructure reflections are too small to be observed by nonresonant diffraction studies to confirm the formation of the long-range cationic order of the pyrochlore phase.\(^{38}\)

As can be seen from Table 1, there is a proportional increase in crystalline size of the GHOE NPs as a function of annealing temperature. This can also be seen from the narrowing of the XRD peaks at a higher annealing temperature. Moreover, the doping of the europium ion does not distort the basic structural network of GHO.

Table 1. Lattice Parameter and Crystallite Size of the GHO and GHOE NPs

| sample     | \(2\theta\) (deg) | FWHM (\(\beta\)) | lattice parameters (Å) | crystal size (nm) |
|------------|-------------------|------------------|------------------------|-------------------|
| GHO-650    | 29.58             | 1.06             | 10.45                  | 7.49              |
| GHOE-650   | 29.74             | 1.03             | 10.39                  | 7.71              |
| GHOE-1100  | 29.72             | 0.22             | 10.40                  | 36.11             |
| GHOE-1300  | 29.66             | 0.16             | 10.43                  | 49.65             |

Figure 1a shows the Raman spectra of the GHO-650, GHOE-650, GHOE-1100, and GHOE-1300 NPs. Raman spectroscopy is one of the most sought out techniques to differentiate the OP and DF phases of \(A_2B_2O_7\) compounds, which is difficult to achieve using XRD. It is well documented in the literature based on the group theory that there are a total of six Raman active vibrational modes existing in the wavenumber range of 200–1000 cm\(^{-1}\) for the OP phase, which are \(\Gamma_{\text{OP}} = A_{1g} + E_{g} + 4F_{2g}\).\(^{39,40}\) On the other hand, because seven \(O_2^{-}\)ions are randomly oriented over the eight anionic sites leading to high level of structural disordering, the DF phase has mainly one active Raman mode \(F_{2g}\). Phase transition from the \(A_2B_2O_7\)O\(^-\)P (\(Fm\overline{3}m\) space group, \(Z = 8\)) to perfect AO\(_2\)F (\(Fd\overline{3}m\), \(Z = 4\)) structure proceeds by disappearance of \(A_{1g}\) and \(E_{g}\) Raman modes and decrease in the number of \(F_{2g}\) modes from 4 to 1. IRR \((r_A/ r_B)\) plays an important role in determining the type of structure which \(A_2B_2O_7\) composition is going to attain.\(^{41}\) It is reported that if IRR is less than 1.46, the DF phase is more likely to form and if it exceeds 1.46, it is the OP phase, which is more likely to be stabilized at room temperature. As discussed earlier, GHO exists in the phase boundary of OP \(\leftrightarrow\) DF phase transition as its IRR value is 1.48.

The Raman spectrum of the GHO-650 NPs (Figure 1a) consists of a single broad peak characteristic of the DF phase. Moreover, europium-doped GHOE-650 NPs also exist in the DF phase, which indicates that europium doping does not change the basic fluorite network of GHO. However, after the GHOE-650 NPs are annealed at 1100 and 1300 °C, there is an induction of pyrochlore ordering in the GHOE NPs. There is an evolution of pyrochlore peaks at 1100 °C, which completely transform to the OP structure at 1300 °C. From the Raman spectra, we could clearly identify six vibrational modes related to Gd–O and Hf–O vibrational frequencies of the GHOE-1100 NPs. The peak positions are approximately around 306, 321, 401, 500, 520, and 640 cm\(^{-1}\), which correspond to \(F_{2g}, E_{g}, F_{2g}, A_{1g}, F_{2g}\), and \(F_{2g}\) respectively.\(^{42}\) The vibrational Raman bands of \(F_{2g}, E_{g}\), and \(F_{2g}\) modes at a lower wavenumber region (300–400 cm\(^{-1}\)) originate from vibrations of the La–O and Hf–O bonds, whereas the \(F_{2g}\) band at higher wavenumber (520 and 640 cm\(^{-1}\)) comes into picture because of the stretching of the Hf–O bonds. The Gaussian deconvoluted Raman spectrum of the GHOE-1300 NPs possessing an ideal pyrochlore structure is shown in Figure S2.

The observed change in phase \(Fm\overline{3}m \rightarrow Fd\overline{3}m\) of the GHOE NPs is in line with the Ostwald’s step rule,\(^{38}\) as it is reported that the OP structure in GHO has a low enthalpy of formation compared to the DF structure.\(^{43}\) The activation energy \((E_a)\) of the thermal growth of the GHO NPs with the DF structure was 65 kJ/mol in the temperature range of 800–1400 °C.
Figure 2 shows the DFT-GGA-calculated distribution of Gd−O, Hf−O, and Eu−O bond lengths in the DF structure with Eu doped at the Gd site (Figure 2a) and the Hf site (Figure 2b). The solid black lines (at 2.29 and 2.56 Å) and dotted black lines (at 2.25 Å) show our DFT-GGA-calculated Gd−O, Hf−O, and Eu−O bond lengths in the OP structure. Dotted blue lines show Eu−O bond distances in the OP structure. The configuration of EuO6/EuO5 polyhedra when doped in OP (DF) is shown in the left (right) side of the figure.

Table 2. DFT-GGA Calculated Equilibrium Lattice Parameters, Atomic Positions, Bond Lengths, and Band Gap of GHO in the OP Structure are Summarized in This Table along with Previous Experimental Measurements and Theoretical Calculations

| system  | a₀ (Å) | X | Gd−O₈b (Å) | Gd−O₄ff (Å) | Hf−O₅eff (Å) | band gap (eV) |
|---------|--------|---|-------------|-------------|-------------|--------------|
| this study GGA | 10.59 | 0.34 | 2.29 | 2.56 | 2.08 | 3.45 |
| previous GGA | 10.53 | 0.34 | 2.28 | 2.53 | 2.07 | 3.42 |
| experiment | 10.52 | | | | | |

Table 3. DFT-GGA-Calculated Cohesive Energies of OP and DF Structures of the GHO and GHOE NPs Tabulated with Respect to the Most Stable Structure*

| system | GHO (eV) | GHOE (eV) |
|--------|---------|-----------|
| OP | 0.00 | Gd site: 6.127, Hf site: 0.000 |
| DF | 8.177 | Gd site: 10.407, Hf site: 9.666 |

*The different energy values are reported for the 88-atom supercell.

with respect to DF. In the bulk state, the OP structure is favorable with respect to the DF structure. Moreover, Jiang et al. and Li et al. have shown that the ground state structure of GHO is OP. They have also calculated OP to DF transformation temperatures for several pyrochlores. Therefore, our DFT results are in agreement with previous DFT calculation results. Further, our DFT-GGA results show that with Eu doping (1 Eu atom in the 88-atom supercell), the OP structure is stable with respect to the DF.

Our experimental results show that the crystallite size increases with increasing annealing temperature (Table 1). Increasing crystallite size implies lower surface to volume ratio with approaching bulk characteristics. The crystallite size of the GHOE-650 NPs is around 7.0 nm, whereas that of the GHOE-1300 NPs is ~50 nm. Raman spectra of the GHOE-1100 and GHOE-1300 NPs confirm the formation of the OP structure. Therefore, the OP structure is favorable in the GHO and GHOE NPs after high-temperature annealing and corroborating with our calculated DFT energetics shown in Table 3.

2.3. Local Site Stability of Eu³⁺ Ions in the GHOE NPs. Figure 2 shows the DFT-GGA-calculated distribution of Gd−O, Hf−O, and Eu−O bond lengths in the DF structure with Eu doped at the Gd site (Figure 2a) and the Hf site (Figure 2b). The scanning electron microscopy (SEM) images (Figure 1b–d) show that the GHOE-650, GHOE-1100, and GHOE-1300 NPs are either spheroidal or spherical and have certain degree of agglomeration. The particle size distribution of the GHOE NPs was calculated from these SEM images by ImageJ software as shown in the insets. There is a progressing increase of the average particle size of these GHOE NPs, that is 14 nm of the GHOE-650 NPs, 48 nm of the GHOE-1100 NPs, and 57 nm of the GHOE-1300 NPs.

2.2. Cohesive Energies of OP and DF Structures: A DFT Study. The DFT-generalized gradient approximation (GGA)-calculated equilibrium lattice parameters, atomic positions, and bond lengths are summarized in Table 2 along with previous DFT calculation results. Table 2 clearly shows that our values calculated via GGA−Perdew−Burke−Ernzerhof agree well with previous GGA−PW91 calculated values and GGA is sufficient to reproduce the insulating character of GHO. The lattice constant (a₀), the internal structural parameter (x) which is related to the position of O₄ff the nearest Gd−O₄ff, Gd−O₄ff and Hf−O₅eff distances and the band gap are tabulated in Table 2. Table 3 shows our DFT-GGA-calculated cohesive energies of OP and DF structures of GHO, and the OP structure is stable with respect to DF. In the bulk state, the OP structure is favorable with respect to the DF structure. Moreover, Jiang et al. and Li et al. have shown that the ground state structure of GHO is OP. They have also calculated OP to DF transformation temperatures for several pyrochlores. Therefore, our DFT results are in agreement with previous DFT calculation results. Further, our DFT-GGA results show that with Eu doping (1 Eu atom in the 88-atom supercell), the OP structure is stable with respect to the DF. Our experimental results show that the crystallite size increases with increasing annealing temperature (Table 1). Increasing crystallite size implies lower surface to volume ratio with approaching bulk characteristics. The crystallite size of the GHOE-650 NPs is around 7.0 nm, whereas that of the GHOE-1300 NPs is ~50 nm. Raman spectra of the GHOE-1100 and GHOE-1300 NPs confirm the formation of the OP structure. Therefore, the OP structure is favorable in the GHO and GHOE NPs after high-temperature annealing and corroborating with our calculated DFT energetics shown in Table 3.
range of 2.16−2.60 Å in the form of GdO₆, GdO₇, and GdO₈ polyhedra. The Hf−O bond distances are distributed over the range of 1.94−2.81 Å in the form of HfO₆ and HfO₇ polyhedra. The Hf−O bond distances are distributed in a wide range compared to an OP HfO₆ bond length of 2.08 Å. In other words, the chemical environment around the Hf site is more distorted compared to that of Gd.

Figure 2 also shows the change in the first and second nearest neighbor bond distances because of Eu doping at Gd and Hf sites. The Gd−Gd/Hf bond lengths change appreciably by Eu doping at the Hf site compared to Eu doping at the Gd site. Moreover, our DFT-GGA-calculated energetics shows that Eu doping in the Hf site is favorable compared to Eu doping at the Gd site. In addition, Figure 2 shows EuO₈ (doped at the Gd site) and EuO₆ (doped at the Hf site) polyhedra in OP (shown on the left) and DF (shown on the right) structures. The distribution of bond lengths and orientation shows that EuO₈ and EuO₆ polyhedra has inversion symmetry when doped in the OP structure and inversion symmetry is absent when doped in the DF structure. The emission spectra from different excitation wavelengths and number of Stark components of the ⁵Dₓ → ⁷F₉ (J = 0−4) transitions of the Eu³⁺ ion in the GHOE-650 NPs (Figures S3b and 5) show that Eu atoms occupy a chemical environment in the DF structure which has no inversion symmetry. These results are consistent with our DFT-calculated results of the local structure around Eu atoms, which also confirm the absence of inversion symmetry.

2.4. PL Properties of the GHO-650 NPs. Figure 3a,b show the PL excitation spectra and the emission spectrum of GHO-650 NPs, respectively. The emission spectrum displayed two emission maxima at ~445 and 720 nm corresponding to blue and red emissions, respectively. Such display of multicolor emissions (blue and red in this case) is a characteristic of nanomaterials wherein the excited state dissipates its excessive energy through various channels because of large number of defect states within band gaps of nanomaterials. It is known that AₓB₇O₃ pyrochlore type ceramics are rich in defects and
more so in oxygen vacancies. 

The Raman spectrum of the GHO-650 NPs (Figure 1a) indicated that it exists in the DF phase with large concentration of oxygen vacancies in its network. 

Eagleman et al. reported that oxygen vacancies are responsible for visible light emission in La\textsubscript{2}Hf\textsubscript{2}O\textsubscript{7}. In addition, we have found that electronic transition involving ionized oxygen vacancies are responsible for such luminescence properties from our earlier work on Nd\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} pyrochlore. 

The used excitation energy (\(\sim 3.37\) eV, 332 nm) is less than the band gap (3.42 eV) of GHO, so direct transition from the valence band (VB) to the conduction band (CB) does not happen, and there exist certain localized defect states within the band gap of the GHO NPs. Such defects could arise during thermal treatment of the GHO NPs or may be present intrinsically in them. 

The responsible oxygen vacancies for blue and red emission in the GHO-650 NPs are presented pictorially as a mechanism in Figure 3c. The blue emission could arise from the electronic transition of singly ionized oxygen vacancies to the VB, and the red emission from that of shallow oxygen defect vacancies to deep ones. The proposed different origins of these two emissions are consistent with the different excitation spectra obtained with \(\lambda_{\text{em}} = 445\) and 720 nm at blue and red regions, respectively (Figure 3a).

2.5. PL Properties of the GHO:Eu\textsuperscript{3+}. 2.5.1. Excitation and Emission Spectroscopy. Figure 4a shows the excitation spectra of the GHOE samples as a function of annealing temperature. These spectra consist of a very strong band peaking at \(\sim 263\) nm, which is known as the charge transfer band (CTB) and attributed to electron transfer from a filled 2p orbital of O\textsuperscript{2−} ions to a vacant 4f orbital of the Eu\textsuperscript{3+} ion. The weak bands at 395 and 465 nm are due to 7F\textsubscript{0} \(\rightarrow\) 5L\textsubscript{6} and 7F\textsubscript{0} \(\rightarrow\) 5D\textsubscript{2} transitions of Eu\textsuperscript{3+} ions. The CTB as a La Porte-allowed transition has higher intensity than the forbidden f-f transitions. The excitation spectra monitored under various emission maxima (591, 630, 654, and 711 nm) are also shown in Figure S3a. Except for the marginal change in intensity, the spectra remain the same at different emission wavelengths. The emission spectra recorded with 263 nm excitation is shown in Figure 4b. For comparison,
emission spectra recorded under 263, 395, and 465 nm excitations are shown in Figure S3b. The intensity of the PL emission recorded with CTB excitation is much more intense than that with f-f excitation bands. The emission spectra for all three GHOE samples consist of five main peaks at 579, 591, 630, 654, and 711 nm corresponding to the $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$, $^5D_0 \rightarrow ^7F_4$, $^5D_0 \rightarrow ^7F_5$, and $^5D_0 \rightarrow ^7F_6$ transitions, respectively. There are several interesting features of these spectra: appearance of $^5D_0 \rightarrow ^7F_4$ transition that is allowed neither by magnetic dipole transition (MDT) nor by EDT, large splitting in the spectral peaks, high asymmetry ratio ($I_{5D0} / I_{7F0}$), and presence of relatively intense $^5D_0 \rightarrow ^7F_2$ transition. The presence of $^5D_0 \rightarrow ^7F_2$ transition and large spectral splitting are signatures of the europium ion in highly disordered environment. 62 This is supported with the fact of relatively high emission intensity of $^5D_0 \rightarrow ^7F_2$ transition due to a distorted chemical surrounding around the Eu$^{3+}$ ions.63 However, there are no changes of the spectral profile in terms of peak symmetry or width on changing the excitation wavelength.

Based on the emission spectra of the GHOE-650, GHOE-1100, and GHOE-1300 NPs (Figure 4b), three effects of annealing on the PL properties of the GHOE NPs were taken into consideration. These effects include (a) emission intensity, (b) spectral width of the $^5D_0 \rightarrow ^7F_0$ emission lines, and (c) the ratio of integrated PL intensities between MDT ($^5D_0 \rightarrow ^7F_1$) and hypersensitive EDTs ($^5D_0 \rightarrow ^7F_2$), that is, the asymmetry ratio ($I_{5D0}$).

First, the emission intensity of the $^5D_0 \rightarrow ^7F_2$ EDT is much higher than that of the $^5D_0 \rightarrow ^7F_1$ MDT for all three GHOE samples, suggesting that the Eu$^{3+}$ ions are localized in low symmetry sites. Moreover, the PL emission intensity increases with increasing annealing temperature, which could be attributed to the different crystallite sizes of the GHOE NPs. The GHOE-650 NPs with the smallest size (~7 nm) have the highest surface to volume ratio, so are rich with surface defects. Such surface defects act as nonradiative pathways to decrease emission intensity. On the other hand, large-sized GHOE-1300 NPs have less surface defects with high emission intensity.

In all three samples, the red emission due to $^5D_0 \rightarrow ^7F_2$ transition is the most intense peak, and the color coordinates are very similar, so only one of the representative samples, that is, the GHOE-650 NPs, is shown with the International de l’Eclairage (CIE) diagram (Figure S3c).

### 2.5.2. Point Group Symmetry and Asymmetry Ratio of Eu$^{3+}$ Ions in the GHOE NPs

Structural change of the GHO host can be corroborated with the change of Stark component numbers from the PL spectral pattern of Eu$^{3+}$ ions, which is related to its point group symmetry.54,55 The original point group symmetry of Gd$^{3+}$/Hf$^{4+}$ sites in both OP and DF structures is $D_5h$.66 Interestingly, the number of Stark components (as highlighted with black asterisks) of the EDT ($\Delta J = \pm 2$ and $\Delta J = \pm 4$) keeps increasing as the annealing temperature of the GHOE NPs increases as can be easily seen from Table S1. Such changes are clearly seen in the PL emission characteristics of $^5D_0 \rightarrow ^7F_0$ (Figure 5a), $^5D_0 \rightarrow ^7F_2$ (Figure 5b), and $^5D_0 \rightarrow ^7F_4$ (Figure 5c) transitions as well. Accordingly, the point group symmetry of the GHO host reduces to $C_{nv}$ for the GHOE-650 NPs because of lattice strain and distortion induced by the small particle size and charge mismatch of ions after Eu$^{3+}$ doping. Furthermore, it changes to $D_2$ (for the GHOE-1100 NPs) and then to $C_{nv}$ (for the GHOE-1300 NPs) because of the effects of annealing and structural change, as depicted schematically in Figure 5e.

The asymmetry ratio $I_{5D0}$ is also highly sensitive to structural change and useful to understand the local symmetry around the Eu$^{3+}$ ions in the GHO host. As the GHO host goes from a highly DF structure to a highly OP structure, there is a progressive decrease of the asymmetry ratio of the Eu$^{3+}$ ions (Figure 5d). The $I_{RO}$ values of the GHOE-650, GHOE-1100, and GHOE-1300 NPs are 2.9, 2.0, and 1.6, respectively. This indicated that the local surrounding of Eu$^{3+}$ ions is highly asymmetric in the GHOE-650 NPs with the DF structure, whereas the asymmetry becomes relatively low in the GHOE-1300 NPs with the OP structure. Therefore, the change of the $I_{RO}$ values is in accordance with the structural difference of the GHOE NPs. Menushenkov et al. also found that the Debye Waller factor as the measure of root-mean-square deviation of the interatomic distance from the average value decreases with increasing annealing temperature for all Gd–O and Hf–O bonds of GHO by means of extended X-ray absorption fine structure measurements.13 This confirms the increase of order of the crystalline state with annealing temperature as reflected in the calculated $I_{RO}$ values.

Neither MDT nor EDT allows $^5D_0 \rightarrow ^7F_0$ transition of Eu$^{3+}$ ions. However, it is still often observed from Eu$^{3+}$-doped inorganic phosphors because of the CF-induced J-mixing effect that lowers the symmetry.56 According to the selection rule governing the EDT, this transition exists in low local symmetry situations of Eu$^{3+}$ ions, including $C_{2v}$, $C_{2}$, $C_{v}$, $C_{sh}$, $C_{2h}$, $C_{4v}$, $C_{4}$, and $C_{nv}$.57 As shown in Figure 5a, the $^5D_0 \rightarrow ^7F_2$ peak of the GHOE-650 NPs which are stabilized in the DF phase shows substantial intensity, and that of the GHOE-1100 and GHOE-1300 NPs is nearly absent because of the pyrochlore ordering.

Based on lifetime spectroscopy (Section 2.5.3), DFT-based cohesive energy calculations (Section 2.2), and local structure study (Section 2.3), Eu$^{3+}$ ions can be stabilized at both Gd$^{3+}$ and Hf$^{4+}$ sites. Whatever the Stark component is considered in this work, it is based on composite emission spectra (Figure 3b) which have the contributions of Eu$^{3+}$ ions at both Gd$^{3+}$ and Hf$^{4+}$ sites. To get individual emission spectra from these Eu@Gd and Eu@Hf sites, we need to carry out time-resolved emission spectroscopy (TRES) which can get individual spectra of Eu$^{3+}$ ions at both Gd$^{3+}$ and Hf$^{4+}$ sites. We are trying to establish collaborations to use TRES as our future projects.

#### 2.5.3. Excited State Lifetime and Quantum Yield

The $^5D_0$ emission decay profiles of all three GHOE samples at the $^5D_0 \rightarrow ^7F_2$ transition display a biexponential behavior (Figure S4). Lifetime values were obtained by fitting with biexponential function

$$I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

where $\tau_1$ and $\tau_2$ are actual lifetime values related to decay rates of corresponding exponential components, and $A_1$ and $A_2$ are biexponential fitting parameters. Based on the PL decay profiles corresponding to the $^5D_0$ excited state of Eu$^{3+}$ ions in the GHOE NPs and the lifetime values obtained after biexponential fitting, the average lifetime values were calculated using the following equation

$$\tau_{av} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

The average and individual lifetime values were mentioned in Table 4. In the GHOE-650 NPs with the DF structure, Gd$^{3+}$ ions exist in highly symmetric GdO$_6$ in the form of a cube, whereas Hf$^{4+}$ ions exist in highly distorted octahedra. The short and long
The distorted GdO8 site. Biexponential decay in other pyrochlore hosts such as the highly symmetric GdO8 site. Eu3+ ions also exhibited scalenohedra and HfO6 exists in highly symmetrical octahedra. In this case, the longer lifetime is attributed to Eu3+ ions sitting at a highly energetic X-ray radiation into visible light based on the RL spectrum.

For the GHOE-650 NPs, the EDT peak around 612 nm is more intense than the MDT peak at 592 nm with intense red emission because of the highly DF structure. After annealing at 1100 and 1300 °C, there is reversal of the EDT and MDT peak pattern. Now, the MDT peak overpowers the EDT one indicating the stabilization of the Eu3+ ion in highly OPP, consistent with previous results. Hence, the emission color changes from red to orange (Figure 6c), showing the RL tunability. Furthermore, the more intense MDT peak of the GHOE-1300 NPs suggests that most of the Eu3+ ions are located at sites with inversion symmetry, consistent with the asymmetry ratio values (Figure 6b). Figure 6d shows the RL emission spectra because of the presence of some divalent europium ion that resulted from the reduction of some of the Eu3+ ions on irradiation with highly energetic X-ray. The peak around 545 nm is ascribed to the electric dipole-allowed transition 4f7→5S2 (4f) of the Eu3+ ions. Interestingly, the GHOE-650 NPs have the highest fraction of the divalent europium ion, whereas the GHOE-1300 NPs have the least. This phenomenon is possibly due to the smallest particle size of the GHOE-650 NPs, and hence the largest numbers of exposed Eu3+ ions on the surface or the subsurface are subjected to the reduction reaction by X-ray.

The emission spectra under UV photon and X-ray are different because the luminescence mechanisms involved in these two cases are distinct. Specifically, under X-ray excitation, e−→h+ pairs (excitons) are generated, and the Eu3+ 4f→4f bands and hosts are excited together.33,58,59,69 In this situation, e− migrates to the Eu3+ centers before luminescence. Under UV excitation, only the Eu3+ (4f→4f) bands are excited, but not the host. Moreover, the conversion of X-ray excitation into visible light usually proceeds in four different steps. In the first step, GHOE absorbs an X-ray through the photoelectric effect and leads to creation of electron and holes. In the second step, these electrons and holes relax to generate large number of secondary

| Table 4. Luminescence Lifetime and Quantum Yield (QY) Values of the GHOE-650, GHOE-1100, and GHOE-1300 NPs |
|-------------------------------------------------|
| samples | τ1 (ms) | τ2 (ms) | τmean (ms) | χ2 | AQY (%) |
|--------|--------|--------|-----------|----|--------|
| GHOE-650 | 1.13 | 2.65 | 2.09 | 1.18 | 6.90 |
| GHOE-1100 | 0.92 | 2.67 | 2.27 | 1.12 | 7.35 |
| GHOE-1300 | 0.98 | 2.96 | 2.45 | 1.23 | 11.48 |

Table 5. Judd–Ofelt Analysis of the GHOE NPs

| samples | Aκ (s−1) | ANR (s−1) | IQY (%) | Ω2 (×10−21) | Ω4 (×10−21) | β1 (%) | β2 (%) | β3 (%) |
|--------|--------|--------|--------|-------------|-------------|--------|--------|--------|
| GHOE-650 | 236 | 198 | 54.3 | 4.97 | 3.12 | 17.8 | 59.7 | 18.8 |
| GHOE-1100 | 265 | 184 | 59.6 | 5.26 | 3.86 | 18.9 | 58.1 | 21.9 |
| GHOE-1300 | 281 | 172 | 62.1 | 4.22 | 3.21 | 21.1 | 56.8 | 21.6 |
electrons, holes, photons, and plasmons. Such relaxation also induces several other electronic excitations. These secondary electrons and holes lose their energy via electron–phonon interaction to give electron–hole pairs with near band gap energy. The third stage involves the transport of the electron–hole pairs (excitons) through the host material to a luminescent center (trap) and the excitation of the luminescent center. The final stage concerns the resulting luminescence. Materials which have a high light output and a short lifetime under photoexcitation may have a very low light output and/or a long lifetime under X-ray excitation. This is due to the energy losses and delays in the energy migration processes, which are absent in PL where the luminescent centers are directly and intentionally excited.

2.5.5. Thermal Quenching Behavior of GHOE NPs. Thermal stability of phosphors is a very important property for their applications toward solid-state lighting and high-power light-emitting diodes. Therefore, we have carried out emission spectroscopy of the GHOE-650 NPs at various temperatures using in situ PL measurements. Figure 7a shows emission spectra of the GHOE NPs measured from room temperature to 973 K. The spectral features do not change with the increase of temperature. At 298 K, the GHOE-650 NPs exhibit intense red emission because of hypersensitive electric dipole $^5D_0 \rightarrow ^7F_2$ transition. However, as temperature increases, there is monotonic reduction in emission intensity (Figure 7b). Such thermal quenching is attributed to a crossover mechanism wherein europium ions are thermally activated through the crossing point between the ground and the excited states. The quenching temperature, $T_{0.5}$, at which the emission intensity drops to 50% of that at room temperature, is about 625 K, indicating an extremely high thermal stability of the GHOE NPs. The thermal population of the charge transfer state ($^5D \rightarrow CT \rightarrow ^7F$) or the excited state ($^5D \rightarrow ^7F$) increases the chances of nonradiative relaxation.

In addition, the thermal quenching activation energy of the GHOE NPs was extrapolated from the slope of Figure 7c denoted from the following Arrhenius equation

$$\ln \left( \frac{I_0}{I} - 1 \right) = \frac{\Delta E}{kT} + C$$

where $I_0$ is initial emission intensity, and $I$ is the emission intensity at a given temperature $T$. For a given constant $A$ and a fixed value of Boltzmann constant $k$, $\Delta E$ denotes the activation energy.

Figure 6. (a) RL spectra, (b) variation of the RL asymmetry ratio, (c) chromaticity coordinate diagram, and (d) RL emission due to the Eu$^{2+}$ ion (because of the reduction of the Eu$^{3+}$ ions by X-ray irradiation) of the GHOE NPs.

Figure 7. (a) Emission spectra at temperatures ranging from 298 to 973 K, (b) corresponding temperature dependence of the PL emission intensity of the $^5D_0 \rightarrow ^7F_2$ transition, and (c) plot of $\ln(I_0/I - 1)$ vs $1/kT$ of the GHOE-650 NPs.
energy involved in thermal quenching process. The relationship of \(\ln(I_0/I - 1)\) and \(1/kT\) displayed linear behavior (Figure 7c). The activation energy calculated from this plot is equal to 0.425 eV for the thermal quenching. In our earlier work on \(\text{La}_2\text{Hf}_2\text{O}_7:\text{Eu}^{3+}\) NPs with an ideal pyrochlore structure, the activation energy value was found to be 0.410 eV which is slightly lower than the defect fluorite GHOE-650 NPs.59

2.6. Efficiency of Host to Dopant Energy Transfer by DFT Calculations. Based on the DFT-GGA-calculated total and partial DOSs, VBs from -4 to 0 eV of the OP structure have a main contribution from the O 2p states and a small contribution from the Gd 5d states (Figure 8a). The energy range is scaled with respect to Fermi energy (\(E_F\)), and the \(E_F\) is set at 0 eV. The upper and lower panels show DOS contributions from spin-up and spin-down components, respectively. The peak around -2.5 eV corresponds to Gd f states in the spin-up component. The lower part of the VB is dominantly contributed by the Hf d states in both spin components. The O 2p states are contributing throughout the VB. In the CB, a peak around 5.0 eV corresponds to Gd f states in the spin-up component. As a result, the electronic band gaps in spin-up and spin-down components are 3.45 and 2.56 eV, respectively. Figure 8bc shows the DFT-GGA-calculated DOSs of GHO with Eu doped at Gd and Hf sites, respectively. The overall DOSs have resemblance with ideal GHO. Eu f states contribute strongly at the VB edge in both spin-up and spin-down components. As a result, impurity states are generated at the VB edge around the \(E_F\) level.

For the DF structure, the DOS features (Figure 8d-f) are similar to those of the OP structure. However, less number of peaks presented in the DOSs of the DF structure signifies positional disordering. In the DOSs of Eu-doped DF, Eu f states contribute solely on the edges of the VB and the CB in spin-up and spin-down components. The electrons present at the VB edges participate in the photoexcitation. High contribution of Eu f states at the VB edges makes optical energy transfer of the GHO host to Eu\(^{3+}\) dopants favorable.

3. CONCLUSIONS

In this work, we have investigated the effect of structural changes of GHO NPs on their PL and RL using europium ions as a spectroscopic probe. GHO and GHO:Eu\(^{3+}\) (GHOE) NPs were synthesized by a MSS method at 650 °C and subjected to annealing at 1100 and 1300 °C with structural evolution. Raman spectroscopy confirms the stabilization of the GHOE-650 NPs with DFP, whereas the GHOE-1300 NPs with a perfectly OP structure. The structure evolution from the fluorite to pyrochlore phase renders a decreased asymmetry ratio of the Eu\(^{3+}\) dopant. Moreover, annealing of the GHOE NPs increases the luminescence emission intensity, quantum efficiency, excited state lifetime, and Stark components, and change the Eu local symmetry from \(C_4v\) (GHOE-650) to \(D_2\) (GHOE-1100) to \(C_{2v}\) (GHOE-1300). The effect of disorder—order transition is also evident from RL wherein the emission color changes from red to orange. High thermal stability is an added advantage of this phosphor for application in solid-state lighting. Our DFT results are corroborating with our experimental findings. Moreover, DFT DOSs analysis shows favorable localization of Eu f states in the VB of GHO, which makes host to dopant optical energy transfer possible.
4. EXPERIMENTAL: SYNTHESIS AND CHARACTERIZATION

Gd$_2$Hf$_2$O$_7$ (GHO) and Eu$^{3+}$-doped GHO (GHOE) NPs were synthesized using MSS at 650 °C (GHO-650 and GHOE-650), similar to our earlier work for La$_2$Hf$_2$O$_7$ NPs. However, by doping europium ions into the GHO host, Gd$^{3+}$ ions are replaced based on closeness in terms of ionic radius and ionic charge. The GHOE-650 sample was further annealed at 1100 and 1300 °C in air for 6 h, and the products are noted as GHOE-1100 and GHOE-1300, respectively. The details of synthesis, characterization, theoretical methodology, Judd–Ofelt analysis, and QY measurements are included in the Supporting Information as S1–S5, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03458. Details of synthesis, characterization, and theoretical methodology (PDF)

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Notes

The authors declare no competing financial interest.

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