Effect of Molten Salt Synthesis Processing Duration on the Photo- and Radioluminescence of UV-, Visible-, and X-ray-Excitable La$_2$Hf$_2$O$_7$:Eu$^{3+}$ Nanoparticles

Jose P. Zuniga,$^{†}$ Santosh K. Gupta,$^{†,§}$ Maya Abdou,$^{†}$ and Yuanbing Mao*,$^{†,‡,‡}$

1 Department of Chemistry and 2 School of Earth, Environmental, and Marine Sciences, University of Texas Rio Grande Valley, 1201 West University Drive, Edinburg, Texas 78539, United States
3 Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

Supporting Information

ABSTRACT: Ln$^{3+}$-ion-doped nanomaterials possess excellent properties because of their high color purity, longer excited state lifetime, narrow emission, and large Stokes shifts. In this work, we studied the correlation between the luminescence properties of La$_2$Hf$_2$O$_7$:Eu$^{3+}$ pyrochlore nanoparticles (NPs) synthesized by a molten salt synthesis (MSS) method at a relatively low temperature and several MSS processing durations (from 1 to 12 h). We synthesized these NPs with different sizes just by changing the MSS processing time without subjecting to high temperature. Raman spectroscopy confirmed the stabilization of the ideal pyrochlore structure of the La$_2$Hf$_2$O$_7$:Eu$^{3+}$ NPs at various MSS processing durations. The synthesized NPs exhibited bright red emission under UV, visible, and X-ray excitations, highlighting their potential applications as a red phosphor and scintillator. As the MSS processing time was increased from 1 to 12 h, a spectral change in the position of the charge transfer state in the La$_2$Hf$_2$O$_7$:Eu$^{3+}$ NPs was observed. The sample processed by the MSS with a duration of 3 h exhibited the highest luminescence intensity, which was attributed to its optimum crystals with least surface defects and less agglomeration. The obtained results strongly and unambiguously indicate the brighter side of this new type of pyrochlore-based NPs in the fast growing field of solid-state lighting and scintillator materials.

1. INTRODUCTION

Materials with A$_2$B$_2$O$_7$-type composition fall into a special class of structure called pyrochlore, in which A represents a trivalent rare-earth (RE) ion and B represents a tetravalent transition metal ion such as Sn$^{4+}$, Ti$^{4+}$, Zr$^{4+}$, and Hf$^{4+}$. Recently, they have gained a significant interest as ceramics because of their unique properties such as high radiation stability, ability to accommodate actinides and lanthanides at both AIII and BIV sites, and ability to dissipate excess radiation energy by forming antisite defects. On the other hand, the pyrochlore structure has a more ordered structure, which causes the cations to prefer the site most suitable for their size. The A$^{3+}$ ions have an eightfold coordination with oxygen, and the B$^{4+}$ ions have a sixfold coordination with oxygen, giving them the capability to swapping sites in the lattice, which leads to antisite defects. Preference for either phase is contingent on the ionic radius of the RE$^{3+}$ ion in the A-site and the B$^{4+}$ ion in the B-site. The pyrochlore structure is favorable if the ionic radii of A$^{3+}$ and B$^{4+}$ ions are similar ($r_A/r_B < 1.46$). The oxygen vacancies are randomly distributed on the anion sites. The similar ionic radii of the A$^{3+}$ and B$^{4+}$ cations give them the capability to swapping sites in the lattice, which leads to antisite defects. On the other hand, the pyrochlore structure has $D_{abcd}$ symmetry and differs from the fluorite in that it has a more ordered structure, which causes the cations to prefer the site most suitable for their size. The A$^{3+}$ ions have an eightfold coordination with oxygen, and the B$^{4+}$ ions have a sixfold coordination with oxygen. The anion Wyckoff sites (8b and 48f) are entirely occupied.

Received: May 13, 2018
Accepted: June 20, 2018
Published: July 12, 2018

DOI: 10.1021/acsomega.8b00987
ACS Omega 2018, 3, 7757–7770
Among pyrochlores, La$_2$Hf$_2$O$_7$ stands out with unique properties such as high density, high refractive index, wide band gap, and high thermal/chemical stability, which are very important from a technical perspective. It has been envisaged to be a very good dielectric material because of its rather small band gap, and high thermal/chemical stability, which are very important from a technical perspective. It has been envisaged to be a very good dielectric material because of its rather low defect densities and less Fermi-level pinning than those of HfO$_2$. Also, because of its high stopping power for X- and γ-rays with $Z_{eff} = 72$ and its high density of 7.9 g/cm$^3$, it was found to be very attractive for novel high-energy radiation detectors. La$_2$Hf$_2$O$_7$ is also known to exhibit defect-induced luminescence on irradiation with ultraviolet photons, and the oxygen vacancies were found to be the most probable reason for the recombination centers in their photoluminescence process.

Doped RE$_2$Hf$_2$O$_7$ nanoceramics with metal ions have proven to be very successful in tailoring their electrical, optical, nuclear, and order–disorder phenomena; scintillation, etc. Our group recently has done some work on photo- and radioluminescence (RL) of the La$_2$Hf$_2$O$_7$:Eu$^{3+}$ nanoparticles (NPs). There are various ways to induce changes in the particle size of nanophase materials, such as changing the pH value of the precursor solution, varying the annealing temperature, altering the synthesis duration, differing the reaction kinetics, and modifying the thermodynamics of reactions. The changes of synthesis duration and temperature may indirectly affect the obtained particle size, crystallinity, coordination number, and geometry around dopant ions in an inorganic phosphor. This also leads to change in the type, size, and density of defects. It was reported that the synthesis temperature and duration have profound effects on the size, morphology, defect density, and surface energy of obtained products, which ultimately alter the optical properties of nanomaterials. Melato and his group investigated the effect of annealing time on the structure, morphology, and photoluminescent properties of MgAl$_2$O$_4$:In$^{3+}$ nanophosphor. On the other hand, Miotloung et al. investigated the effects of the annealing time on the optical properties of ZnAl$_2$O$_4$. There are a few more reports on the effect of annealing time on optical properties of YAG:Ce$^{3+}$ and ZnAl$_2$O$_4$:Gd$^{3+}$, etc. Not many studies in this direction have been carried out to explore the effect of synthesis processing time on the optical properties of nanophosphors, not to mention those during the molten salt synthesis (MSS) process, until the current study.

Exploitation of a luminescence probe that is sensitive to the local structure is expected to give useful information on its local site, site symmetry, and distribution ratio at the A$^3+$ and B$^{4+}$ sites in A$_2$B$_2$O$_7$-type compounds, which are very important for designing efficient optoelectronic devices. A 4f electron exhibits special photophysical characteristics compared with 3d and 5f electrons and therefore exploring nanomaterials doped with luminescent lanthanide ions has been found to be an indispensable approach for designing high-quality nanophosphors for future applications. Once doped with the La$^{3+}$ ion, NPs exhibit photophysical properties that are different from those of their bulk counterparts because of their small grains. Meltzer et al. reported increased photoluminescence efficiency of nanophase materials compared to that of their bulk counterparts.

It is well documented that Eu$^{3+}$ ions form an ideal spectroscopic probe for lanthanide sites due to their distinct spectroscopic signature, integer J-numbers, and the ease of assessing their site symmetry. Their ground-state $^5D_0$ and the most informative excited state $^5D_2$ are nondegenerate. Therefore, they are not split by crystal-field effects. Eu$^{3+}$ ions with the characteristic orange red emission at 592 and 614 nm are highly sensitive to the local surroundings. The Eu$^{3+}$ photoluminescence and spectral data can give highly reliable information on whether the dopant ions are localized on the surface of A$_2$B$_2$O$_7$ NPs or they have percolated either interstitially or substitutionally inside the A$_2$B$_2$O$_7$ lattice. Although closeness in size and charge guarantees most of the Eu$^{3+}$ ions to occupy the A$^3+$ site, there may be lattice strain to mismatch in ionic radii between eight-coordinated Eu$^{3+}$ and RE$^{3+}$ ions, which may affect the optical properties of Eu$^{3+}$ ions. Despite the wide array of applications, investigations on RE$_2$Hf$_2$O$_7$-type compositions are limited. To the best of our knowledge, among the available literature, only Papan and his group have carried out luminescence spectroscopy and Judd–Ofelt (JO) analyses on their combustion-synthesized europium-doped Y$_2$Hf$_2$O$_7$, Gd$_2$Hf$_2$O$_7$, and Lu$_2$Hf$_2$O$_7$. In this study, we have correlated the changes in optical properties of europium-doped lanthanum hafnate La$_2$Hf$_2$O$_7$:Eu$^{3+}$ NPs synthesized by an environmentally friendly MSS method as a function of processing duration with the Judd–Ofelt parameter and other related photophysical parameters.

2. RESULTS AND DISCUSSION

2.1. Raman Spectroscopy. Raman spectroscopy is one of the most sensitive techniques to probe metal–oxygen (M–O) vibrational modes, so it is one of the most sought-out techniques to differentiate between ordered pyrochlore and disordered fluorite phases (DFP), which is very difficult to achieve by X-ray diffraction (XRD) most of the time. The disordered fluorite phase (DFP) exists in the $Fm\bar{3}m$ space group wherein all of the cationic ions (A$^3+$ and B$^{4+}$) are randomly distributed. On the other hand, the ordered pyrochlore phase (OPP) known to exist in the $Fd\bar{3}m$ space group exhibits close structural resemblance to the fluorite phase except that there are two cationic sites and three anionic sites (i.e., 48f(O$_1$), 8a(O$_2$), and 8b(O$_{III}$)) with one-eighth of the oxygen ions (O$_{III}$) at the 8b site absent in the OPP. Therefore, Raman spectroscopy provides unambiguous information in determining whether a synthesized A$_2$B$_2$O$_7$-sample exists in an OPP or a DFP structure.

On the basis of the group theory, it is well documented in the literature that there are a total of six Raman-active vibrational modes for OPP existing in the wavenumber range of 200–1000 cm$^{-1}$, specifically, $\Gamma_{OPP} = A_{1g} + E_g + 4F_{2g}$. On the other hand, the DFP has mainly one active Raman mode, that is $\Gamma_{DFP} = F_{2g}$ because the seven O$^{2-}$ ions are randomly oriented over the eight anionic sites in this particular phase, leading to a high level of structural disordering. The transition from the OPP ($Fd\bar{3}m$ (A$_2$B$_2$O$_7$O$^-$), space group, Z =
have started to appear around 320, 400, and 520 cm$^{-1}$. The peak positions for the other La$_2$Hf$_2$O$_7$ NPs are around 304, 321, 401, 506, 520, and 610 cm$^{-1}$, which correspond to F$_{2g}$, E$_u$, F$_{3g}$, A$_{1g}$, F$_{2g}$, and F$_{5g}$.

The vibrational Raman bands of F$_{2g}$, E$_u$, and F$_{5g}$ modes at a low wavenumber region (300–400 cm$^{-1}$) originate from vibrations of the La–O and Hf–O bonds, whereas the F$_{2g}$ modes at high wavenumbers (522 and 641 cm$^{-1}$) come into picture due to stretching of the Hf–O bonds. There is a small kink around 750 cm$^{-1}$, which is attributed to the distortion of HfO$_6$ octahedral geometry. The Raman spectroscopy data acquired suggested that the as-synthesized La$_2$Hf$_2$O$_7$:Eu$^{3+}$ NPs are indeed in the pyrochlore phase based on the observed six typical Raman-active vibrational modes existing in the wavenumber range of 200–1000 cm$^{-1}$. On the other hand, a defect fluorite phase only processes one active vibrational mode. This mode usually occurs at ~300 cm$^{-1}$ similar to the naturally occurring defect fluorite rare-earth hafnate.

There are not much appreciable differences in the Raman spectra of the Eu$^{3+}$-doped La$_2$Hf$_2$O$_7$ samples (Figure 1b) from their undoped counterparts, indicating that europium doping does not alter the basic pyrochlore network of lanthanum hafnate.

2.2. XRD Patterns and Refinement. Differentiation of the structures of DFP ($Fm3m$) and OPP ($Fd3m$) using X-ray diffraction (XRD) is very difficult because of their phase resemblance within the cubic structure family. XRD in most cases using a Cu Kα source in common research labs fails to detect weaker superlattice reflections of the pyrochlore phase. A stronger source such as synchrotron radiation is needed to resolve the very weak lattice reflection. As reported in the literature, pertaining to the Rietveld refinement of the pyrochlore phase La$_2$Zr$_2$O$_7$ and La$_2$Hf$_2$O$_7$, a synchrotron X-ray source is really needed. More specifically, these superlattice reflections are relatively strong in the neutron patterns, likely a consequence of the greater relative sensitivity of neutrons to O atoms in the presence of Hf and Ln atoms. For this reason, our lab XRD instrument identified only the defect fluorite phase from our LHO and LHOE NPs, which should not be considered as a discrepancy with the Raman data (Figure 1).

In our case, we have used XRD to confirm that our samples are free of impurities and to estimate their particle size.

Figure 2 shows the XRD patterns of the La$_2$Hf$_2$O$_7$ and La$_2$Hf$_2$O$_7$:5.0%Eu$^{3+}$ powder samples synthesized at 650 °C by the MSS method with various processing durations. No visible impurity phases such as La$_2$O$_3$, Eu$_2$O$_3$, and HfO$_2$ were detected. Meanwhile, it is well known that the presence of weak reflections due to the ordered pyrochlore phase (OPP) cannot be ruled out, as they are sometimes not detected in Cu Kα-based XRD. Therefore, the ideal scenario would be probing the crystal phase of these samples using laser-based Raman spectroscopy, synchrotron X-ray diffraction, or neutron diffraction. Here, all of the XRD patterns and the corresponding 2θ angles and (hkl) indexes are in agreement with reported XRD pattern of La$_2$Hf$_2$O$_7$ (JCPDS No. 78-1292). When comparing the undoped and europium-doped samples, the results indicate that doping does not change the crystal structure of the La$_2$Hf$_2$O$_7$ host. In addition, changing the MSS processing duration did not change the crystal structure of the prepared NPs.

The determined particle size is given in Table 1, which displays the lattice parameter and particle size as a function of the MSS processing duration for both the undoped and doped La$_2$Hf$_2$O$_7$ samples. As far as the lattice parameter is concerned,
as the MSS processing duration increases, there is not much change in the case of the undoped La$_2$Hf$_2$O$_7$ samples, but the lattice parameter decreases in the case of the La$_2$Hf$_2$O$_7$:Eu$^{3+}$ samples.

Regarding the particle size, it can be seen that there is an increase with an increase in the MSS processing duration. The increased particle size is a result of the longer MSS processing time to allow the continuous growth of the NPs. Furthermore, it can be seen that the particle size decreases after doping La$_2$Hf$_2$O$_7$ with 5% Eu$^{3+}$ at the same MSS processing duration.

On doping a foreign ion into a crystal lattice, the crystallite size is reduced because of the lattice distortion caused by the difference in the ionic radius of the dopant and the original ion replaced. There is also a possibility that a fraction of the Eu$^{3+}$ dopants substitutes the Hf$^{4+}$ sites, which leads to the creation of oxygen vacancies and consequently significant strain and reduction in particle size in the La$_2$Hf$_2$O$_7$ lattice.

To rule out the formation of any metastable state in the La$_2$Hf$_2$O$_7$:Eu$^{3+}$ NPs by the MSS at a relatively low temperature of 650 °C, the Rietveld refinement of the XRD data and thermogravimetric analysis (TGA) were carried out using LHO-6h and LHOE-6h NPs as representatives. The Rietveld-refined XRD patterns of these two samples are shown in Figure 3a,b. The lattice parameter, cell volume, space group, and bond angle estimated from the refinement along with other refinement parameters are tabulated in Table S1. Our original XRD data were fitted well by the Rietveld refinement with the fluorite structure instead of the pyrochlore phase with superlattice reflection. The crystal structure of the LHO-6h and LHOE-6h NPs (Figure S1) is in agreement with previous reports for La$_2$Hf$_2$O$_7$. The estimated uncertainty on the lattice parameter is 10.777 ± 0.001 from the LHO-6h NPs and 10.765 ± 0.001 from the LHOE-6h NPs (Table S1). It can also be seen that doping Eu$^{3+}$ into the La$_2$Hf$_2$O$_7$ lattice does not distort its basic fluorite network, which can be easily visualized from Figures 4 and S1b. The chemical content of the unit cell is 16.0000 La + 48.0002 O + 16.0000 Hf + 8.0001 O.

As the MSS processing duration increased from 1 to 12 h, SEM images (Figure 4) confirmed that the particle size of the LHOE NPs kept increasing, which is consistent with the calculated values from the XRD data (Figure 2 and Table 1). Moreover, the particles look spherical at a short MSS processing duration but they tend to form large clusters and finally agglomerate at longer MSS processing times of 9 and 12 h. The particle size distribution of the LHOE NPs was calculated by ImageJ from these SEM images (Figure S2). There is a progressing enhancement of the obtained mean diameter of these LHOE NPs from 19 to 50 nm as the MSS processing time increased from 1 to 12 h. The representative transmission electron microscopy (TEM) image of the LHOE-6h NPs clearly shows that the synthesized NPs have well-defined morphology (Figure S3) and their size is in a nanometer range with uniform distribution.

**2.3. TGA Measurements.** TGA data (Figure 5) were also collected to rule out the possible formation of any metastable state in the LHO and LHOE NPs synthesized by the MSS method. There is barely any weight change from the LHO-6h and LHOE-6h NPs other than the initial weight loss due to physisorbed water molecules and residual nitrate ions from the molten salt. Both samples are very stable throughout the temperature range up to 1000 °C. This again suggested the

| samples | $2\theta$ (deg) | FWHM (β) | lattice parameter (Å) | particle size (nm) |
|---------|----------------|----------|-----------------------|-------------------|
| LHO-1h  | 28.67          | 0.74     | 10.77                 | 10.7 ± 1.7        |
| LHO-3h  | 28.68          | 0.36     | 10.77                 | 22.1 ± 1.2        |
| LHO-6h  | 28.67          | 0.34     | 10.77                 | 23.4 ± 1.2        |
| LHO-9h  | 28.68          | 0.31     | 10.77                 | 25.6 ± 1.1        |
| LHO-12h | 28.70          | 0.29     | 10.77                 | 27.4 ± 1.1        |
| LHOE-1h | 28.63          | 0.47     | 10.77                 | 14.9 ± 0.9        |
| LHOE-3h | 28.66          | 0.43     | 10.78                 | 18.5 ± 0.8        |
| LHOE-6h | 28.68          | 0.36     | 10.77                 | 22.1 ± 0.7        |
| LHOE-9h | 28.70          | 0.34     | 10.77                 | 23.4 ± 0.7        |
| LHOE-12h| 28.67          | 0.33     | 10.77                 | 24.1 ± 0.7        |
thermal stability of the La$_2$Hf$_2$O$_7$ NPs for potential high-temperature applications such as nuclear waste host, thermal barrier coatings, and luminescence host.

2.4. Excitation and Emission Spectra of Photoluminescence. From the excitation spectra of the La$_2$Hf$_2$O$_7$:5%Eu$^{3+}$ NPs processed by MSS at 650 °C for different time intervals (Figure 6a), we could see a broad band ranging from 220 to 320 nm, and there are several very fine features from 350 to 500 nm. Such a broad band is attributed to the allowed charge transfer state (CTS) with three possible origins: (a) host absorption band due to electronic transition from O$^{2-} \rightarrow$ Hf$^{4+}$, (b) intervalence charge transfer between Hf$^{4+}$ and Eu$^{3+}$, and (c) the predominant contribution would be due to electron transfer from O$^{2-} \rightarrow$ Eu$^{3+}$. The fine structure in the region of 350–500 nm is attributed to the intra$f$–$f$ transition of Eu$^{3+}$ ions with peaks at 362, 383, 395, 414, and 464 nm assigned to $^7$F$_0 \rightarrow ^5$D$_0$, $^7$F$_0 \rightarrow ^5$G$_{2-4}$, $^7$F$_0 \rightarrow ^5$L$_{6'}$, $^7$F$_0 \rightarrow ^5$D$_2$, and $^7$F$_0 \rightarrow ^5$D$_{4'}$, respectively. Among them, the intensities of the 395 nm (near UV) and 464 nm (blue light) peaks are the highest. This indicated that our La$_2$Hf$_2$O$_7$:5%Eu$^{3+}$ NPs have the ability to be effectively pumped by far UV, mid UV, near UV, blue light, and green light for being used as a photoluminescence host. From all of our La$_2$Hf$_2$O$_7$:5%Eu$^{3+}$ NPs synthesized by the MSS route, we could see that the photoluminescence excitation (PLE) intensity of the $f$–$f$ band is higher than that of the CTS. This is very unusual and highly desirable because intuitively the $f$–$f$ transition is forbidden in nature, whereas the CTS is an allowed transition. This can be attributed to two reasons: (i) overlap of the CTS and the absorption band of the

Figure 3. Rietveld-refined XRD patterns of the (a) LHO-6h and (b) LHOE-6h NPs.
host$^{51}$ and (ii) the forbidden $4f-4f$ transition “steals” some intensity from the allowed CTS transition.$^{52}$ Excitation lines originating from the $^7F_0 \rightarrow ^5L_6$ ($\approx 395$ nm) and $^7F_0 \rightarrow ^5D_2$ ($\approx 464$ nm) transitions are highly suitable as color converters in light-emitting diodes (LEDs) because they overlap very well with the emission spectra of efficient near-UV and blue LEDs, respectively.$^{53}$ However, there is no perfect correlation between the MSS processing duration and the variation in the wavelength position of the CTS maxima of our LHOE NPs (Figure 6b). Initially, the LHOE-1h sample with the smallest particle size displayed the maximum blue shift compared to that in the LHOE-3h sample, indicating the widening of band gap. From the LHOE-3h sample to the LHOE-6h sample and then to the LHOE-9h sample, the CTS maxima exhibited a blue shift although there is a continuous increase in particle size. Finally, there was a red shift in the CTS maxima from the LHOE-9h sample to the LHOE-12h sample. The lack of perfect correlation between the CTS maxima and the MSS processing duration can be attributed to the fact that there were accompanying structural changes along with the MSS processing duration and particle size variation. Although the reason is unknown, further control of the identity of these particles by proper synthesis procedures and detailed investigation by various characterization techniques are guaranteed. Moreover, such observation in this case cannot be attributed to quantum confinement, which is normally observed when nanoparticles are sufficiently small, typically 10 nm or less. Such a phenomenon is more prevalent in systems with simple energy-level diagrams, such as metal or semiconductor nanoparticles. Pyrochlore oxides, such as $\text{La}_2\text{Hf}_2\text{O}_7$,

Figure 4. Scanning electron microscopy (SEM) micrographs of the LHOE NPs as a function of the MSS processing duration: (a) 1 h, (b) 3 h, (c) 6 h, (d) 9 h, and (e) 12 h.

Figure 5. TGA graphs of the (a) LHO-6h and (b) LHOE-6h NPs.
have complex band diagrams: the valence band (VB) is mainly contributed from O 2p, whereas the conduction band (CB) has contributions from Hf 4d, La 4d, and La 4f states. The La$_2$Hf$_2$O$_7$:5%Eu$^{3+}$ NPs processed by MSS for different durations displayed similar emission spectral features of the Eu$^{3+}$ ion after being excited at 265 nm (Figure 7a). The peaks at 579, 592, 612, 655, and 710 nm are related to the $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$ (magnetic dipole transition, MDT, $\Delta J = \pm 1$), $^5D_0 \rightarrow ^7F_2$ (hypersensitive electric dipole transition, EDT, $\Delta J = \pm 2$), $^5D_0 \rightarrow ^7F_3$, and $^5D_0 \rightarrow ^7F_4$ transitions, respectively. A few important observations can be made from these emission spectra: (i) appearance of the $^5D_0 \rightarrow ^7F_0$ transition, (ii) significant stark splitting of the $^5D_0 \rightarrow ^7F_1$ (MDT), $^5D_0 \rightarrow ^7F_2$ (hypersensitive EDT), and $^7D_0 \rightarrow ^7F_2$ (EDT) transitions, and (iii) higher intensity of the $^5D_0 \rightarrow ^7F_2$ transition than that of the $^5D_0 \rightarrow ^7F_1$ transition. The intensity of the $^5D_0 \rightarrow ^7F_1$ MDT peak at 592 nm is independent of the local environment of the Eu$^{3+}$ ion. On the other hand, the intensity of the hypersensitive EDT peak is easily affected by the local symmetry/environment of Eu$^{3+}$ ions and the crystal field induced by surrounding ligands. The ratio of integral areas of the $^5D_0 \rightarrow ^7F_2$ and $^7D_0 \rightarrow ^7F_2$ transitions, known as asymmetry factor, gives information related to the local symmetry of Eu$^{3+}$ ions in hosts. The origins of certain transitions, such as $^5D_0 \rightarrow ^7F_0$, $^7D_0 \rightarrow ^7F_2$, and $^7D_0 \rightarrow ^7F_2$, are governed by neither MDT nor EDT. Their appearance in an emission spectrum indicated a highly asymmetric environment around the europium ion. Therefore, we concluded that the Eu$^{3+}$ ions in the La$_2$Hf$_2$O$_7$:5%Eu$^{3+}$ NPs are localized in a highly asymmetric and distorted environment.

In fact, on the basis of the selection rule allowed for electric dipole, the $^5D_0 \rightarrow ^7F_0$ transition is allowed only with point group symmetry designated as $C_{4v}$, $C_{3v}$, $C_{4h}$, $C_{3h}$, $C_{2h}$, $C_{4i}$, $C_{3i}$, and $C_{2i}$. On the basis of the splitting pattern in the emission characteristics of our La$_2$Hf$_2$O$_7$:Eu$^{3+}$ NPs, there is no splitting observed in the $^5D_0 \rightarrow ^7F_0$ transition. By Gaussian deconvolution of the $^5D_0 \rightarrow ^7F_2$, $^7D_0 \rightarrow ^7F_2$, $^7D_0 \rightarrow ^7F_2$, and $^7D_0 \rightarrow ^7F_2$ transitions, the numbers of stark components were found to be 3, 2, 2, and 3, respectively (Figure 8). This phenomenon suggests the $C_{4v}$ point group symmetry for Eu$^{3+}$ ions in our doped La$_2$Hf$_2$O$_7$ NPs, whereas the actual symmetry of both A and B sites of A$_2$B$_2$O$_7$ compounds is $D_{3d}$. The reduction of the symmetry of Eu$^{3+}$ ions in the La$_2$Hf$_2$O$_7$ host of these NPs could be induced by the lattice strain due to the mismatch of the ionic radii of La$^{3+}$ and Eu$^{3+}$ ions. It is also

Figure 6. (a) Excitation spectra and (b) variation of the CTS maxima of the La$_2$Hf$_2$O$_7$:Eu$^{3+}$ NPs as a function of the MSS processing duration varying from 1 to 12 h.

Figure 7. (a) Emission spectra and (b) variation of the integral emission intensity of the La$_2$Hf$_2$O$_7$:5%Eu$^{3+}$ NPs as a function of the MSS processing duration varied from 1 to 12 h.
possible that the 5.0% Eu³⁺ ions are not entirely stabilized at the La³⁺ site in the host lattice. In other words, some of the Eu³⁺ ions may get localized at the Hf⁴⁺ site, which invokes the need for charge compensation by oxygen vacancies. Such defects in the vicinity of Eu³⁺ ions further reduce the local structural symmetry of the Eu³⁺ ions. Moreover, the hyper-sensitive EDT band is more intense than the MDT band, which also indicates the lower symmetry of the Eu³⁺ ion. In fact, the LHOE-3h sample has the maximum asymmetry ratio and maximum emission intensity (Table 2 and Figure 7b). By correlating the asymmetry ratio with the particle size/surface defects of our La₂Hf₂O₇:5%Eu³⁺ NPs, there are two ways to look into this phenomenon. The highest asymmetry ratio from the LHOE-3h sample suggests a highly asymmetric local environment around the Eu³⁺ ions compared with other LHOE samples. Therefore, Laporte’s selection rules are more relaxed for the LHOE-3h sample compared with the other samples, which means higher transition probability as well as oscillator strength for the f−f transition, leading to enhanced emission output. Further, this phenomenon can also be explained in terms of size/surface defects. The LHOE-3h sample has minimal surface defects and least agglomeration that favor high radiative transition and low scattering of excited and emitted light, respectively, leading to high luminescence output. The PL emission enhancement up to 3 h MSS processing duration can be ascribed to the reduction in nonradiative pathways as a result of reduction in surface defects with the increased particle size. Beyond 3 h MSS processing duration, the La₂Hf₂O₇:5%Eu³⁺ NPs tend to agglomerate, which may cause scattering of the emitted light and therefore reduction in emission intensity. These observations could be explained on the basis of our SEM results (Figure 4). Figure 9 schematically shows the progressive increase in particle size along the increasing MSS processing duration, which reflects the increased particle size but reduced surface defects.

Furthermore, the application of X-ray-excited luminescence (XEL) has been explored for scintillating and bioimaging purposes, which require bright luminescent particles. Studies related to the variation of the radioluminescence output of the La₂Hf₂O₇:5%Eu³⁺ NPs as a function of the MSS processing duration will give highly useful information with respect to the optimized processing time of Eu³⁺ ions for X-ray luminescence. The emission spectra under X-ray excitation with the power of 12 W (Figure 10a) display typical spectral features of the Eu³⁺ ions similar to those obtained under UV excitation (Figure 7a). The X-ray luminescence from the LHOE-3h sample was the brightest among all of the samples we studied (Figure 10b).

Table 2. Asymmetry Ratio of the La₂Hf₂O₇:5%Eu³⁺ NPs as a Function of the MSS Processing Time Varied from 1 to 12 h

| samples       | PL     | RL  |
|---------------|--------|-----|
| LHOE-1h       | 1.57   |     |
| LHOE-3h       | 3.99   | 2.57|
| LHOE-6h       | 3.19   |     |
| LHOE-9h       | 3.49   |     |
| LHOE-12h      | 3.34   |     |

Figure 8. Stark splitting patterns of the ⁵D₀ → ⁷F₉ (J = 0−4) transitions of the LHOE-3h NPs.

Figure 9. Schematic showing the increase in the particle size of the La₂Hf₂O₇:5%Eu³⁺ NPs as a function of the MSS processing duration.
Eu3+ ions are localized at both La3+ (EuLa) and Hf4+ sites. For UV luminescence decay measurement, it was found that the Eu3+ ions get distributed at both La3+ and Hf4+ sites in the La2Hf2O7:Eu3+ NPs. Excitation with an energetic X-ray beam leads to the formation of negative antisite defects (EuHf′) and positive oxygen vacancy defects (V̈O) as indicated below by the Kroger–Vink notation.

$\text{Eu}^{3+} + \text{Hf}^{4+} \rightarrow \text{Eu}_{\text{Hf}} + V_O$

High-energy X-rays are produced by events that occur to disrupt the nuclear stability of atoms. Radiation having lower energy, such as ultraviolet, originates from the electron clouds that surround the nucleus or from the interaction of one atom with another. These forms of radiation occur due to the fact that electrons moving in orbits around the nucleus of an atom are arranged in different energy levels within their probability distribution functions. When a sample is excited by energetic X-ray beams, a large number of free charge carriers or excitons (bound state of e− and h+ pairs) are generated in the crystal lattice because of the photoelectric effect. In the case of La2Hf2O7, there are two crystallographic sites: eight-coordinated La3+ and six-coordinated Hf4+ sites. On the basis of the UV luminescence decay measurement, it was found that the Eu3+ ions are localized at both La3+ (EuLa) and Hf4+ sites (EuHf′). The Eu3+ ions occupying Hf4+ sites may lead to the generation of negative antisite defects (EuHf′) and positive oxygen vacancy defects (V̈O) as indicated below by the Kroger–Vink notation.

$\text{Eu}^{3+} + \text{Hf}^{4+} \rightarrow \text{Eu}_{\text{Hf}} + V_O$

UV-excited PL spectra displayed both EDT and MDT (Figure 7a). EDT is attributed to EuHf′ whereas MDT is attributed to EuLa. As discussed earlier, the Eu3+ ions get distributed at both the La3+ and Hf4+ sites in the La2Hf2O7:Eu3+ NPs. For La2Hf2O7, the valence band (VB) is composed of O 2p orbitals hybridized with Hf 5d orbitals along with a minor contribution from La 4f states. On the other hand, the conduction band (CB) is mainly composed of La 4d states (in majority spin component), 4f states (in minority spin component), and Hf 5d states. Hf 5d states contribute solely to the lower part of the conduction band.

The EuHf′ defects are XEL-active and amenable to emission under X-ray excitation. This is similar to what Dobrowolska et al. have observed in europium-doped barium hafnate. Excitation with an energetic 12 W X-ray beam leads to the formation of excitons (bound electron–hole pairs) between electrons in the lower part of the CB comprising Hf 5d states (5d1 Hf3+) and holes in the VB, if they possess similar momentum. The energy absorbed by excitons can be transported through the La2Hf2O7 lattice. They will be trapped in the EuHf′ defect sites, and then radiative recombination is followed. The $^3D_0 \rightarrow ^7F_j/^3D_0 \rightarrow ^7F_1$ ratio ($I_{AB}$) indicates a local crystal structure surrounding the doped Eu3+ ions. For the same LHOE-3h sample, the X-ray-excited luminescence shows an $I_{AB}$ value of 2.57, which is much lower as compared to that for the UV-excited luminescence (3.99). This indicated that the crystal symmetry surrounding the Eu3+ ions under X-ray excitation was predominantly from a high-symmetry site compared with that under UV excitation. This is due to the contribution of both EuHf′ and EuHf to the X-ray-excited luminescence, whereas only EuHf′ contributes to X-ray-excited luminescence.

Furthermore, the emitted photon counts corresponding to green and red emission under the UV excitation (Figure 7) are much larger than the ones under X-ray excitation (Figure 10). La2Hf2O7 is a material with high dielectric constant, and excitons formed in these cases on exposure to ionizing radiation such as X-ray are weakly bonded and are known as Wannier–Mott-type excitons. They break easily on collision with phonons. The number of excitons thus available for energy transfer to Eu3+ ions is small and hence low RL output. On the other hand, under UV excitation of 265 nm, the La2Hf2O7 host absorbs the energy and transfers it to radiative Eu3+ centers directly. This is known as host-sensitized energy transfer.

2.5. Potential Red-Emitting Phosphor Excitable by Various Lights. Commercial red phosphors for near-ultraviolet (NUV)-based white light-emitting diodes are excited by NUV or blue LEDs. On the basis of the Laporte selection rules, the intra f–f transitions are forbidden in nature; therefore, Eu3+-based phosphors have poor absorptivity in the near-ultraviolet/blue region. As a result, they exhibit weaker emission under similar excitation. Because the excitation spectra of our samples are very rich in near-, mid-, and far-UV regions as well as blue and green regions, they exhibit intense red emission corresponding to the $^3D_0 \rightarrow ^7F_2$ transition of Eu3+ ions under excitations by far UV (at 200 nm), mid UV (at 265 nm), near UV (at 393 nm), blue light (at 463 nm), and green light (at 534 nm) (Figure 11). Such intense red-emitting NPs can be explored for white LEDs based on phosphor-converted LEDs, wherein blue LEDs are combined with red and green phosphors.

Figure 10. (a) X-ray-excited luminescence of the La2Hf2O7:5%Eu3+ NPs, (b) corresponding XEL intensity expressed as an integrated area under the XEL spectra in the range of 550–750 nm as a function of the MSS processing time.
The unusual behavior of the LHOE-1h sample is attributed to S4. The LHOE-1h sample exhibited monoexponential decay. All other LHOE samples demonstrated bi-exponential decay behavior based on the exponential fitting equation given below

\[ I(t) = A_1 \exp\left(-\frac{t}{T_1}\right) + A_2 \exp\left(-\frac{t}{T_2}\right) \]  

(1)

where \( I(t) \) is the intensity at time \( t \), \( T_1 \) and \( T_2 \) are luminescence lifetimes, and \( A_1 \) and \( A_2 \) are their relative magnitudes. For all other samples, it is possible that Eu\(^{3+}\) ions have been stabilized at two different lattice sites in the La\(_2\)Hf\(_2\)O\(_7\) host. The fitted lifetime values and their relative percentage for all samples are tabulated in Table 3. Unlike in Nd\(_2\)Zr\(_2\)O\(_7\):Eu\(^{3+}\), we could not find any splitting in the \( ^{5}D_0 \rightarrow ^{7}F_0 \) transition at room temperature.\(^ {61} \) This may get resolved at a very low temperature close to that of liquid N\(_2\). The presence of more than one spectral peak in the \( ^{5}D_0 \rightarrow ^{7}F_0 \) transition shows that more than one site or species is present, but it does not allow the determination of the exact number of sites or species because the sites or species with a symmetry other than \( C_{av}, C_{va} \) or \( C_l \) do not give an observable \( ^{5}D_0 \rightarrow ^{7}F_0 \) transition.\(^ {62} \)

In a pyrochlore structure, there are two lattice sites, i.e., the eight-coordinated La\(^{3+}\) ion site with scalenohedra geometry and the six-coordinated Hf\(^{4+}\) ion site with distorted octahedral geometry. The stabilization of the Eu\(^{3+}\) ions at the Hf\(^{4+}\) sites invokes the need for charge compensation by forming negatively charged antisite defect Eu\(_{\text{Hf}}\) and positively charged oxygen vacancies V\(_{\text{O}}\) according to eq 2

\[ \text{Eu}^{3+} + \text{Hf}^{4+} \rightarrow \text{Eu}_{\text{Hf}}^- + \text{V}_{\text{O}}^+ \]  

(2)

The long lifetime is mostly associated with the symmetric La\(^{3+}\) sites, whereas the short one is due to the asymmetric Hf\(^{4+}\) sites where the \( f-f \) transition rules are relaxed and they become allowed. In our case, the long lifetime having a higher percentage could be ascribed to the Eu\(^{3+}\) ions sitting at the La\(^{3+}\) sites, whereas the short-lifetime species is because the Eu\(^{3+}\) ions are localized at the Hf\(^{4+}\) sites. The reason is obviously the closeness of the ionic radii of the Eu\(^{3+}\) and La\(^{3+}\) ions, and furthermore, there is no need for charge compensation. Another interesting observation from Table 3 is that there is a monotonous increase in the lifetime values for both short- and long-lived species as a function of the MSS processing duration. The increase in the lifetime values with the MSS processing time is ascribed to the reduction of surface defects, which ultimately results in the reduction of non-radiative transitions in the LHOE NPs.

2.7. Judd–Ofelt Analysis. Judd–Ofelt (JO) analysis is one of the most useful techniques to get information on rare-earth-doped phosphors by correlating the emission spectrum with the local structure, polarizability, and covalency. In the case of the europium ion, this hypothesis is valid only when its doped samples show a pure magnetic dipole transition. In case of other ions, an invariable absorption spectrum is used to carry out such analysis. The details of these calculations have already been reported in one of our earlier studies.\(^ {63} \) There are two phenomenal parameters, i.e., \( \Omega_2 \) and \( \Omega_4 \), which are known as short- and long-range JO parameters. Normally, \( \Omega_2 \) gives information related to the symmetry, covalency, and polarizability, whereas \( \Omega_4 \) gives information related to the rigidity and viscosity of the metal–oxygen bond.

Among all of the LHOE samples, the LHOE-3h sample was found to have the highest \( \Omega_2 \) and \( \Omega_4 \) values. The large \( \Omega_2 \) value reflects the high covalency around the Eu–O bond and maximum distortion, and the large \( \Omega_4 \) value indicates the rigid structure of the Eu–O bond.\(^ {64} \) The trend from all of the La\(_2\)Hf\(_2\)O\(_7\):5%Eu\(^{3+}\) NP samples is that \( \Omega_2 \) is greater than \( \Omega_4 \), which confirms the highly asymmetric environment around the Eu\(^{3+}\) ions in the La\(_2\)Hf\(_2\)O\(_7\):5%Eu\(^{3+}\) NPs, which is consistent with the discussed luminescence data. Therefore, the Judd–Ofelt analysis also supports our previous interesting observation that the LHOE-3h sample possesses the best optical properties.

Furthermore, as can be easily seen from Table 4, the radiative transition probability was maximum in the case of the LHOE-3h sample. Accordingly, its nonradiative transition rate is minimal. This may be attributed to the fact that the 3 h MSS

![Image](https://example.com/image.png)

**Figure 11.** (a) Emission spectra and (b) schematic of the LHOE-3h NPs under various excitations, including far UV, mid UV, near UV, blue light, and green light.

**Table 3. Photoluminescence Lifetime Values of the LHOE NPs at \( \lambda_{em} = 265 \text{ nm} \) and \( \lambda_{em} = 612 \text{ nm} \)**

| samples    | \( r_1 \) | \( r_2 \) | \( r_{1\%} \) | \( r_{2\%} \) |
|------------|----------|----------|----------------|----------------|
| LHOE-1h    | 1.6      | 100      | 0.00           |                |
| LHOE-3h    | 1.0      | 2.6      | 29.0           | 71.0           |
| LHOE-6h    | 1.0      | 2.7      | 29.0           | 71.0           |
| LHOE-9h    | 1.2      | 2.9      | 35.0           | 65.0           |
| LHOE-12h   | 1.0      | 2.9      | 27.0           | 73.0           |
processing duration is optimum to lower the surface defect density but not to create agglomerates. From the branching ratio measurements, we can see that the maximum photon emission from all of the LHOE samples comes from the red emission at 612 nm due to the $5D_0 \rightarrow 7F_2$ transition. Interestingly, $\beta_2$ is the highest for LHOE-3h (Table 4), which suggests that the red emission intensity is maximum for the LHOE-3h sample. On the other hand, its $\beta_1$ is the lowest, which indicated that the optical purity of red emission for this sample would be very high due to the least contribution from orange emission at 593 nm.

### 3. CONCLUSIONS

In summary, we demonstrated that the europium-doped lanthanum hafnate (La$_2$Hf$_2$O$_7$:Eu$^{3+}$) nanoparticles with an ordered pyrochlore phase structure could be successfully prepared at 650 °C by a molten salt synthesis method for various durations. The emission output and quantum yield were found to be the highest for the MSS-processed sample for 3 h owing to its least surface defect and least agglomeration. The emission spectrum revealed the predominant asymmetric environment of Eu$^{3+}$ ions with large spectral splitting and the presence of the forbidden $5D_0 \rightarrow 7F_2$ transition. The optical purity of red emission was also very high for the LHOE-3h NPs because of the least contribution among all of the LHOE samples from orange emission at 593 nm as seen from the branching ratio calculations. The large spectral splitting could be seen in the reduction of point group symmetry from $D_{2d}$ to $C_{4v}$ because of the created lattice strain and distortion due to the localization of the Eu$^{3+}$ ions at La$^{3+}$/Hf$^{4+}$ sites. The synthesized nanoparticles displayed a unique ability of emitting bright red light under far-UV to green light excitations. These La$_2$Hf$_2$O$_7$:Eu$^{3+}$ nanoparticles were further explored for their applications as radioluminescent phosphors. Interestingly, the synthesized La$_2$Hf$_2$O$_7$:Eu$^{3+}$ NPs have the ability to converting highly energetic X-ray into red light, which highlights its suitability for X-ray scintillators. Our results indicate the important role that the molten salt synthesis processing duration plays in optimizing nanophosphors for optoelectronic applications. This work opens a new pathway to optimize the molten salt synthesis conditions suitably for getting highly efficient luminescent materials for phosphor and scintillator applications.

| samples    | $A_R$ (s$^{-1}$) | $A_{NR}$ (s$^{-1}$) | $\eta$ (%) | $\Omega_2$ (x10$^{-20}$) | $\Omega_4$ (x10$^{-20}$) | $\beta_1$ (%) | $\beta_2$ (%) | $\beta_3$ (%) |
|------------|------------------|---------------------|-------------|--------------------------|--------------------------|--------------|--------------|--------------|
| LHOE-1h    | 189              | 437                 | 30.2        | 1.02                     | 0.99                     | 26.5         | 41.8         | 20.4         |
| LHOE-3h    | 294              | 186                 | 61.2        | 2.37                     | 1.40                     | 17.0         | 62.4         | 18.4         |
| LHOE-6h    | 269              | 177                 | 60.3        | 2.06                     | 1.38                     | 18.6         | 59.3         | 19.7         |
| LHOE-9h    | 282              | 151                 | 65.1        | 2.25                     | 1.32                     | 17.7         | 61.9         | 18.0         |
| LHOE-12h   | 274              | 148                 | 64.8        | 2.16                     | 1.28                     | 18.3         | 61.2         | 18.1         |

$A_R$, radiative rate; $A_{NR}$, nonradiative rate; $\Omega$, Judd–Ofelt parameter; and $\beta$, branching ratio.
4. EXPERIMENTAL DETAILS

4.1. Synthesis of \( \text{La}_2\text{Hf}_2\text{O}_7:5\%\text{Eu}^{3+} \) NPs. In this study, we synthesized the \( \text{La}_2\text{Hf}_2\text{O}_7:5\%\text{Eu}^{3+} \) NPs through the facile MSS method as reported before but with various processing durations (from 1 to 12 h) instead of the standard 6 h. The chemicals used are all of analytical grade and were used without any further purification. Lanthanum nitrate hexahydrate (\( \text{La(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}, 99.0\% \)), hafnium dichloride oxide octahydrate (\( \text{HfOCl}_2\cdot8\text{H}_2\text{O}, 99.0\% \)), and europium(III) nitrate hexahydrate (\( \text{Eu(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}, 99.9\% \)) were first measured in stoichiometric ratio and dissolved in water (Millipore, 18.2 mΩ at 25 °C). After 30 min of stirring, 200 mL of ammonium hydroxide was titrated into the mixture solution dropwise within ~2 h. This first step allows the formation of a single-source precursor via a co-precipitation technique. In the next step, potassium nitrate (\( \text{KNO}_3, 99.9\% \)), sodium nitrate (\( \text{NaNO}_3, 98\% \)), and the formed single-source precursor were mixed in a ratio of 30:30:1 and grinded together into fine powder. The fine powder was then MSS-processed at 650 °C for various hours, more specifically, 1, 3, 6, 9, and 12 h, as shown in Scheme 1. The synthesized \( \text{La}_2\text{Hf}_2\text{O}_7:5\%\text{Eu}^{3+} \) NPs were finally washed multiple times with deionized water to remove any residual salt from the surface of the obtained NPs. On the basis of the MSS processing durations, the \( \text{La}_2\text{Hf}_2\text{O}_7:5\%\text{Eu}^{3+} \) NPs were denoted LHOE-1h, LHOE-3h, LHOE-6h, LHOE-9h, and LHOE-12h, respectively. Similarly, undoped \( \text{La}_2\text{Hf}_2\text{O}_7 \) NP counterparts were synthesized and labeled as LHO-1h, LHO-3h, LHO-6h, LHO-9h, and LHO-12h, respectively. On the basis of the authors’ experience, the MSS method allows for a size-controllable synthesis of these \( \text{A}_2\text{B}_2\text{O}_7 \) refractory metal oxide NPs at a relatively low temperature while ensuring no fluorite–pyrochlore phase transformation.\(^{4,13,16,36}\)

4.2. Characterization. All synthesized \( \text{La}_2\text{Hf}_2\text{O}_7:5\%\text{Eu}^{3+} \) NPs were systematically characterized using X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), photoluminescence (PL), radioluminescence (RL), fluorescence decay, quantum yield, and time-resolved emission spectroscopy. Powder XRD was used to distinguish any phase formation of a single-source precursor via a co-precipitation technique. In the next step, potassium nitrate (\( \text{KNO}_3, 99.9\% \)), sodium nitrate (\( \text{NaNO}_3, 98\% \)), and europium(III) nitrate hexahydrate (\( \text{Eu(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}, 99.9\% \)) were first measured in stoichiometric ratio and dissolved in water (Millipore, 18.2 mΩ at 25 °C). After 30 min of stirring, 200 mL of ammonium hydroxide was titrated into the mixture solution dropwise within ~2 h. This first step allows the formation of a single-source precursor via a co-precipitation technique. In the next step, potassium nitrate (\( \text{KNO}_3, 99.9\% \)), sodium nitrate (\( \text{NaNO}_3, 98\% \)), and the formed single-source precursor were mixed in a ratio of 30:30:1 and grinded together into fine powder. The fine powder was then MSS-processed at 650 °C for various hours, more specifically, 1, 3, 6, 9, and 12 h, as shown in Scheme 1. The synthesized \( \text{La}_2\text{Hf}_2\text{O}_7:5\%\text{Eu}^{3+} \) NPs were finally washed multiple times with deionized water to remove any residual salt from the surface of the obtained NPs. On the basis of the MSS processing durations, the \( \text{La}_2\text{Hf}_2\text{O}_7:5\%\text{Eu}^{3+} \) NPs were denoted LHOE-1h, LHOE-3h, LHOE-6h, LHOE-9h, and LHOE-12h, respectively. Similarly, undoped \( \text{La}_2\text{Hf}_2\text{O}_7 \) NP counterparts were synthesized and labeled as LHO-1h, LHO-3h, LHO-6h, LHO-9h, and LHO-12h, respectively. On the basis of the authors’ experience, the MSS method allows for a size-controllable synthesis of these \( \text{A}_2\text{B}_2\text{O}_7 \) refractory metal oxide NPs at a relatively low temperature while ensuring no fluorite–pyrochlore phase transformation.\(^{4,13,16,36}\)

Crystal structure, Rietveld-refined parameters from the XRD patterns, structure parameters obtained from the Rietveld refinement of the XRD patterns, and luminescence decay profiles (PDF)

AUTHOR INFORMATION

Corresponding Author
E-mail: yuanbing.mao@utrgv.edu. Tel: +1-956-665-2986.

ORCID
Santosh K. Gupta: 0000-0002-1178-0159
Yuanbing Mao: 0000-0003-2665-6676

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the financial support by the National Science Foundation under CHE (award #1710160) and DMR (grant #1523577) and the USDA National Institute of Food and Agriculture (award #2015-38422-24059, for the Integrating Food Science/Engineering and Education Network (IFSEEN) program). The Department of Chemistry at the University of Texas Rio Grande Valley is grateful for the generous support provided by a Departmental Grant from the Robert A. Welch Foundation (Grant No. BX-0048). S.K.G. would like to thank the United States-India Education Foundation (USIEF) and Institute of International Education (IIE) for his Fulbright Nehru Postdoctoral Fellowship (Award# 2268/FNPDR/2017). The authors would also like to thank Melanie Thomas for TEM measurements.

REFERENCES

(1) Gupta, S. K.; Reghukumar, C.; Pathak, N.; Sudarshan, K.; Tyagi, D.; Mohapatra, M.; Pujari, P.; Kadam, R. Spectration of uranium and doping induced defects in \( \text{Gd}_{0.98}\text{U}_{0.02}\text{Zr}_2\text{O}_7 \). Photoluminescence, X-
ray photoelectron and positron annihilation lifetime spectroscopy. Chem. Phys. Lett. 2017, 669, 245–250.
(2) Martel, L.; Najj, M.; Popa, K.; Vigier, J.-F.; Somers, J. Fingerprint of local disorder in long range ordered isometric pyrochlores. Sci. Rep. 2017, 7, No. 12269.
(3) Gupta, S. K.; Ghosh, P. S.; Reghukumar, C.; Pathak, N.; Kadam, R. M. Experimental and theoretical approach to account for green luminescence from Gd2Zr2O7 pyrochlore: exploring the site occupancy and origin of host-dopant energy transfer in Gd2Zr2O7:Eu3+. RSC Adv. 2016, 6, 44908–44920.
(4) Pokhrel, M.; Wahid, K.; Mao, Y. Systematic studies on RE2Hf2O7:5%Eu3+ (RE = Y, La, Pr, Gd, Er, and Lu) nanoparticles: effects of the A-site RE3+ cation and calcination on structure and photoluminescence. J. Phys. Chem. C 2016, 120, 14828–14839.
(5) Zhang, B.; Dewasurendra, S.; Zhang, F. Blue and red upconversion light emission in TM-doped A2B2O7 oxides. Mater. Lett. 2016, 170, 53–57.
(6) Renju, U. A.; Rao, P. P.; Thampi, D. S. V. Influence of phase transition from order to disorder and Philip’s ionicity on the thermal expansion coefficient of pyrochlore type compositions with a multivalent environment. New J. Chem. 2017, 41, 245–255.
(7) Nguyen, T. M. H.; Sandilands, L. J.; Sohn, C. H.; Kim, C. H.; Wysocki, A. L.; Yang, I.-S.; Moon, S. J.; Ko, J.-H.; Yamaura, J.; Hiroi, Z.; Noh, T. W. Two-magnon scattering in the 5d all-in-all-out expansion coefficient of pyrochlore type compositions with a transition from order to disorder and Philip. 2016, ACS Omega.
(8) Eagleman, Y.; Weber, M.; Chaudhry, A.; Derenzo, S. Luminescence study of cerium-doped La2Hf2O7: Effects due to trivalent and tetravalent cerium and oxygen vacancies. J. Lumin. 2012, 132, 2889–2896.
(9) Gupta, S. K.; Sadasharan, K.; Ghosh, P. S.; Sanjaly, K.; Srivastava, A. P.; Arya, A.; Pujari, P. K.; Kadam, R. M. Luminescence of undoped and Eu3+ doped nanocrystalline SrWO4 scheelite: time resolved fluorescence complemented by DFT and positron annihilation spectroscopic studies. RSC Adv. 2016, 6, 3792–3805.
(10) Gupta, S. K.; Sadasharan, K.; Ghosh, P.; Srivastava, A.; Bevara, S.; Pujari, P.; Kadam, R. Role of various defects in the photoluminescence characteristics of nanocrystalline Nd2Zr2O7: an investigation through spectroscopic and DFT calculations. J. Mater. Chem. C 2016, 4, 4988–5000.
(11) Gupta, S. K.; Sadasharan, K.; Srivastava, A.; Kadam, R. Visible light emission from bulk and nano SrWO4: Possible role of defects in photoluminescence. J. Lumin. 2017, 192, 1220–1226.
(12) Melato, L.; Motaung, T.; Ntwaebaborwa, O.; Motloung, S. Effect of annealing at different time intervals on the structure, morphology and luminescent properties of MgAl2O4:0.3%In3+ nanophosphor prepared by citrate sol-gel method. Opt. Mater. 2017, 66, 319–326.
(13) Motloung, S. V.; Kumari, P.; Koa, L. F.; Motaung, T. E.; Hlatshwayo, T. T.; Mochane, M. J. Effects of annealing time on the structure and optical properties of ZnAl2O4:ZnO prepared via citrate sol-gel process. Mater. Today Commun. 2018, 14, 294–301.
(14) Abd, H. R.; Hassan, Z.; Ahmed, N. M.; Almessiere, M. A.; Omar, A.; Alsultany, F. H.; Sabah, F. A.; Osman, U. S. Effect of Annealing Time of YAG:Ce3+ Phosphor on White Light Chromaticity Values. J. Electron. Mater. 2018, 47, 1638–1646.
(15) Menon, S. G.; Choudhari, K.; Shivashankar, S.; Santhosh, C.; Kulkarni, S. D. Rapid annealing: A novel processing technique for Cr:ZnAl2O4 nanoparticles. J. Alloys Compd. 2017, 728, 484–489.
(16) Motloung, S.; Motloung, S.; Swart, H.; Hlatshwayo, T. T. The Effect of Annealing Time on the Structural and Optical Properties of ZnAl2O4:ZnO Nanoporph Prepared via the Sol–Gel Method. J. Electron. Mater. 2018, 47, 521–529.
(17) Meltzer, R.; Feofilov, S.; Tissue, B.; Yuán, H. Dependence of fluorescence lifetimes of Y2O3:Eu3+ nanoparticles on the surrounding medium. Phys. Rev. B: Condens. Matter Mater. Phys. 1999, 60, No. R14012.
(18) Gupta, S. K.; Ghosh, P. S.; Yadav, A. K.; Jha, S. N.; Bhattacharyya, D.; Kadam, R. M. Origin of Blue-Green Emission in Cr:ZnAl2O4 and Local Structure of Ln3+ Ion in Cr:ZnAl2O4 nanoparticles. J. Alloys Compd. 2017, 728, 484–489.
(19) Motloung, S.; Motloung, S.; Swart, H.; Hlatshwayo, T. T. The Effect of Annealing Time on the Structural and Optical Properties of ZnAl2O4:0.01%Cr3+ Nanophosphor Prepared via the Sol–Gel Method. J. Electron. Mater. 2018, 47, 521–529.
(20) Meltzer, R.; Feofilov, S.; Tissue, B.; Yuán, H. Dependence of fluorescence lifetimes of Y2O3:Eu3+ nanoparticles on the surrounding medium. Phys. Rev. B: Condens. Matter Mater. Phys. 1999, 60, No. R14012.
(37) Sayed, F. N.; Grover, V.; Bhattacharyya, K.; Jain, D.; Arya, A.; Pillai, C.; Tyagi, A. Sm2–xDy;xZr2O5. Pyrophores: Probing Order–Disorder Dynamics and Multifunctionality. Inorg. Chem. 2011, 50, 2354–2365.

(38) Turner, K. M.; Rittman, D. R.; Heymach, R. A.; Tracy, C. L.; Turner, M. L.; Fuentes, A. F.; Mao, W. L.; Ewing, R. C. Pressure-induced structural modifications of rare-earth hafnate pyrophlore. J. Phys.: Condens. Matter 2017, 29, No. 255401.

(39) Subramanian, M.; Aravamudan, G.; Rao, G. S. Oxide pyrophlores—a review. Prog. Solid State Chem. 1983, 15, 55–143.

(40) Stanek, C.; Jiang, C.; Uberuaga, B.; Sickafus, K.; Cleave, A.; Grimes, R. Predicted structure and stability of $\text{A}_2\text{B}_3\text{O}_7$: $\delta$-phase compositions. Phys. Rev. B: Condens. Matter Mater. Phys. 2009, 80, No. 174101.

(41) Garg, N.; Pandey, K.; Murli, C.; Shanavas, K.; Mandal, B. P.; Tyagi, A.; Sharma, S. M. Decomposition of lanthanum hafnate at high pressures. Phys. Rev. B: Condens. Matter Mater. Phys. 2008, 77, No. 214105.

(42) Popov, V.; Menushenkov, A.; Yaroslavtsev, A.; Zubavichus, Y. V.; Givanov, B.; Yastrebtsev, A.; Leschhev, D.; Chernikov, R. Fluorite–pyrophlore phase transition in nanostructured $\text{Ln}_2\text{H}_2\text{O}_6$ ($\text{Ln} = \text{La–Lu}$). J. Alloys Compd. 2016, 689, 669–679.

(43) Blanchard, P. E.; Liu, S.; Kennedy, B. J.; Ling, C. D.; Avdeev, M.; Atiken, J. B.; Cowie, B. C.; Tadich, A. Investigating the local structure of lanthanoid hafnates $\text{Ln}_2\text{H}_2\text{O}_6$, via diffraction and spectroscopy. J. Phys. Chem. C 2013, 117, 2266–2273.

(44) Min, X.; Sun, Y.; Kong, L.; Guan, M.; Fang, M.; Liu, Y.; Wu, X.; Huang, Z. Novel pyrophlore-type $\text{La}_2\text{Zr}_2\text{O}_7$: $\text{Eu}^{3+}$ red phosphors: Synthesis, structural, luminescence properties and theoretical calculation. Dyes Pigments. 2018, 157, 47–54.

(45) Cojocaru, B.; Avram, D.; Kessler, V.; Parvulescu, V.; Seisenbaeva, G.; Tiseanu, C. Nanoscale insights into doping behavior, particle size and surface effects in trivalent metal doped $\text{SnO}_2$. Sci. Rep. 2017, 7, No. 9598.

(46) Ma, D.; Lu, Z.; Tang, Y.; Li, T.; Tang, Z.; Yang, Z. Effect of lattice strain on the oxygen vacancy formation and hydrogen adsorption at $\text{CeO}_2$ (111) surface. Phys. Lett. A 2014, 378, 2570–2575.

(47) Blanchard, P. E.; Liu, S.; Kennedy, B. J.; Ling, C. D.; Avdeev, M.; Atiken, J. B.; Cowie, B. C.; Tadich, A. Investigating the local structure of lanthanoid hafnates $\text{Ln}_2\text{H}_2\text{O}_6$, via diffraction and spectroscopy. J. Phys. Chem. C 2013, 117, 2266–2273.

(48) Gupta, S. K.; Ghosh, P.; Sudarshan, K.; Gupta, R.; Pujari, P.; Kadam, R. Multifunctional pure and $\text{Eu}^{3+}$ doped $\beta$-$\text{Ag}_2\text{MoO}_4$: photoluminescence, energy transfer dynamics and defect induced properties. Dalton Trans. 2015, 44, 19097–19110.

(49) Keskar, M.; Gupta, S. K.; Phatak, R.; Kannan, S.; Natarajan, V. Optical properties of $\text{Eu}^{3+}$ activated thorium molybdate and thorium tungstate: Structure, local symmetry and photophysical properties. J. Photochem. Photobiol., A 2015, 311, 59–67.

(50) Krumpel, A. H.; Boutinaud, P.; van der Kolk, E.; Dorenbos, P. Charge transfer transitions in the transition metal oxides $\text{ABO}_3$: $\text{Ln}^{3+}$ and $\text{APO}_4: \text{In}^{3+}$ ($\text{A} = \text{La}, \text{Gd}, \text{Y}, \text{Sc}; \text{B} = \text{V}, \text{Nb}, \text{Ta}; \text{Ln} = \text{lanthanide}$). J. Lumin. 2010, 130, 1357–1365.

(51) Li, Y.-C.; Chang, Y.-H.; Lin, Y.-F.; Chang, Y.-S.; Lin, Y.-J. Green-emitting phosphor of $\text{LaAlGe}_2\text{O}_7$: $\text{Te}^{5+}$ under near-UV irradiation. Electrochem. Solid-State Lett. 2006, 9, H74–H77.

(52) Blasse, G.; Grabmaier, B. A General Introduction to Luminous Materials. In Luminescent Materials; Springer: New York, 1974, p. 687.

(53) Janulievicis, M.; Marmokas, P.; Misevicius, M.; Grigorjevaite, J.; Mikelionaita, L.; Sakirzanos, S.; Katelnikovas, A. Luminescence and luminescence quenching of highly efficient $\text{Y}_2\text{Mo}_4\text{O}_{13}$:$\text{Eu}^{3+}$ phosphors and ceramics. Sci. Rep. 2016, 6, No. 26098.

(54) Gupta, S. K.; Bhide, M. K.; Godbole, S. V.; Natarajan, V. Probing Site Symmetry Around $\text{Eu}^{3+}$ in Nanocrystalline $\text{ThO}_2$ Using Time Resolved Emission Spectroscopy. J. Am. Ceram. Soc. 2014, 97, 3694–3701.