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Pressure-induced site swapping, luminescence quenching, and color tunability of $Gd_2Hf_2O_7$:Eu³⁺ nanoparticles

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ABSTRACT

High-pressure (HP) studies have been an active research area in fundamental physics and to meet demand of several technological applications. In this paper, we have explored the HP effect on optical properties of pyrochlore $Gd_2Hf_2O_7$:5%Eu³⁺ (GHOE) nanoparticles (NPs). We have investigated several aspects of their optical properties under HP such as charge transfer transitions, emission dynamics, asymmetry ratio, excited state lifetime, and color coordinates. HP photoluminescence (PL) spectra indicate the irreversible and complete disappearance of charge transfer beyond ~5.4 GPa (up to 53 GPa) owing to the reduced charge density around O^{2-} ion in the GHOE NPs. Elevated pressure induces peak broadening, evolution of emission from ⁵D₁/⁵D₂ states, and reduction of ⁵D₀ \rightarrow ⁷F₂ red emission intensity due to enhanced defect density and cross relaxation. Moreover, there is systematic reduction in asymmetry ratio which suggests improving symmetry around Eu³⁺ ion and covalency reduction of Eu–O bond. PL lifetime spectroscopy suggests that a large fraction of Eu³⁺ ions is localized at Gd³⁺ site at lower pressure induced color tunability in the red-orange-yellow domain. Hence, we demonstrated pressure induced site swapping, luminescence quenching, Eu–O covalency change, and color tunability of the GHOE NPs for high pressure research on optical materials.

1. Introduction

High pressure spectroscopy research has been attracting a lot of attention in recent years owing to associated interesting features and application potentials such as high-pressure sensing capability, phase transition, evolution of new phases, dopant site swapping, spectral shift, band gap alteration, etc.[1–6] It is also very important from the perspective of understanding high pressure physicochemical changes of materials. At the same time, several researcher groups have investigated high pressure performance of luminescent materials to understanding the photochemical changes happening at elevated pressure. Such studies are crucial for designing optical materials which needed to be subjected to extreme conditions of temperature and pressure. For example, Liu et al. observed enhanced emission and blue shift in spectral band of 9-(3-(1,2,2-triphenylvinyl)phenyl) anthracene crystal under high pressure[3]. Wozny et al. investigated the high pressure luminescence of monoclinic (α) and triclinic (β) GdBO₃ submicron-sized crystals and

observed peak broadening, changes in stark splitting, spectral shift, etc. [7] Chen et al. observed the evolution of new energy peaks in CaS:Eu²⁺ with increasing pressure.[8] Hou et al. observed interesting discontinuity on luminescence intensity ratio between ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transitions with increasing pressure, indicating a phase transition occurred at 7.3 GPa.[9] Runowski et al. observed shortening of lifetime from SrF₂:Yb³⁺,Er³⁺ nanocrystals reversibly and linearly with pressure up to 5.29 GPa.[10]

These high-pressure luminescence spectroscopic results among various studies indicate that most of the studied lanthanide ions are not affected much by external field. There are no or little change in their local vicinity because they are deeply buried inside the nucleus and well protected by overlying $5s^2$ and $5p^6$ shells. Among all these lanthanide ions, Eu^{3+} is the unique representation which is strongly influenced by external changes including thermal, pressure, etc.[11–14] This is because of its highly sensitive electronic transitions such as ${}^5D_0 \rightarrow 7F_2$ (forced electric dipole transition, FEDT) and ${}^5D_0 \rightarrow {}^7F_1$ (pure magnetic

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Research Article





dipole transition, PMDT). The ground and excited states of ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition has non-degenerate state. It is not allowed by either PMDT or FEDT, but its splitting gives information on the number of sites occupied by Eu³⁺ in doped hosts.

Among luminescent materials, Eu³⁺ doped nanocrystals are in high demand owing to the narrow red emission bands for various applications such as thermal sensors, scintillators, phosphor converted light emitting diodes, biomedical imaging, and anticounterfeiting.[15-21] In particular, Eu³⁺ doped rare earth hafnate based pyrochlores are one type of the most sought out optical materials for a variety of applications in the area of X-ray phosphors, thermographic phosphors, pressure sensors, nuclear waste hosts, solid state lighting, etc.[1,11,15,20,22] Gd₂Hf₂O₇ is one of important pyrochlore composition owing to its unique properties such as low thermal conductivity, ability to accommodate lanthanide dopants at both A- and B-sites, high structural and mechanical stability, high radiation stability which render it with applications for scintillators, thermal barrier coating, nuclear waste hosts, luminescence host, etc.[15,23-26] Previously, fundamental photophysical properties of $Gd_2Hf_2O_7$ doped with either actinides (U^{6+}) or lanthanides (Eu^{3+}) have been explored by us under ambient pressure towards photoluminescence and radioluminescence applications. [15,27,28] There is no report on the study of the high-pressure luminescence spectroscopy of GHOE. It will be interesting to understand the behaviors of Gd₂Hf₂O₇: Eu³⁺ (GHOE) nanoparticles (NPs) at high pressure and consequently pressure-induced structural and property changes. Hence, we probed the excitation, emission, and lifetime spectroscopy of the GHOE NPs at elevated pressure up to 53 GPa in this study. Moreover, we calculated the values of asymmetry ratio and color coordinates of the GHOE NPs, which provide insight in local structure and emission color of Eu^{3+} ions at a wide pressure range.

2. Experimental

2.1. Synthesis

The GHOE NPs were synthesized using a molten-salt synthesis method at 650 °C as reported in our previous publications.[11,15,20,22] More specifically, the chemicals used are all analytical grade and were used without any further purification. Gadolinium nitrate hexahydrate (Gd(NO₃)₃•6H₂O, 99.0%), europium (III) nitrate hexahydrate (Eu (NO₃)₃•6H₂O, 99.9%), and hafnium dichloride oxide octahydrate (HfOCl₂•8H₂O, 99.0%) in molar ratio of 0.95:0.05:1 were first measured in stoichiometric ratio and dissolved in water (Millipore, 18.2 M Ω at 25 °C). After 30 min of stirring, 200 ml ammonium hydroxide was titrated into the mixture solution dropwise within ~ 2 h. This first step allows the formation of a single source precursor 95%Gd(OH)3.5%Eu $(OH)_3$ ·HfO $(OH)_2$ ·*n*H₂O via coprecipitation technique. In the next step, potassium nitrate (KNO₃, 99.9%), sodium nitrate (NaNO₃, 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 6 h. The synthesized GHOE NPs were finally washed multiple times with DI water to remove any residual salt from the surface of the obtained NPs.

2.2. Characterization

X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), PL spectroscopy, *in situ* high-pressure Raman spectroscopy, and *in situ* high-pressure PL spectroscopy were used to characterize the synthesized GHOE NPs. Specifically, BrukerD8 Advance X-ray diffractometer equipped with a copper X-ray source with a K α 1 radiation of $\lambda = 0.15406$ nm was used for taking the XRD patterns. The instrument was operated at 40 kV and 40 mA and the scans were taken in a mode of 20 with a range of 10–90° with a scanning step of 0.04° at a rate of 2.0 deg. min⁻¹. Raman Spectra were taken with a Bruker Senterra system couple with a helium lamp.

The scans were taken from a range of 80 cm^{-1} to 1530 cm^{-1} for a total of 10 accumulations with a rate of 1.0 cm^{-1} for every 10 s. Cosmic spikes were removed from the background of the scans through the calibration of the instrument. SEM images were taken by a Carl Zeiss sigma VP scanning electron microscope with a 5 kV field emission gun. PL studies were conducted on a FLS 980 fluorometer (Edinburgh Instrument). The PL instrument was coupled with a Xenon lamp and a pulse lamp at a frequency range of 1–100 Hz and equipped with a sensitive photomultiplier tube (PMT).

In situ high pressure PL studies were conducted using a DAC equipped with a 1-carat diamond on each half of the device. Mounting the GHOE NPs into the DAC was done using the following technique: a preindented gasket (~2.8 mm diameter hole) was placed under a 10X microscope lens, and then the powder of GHOE NPs was added to the gasket carefully. About a 30 μ L of hydrostatic fluid made of 1:4 methanol/water then was added to the gasket to provide homogenous pressure distribution. After that, ruby powder was added to the gasket as a pressure sensor to estimate the pressure. More details on the *in situ* measurements are included in ESI. Then the mix of the GHOE sample, ruby powder and hydrostatic fluid was centered and aligned on the gasket hole. The FLS 980 instrument optics were modified to adjust and calibrate the DAC device. 3D printing technology was used to design a sample stage to center the loaded DAC into the Xenon beam properly.

3. Results and discussion

3.1. Phase purity and structure

The purity, phase, and shape of the GHOE NPs were characterized using XRD, Raman spectroscopy and SEM. The XRD peaks of the GHOE NPs are sharp and intense which are attributed to the highly crystalline nature of the molten salts synthesized GHOE NPs (Fig. 1a). The XRD pattern of these NPs confirms the formation of pure Gd₂Hf₂O₇ and complete absence of any impurity such as Gd₂O₃, HfO₂, or Eu₂O₃. Our XRD pattern matches completely with those reported earlier by other groups as well as our own group for pure Gd₂Hf₂O₇.[15,29,30]

As reported in our previous publications, the $A_2B_2O_7$ -type oxides tend to stabilize in two different phases: ordered pyrochlore (OP) and disordered fluorite (DF). The distribution of the oxide ions and their location in the unit cell is the main difference between the two phases. The OP phase tends to have an Fd-3m space group with high degree of ordering. On the other hand, the DF phase belongs to the Fm-3m space group with predominant disordering in the lattice. Based on the ionic radius ratio of Gd³⁺ and Hf⁴⁺ ions, GHOE can stabilize in either OP or DF as the ionic radius ratio (IRR) falls at the boundary. However, due to the poor resolution of lab-scale Cu K α XRD, the XRD pattern of our GHOE NPs shows only the peaks that corresponds to the DF phase. No superlattice peaks of the OP phase were detected, which need stronger sources such as synchrotron X-rays.

To identify the actual structure of the GHOE NPs, Raman spectra were taken. It is well known that the OP phase of A2B2O7 oxide is characterized with the presence of 6 closely spaced peaks in the range of 200–1000 cm⁻¹ in the Raman spectrum, which are attributed to $\Gamma_{OP} =$ $A_{1g} + E_g + 4F_{2g}$. Due to the large structural disordering that is caused by the random distribution of oxygen ions over eight available positions, the DF phase shows only a single broad peak ($\Gamma_{DF} = F_{2g}$). As mentioned before, IRR is a critical parameter in deciding the phase of A2B2O7 oxides. The DF phase is favored when IRR is less than 1.46, whereas the OP phase is the prevailing one when it is greater than 1.46. Our Raman spectra here (Fig. 1b) shows a single broad peak around 300 $\rm cm^{-1}$ that is attributed to the F_{2g} metal-oxygen vibrational mode of the DF phase. This therefore agrees with our XRD results. What is interesting about GHO is that its IRR ($r_{\rm Gd}/r_{\rm Hf}$) is about 1.48 which makes it an excellent host for studying the phase shift between the OP and DF phase. As we mentioned in one of our previously published articles, we induced this phase shift thermodynamically.[15]



Fig. 1. (a) XRD pattern and (b) Raman spectrum of the GHOE NPs.

3.2. Particle size and distribution

To identify the morphology and size of the GHOE NPs, SEM images were taken which clearly confirmed the formation of nano-size GHOE particles (Fig. 2). The SEM image shows that a few of these particles are connected with each other and form aggregates. The corresponding size distribution histogram confirms that the average size of these GHOE NPs is ~31 nm, which agrees with our previous work on the GHO and GHOE NPs synthesized at the same temperature (650 °C).[15]

3.3. Pressure dependent optical properties

3.3.1. PL excitation spectra

Fig. 3 shows the excitation spectra of the GHOE NPs in the range of 0–53 GPa. The ambient pressure excitation spectrum consists of a broad and strong charge transfer band (CTB) peaking at 269 nm and many weak intra-configuration Eu^{3+} f-f bands in the range of 350–500 nm. The intense and broad CTB is ascribed to three different contributions [31]: (a) $O^{2-} \rightarrow Eu^{3+}$ charge transfer transition, (b) $Hf^{4+} \rightarrow Eu^{3+}$ intervalence charge transfer (IVCT), and (c) $O^{2-} \rightarrow Hf^{4+}$ host absorption band (HAB). As far as the intra-configuration f-f transitions, two main Eu^{3+} excitation peaks at 395 and 465 nm due to ${}^7F_0 \rightarrow {}^5L_6$ and ${}^7F_0 \rightarrow {}^5D_2$ are clearly seen in the excitation spectra at ambient pressure.

As a function of pressure, there is not much change of the intraconfiguration $\rm Eu^{3+}$ f-f bands. Both of these two typical $\rm Eu^{3+}$ peaks at



Fig. 3. Pressure dependent PL excitation spectra of the GHOE NPs ($\lambda_{em}=612$ nm).



Fig. 2. SEM image of the GHOE NPs. Inset shows the size distribution plot analyzed by the ImageJ software.

395 and 465 nm persist until 53.16 GPa. Such observation is quite in line with analogy that Eu^{3+} f-shell is deeply buried inside the nucleus so is strongly shielded from the electron in the valence shell. This makes the f-f transitions feebly independent on applied pressure.[32]

However, as a function of applied pressure, the intensity of the CTB kept gradually decreasing until 5.38 GPa. Beyond that pressure, there was an even more significant CTB intensity reduction. Complete disappearance of the CTB is quite difficult due to its quite broad feature. Even on releasing the pressure, substantial intensity of the CTB would not be retracted as can be seen from Fig. 3. In our earlier work, we have observed similar reduction in intensity of CTB at lower pressure of 2.75 GPa and beyond.[1] CTB mainly has electronic contribution from oxygen ion either to Eu³⁺ or Hf⁴⁺, whose charge density is strongly dependent on applied pressure. Such intensity reduction of CTB and its gradual disappearance have been ascribed to the reduction of effective charge on oxygen at high pressure.[33] Another reason could be the volumetric compression of the GHOE NPs, which endows various contributions to charge transfer such as CTT, IVCT and HAB difficult to occur. Behrendt et al. have observed that CTB displayed blue shift with increasing pressure from LaAlO₃:Eu³⁺ and Y₂O₂S:Eu³⁺.[34,35] Their study was limited to a low-pressure range up to 250 kBar whereas we have extended our work up to 53 GPa.

3.3.2. PL emission spectra

Pressure dependent luminescence from lanthanide ion doped in crystalline host matrix is governed by several factors including the shielding of 4f electrons, hybridized state of ground and excited state 4f wave functions, and host crystal and electronic fields.[36] Pressure dependent PL features such as peak shift, peak broadening, stark splitting, intensity, etc. from lanthanide luminescence arise from the balance of these three contributions. Ambient pressure emission spectrum of the GHOE NPs under 269 nm excitation wavelength (Fig. 4) consists of peaks in the range of 570–680 nm corresponding to the Eu^{3+} electronic transition from the excited ${}^{5}D_{0}$ state to the ${}^{7}F_{J}$ levels (J = 1, 2 and 3). The reason that we chose the excitation at 269 nm although its intensity reduced substantially beyond 5.38 GPa was mainly because there was no emission output when the GHOE NPs were excited at either 395 nm or 465 nm. This may be because the luminescence of the GHOE NPs mainly occur via the host sensitization. Even though the CTB intensity was weak beyond 5.38 GPa, photons via host absorption could transfer energy to Eu^{3+} ions leading to ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ emission. We realize it need much deeper



Fig. 4. Pressure dependent PL emission spectra of the GHOE NPs ($\lambda_{\rm ex}=269$ nm).

analysis to confirm this hypothesis, e.g. via *in situ* low temperature PL measurements. The most intense peaks are located at 592, 615 and 653 nm due to ${}^5D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow {}^7F_2$, and ${}^5D_0 \rightarrow {}^7F_3$, respectively. Among these three transitions, ${}^5D_0 \rightarrow {}^7F_1$ is induced by magnetic dipole transition (MDT). MDT is not affected much by the local environment around Eu³⁺ ions and usually displays high intensity in the presence of inversion center around Eu³⁺ ions. ${}^5D_0 \rightarrow {}^7F_2$ is induced by electric dipole transition (EDT). It is strongly affected by the local environment around Eu³⁺ ions and usually displays high intensity when localized at distorted and asymmetric environment when lacking inversion center. In fact, EDT has two Stark components at 611 and 630 nm due to the crystal field effect of Gd₂Hf₂O₇ host. On comparing the peak intensity at 592 and 615 nm (Fig. 4), it is clear that Eu³⁺ ions in the GHOE NPs are localized at a site which lacks inversion symmetry. The weak emission peak around 653 nm is ascribed to ${}^5D_0 \rightarrow {}^7F_3$ transition which is allowed by neither MDT nor EDT.

The emission spectra of the GHOE NPs at different pressures up to 53 GPa is also shown in Fig. 4. Firstly, there is no change in spectral position or intensity of the MDT as expected that it is not affected much by physical or chemical variations such as temperature, pressure, or host symmetry. Secondly, the emission from ${}^{5}D_{1}$ and ${}^{5}D_{2}$ levels (560 nm peak) along that from ${}^{5}D_{0}$ level evolves with increasing pressure beyond 5.38 GPa, which is in line with one observed by Behrendt et al. from LaAlO₃:Eu³⁺ and Y₂O₂S:Eu³⁺.[34,35] Finally and most importantly, the red emission at 611 and 630 nm due to ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition gradually reduces with the applied pressure increased up to 16.91 GPa, and then significant intensity reduction of this transition is observed beyond 16.91 GPa up to the highest applied pressure of 53 GPa in this study. The red emission cannot be retracted when the applied pressure was released. This phenomenon suggests the pressure induced intensity change is irreversible in nature. This is attributed to enhanced electron-phonon coupling and non-radiative transition induced by defects and cross relaxation at elevated pressure. The other mechanism that can be attributed to the reduced red emission intensity at elevated pressure is the non-radiative depopulation of the ⁵D₀ level through trap levels.[37] Moreover, emission peaks are slightly broadened at elevated pressure due to increases in electron-phonon coupling.[38] Fig. S1 shows the change in emission intensity of ruby under different pressures. Also, the method for pressure calibration is mentioned in the ESI. We realize that the pressure measurement using the ruby scale has its own limitations. On one hand, non-hydrostatic stresses would induce overlap of the R1 and R2 lines. On the other hand, measurement temperature increase could cause wavelength shift, intensity lost, and overlap of the doublet. As a result, significant non-hydrostatic pressure may have impacted our studies and played a major role on the peak profile and local structure of Eu³⁺ ion in our study.

3.3.3. Pressure effect on asymmetry ratio

Asymmetry ratio ($I_{21} = I_{EDT}/I_{MDT}$) is one of the critical parameters in assessing the local structure, symmetry and environment around Eu³⁺ ions. Higher the I_{21} value, higher the asymmetry around Eu³⁺ ions, and higher covalency of Eu–O bond. [39] The I_{21} of the GHOE NPs increases slightly from ambient pressure to 3.46 GPa, and then there is systematic reduction until 53 GPa throughout the applied pressure range (Fig. 5). This observation suggests improved symmetry around Eu^{3+} ions and reduced Eu-O bond covalency with increasing applied pressure.[40] Similar results were observed by other researchers on high pressure luminescence studies of YF₃:Eu³⁺ and TiO₂:Eu³⁺.[39,40] In GHO pyrochlore, there are two different polyhedral: distorted GdO8 scalenohedra and relatively symmetric HfO₆ octahedra. Based on our emission spectra at ambient pressure and low-pressure zone, the predominant EDT over MDT suggests that a large fraction of Eu³⁺ ions occupies the GdO₈ scalenohedra in the low-pressure zone. With increasing pressure, Eu^{3+} ions started moving into symmetric HfO₆ octahedra. Moreover, beyond 16.91 GPa, the local environment of Eu³⁺ ions changes from GdO₈ scalenohedra to HfO₆ octahedra. Hence, this study suggests that Eu³⁺



Fig. 5. The function of applied pressure on the asymmetry ratio of the GHOE NPs.

ions in our GHOE NPs underwent pressure induced symmetric and orderly distribution in the $Gd_2Hf_2O_7$ host. We cannot rule out the fact that the applied pressure may have induced phase transition from the defect fluorite to order pyrochlore structure, which may inculcate

significant reduction in asymmetry ratio of Eu^{3+} dopant local environment. In complex system like $A_2B_2O_7$ with high oxygen density, to probe pressure induced structural transition, one needs to use synchrotron based XRD or reactor-based neutron diffraction for *in situ* structural transition analysis. Currently we are seeking opportunities to get access to such facilities.

3.3.4. Pressure effect on lifetime of ${}^{5}D_{0}$ excited state of Eu^{3+} ion

The luminescence lifetime profiles of the GHOE NPs at different applied pressures (Fig. 6) display biexponential fittings with two different lifetime values. The short lifetime value τ_1 is in the range of 870–570 μ s whereas the long lifetime value τ_2 is in the range of 2.06–1.26 ms. These two lifetimes τ_1 and τ_2 are attributed to the stabilization of Eu³⁺ ions at two different local sites in the GHOE NPs. τ_1 is attributed to Eu^{3+} ions occupying GdO₈ site whereas τ_2 is the ones occupying HfO₆ site. This is in line with the fact that f-f transitions are more allowed in asymmetric sites and forbidden in symmetric sites which offer short and long lifetimes at asymmetric GdO₈ and symmetric HfO_6 sites, respectively. [41–43] The fractional distribution of these two lifetimes τ_1 and τ_2 as P1 and P2 in terms of percentage, respectively (Table 1), indicates that the fraction of Eu^{3+} ions residing at GdO₈ sites decreased systematically and that of Eu^{3+} ions residing at HfO₆ sites increased with increasing applied pressure. This observation clearly suggests pressure-induced change in local environment of Eu³⁺ ions from asymmetric GdO₈ sites to symmetric HfO₆ sites, which is in line with our asymmetric ratio study described in the preceding section. On releasing pressure from the GHOE NPs, the excited state lifetime is also



Fig. 6. Pressure dependent in situ lifetime profiles of the GHOE NPs. The numbers above the decay curves indicate the designated pressure at which it was recorded.

Table 1

Excited state lifetimes of $^5\text{D}_0$ level of Eu^{3+} from the GHOE NPs at different pressures.

PL lifetime analysis					
Pressure (GPa)	τ_1 (µs)	P1 (%)	τ_2 (ms)	P2 (%)	Chi ²
0	872	83	2.06	17	1.195
3.46	788	81	1.92	19	1.178
4.13	642	79	1.72	21	1.105
5.38	309	73	1.26	27	1.005
8.33	716	68	1.81	32	1.166
16.90	615	56	1.65	44	1.175
31.80	574	23	1.63	77	1.178
51.09	559	18	1.609	82	1.166
53.16	604	16	1.67	84	1.181
Pressure released	587	16	1.57	84	1.127

irreversible as the excitation spectra, emission spectra, and asymmetry ratio described above.

The gradually decreasing lifetime with increasing pressure initially was in line with other reported high pressure studies.[33,44] Once the external pressure was increased to a few GPa, the local environment of Eu^{3+} ions changes from GdO_8 scalenohedra to HfO_6 octahedra, which endowed the sudden increase of lifetime. Further experimental studies are necessary to clarify the exact reasons.

Moreover, we have noticed the same that there was no linear trend in the lifetime value as the applied pressures increased (Table 1). There was also no one-to one correlation of lifetime and emission intensity variation with pressure. This may be due to more predominate effect of crystal field and defects on lifetime at elevated pressure compared to emission intensity. On the other hand, the change trend of the populations of both short- and long-lived species is linear with the pressure increase. Specifically, in one hand, population of short-lived species gradually decreased at higher pressure whereas that of long-lived species monotonically increased. As we have ascribed, the short-lived species of Eu^{3+} ions occupy GdO₈ site whereas the long-lived ones are ascribed to Eu^{3+} ions occupying HfO₆ site. This observation clearly suggests pressure-induced change in local environment of Eu^{3+} ions from asymmetric GdO₈ sites to symmetric HfO₆ sites, which is in line with our asymmetric ratio study described in the preceding section.

3.3.5. Pressure effect on color coordinates

Spectral change in the emission profiles of the GHOE NPs (Fig. 4) clearly shows significant difference in terms of the intensity ratio of the EDT and MDT peaks as well as the asymmetry ratio (Fig. 5). At room temperature and ambient pressure and at low pressure zone up to 8.33 GPa, the GHOE NPs displayed bright red color emission, which was varied to orange color emission in medium pressure range and to yellow color at high pressure range. The plotted color index diagram of the actual color coordinates of the GHOE NPs at different pressures (Fig. 7) clearly shows a pressure-induced color tunability in the domain of red-orange-yellow.

4. Conclusion

In this work, we have investigated the effect of pressure (up to 53 GPa) on optical properties of the molten-salt synthesized GHOE NPs. The formed NPs are spherical with defect fluorite structure. The excitation peak intensity of the charge transfer transition gradually decreased until 5.38 GPa and then completely disappeared, which was ascribed to charge density reduction around oxygen ion. The red emission from the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition at 611 and 630 nm gradually reduced up to 16.91 GPa and then completely quenched up to the highest applied pressure of 53 GPa in this study. The asymmetry ratio systematically reduced throughout the applied pressure range up to 53 GPa, which suggests improving symmetry around Eu³⁺ ions and reducing Eu–O bond covalency. The shorter lifetime value t_1 is in the range of 870–570 μ s is attributed to europium ion occupying GdO8 site whereas longer lifetime value t_2 is in the range of 2055–1258 µs is one occupying HfO₆ site. The emission lifetime spectroscopy data suggest that a large fraction of Eu³⁺ ions occupies GdO₈ scalenohedra in the low-pressure zone and then



Fig. 7. Color coordinates of the GHOE NPs from low to high pressure ranges indicated along the arrow. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

started moving into symmetric HfO_6 octahedra as the applied pressure was increased. Specifically, beyond 16.91 GPa, a remarkably high fraction of Eu^{3+} ions changes its local environment from GdO_8 scalenohedra to HfO_6 octahedra. Therefore, our study indicates that Eu^{3+} ions can undergo pressure-induced symmetric and orderly distribution in the $Gd_2Hf_2O_7$ host. The change of color coordinates through the applied pressure range suggested the pressure induced color tunability in our GHOE NPs in the domain of red-orange-yellow. Overall, our current work throws scientific light on understanding pressure induced site swapping, luminescence quenching, Eu-O covalency change, and color tunability of the GHOE NPs, which would be quite useful to understand high pressure research on luminescent materials in the future.

CRediT authorship contribution statement

Santosh K. Gupta: Conceptualization, Data curation, Formal analysis, Visualization, Writing. Hisham Abdou: Data curation, Methodology, Investigation. Yuanbing Mao: Conceptualization, Supervision, Visualization, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.optmat.2020.110789.

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