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High pressure induced disappearing $^5D_0 \rightarrow {}^7F_2$ and broadening $^5D_0 \rightarrow {}^7F_1$ transitions from $Y_2Hf_2O_7:Eu^{3+}$ nanoparticles

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ABSTRACT

Design of color tunable phosphors as pressure sensors has drawn immense attention. In this work, luminescent $Y_2Hf_2O_7:Eu^{3+}$ nanoparticles upon high pressure demonstrate lowered phonon frequency, enhanced crystal field, and increased local site swapping effect as manifested with appearing emission of $^5D_1/^5D_2$ levels, increasing width of magnetic dipole transition (up to ~11.43 GPa), and increased symmetry around Eu^{3+} ion with disappeared $^5D_0 \rightarrow {}^7F_2$ transition beyond 5.7 GPa. Our results indicate the potential of the $Y_2Hf_2O_7:Eu^{3+}$ nanoparticles as medium range pressure sensors with tunable luminescence from red to orange to yellow in the pressure range of 0–49.4 GPa.

1. Introduction

Pressure as a critical parameter can induce restricted vibration and enhanced intermolecular attraction to materials. It can lead to changes of bond length, crystal field and hence photoluminescence (PL) properties of phosphors [1,2]. Investigation of the high-pressure effect on luminescent materials, usually in diamond anvil cells (DAC), is of importance to understand their behaviors under high stress, electromagnetic noise, or elevated mechanical push and the pressure induced structural behavior.

Europium ion is one of the most sensitive lanthanide ions whose PL is strongly influenced by external factors on its magnetic dipole transition (MDT, $\triangle J = \pm 1$), hypersensitive electric dipole transition (h-EDT, $\triangle J = \pm 2$), and non-degenerate emissive state ($^5D_0$) [3]. Owing to its bright red emission from $^5D_0 \rightarrow {}^7F_2$ transition, europium doped phosphors are widely used for solid state lighting, bioimaging, anti-counterfeiting, sensors, solar cell, display panels, etc. [4,5]. Its full potential can be manifested when accommodated inside suitable host lattices.

Pyrochlore $Y_2Hf_2O_7$ (YHO) is a good luminescent host owing to its high chemical stability, non-toxicity, moderate phonon energy, high structural flexibility, high radiation stability, and strong ability to accommodate dopants at both Y^{3+} and Hf^{4+} sites as demonstrated by our early exploration of $Y_2Hf_2O_7:Eu^{3+}$ (YHOE) for phosphor and scintillator applications [3,4,6].

In this work, we demonstrated the impact of high pressure on PL properties of YHOE nanoparticles (NPs) for color tunable phosphor and pressure sensor based on asymmetry ratio (R_{21}), color coordinates, and excited state lifetime. The YHOE NPs were synthesized by a molten salt synthesis method and characterized using X-ray diffraction (XRD), Raman spectroscopy, field emission scanning electron microscopy (FESEM), and energy dispersive X-ray spectroscopy (EDX) with the same experimental details as mentioned in our earlier work [6,7].

2. Results and discussion

2.1. Phase, structure, purity and morphological analysis

XRD pattern and its Rietveld refinement of the YHOE NPs (Fig. 1a) matched with cubic pyrochlore structured $Y_2Hf_2O_7$. The refined structural data such as lattice parameter, space group and unit cell volume (Table 1) is in agreement with reported results of $Y_2Hf_2O_7$ [8]. The crystal structure of the YHOE NPs (Fig. 1*b*) showed random distribution of Y/Hf at *4a* position and oxygen and oxygen vacancies (OVs) at *8c* site. EDX spectrum of the synthesized YHOE NPs confirmed the presence of Y, Hf, O, and Eu elements (Fig. 1c). The peak at 0.277 keV was ascribed to C $K\alpha_1$ which may come from the used carbon tape.

As a sensitive spectroscopy to metal–oxygen vibration, Raman spectrum of the YHOE NPs (Fig. 2a) showed a broad Raman peak at around 400 cm^{-1} as a signature of defect fluorite structure owing to the random distribution of 7 oxygens at 8 lattice site unlike sextet A_{1g} +

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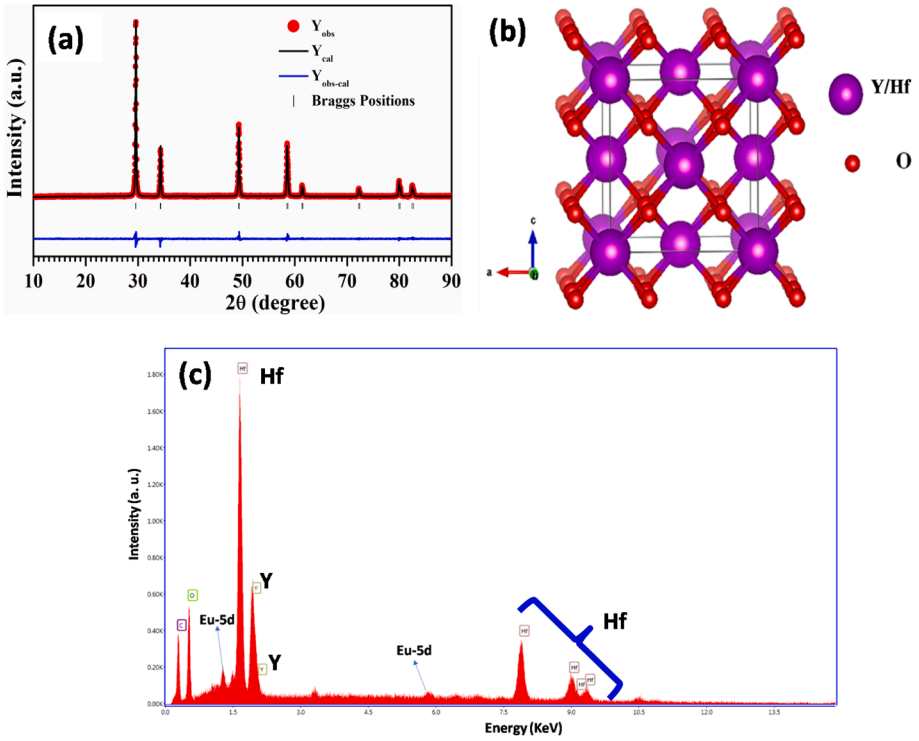

Fig. 1. (a) Riveted refined XRD pattern, (b) crystal structure, and (c) EDX spectrum of the YHOE NPs.

Table 1
Rietveld refined structural parameters of the YHOE NPs.

Structural parameters	Obtained values
$a = b = c$ (Å)	5.1822 (1)
Unit cell volume (Å^3)	139.17
Space Group	Fm-3m
R_p	8.03
R_{wp}	10.7
R_{exp}	7.78
Chi^2 (χ^2)	1.88

$4F_{2g} + E_g$ peaks of ideal pyrochlore phase [8]. Other broad humps at ~600 and 800 cm^{-1} indicated the high level of disordering and distortion of HfO_6 octahedra, respectively. FESEM micrograph (Fig. 2b) showed the formation of nanocrystallites having spherical morphology and an average size of ~32 nm (Inset of Fig. 2b). The presented certain level of aggregation may be due to the fast nucleation in the presence of molten salt and air-drying process. Stabilization of the slightly aggregated YHOE NPs suggested that the Columbic repulsion among them was unable to overcome the van der Waals forces in the presence of KNO_3-$NaNO_3$ molten salt.

2.2. *High pressure PL Spectroscopy:*

High pressure was applied using a DAC under hydrostatic fluid of methanol and ethanol (4:1). Ruby emission at 694.2 nm (R1 band) was used as the pressure reference by placing a small piece of ruby between two diamonds anvils [9]. The R1 band directly proportionally shifts to higher wavelength under elevated pressure. The PL emission spectrum of the YHOE NPs at ambient condition (Fig. 3a) depicted three different characteristics peak of Eu^{3+} ion at 590 orange emissions due to the MDT of $^5D_0 \rightarrow {}^7F_1$, doublet h-EDT red emission of $^5D_0 \rightarrow {}^7F_2$ transition spanning 600–640 nm, and a peak at 655 nm from $^5D_0 \rightarrow {}^7F_3$ transition which is neither allowed by MDT nor by EDT. Stronger intensity of h-

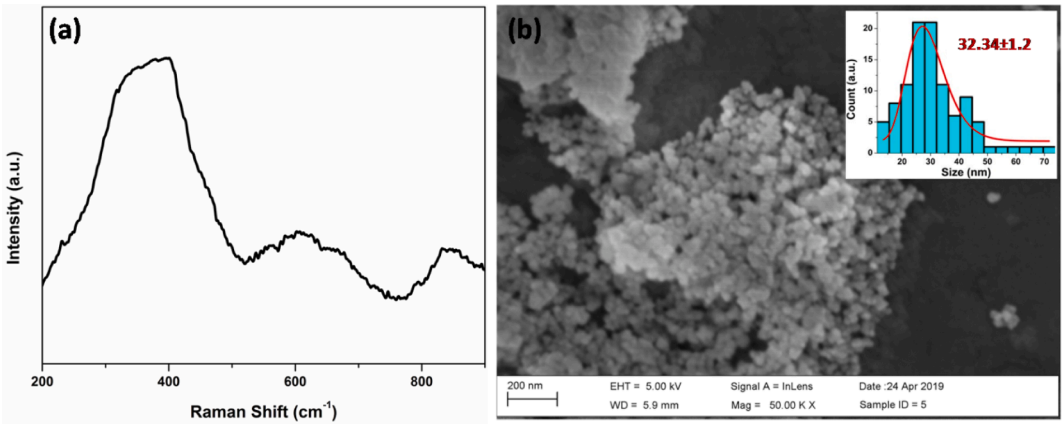

Fig. 2. (a) Raman spectrum and (b) FESEM image of the YHOE NPs. The size distribution of the YHOE NPs obtained using ImageJ software was shown as the inset of Fig. 2b.

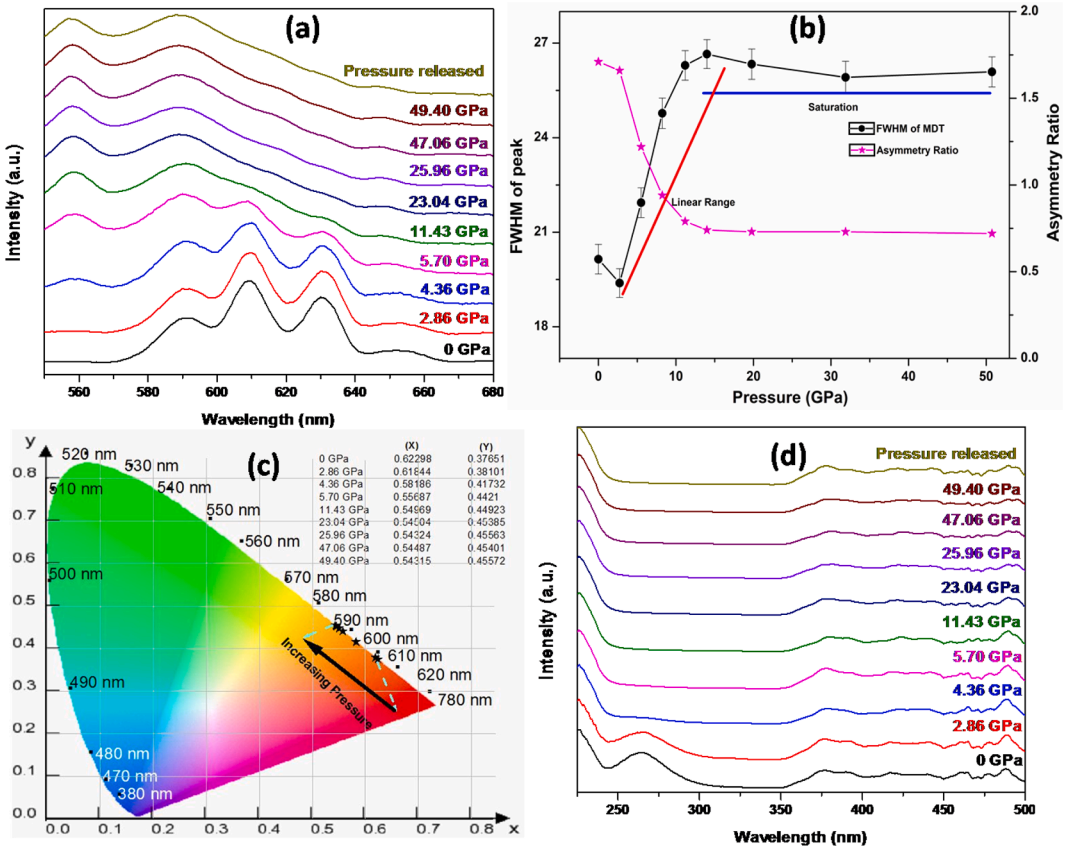

Fig. 3. (a) Emission spectra (λ_{ex} = 370 nm), (b) variation of asymmetry ratio and FWHM of the MDT peak with pressure, (c) color coordinate diagram and (d) excitation spectra (λ_{ex} = 590 nm) of the YHOE NPs.

EDT compared to MDT suggested that the symmetry around Eu^{3+} ion was quite low for the YHOE NPs at ambient conditions.

Several interesting features appeared in the PL emission spectra as the applied pressure increased. Evolution of peaks from $^5D_1/^5D_2$ levels at around 550 nm was first observed at around 4.36 GPa, which was retained until 49.4 GPa. This indicated lowering of phonon frequency of Hf-O at higher pressure as observed by Behrendt et al. in $LaAlO_3:Eu^{3+}$ and $Y_2O_2S:Eu^{3+}$ as well as in our earlier work on $Gd_2Hf_2O_7:Eu^{3+}$, PVDF: Eu^{3+} and $La_2Hf_2O_7:Eu^{3+}$ [10–14].

With increasing pressure, the h-EDT peak gradually decreased its intensity and completely disappeared beyond 5.70 GPa while the MDT peak demonstrated no change in intensity. This concurrent disappearance of the h-EDT peak suggested enhanced symmetry around Eu^{3+} ion with elevating pressure. In defect fluorite structured YHOE NPs, yttrium-oxygen polyhedra have distorted scalenohedra coordination with low symmetry whereas hafnium-oxygen polyhedra have symmetric octahedron coordination. The PL spectral feature of the YHOE NPs indicated that Eu^{3+} ions occupied Y^{3+} sites in majority at ambient condition and below 5.70 GPa and there was a complete site swapping from Y^{3+} to Hf^{4+} sites beyond 5.70 GPa under the influence of high pressure.

At pressure below 5.70 GPa, Eu^{3+} occupies Y^{3+} site where there is no need for charge compensating defects and the lattice still feels strain and distortion of size mismatch. Beyond 5.7 GPa, there is a site swapping of Eu^{3+} ion from Y^{3+} to Hf^{4+} which invokes the necessity of charge compensating defect owing to charge mismatch via the formation of positively charged oxygen vacancy ($V_O^{\cdot\cdot}$) and negatively charge antisite defects ($Eu_{Hf}^{'}$) as shown in equation (1) below:

$$Eu^{3+} + Hf^{4+} \rightarrow Eu_{Hf}^{'} + V_O^{\cdot\cdot} \quad (1)$$

These defects are expected to affect the PL of the YHOE NPs in two different ways. $Eu_{Hf}^{'}$ can provide an additional pathway for non-radiative relaxation and may quench the emission output. On the other hand, $V_O^{\cdot\cdot}$ can act as a sensitizer and help enhance emission output by transferring host emission to Eu^{3+} ion.

The variation of asymmetry ratio as a function of pressure (Fig. 3b) also clearly showed a gradual increase of symmetry up to 5.70 GPa and then followed with an extremely low asymmetry around Eu^{3+} ion to 49.4 GPa, the maximum external pressure applied in this study. These changes were irreversible even upon releasing the external pressure. Based on our earlier work on high pressure luminescence of $A_2B_2O_7$ pyrochlores, it was found that there is structural phase transition at some critical pressure values which may differ depending on the A/B ratio. We believe the enhanced symmetry ratio at high pressure may be attributed to the structural phase transition from disordered defect fluorite structure (ambient structure of YHOE) to ordered ideal pyrochlore structure. This hypothesis needs to be ascertained using *in situ* Raman spectroscopy in the future.

These changes could be realized in stimulating tunable color emission from the YHOE NPs as seen from the corresponding color coordinate diagram (Fig. 3c). Bright red emission coming from intense h-EDT of the YHOE NPs was observed at ambient condition. Beyond 5.70 GPa, orange emission was seen due to the disappearance of h-EDT emission. With increasing pressure, an inclusion of yellow hue was observed due to increasing full width half maxima (FWHM) of MDT. The change of FWHM of the MDT peak as a function of pressure was linear from 18 to 27 nm up to ~11.43 GPa and followed with a saturation (Fig. 3b). This peak broadening can be ascribed to enhanced electron–phonon coupling, defects, distortion and crystal field leading to larger band splitting at increased pressure [15]. Another interesting feature was that no change in the intensity of MDT up to 49.4 GPa was observed as expected by minor influence of external factors such as pressure in this study. These changes in spectral features under pressure as

demonstrated here are related to pressure sensitivity. It highlights the potential of the YHOE NPs to be used as medium range pressure sensor.

The excitation spectra at ambient conditions shown in Fig. 3d showed charge transfer band (CTB) at 250 nm due to $O^{2-} \rightarrow Eu^{3+}$ electron transfer and intra-configurational f-f (IFF) band of Eu^{3+} spanning 360–500 nm. As expected, not much change of the IFF band was seen with enhanced pressure as f orbitals are deeply buried beneath the valence shell while the CTB peak disappeared completely beyond 2.86 GPa. Similar spectral changes were observed in other pyrochlores probably due to enhanced structural distortion at high pressure or stabilization of ordered pyrochlore or cotuunite phase at higher pressure [10,11,16].

3. Conclusion

In this work, we have carried out high pressure luminescence measurement on molten salt synthesized YHOE NPs. High pressure effects on the YHOE NPs led to lowering of phonon frequency, local site swapping of Eu^{3+} ions from Y^{3+} to Hf^{4+} sites, and increased in FWHM of the MDT peak up to 11.43 GPa. We further demonstrated how the luminescence tunability from red to orange to yellow endowed by the disappearance of h-EDT peak of the YHOE NPs at high pressure. Moreover, these demonstrated changes in spectral features under pressure can be explored for designing future medium range pressure sensors.

CRediT authorship contribution statement

Santosh K. Gupta: Formal analysis, Writing - original draft, Visualization. **Yuanbing Mao:** Conceptualization, Writing - review & editing, Supervision.

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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