

# MATERIALS CHEMISTRY FRONTIERS





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## **RESEARCH ARTICLE**



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## 1. Introduction

Compounds with a general formula of  $A_2B_2O_7$  have received intense attention due to their high thermodynamic stability, high radiation stability, capability to incorporate lanthanides and actinides, and ability to form antisite defects by swapping A and B positions.<sup>1–6</sup> Among these compounds, rare-earth hafnates RE<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> possess various desirable properties, which are very important for different technological applications, such as computer tomography (CT),<sup>7</sup> positron emission tomography (PET),<sup>8</sup> high-energy radiation detectors,<sup>9</sup> scintillation host materials,<sup>10</sup> magnetic materials,<sup>11</sup> among others.<sup>4,9,12–15</sup>

Uranium and its radioactive isotopes contribute to a highlevel of nuclear waste, which needs to be properly disposed.

## On structure and phase transformation of uranium doped La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> nanoparticles as an efficient nuclear waste host<sup>†</sup>

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The design and development of efficient and stable nuclear waste hosts has drawn intensive interest for long-lived lanthanides and actinides. A detailed investigation of their structure and potential structural evolution are crucial. In this study, we have synthesized lanthanum hafnate La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> nanoparticles (NPs) doped with uranium at different concentrations (0-10%) and investigated their structural transition. We have discovered that in our La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:U NPs, the uranium dopants are stabilized at both  $U^{4+}$  and  $U^{6+}$  oxidation states in which the  $U^{6+}$  oxidation state exists in octahedral uranate  $UO_6^{6-}$  form. We also confirmed that the U<sup>4+</sup> ions substituted the Hf<sup>4+</sup> ions with a lifetime of  $\sim$ 1.0  $\mu$ s and the UO<sub>6</sub><sup>6-</sup> ions resided at the La<sup>3+</sup> sites with a lifetime of ~9.0  $\mu$ s. More interestingly, the proportion of the U<sup>4+</sup> ions in the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:U NPs was higher than that of the  $UO_6^{6-}$  ions at low doping level, but at the doping level higher than 2.5%, the fraction of the  $UO_6^{6-}$  ions was greater than that of the  $U^{4+}$  ions. Furthermore, we studied the structural phase transformation from order pyrochlore to cotunnite of these La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:U NPs with increasing uranium doping level, and found that ordered pyrochlore phase favors the U<sup>4+</sup> ions whereas disordered cotunnite phase favors the  $UO_6^{6-}$  ions. We further used *in situ* Raman spectroscopy to confirm the reversible cotunnite to pyrochlore phase transformation of the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:10%U NPs at 900 °C. Therefore, this work demonstrated the successful development of uranium doped La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> NPs and thorough characterization of the fundamental spectra of uranium ions, doping induced phase transformation, and structure-optical property correlation.

> Uranium ion has multiple oxidation states (*i.e.* +3, +4, +5 and +6), all of which are luminescence active with characteristics emission.<sup>16-19</sup> Speciation studies of uranium ion in A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> compounds will be highly beneficial for fundamental uranium chemistry and nuclear industry. However, because of its complex nature and various existing valence states, the incorporation mechanism, oxidation state and structural environment of uranium ions in A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> compounds are uncharted and vague. For example, Zhang and coworkers investigated the phase evolution of U doped Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>.<sup>20</sup> They have carried out detailed phase evolution investigation from Ln2Ti2O7 pyrochlores to  $Ln_{0.5}U_{0.5}Ti_2O_6$  (Ln = Y and Gd) brannerites in glasses using various techniques such as X-ray diffraction, Raman spectroscopy, diffuse reflectance spectroscopy and electron microscopy. Shu et al. studied the effect of alpha irradiation on U doped Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>.<sup>21</sup> Their study revealed that main crystal structure does not change but weak structural ordering takes place on alpha irradiation. They have also found increase in radiation stability of Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> at high uranium concentrations. Lu et al. explored the effects of U3O8 on the phase and microstructure evolution of Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and found that uranium is homogenously distributed in +4 and +6 oxidation states at

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 $Gd^{3+}$  and  $Zr^{4+}$  sites, respectively.<sup>22</sup> One of us studied the speciation of uranium using luminescence spectroscopy for  $A_2Zr_2O_7$  (A = La, Nd and Gd) and the results show that uranium is stabilized as  $U^{4+}$  and  $UO_6^{6-}$  in  $Gd_2Zr_2O_7$ , only as  $UO_6^{6-}$  in  $Nd_2Zr_2O_7$ , and as both  $UO_6^{6-}$  and  $UO_2^{2+}$  in  $La_2Zr_2O_7$ .<sup>23-25</sup> There are few more reports on uranium doped  $Gd_2Zr_2O_7$  wherein speciation of uranium was carried out in bulk phase using X-ray diffraction, Raman spectroscopy and X-ray photoelectron spectroscopy along with other suitable techniques.<sup>26-28</sup> However, none of these reports includes studies on structure and phase evolution of uranium doped  $La_2Hf_2O_7$  nanoparticles (NPs).

Photoluminescence (PL) spectroscopy is an indispensable technique to probe optical properties and local structure of phosphors. It is also the most acceptable technique for detecting and estimating uranium in ultra-trace level in both solids as well as aqueous media.<sup>29</sup> Meanwhile, Raman spectroscopy has been widely utilized as a tool to distinguish between the disordered fluorite and the ordered pyrochlore phases of A2B2O7 compounds. Due to its high sensitivity to oxygen-cation vibrations, Raman spectroscopy has the capability to probe local structure and to further identify disorder within the pyrochlore structure, which emerge from vacancies and defects that disrupt the translational symmetry. Moreover, X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. It is also one of the highly sensitive methods to probe oxygen vacancies. Therefore, in this work, we have used these three techniques together along with other traditional materials characterization techniques complementarily to investigate the structure and phase transition of the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> NPs with different uranium doping levels. Lastly, for the first time, we observed reversible phase transformation in the La2Hf2O7:10%U NPs using in situ Raman measurement. Therefore, through the successful development of uranium doped La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> NPs and their thorough characterization of the fundamental spectra of uranium ions, doping induced phase transformation, and structure-optical property correlation, we believe this work open new research areas important for safe nuclear energy and sustainable environment.

## 2. Experimental

Fig. S1 (ESI<sup>†</sup>) depicts the schematic of the combined coprecipitation and molten-salt synthesis (MSS) procedure adopted to synthesize the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:x mol%U NPs (x = 0.5-10.0).<sup>4,9,30,31</sup> Additional synthesis and characterization details are provided in ESI<sup>†</sup> (S.1 and S.2).

### 3. Results and discussion

#### 3.1 Phase, structure and morphological analysis

XRD is used to confirm the phase of the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:x%U (x = 0, 0.5, 1, 2.5, 5, 7.5, and 10) NPs (Fig. S2, ESI<sup>†</sup>). Fourier transformed infrared (FTIR) spectra were collected (Fig. S3, ESI<sup>†</sup>) to

identify the phase and rule out the formation of any additional phase of the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:x%U NPs. Morphostructural characterization of the synthesized NPs was performed with scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) as shown in Fig. S4 and S5 (ESI†). The presence of uranium dopant was confirmed by energy dispersive spectroscopy (EDS) (Fig. S6, ESI†). The doping efficiency and uniform distribution of constituent element were investigated using elemental mapping (Fig. S7, ESI†).

#### 3.2 Raman spectroscopy

It is well known that the ideal pyrochlore phase has six well-resolved Raman active vibrational modes in the range of 200–1000 cm<sup>-1</sup> which are represented as  $\Gamma_P = A_{1g} + E_g + 4F_{2g}$ , whereas the fluorite phase has mainly one Raman active mode that is  $\Gamma_F = F_{2g}$ .<sup>32</sup> This is because seven oxygen ions are randomly distributed at eight anion positions, which leads to structural disordering in the fluorite phase, and hence all the fine peaks of pyrochlore collapsed into one broader peak. More specifically, phase transformation from  $A_2B_2O_6O'$  pyrochlore (*Fd* $\bar{3}m$  space group) to AO<sub>2</sub> fluorite (*Fm* $\bar{3}m$ , *Z* = 4) structure takes place through the disappearance of  $A_{1g}$  and  $E_g$  Raman modes and decrease in the number of  $F_{2g}$  modes from 4 to 1.

Radius ratio  $(r_A/r_B)$  plays an important role in determining which structure of A2B2O7 compounds attain.33 It has been reported that fluorite phase is more likely to form if  $r_A/r_B < 1.46$ and while ordered pyrochlore phase is more likely to be stabilized if  $r_A/r_B$  is greater than 1.46 at room temperature. It was propose that  $r_A/r_B$  for different  $A_2B_2O_7$  compositions follows this trend: disordered fluorite phase (DFP)  $r_{\rm A}/r_{\rm B} < 1.21 <$  $\delta$ -phase  $r_A/r_B < 1.42-1.44 < ordered pyrochlore phase (OPP)$  $r_{\rm A}/r_{\rm B}$  < 1.78–1.83 < monoclinic pyrochlore  $r_{\rm A}/r_{\rm B}$  < 1.92.<sup>34</sup> La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> is the most favorable candidate with radius ratio of 1.45 to be stabilized in pyrochlore phase. Fig. 1a shows the Raman spectra of the as-synthesized La2Hf2O7:U NPs with different uranium concentrations. Undoped sample has six wellresolved Raman peaks at 306, 324, 402, 501, 521 and 601  $cm^{-1}$ pertaining to the vibrations of La-O and Hf-O bonds. These peaks are assigned to  $F_{2g},\;E_g,\;F_{2g},\;A_{1g}\;F_{2g}$  and  $F_{2g}$  modes, respectively.<sup>35</sup> The vibrational modes of  $F_{2g}$ ,  $E_g$ , and  $F_{2g}$  at low frequency region of 300–400  $\text{cm}^{-1}$  arise from vibrations of the La-O and Hf-O bonds. On the other hand, the high frequency bands at 501, 522 and 601 cm<sup>-1</sup> arise from the stretching of the Hf-O bonds.<sup>35</sup> However, the complete pyrochlore phase is preserved only up to 1.0% uranium doping level. After that, the fine OPP structure starts to collapse into broader peaks and disordered fluorite phase or cotunnite phase evolves and coexists with OPP. At 2.5% uranium doping level and above, there is complete disordering of the La2Hf2O7 pyrochlore phase and a broad peak around 715  $\text{cm}^{-1}$  appears. Its intensity keeps increasing and even overpowers the broad fluorite peak at 7.5% and 10% uranium doping levels. This peak is not a fundamental Raman vibrational mode of pyrochlore-structured A2B2O7 type oxides. It is believed to appear due to the distortions of the BO<sub>6</sub> octahedra.<sup>35,36</sup> In La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>, it has been attributed to distortion in HfO<sub>6</sub> octahedra and other kind of structural defects due to



Fig. 1 (a) Raman spectra of the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:x%U NPs (x = 0, 0.5, 1, 2.5, 5, 7.5, and 10) and (b) corresponding integrated Raman intensity ratio of the distorted HfO<sub>6</sub> octahedra ( $I_2$ ) and the main F<sub>2g</sub> Raman mode of the ordered pyrochlore ( $I_1$ ). This Raman intensity ratio serves as a qualitative indicator of the progression of anion disorder as a function of uranium doping concentration in the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> host.

doping of uranium at La/Hf site. The average metal-oxygen bond lengths in the fluorite phase is close to those existing in ideal pyrochlore structure, but is relatively much smaller than those in cotunnite-type  $A_2B_2O_7$  structure, suggesting that the fluorite phase has more covalent character than the cotunnitetype structure.<sup>37</sup> In the cotunnite-type structure, coordination number of metal ions is generally 8- or 9-fold, whereas in the fluorite-type structures, metal ions coordinate with oxygen ion in 7- or 8-fold coordination. This suggests La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> has the tendency to form ionic bonding with higher coordination number at high uranium doping concentration. Furthermore, based on Raman spectroscopy data, the increase of uranium doping level induces the gradual phase transformation from pyrochlore to fluorite and then cotunnite as observed by the appearance of broad peaks at 307 and 715 cm<sup>-1</sup>. Zhang et al. have also observed such process in U doped Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> but by applying pressure of 22 GPa, which finally transformed into a disordered fluorite structure on release of pressure.<sup>28</sup>

As a quantitative measure of the extent of anion disordering in the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:U NPs as a function of uranium doping concentration, the ratio of integrated Raman intensity between Raman active vibration mode of the distorted HfO<sub>6</sub> octahedra and the main F<sub>2g</sub> Raman mode at  $\omega_0 \approx 307 \text{ cm}^{-1}$  is plotted in Fig. 1b.<sup>38</sup> Moreover, we annealed our samples at high temperature to enhance cation ordering and reduce strain, but there was little effect on the Raman spectra of our La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:U NPs.<sup>39</sup> Thus, this ratio selectively indicates disorder on the anion sub-lattice.

#### 3.3 XPS analysis

To confirm the oxidation state of uranium ion and other constituent elements in the  $La_2Hf_2O_7$ :U NPs, XPS was carried out for the lowest and highest composition. Fig. S8 (ESI<sup>†</sup>) depicts the XPS spectra of La 3d, Hf 4f and O 1s core level electron for

the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:U NPs at various doping levels. Fig. S8a (ESI<sup>†</sup>) shows the La 3d XPS spectra that indicated the binding energies (BE) values for La 3d<sub>5/2</sub> and La 3d<sub>3/2</sub> are approximately 839.7 and 852 eV in addition to satellite peaks at 865.6 and 877.4 eV at 0.5% uranium doping. The La 3d X-ray photoelectron peak splits into 3d<sub>5/2</sub> and 3d<sub>3/2</sub> due to strong orbit coupling. There may be some additional contribution of ligand to metal charge transfer (oxygen to hafnium) which cause further splitting to these lines.<sup>40</sup> The BE difference in 3d<sub>3/2</sub> and 3d<sub>5/2</sub> states is around 16.5 eV, which indicates the stabilization of lanthanum ion in +3 oxidation state.<sup>41</sup> Most of the report on XPS spectra of HfO<sub>2</sub><sup>42-44</sup> clearly shows spin-orbit coupling induced splitting in Hf 4f peak to  $4f_{7/2}$  and  $4f_{5/2}$  similar to what we have observed in our La2Hf2O7:U NPs (Fig. S8b, ESI<sup>+</sup>). The BE values for these two peaks is approximately around BE = 18.9 eV and BE = 20.6 eV for 0.5% uranium doped La2Hf2O7 NPs with 4f spin-orbit splitting energy values around  $\sim$  1.92 eV. All these data are in concordance with Hf in +4-oxidation state. Although it can be seen from Fig. S8b (ESI<sup>+</sup>) that the Hf 4f peaks become more pronounced for the higher doping concentrations of U, due to the overlap between the La 5p and Hf 4f spectra, the peak contributions are not clear. On increasing the concentration of uranium ion, there is slight variation in peak position for X-ray photoelectron of La-3d and Hf-4f due to slight doping inducing change in electronic localization as well as density. The Hf 4p and U 4f spectra have overlapping peaks. The O 1s XPS spectra are shown in Fig. S8c (ESI<sup>†</sup>). As to-be-confirmed by PL data that there is uranium distribution (both U<sup>4+</sup> and U<sup>6+</sup>) at both La<sup>3+</sup>/Hf<sup>4+</sup> site, there are large density of charge compensating defect formation in our La2Hf2O7:U NPs to take care of charge neutrality. One of predominant defects would be oxygen vacancy. The area under the surface hydroxyl/under-coordinated O 1s peak (Ov) is increasing with uranium doping concentration, suggesting the formation of oxygen vacancies due to charge neutrality.



Fig. 2 (a) Uranium  $4f_{7/2}$  XPS spectra of the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:U NPs at different doping levels and (b) variation of the U<sup>4+</sup>/U<sup>6+</sup> ratio as a function of uranium doping levels (2.5–10%).

Since XPS studies can distinguish different oxidation states of uranium according to the binding energy of 4f orbit, we have used XPS to confirm the oxidation state of uranium in our  $La_2Hf_2O_7$  NPs (Fig. 2a). From the XPS analysis, we confirmed the presence of both U<sup>4+</sup> and U<sup>6+</sup> in all samples with different concentrations. At higher concentrations the XPS spectra displayed two peaks at binding energies values of 382.5 and 393.3 corresponding to U  $4f_{7/2}$  and U  $4f_{5/2}$ , respectively. This difference is because of spin orbit coupling. However, at lower doping concentrations (0.5%, and 1%) the U  $4f_{5/2}$  peak was absent. Because the U  $4f_{5/2}$  peak was not observed at lower concentrations, we were unable to calculate the fractional ratio of U<sup>4+</sup> and U<sup>6+</sup> species in the 0.5% and 1% uranium doped La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:U samples. The XPS parameters as calculated for the rest of the samples are shown in Table S2 (ESI<sup>†</sup>). From the ratio analysis, it is clearly evident that as the concentration of uranium dopant increases, there is an exponential decrease in the U<sup>4+</sup>/U<sup>6+</sup> ratio (Fig. 2b), confirming that U<sup>4+</sup> is dominating at lower concentrations, while at higher concentrations it is U<sup>6+</sup>. This observation is consistent with our



Fig. 3 (a) Emission spectrum and (b) excitation spectrum of the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:1.0 mol%U NPs.

PL emission spectroscopy and lifetime studies as discussed in the next section.

#### 3.4 Photoluminescence

**3.4.1 Emission and excitation spectroscopy.** PL emission spectrum (Fig. 3a) of the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:1.0%U NPs at  $\lambda_{ex}$  = 230 nm showed two different features in region a ( $R_a$ : 440–500 nm) and region b ( $R_b$ : 540–570 nm). In  $R_a$ , there is a cluster of four observable featureless bands centered at 451, 468, 482 and 493 nm in the blue region. In  $R_b$ , there is a single broadband at 550 nm in the green region.

The cluster of four bands in blue region is definitely not arising because of uranyl ions as they have unique signature of equally spaced vibronically coupled emission band whose value is close to symmetric stretching Raman mode of uranyl ion. Moreover, the position of the first band in the emission spectrum  $(v_{0-0})$  is a unique signature for deciding the number of oxygen atom coordinated to uranium and its bond order, which is known as zero phonon line (ZPL). It corresponds to the electronic transition from triplet  ${}^{3}\Pi_{u}$  state to singlet  ${}^{1}\Sigma_{g}^{+}(D_{\infty h})$ state from oxygen to the non-bonding orbital of uranium  $(5f\delta_{\mu})$  and  $5f\phi_{\mu}$ ). In our spectrum, it is located at 451 nm, which is much lower than the normally observed in case of  $UO_2^{2+45-47}$ . This feature further supports the fact that the sharp features in  $R_{\rm a}$  region corresponds to uranium in +4 oxidation state. It has been also reported previously that uranium has high tendency to be stabilized in both  $U^{4+}$  and  $U^{5+}/U^{6+}$  in  $A_2B_2O_7$  type pyrochlore oxides.<sup>48,49</sup> Indeed, in our earlier work on U doped Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>, we could confirm that uranium has a tendency to stabilize in both U(+4) and U(+6) states.<sup>24</sup> In our case here, the emission peaks in region  $R_a$  are attributed to  $f \rightarrow f$  transitions of the U<sup>4+</sup> 5f<sup>2</sup> ion.<sup>24,50–52</sup> The spectral splitting of the U(rv) bands is the result of ligand field induced by hafnate ion. This particular emission is attributed to the relaxation of the highest energy <sup>3</sup>F<sub>2</sub> chargetransfer excited-state manifold (5f<sup>1</sup>6d<sup>1</sup>) to Russell-Saunders coupled <sup>3</sup>H<sub>4</sub>(5f<sup>2</sup>) ground state and higher lying energy states derived from the 5f<sup>2</sup> electronic configuration.<sup>24</sup>

On the other hand, the broad peak in the green emission zone  $R_{\rm b}$  at 550 nm is originated from uranium ion in +6 oxidation state, which allowed for oxygen to uranium charge transfer.<sup>23–25,45–47,53,54</sup> Therefore, it is due to ligand to metal charge transfer (LMCT) transition and is typical of uranium stabilizing in octahedral uranate ion  $UO_6^{6-23,53}$  Visible emission in the green region emerges due to ligand to metal charge transfer (LMCT) involving bonding oxygen orbitals ( $\Pi_u$ ,  $\Pi_g$ ,  $\Omega_g$ , and  $\Omega_u$ ) to nonbonding 5f<sub>δ</sub> and 5f $\varphi$  orbitals of uranium ion.

Apparently, uranyl ion (UO2<sup>2+</sup>) vibronic features are very distinct from those that arises due to LMCT transitions. Normally LMCT induced vibronic transitions are very broad and often structureless. It is very difficult to identify the zero-phonon lines (ZPLs) and vibration modes from there. This is because of the fact that broadening due to LMCT induces lattice displacements and charge-hole relaxation in the valence band.55 Previously published work has shown that uranyl ion has a unique emission peak with constant spacing.<sup>23-25,45-47,53,54</sup> The origin of such vibronic coupling is the strong interaction of the ground state Raman active O=U=O symmetric stretching mode with the  ${}^{3}\Pi_{u}$  electronic triplet excited state (generally observed between 780 and 900 cm<sup>-1</sup>). Isolated uranyl ion has three Raman active modes at ground state vibrational frequencies of 830 ( $\omega_2$ ), 920 ( $\omega_2$ ) and 250 ( $\omega_3$ ) cm<sup>-1</sup> due to symmetric stretching, asymmetric stretching and bending, respectively. However, based on Franck-Condon principle only symmetric stretching modes are allowed to couple with the electric dipole transition of uranyl ion.<sup>56</sup> Therefore, as a unique signature of the uranyl ion, vibronic band progresses harmonically in the frequency of the O=U=O symmetric stretching. These are known as false origins:<sup>57</sup>  $\omega_2$  and  $\omega_2$  are coupled to the vibronic transitions of the symmetric stretching mode that progress in the frequency of  $\omega_1$ . No harmonics of asymmetric stretching  $\omega_2$ and bending mode  $\omega_3$  appear in the uranyl vibronic spectra because they are non Franck-Condon mode. Absence of such signature clearly rules out the stabilization of uranium ion as  $UO_2^{2+}$  in La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>.

Among various stable forms, hexavalent uranium ions depending on the conditions of concentration, annealing temperature, and structure of host can have different molecular structures leading to tetrahedral uranate  $UO_4^{2-}$ , octahedral uranate  $UO_6^{6-}$  or uranyl UO2<sup>2+</sup> species. Of these uranyl ions, UO2<sup>2+</sup> have been studied most extensively, because it is the most prevalent form of natural uranium in the ecological system. Uranyl ions are characterized by uranium-oxygen partial triple bond character, whereas octahedral and tetrahedral uranate ions are characterized by uranium-oxygen single bond. Crystal lattice hosts that favor the formation of U-O bond (singly bonded) will stabilize uranium ion in the form of uranate ions while those that offer close packed environments favor shorter triply bonded uranium-oxygen bonds to stabilize uranium in the form of UO22+ ions.58 From our earlier work on magnesium aluminate spinel and strontium silicate,<sup>45,46</sup> uranium stabilizes as  $UO_2^{2+}$  in MgAl<sub>2</sub>O<sub>4</sub> whereas as both U(+4) and UO<sub>6</sub><sup>6-</sup> in Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>.<sup>24</sup> On the other hand, it tends to stabilize as  $UO_6^{6-}$  in SrZrO<sub>3</sub>,  $Nd_2Zr_2O_7$ , and  $Sr_2CeO_4$ .<sup>23,53,54</sup> In this case here, uranium stabilizes as both +4 and +6 oxidation state in the form of U<sup>4+</sup> ion as well as  $UO_6^{6-}$  ion at 1.0% uranium doped La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>.

The representative excitation bands corresponding to  $U^{4+}$ and  $UO_6^{6-}$  emissions were taken from the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:1.0 mol%U NPs (Fig. 3b). The distinct features in the two cases are another indication of the fact that the emission features in blue and green region has different origin altogether. The shoulder around 200–250 nm is attributed to oxygen to uranium charge transfer transition whereas the fine structure from 300–400 nm is the intra f–f band of uranium ion.

Fig. 4a depicts the emission spectra of the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:U NPs for various uranium concentrations and Fig. 4b displayed the effect of uranium ion concentration on emission intensity for both  $U^{4+}$  emission at 458 nm and  $UO_6^{6-}$  emission at 550 nm. The emission intensity increases up to 1.0% uranium doping, and after that, there is an emission intensity reduction. Such phenomenon is attributed to concentration quenching. At higher doping concentration, the distance between two-activator ions decreased to an extent where non-radiative energy transfer between them is facilitated. That distance in photophysical parlance is called critical distance. To confirm the non-radiative energy transfer mechanism, which leads to concentration quenching, the critical distance ( $R_c$ ) needs to be determined using the following equation:

$$R_{\rm c} = 2 \left( \frac{3V}{4\pi X_{\rm c} N} \right)^2$$



Fig. 4 (a) Emission spectra of the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:U NPs with various uranium doping concentrations with  $\lambda_{ex}$  = 230 nm, and (b) corresponding plot of emission intensity and (c) ratio of emission intensity from the U<sup>4+</sup> and UO<sub>6</sub><sup>6-</sup> ions as a function of the uranium doping concentration.

where  $R_c$  is called critical distance and is defined as the minimum possible distance between the dopant ions at which non-radiative energy transfer takes place, *V* is the volume of the unit cell,  $X_c$  is the critical concentration of dopant ion, and *N* is the number of cations present in one formula unit of host. The values of *V* and *N* for La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> are 1250.32 Å<sup>3</sup> and 16, respectively. Considering  $X_c = 1.0\%$  (0.01), critical energy transfer distance  $R_c$  in the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:1.0%U NPs was estimated to be 24.62 Å. In this case, non-radiative energy transfer takes place at the U–U distance greater than 10 Å *via* electric multipolar interaction.

In addition, uranium was stabilized as both  $U^{4+}$  and  $UO_6^{6-}$  ions in all doping concentrations in the La2Hf2O7 host, but their relative intensity changes (Fig. 4a). At low concentrations, the fraction of  $U^{4+}$  is more than that of  $UO_6^{6-}$  whereas the trends reverses at high doping concentrations as plotted in Fig. 4c. This in an interesting observation consistent with XPS data, which can be correlated to some kind of structural changes. At low uranium doping, A2B2O7 structure favors the stabilization of  $U^{4+}$  over that of  $UO_6^{6-}$ . At high doping level,  $A_2B_2O_7$  structure favors  $UO_6^{6-}$  over  $U^{4+}$ . It has been reported that the structure of host materials plays huge roles in stabilizing different oxidation states and coordinations of doping ions. Perovskite structure tends to stabilize the U(v1) oxidation state in UO<sub>6</sub><sup>6-</sup> coordination<sup>53</sup> whereas spinel structure tends to favor the same oxidation state but in a different geometry as UO2<sup>2+</sup> ion.<sup>45</sup> On the other hand, fluorite type A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> composition favors the stabilization of both U4+ and U6+24 In this case, our Raman spectroscopy results are assimilate our PL observations, supporting the fact that oxidation stabilization of uranium is dependent on the structural and phase evolution of the NPs.

**3.4.2 Lifetime spectroscopy.** Investigating the local site occupied by U ions in the  $A_2B_2O_7$  type pyrochlore structure is very important from the point of view of nuclear waste immobilization. In ideal pyrochlore lattice, there are two cationic sites having 16c and 16d Wyckoff positions with different coordination numbers (CNs). In addition, there are two anionic sites at 8a and 48f Wyckoff positions. Dopant ion occupancy on these sites depends on their ionic radii. The 16c cation site having CN of six anions on

the 48f sites and two on the 8a sites is usually occupied by large size dopant ions, whereas the 16d cationic site having CN of six anions on the 48f sites is usually occupied by small sized ions.<sup>28</sup>

As far as ionic radius is concerned, uranium in 8-coordination (100 pm) is shorter than 8-coordinated  $La^{3+}$  ion (116 pm), so it can easily reside on the lanthanum site. On the other hand, 6-coordinated Hf<sup>4+</sup> ion (71 pm) is smaller, and its site is difficult to accommodate large sized uranium ion (89 pm). On the other hand, for U<sup>4+</sup> ion substitution, Hf<sup>4+</sup> site favors charge matching whereas there is a need for charge compensation at La<sup>3+</sup> site. Charge matching is energetically more favorable situation than size matching. Therefore, U<sup>4+</sup> ion feels less distortion at Hf<sup>4+</sup> site relative to at La<sup>3+</sup> site due to its same ionic charge with Hf<sup>4+</sup> ion. Therefore, room temperature luminescence decay profiles of the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:1.0%U NPs were measured with emission wavelengths of 468 nm and 552 nm after excited at 230 nm (Fig. 5a and b). The luminescence decay profile corresponding to U<sup>4+</sup> ion (468 nm) displayed a biexponential behavior with two lifetime values. It indicates that U<sup>4+</sup> ion is not homogeneously distributed in the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> matrix.

Based on the fitting data, the decay curve shows two different lifetime values of 1.01 and 9.68  $\mu$ s with magnitudes 60% and 40%, respectively. The long lifetime measured from the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:1.0%U NPs (9.68  $\mu$ s) is ascribed to uranate ion localized at the La<sup>3+</sup> site whereas the fast decaying uranyl ion (1.01  $\mu$ s) is attributed to U<sup>4+</sup> ion localized at Hf<sup>4+</sup> site. The PL decay profile corresponding to UO<sub>6</sub><sup>6-</sup> ion (550 nm) also displayed a biexponential behavior with lifetime values of 1.01  $\mu$ s (39%) and 9.09  $\mu$ s (61%). Here the fast decaying uranium is attributed to U(w) ion localized at the Hf<sup>4+</sup> site whereas the slow decaying uranium ion is attributed to UO<sub>6</sub><sup>6-</sup> ion at La<sup>3+</sup> site. In this case, one U<sup>6+</sup> ion replaces two La<sup>3+</sup> sites and charge-compensating defects are cation vacancies.

#### 3.5 Structural evolution of the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:10%U NPs by *in situ* Raman spectroscopy

To further investigate the structural evolution of our  $La_2Hf_2O_7:x\%U$ NPs, we took *in situ* Raman spectra of  $La_2Hf_2O_7:10\%U$  NPs as an



Fig. 5 Luminescence decay profiles of the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:1.0%U NPs with emission wavelengths of (a) 468 nm and (b) 552 nm after excited at 230 nm.



example with our initial effort. From the discussion above, the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:10%U NPs exists in complete cotunnite structure. The average metal–oxygen bond length in the fluorite-phase is much closer to those existing in ideal pyrochlore structures, but is relatively much smaller than that in cotunnite-type  $A_2B_2O_7$  structures, suggesting that the fluorite phases have more covalent character than the cotunnite-type.<sup>37</sup> In the cotunnite-type structures metal ion is generally 8 or 9-fold whereas in the fluorite-type structures metal ion coordinates with oxygen ion in 7 or 8 fold coordination. This suggest that at high uranium concentration hafnate pyrochlore has tendency to form ionic bonding with higher coordination number.

With increasing temperature from 25 °C to 950 °C (Fig. 6a), this particular the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>:10%U sample underwent phase transformation from cotunnite phase to ordered pyrochlore phase. At the highest reached measurement temperature, *i.e.* 950 °C, all the Raman modes expected for ordered pyrochlore phase were found from the heated sample with the almost complete disappearance of the 715 cm<sup>-1</sup> peak originated from the structurally disorder cotunnite phase (top panel of Fig. 6a) while the disordered fluorite phase was probably unseen. The complete phase transformation took place around 900 °C. Even more interestingly and for the first time, we found that the phase change is reversible, *i.e.*, the Raman band corresponding to cotunnite phase reappear after the sample was cooled down back to room temperature (Fig. 6b). With the initial exciting Raman results collected so far, further investigations are undergoing, including in situ Raman studies of other composition along with in situ PL, X-ray absorption spectroscopy and neutron diffraction measurements, and will be reported separately in the near future.

## 4. Conclusion

In this work, uranium doped La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> nanoparticles were successfully synthesized using a combined co-precipitation

and molten salt synthesis method. XRD and FTIR demonstrated the formation of pure La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> phase with particle size in the nanodomain as confirmed using electron microscopy. Emission and lifetime spectroscopy further suggested the existence of  $U^{4+}$  ions along with  $U^{6+}$  ions as  $UO_6^{6-}$  species. The same has been further corroborated by more oxidation state sensitive XPS. Luminescence lifetime measurement confirmed the stabilization of fast decaying U<sup>4+</sup> at Hf<sup>4+</sup> site whereas slowly decaying U<sup>6+</sup> tends to stabilize at La<sup>3+</sup> site. Further concentration dependence studies showed maximum emission output for 1.0% uranium doped samples and the concentration quenching in these NPs was attributed to non-radiative energy transfer via multipolar interaction. Another interesting phenomenon was observed from the emission spectra as well as XPS: at low uranium doping concentration, the proportion of U<sup>4+</sup> ion was more than that of U<sup>6+</sup>, whereas at high uranium doping concentration, the opposite happened. We successfully explained this phenomenon using Raman spectroscopy, which demonstrated a structural phase transition from order pyrochlore to cotunnite with increasing uranium doping concentration. It was concluded that ordered pyrochlore phase favors uranium stabilization in +4-valence state whereas disordered cotunnite phase energetically favors octahedral uranate ions UO<sub>6</sub><sup>6-</sup>. To further understand the structural evolution, in situ Raman measurements were carried out on the La2Hf2O2:10%U NPs between room temperature and 950 °C. A reversible structural transition was found at 900 °C between ordered pyrochlore phase and disorder cotunnite phase. Therefore, it is expected that this work open new research areas of fundamental solid-state spectroscopy of uranium, doping induced pyrochlore to fluorite phase transition, and structure-optical property correlation in doped A2B2O7 with urgent importance to nuclear power industry and sustainable environment.

## Conflicts of interest

There are no conflicts to declare.

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