Europium(III)-doped $A_2Hf_2O_7$ ($A = Y, \text{Gd, Lu}$) nanoparticles: Influence of annealing temperature, europium(III) concentration and host cation on the luminescent properties

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Abstract

The detailed analyses of structure and luminescence of europium(III)-doped $A_2Hf_2O_7$ ($A = Y, \text{Gd, Lu}$) nanoparticles is presented. Samples were prepared by time and cost effective combustion method that utilize polyethylene glycol both as a chelating agent and as a fuel, with different europium(III) concentrations (from 1 to 12 at.%), annealed at temperatures ranging from 800 to 1400 °C, and with alternating $A^{3+}$ cation in the $A_2Hf_2O_7$ host. Then, structural variations between materials were analysed by X-ray diffraction and structural refinement, while the changes in the luminescence were assessed from the Judd-Olfelt analyses of emission spectra. Nanoparticles prepared at the lowest temperature (800 °C) had the smallest particle size of ~6 nm and showed the highest quantum efficiency when doped with 1 and 2 at.% of europium(III). Radiative transition rate and quantum efficiency of emission showed $Lu_2Hf_2O_7 > Gd_2Hf_2O_7 > Y_2Hf_2O_7$ trend.

1. Introduction

Compounds of general formula $A_2B_2O_7$, where $A$ element is a rare earth (RE) or an element with inert lone-pair of electrons and $B$ element is a transition metal with variable oxidation state or a post transition metal, display interesting physical properties like high melting point (~2700 K), catalytic activity, piezoelectric behaviour, ferro- and ferrimagnetism, giant magnetoresistance, and could be used as solid oxide fuel cells, dielectric materials, catalysts, immobilizers of nuclear waste and hosts for luminescent materials [1-5]. To achieve electroneutrality in these compounds, two combinations of $A$ and $B$ cations are possible $A^{3+}/B^{4+}$ or $A^{4+}/B^{5+}$. Crystal structures of $A_2B_2O_7$ are in direct correlation with the ratio of their ionic radii, $r(A^{3+})/r(B^{4+})$. If the ratio is low ($r(A^{3+})/r(B^{4+}) < 1.46$) they crystallize in fluorite crystal structure with $Fm\bar{3}m$ symmetry, while both cations are in 8-fold coordination with one anion vacancy per unit cell. In the case where $r(A^{3+})$ is larger and/or $r(B^{4+})$ is smaller, the ratio is larger ($r(A^{3+})/r(B^{4+}) = 1.46-1.78$), and these materials crystallize in pyrochlore crystal structure with $Fd\bar{3}m$ symmetry, where $A^{3+}$ is also in the 8-fold coordination while $B^{4+}$ is in 6-fold coordination [6,7].

In the field of transition metal or lanthanide doped materials for luminescence applications, $A_2B_2O_7$ compounds activated with Mn$^{2+}$ have been used as deep-red emitting phosphors for white LEDs [8,9], and as conventional downconversion phosphors when activated with Eu$^{3+}$ and Sm$^{3+}$ [10,11]. Also, these materials could be applied as scintillators due to their high density (7.93–9.95 g cm$^{-3}$) [12] which results in the excellent gamma-ray stopping power, and in the computer tomography and positron emission tomography [13]. Recently, luminescence thermometry with Eu$^{3+}$ and Sm$^{3+}$ doped Gd$_2Ti_2O_7$ has been demonstrated [14,15]. To date, only few reports have been published on the synthesis of rare earth based $A_2B_2O_7$ ($A = Y, \text{Gd, Lu}; B = Ti^{4+}, Hf^{4+}, \text{Sn}^{4+}, Zr^{4+}$) pyrochlores and on their luminescence when doped with trivalent rare earths, even though they are promising candidates for the activation with trivalent rare earth ions due to similarities of ionic radii and valence [16]. $Y_2Hf_2O_7$ was synthesized with a classic solid-state method, while Gd$_2Hf_2O_7$ by a vaporization method [17,18]. However, the disadvantage of these synthesis methods is the use of high temperatures (1300–1900 °C) or high pressures [18,19]. The use of soft...
chemical synthesis methods, Pechini modification of self-propagating high-temperature synthesis, co-precipitation, and combustion synthesis has yielded a cost-effective preparation of $Y_2Hf_2O_7$ [13,20,21]. Until now, properties of $Y_2Hf_2O_7$ phosphors doped with La$^{3+}$ and Ti$^{4+}$ ions, and Lu$_2$Hf$_2$O$_7$ doped with Tb$^{3+}$ ions have been reported [22–24].

In this work we show time and cost effective synthesis of high-density $A_2Hf_2O_7$ nanoparticles by combustion method that utilize polyethylene glycol (PEG) both as a chelating agent and as a fuel. Then, we systematically analyse how structure of nanoparticles and emission of europium(III) ions that are introduced into nanoparticles depends on the variation of nanoparticle’s composition and on the temperature of synthesis. For this purpose nanoparticles are prepared at 800, 1100 and 1400 °C, europium(III) concentration is varied between 1 and 12 at.%, and, finally, different A$^{3+}$ cations (Y, Gd, Lu) were used for the $A_2Hf_2O_7$ host. Judd-Ofelt theory was applied for the analysis of europium(III) emission which allowed calculation and comparison of radiative and nonradiative transition rates, Judd-Ofelt intensity parameters, and quantum efficiencies.

2. Experimental

All chemicals: HfCl$_4$ (99.9%, Alfa Aesar) Y$_2$O$_3$ (99.9%, Alfa Aesar), Eu$_2$O$_3$ (99.9%, Alfa Aesar), HNO$_3$ (69–70%, J.T. Baker), NH$_3$ (30–33%, Roth) and PEG 200 (Alfa Aesar) were of the highest purity available and were used without any further purification. The direct use of HfCl$_4$ in the synthesis is undesirable because Cl$^-$ ions could quench optical signal [25]. To eliminate Cl$^-$ ions, HfCl$_4$ was first dissolved in water and Hf$^{4+}$ ions formed HfO$^{2+}$. These ions are then transformed in HfO(OH)$_2$ in the presence of aqueous 6.7 M ammonia solution and precipitate was washed until pH value was neutral to remove access of Cl$^-$ and NH$_4^+$ ions. The obtained precipitate (HfO(OH)$_2$) was used further in the synthesis after dissolution in HNO$_3$ acid as shown in the following three steps:

$$\text{HfCl}_4 + \text{H}_2\text{O} \rightarrow \text{HfO}^{2+} + 2\text{H}^+ + 4\text{Cl}^-$$
$$\text{HfO}^{2+} + 2\text{NH}_3\text{OH} \rightarrow \text{HfO(OH)}_2\downarrow + 2\text{NH}_4^+$$
$$\text{HfO(OH)}_2 + 4\text{HNO}_3 \rightarrow \text{Hf(NO}_3)_3\downarrow + 3\text{H}_2\text{O}$$

In the obtained Hf$\text{[NO}_3\text{]}_4$ transparent solution an appropriate amounts of Y$_2$O$_3$ and corresponding stoichiometric ratio Eu$_2$O$_3$ ($x = 1, 2, 4, 8, 12$ at.%) were added, and the mixture was stirred at 80 °C. After 1 h solution becomes transparent and PEG 200 was added to the solution in the 1:1 ratio (to the mass of Y$_2$Hf$_2$O$_7$). Solution was further heated at 120 °C until it formed the gel, which was then transferred to the crucible and calcined at different temperatures ($T = 800, 1100$ and $1400$ °C) for 24 h. The europium(III) doped Gd$_2$Hf$_2$O$_7$ and Lu$_2$Hf$_2$O$_7$ samples were obtained under identical experimental procedure and conditions.

XRD measurements were obtained using a Rigaku Smart Lab diffractometer. Diffraction data were recorded in a 20 range from 10° to 90°, counting 0.7°/min in 0.02° steps. The structural analysis results (unit cell parameter, crystal coherence size, microstrain values, and data fit parameters) were obtained using PDFXL Integrated X-ray powder diffraction software.

Luminescence measurements were obtained at room temperature with Fluorolog-3 Model FL3-221 spectrophotometer system (Horiba JobinVyon), utilizing a 450 W Xenon lamp as an excitation source for steady-state emission measurements, and a Xenon—Mercuory pulsed lamp for emission decay measurements.

Transmission electron microscopy (TEM) studies were made on a Tecnai G20 (FEI) operated at an accelerating voltage of 200 kV. Samples were supported on a perforated carbon film (S147-4, Agar scientific) and were dried in air for one day. It was observed that at a high electron radiation dose defects were induced into the crystals until their crystal structure disappeared. Therefore, for HRTEM images the electron beam intensity was reduced strongly by inserting a condenser aperture and by decreasing the spot size.

3. Results and discussion

3.1. Structure and morphology of nanoparticles

Typical HRTEM images of $Y_2Hf_2O_7$ nanoparticles doped with 2 at.% of europium(III) and annealed at different temperatures are shown in Fig. 1a, b, c. All samples reveals clear crystal structure visible in HRTEM images and also in SADP. The SADP and reconstructed electron diffraction pattern of sample annealed in 800 °C is shown Fig. 1a (right side) and corresponds to cubic structure. The crystallite sizes for sample annealed at 800 °C was in range from 3 till 7 nm, whereas for sample annealed at 1100 °C in range from 5 till 15 nm. The crystallite size distribution and average size 11.7 nm of sample annealed in 1100 °C was estimated from TEM DF images and are shown in Fig. 1b (right side) together with selected DF patterns. The particles of sample annealed at 1400 °C was too large to evaluate the crystallite size in TEM. All samples shows nanoparticle agglomerates with different sizes (Fig. 1c (right side)), and particle size up to 300 nm for sample annealed at 1400 °C.

Fig. 2a displays XRD patterns of the $Y_2Hf_2O_7$:2 at.% Eu$^{3+}$ samples annealed at different temperatures ($T = 800, 1100$ and $1400$ °C) for 24 h, while Table 1 presents structural parameters of the samples obtained after Rietveld refinement of experimental data. All patterns clearly show presence of the cubic fluorite structure (Fm$\bar{3}$m (2 2 5)) in samples, with diffraction peaks indexed according to the ICDD 00-024-1406 card. With the increase of annealing temperature diffraction peaks became narrower and an average crystallite size of powders increases from 6 nm to 66 nm. The calculated average crystalline sizes for samples annealed at 800 °C and 1100 °C are very close to that observed in TEM images. The increase in annealing temperature did not significantly alter the unit cell parameter ($a$), therefore, the local environments around dopant europium(III) ions are similar in all samples in term of the distance between europium(III) and neighbouring ions. However, the values of microstrain are ten times lower in samples annealed at higher temperatures. XRD patterns of the $A_2Hf_2O_7$:1 at.% Eu$^{3+}$ ($A = Y, Gd, Lu$) samples and structural parameters of the samples obtained after Rietveld refinement of experimental data are presented in Fig. S1. The patterns clearly show pure cubic fluorite structure (Fm$\bar{3}$m (2 2 5)) in the samples, with diffraction peaks indexed according to the ICDD 00-024-1406 card (for $A = Y$ and Lu) and ICDD 00-024-0425 (for $A = Gd$).

Fluorite $Y_2Hf_2O_7$ crystallize in space group Fm$\bar{3}$m ($O_h^6$) No.225, with one formula unit in the primitive cell; the basic crystallo- graphic properties are listed in Table 2. Y$^{3+}$ and Hf$^{4+}$ cations randomly occupy $m$ $3$ $m$ site, each having occupancy factor of 0.5. To maintain charge balance, there are seven oxygens and a vacancy occupying 8 $3$ $m$ site of the unit cell, as can be seen in Fig. 2b. In this type of oxygen deficient fluorite structure the occupancy for each anion site is 0.875, where any of the eight oxygen sites in the structure have an equal probability to become vacant. In Fig. 2b blue spheres represent cations, red spheres represent oxygen’s, while yellow sphere is the vacancy. Blue tetrahedrons are coordination polyhedron around oxgens, yellow tetrahedron is the vacancy coordination polyhedron that also retains the shape in the crystalline structure, while coordination polyhedrons around cations are cubes as presented in red on the picture. In the 8-fold coordination, the values of ionic radii of constituting cations are:
$r_{\text{III}}(Y) = 1.019$ Å, $r_{\text{III}}(\text{Gd}) = 1.053$ Å, $r_{\text{III}}(\text{Lu}) = 0.977$ Å, $r_{\text{IV}}(\text{Hf}) = 0.83$ Å, which gives $r(Y^{3+}/Hf^{4+}) = 1.23$, $r(\text{Gd}^{3+}/Hf^{4+}) = 1.27$ and $r(\text{Lu}^{3+}/Hf^{4+}) = 1.18$ [16]. In the pyrochlore structure, hafnium(IV) ion is in 6-fold coordination and value of ionic radius is $r_{\text{IV}}(\text{Hf}) = 0.71$ Å, that was taken into account for $rA^{3+}/rB^{4+}$ in previous reports [1,2]. The ionic radius for dopant europium(III) ion is $r_{\text{III}}(\text{Eu}) = 1.066$ Å [16], that gives great probability of isomorphic ion exchange in the fluorite $A_2B_2O_7$ structure, without significant disturbing of the lattice. The surrounding of europium(III) in the crystal lattice is cube, but the oxygen vacancy significantly changes the symmetry of the crystal field effecting the luminescence properties.

### 3.2. Luminescent properties

The representative excitation and emission luminescence spectra of europium(III)-doped $Y_2\text{Hf}_2\text{O}_7$ nanoparticles annealed at 800 °C are presented in Fig. 3. Fig. 3a shows excitation spectrum in the 350–550 nm spectral range (recorded at $\lambda_{\text{max}} = 612$ nm) that is composed of characteristic europium(III) absorption bands
The ratio of intensities of 5D0 → 7F2 transition and it is hypersensitive on the local environment of europium(III). Single emission peak at 579 nm originate from 5D0 → 7F1 magnetic-dipole transition. The intensity of this transition does not depend on the local environment, therefore it can be used as a reference for Judd-Ofelt calculations. The most intensive transition is centered at 612 nm; intensity of this transition does not depend on the local environment, therefore it can be used as a reference for Judd-Ofelt calculations. The 5D0 → 7F1 transition is largely independent of the environment and can be considered in a first approximation to be constant.

3.2.1. Judd-Ofelt calculations

Transition probabilities of the rare earths are composed mainly of the electric dipole contribution 5D0 → 7FJ (J = 2, 4, 6) and to a much lesser extent by the magnetic-dipole contribution 5D0 → 7F1. The 5D0 → 7F3 transition is forbidden according to Judd-Ofelt theory, both in magnetic and induced electric dipole scheme, and this transition can only gain intensity via J-mixing [32,33]. Moreover, according to the standard Judd-Ofelt theory the 5D0 → 7F0 transition is strictly forbidden. Due to the above mentioned, these two transitions will not be considered in determining of transition probabilities and Judd-Ofelt parameters. The intensity of 5D0 → 7F1 magnetic dipole transition is largely independent of the environment and can be considered in a first approximation to be constant [34].

The Judd-Ofelt theory is a powerful tool for analysing 4f → 4f electronic transitions in lanthanide series [35,36]. Study of the optical properties of the rare earth ions in different host materials provides information about radiative and nonradiative emission rates, branching ratio, and quantum efficiency of emission.

In the standard theory radiative transition probability, A, of spontaneous emission of a transition between two manifolds J and J’ is given by:

\[ A(J \rightarrow J') = \frac{64 \pi^4 e^2}{3h(2J + 1)^3} \left[ n \left( \frac{n^2 + 2}{9} \right)^2 D_{ED} + n^2 D_{MD} \right] \]  

(1)

where \( h \) denotes Planck constant \( (6.63 \times 10^{-27} \text{ erg s}) \), \( 2J + 1 \) is the degeneracy of the initial state, \( n \) is the refractive index and \( e \) is charge of electron. The electric and magnetic dipole strengths, respectively, \( D_{ED} \) and \( D_{MD} \), are given by Ref. [37].

\[ D_{MD} = 9.6 \times 10^{-42} \text{ esu}^2\text{cm}^2 \]  

(2)

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>800 °C</th>
<th>1100 °C</th>
<th>1400 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a ) (Å)</td>
<td>5.19920 (6)</td>
<td>5.21227 (17)</td>
<td>5.19985 (17)</td>
</tr>
<tr>
<td>Crystalite size (nm)</td>
<td>5.83</td>
<td>13.32</td>
<td>66.60</td>
</tr>
<tr>
<td>Microstrain (%)</td>
<td>1.19 (21)</td>
<td>0.14 (5)</td>
<td>0.1589 (11)</td>
</tr>
<tr>
<td>Rwp (%)</td>
<td>3.17</td>
<td>5.48</td>
<td>4.72</td>
</tr>
<tr>
<td>Re (%)</td>
<td>1.99</td>
<td>1.91</td>
<td>1.98</td>
</tr>
<tr>
<td>Microstrain (%)</td>
<td>1.19 (21)</td>
<td>0.14 (5)</td>
<td>0.1589 (11)</td>
</tr>
<tr>
<td>Crystallite size (nm)</td>
<td>5.83</td>
<td>13.32</td>
<td>66.60</td>
</tr>
<tr>
<td>a (Å)</td>
<td>5.19920 (6)</td>
<td>5.21227 (17)</td>
<td>5.19985 (17)</td>
</tr>
</tbody>
</table>

\( a \) Rwp – regression sum of weighted squared errors of fit.

\( b \) Re - regression sum of relative errors of fit.

\( c \) GOF - goodness-of-fit (– Rwp/Re).

Table 2

Basic crystallographic properties of the fluorite A2Hf2O7 (Fm\( \overline{3} \) m) structure.

<table>
<thead>
<tr>
<th>No</th>
<th>Atom</th>
<th>Oxidation</th>
<th>Multiplicity</th>
<th>Wyckoff</th>
<th>Site symmetry</th>
<th>Coordinates</th>
<th>Site occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>+3</td>
<td>2</td>
<td>4a</td>
<td>m( \overline{3} )m</td>
<td>x 0 0</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>Hf</td>
<td>+4</td>
<td>2</td>
<td>4a</td>
<td>m( \overline{3} )m</td>
<td>0 0 0</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>O</td>
<td>-2</td>
<td>7</td>
<td>8c</td>
<td>Fm( \overline{3} )m</td>
<td>0.25 0.25 0.25</td>
<td>0.875</td>
</tr>
</tbody>
</table>
calculate non-radiative transition rate as the sum of all radiative rates:

\[ D_{\text{ED}}(\Psi_f, \Psi_j) = \varepsilon^2 \sum_{\lambda=2, 4, 6} \Omega_{\lambda}(\langle \Psi_f | U^{(\lambda)} | \Psi_j \rangle)^2, \]  

(3)

where squared reduced matrix elements \( |\langle \Psi_f | U^{(\lambda)} | \Psi_j \rangle|^2 \) have values independent of the host matrix. For calculation of intensity parameters, \( \Omega_{\lambda} (\lambda = 2, 4 \text{ and } 6) \), the following equation can be used [27,38]:

\[ \Omega_{\lambda} = \frac{D_{\text{MD}}^2}{\varepsilon^2 P_{\lambda}^2} \frac{9 n^3}{n (n^2 + 2)^2} \int \frac{I_i'(\nu_j)}{I_1'(\nu_1)}, \]  

(4)

where non-diagonal elements of the \( |\langle \Psi_f | U^{(\lambda)} | \Psi_j \rangle|^2 \) matrix have zero values, and values of squared reduced matrix element for the \(^{5}D_0 \rightarrow ^{7}F_2\) transition is 0.0032 and 0.0023 for the \(^{5}D_0 \rightarrow ^{7}F_4\) transition [39].

For calculation, the value of refractive index of 1.691 is taken from the literature [40].

We have calculated radiative emission probabilities of all transitions originating from the \(^{5}D_0\) excited state in terms of the ratio of areas \( S \) under corresponding emission curves [27,38]:

\[ A_i(^{5}D_0 \rightarrow ^{7}F_{2,4}) = A_i(^{5}D_0 \rightarrow ^{7}F_1) \times \frac{S(^{5}D_0 \rightarrow ^{7}F_{2,4})}{S(^{5}D_0 \rightarrow ^{7}F_1)}. \]  

(5)

The total radiative emission rate, \( A_R \), for an excited state is given as the sum of all radiative rates:

\[ A_R = \sum_{i=2, 4} A_i. \]  

(6)

The radiative lifetime \( (\tau_R) \) of an excited level \( \Psi_j \) is given by the reciprocal of the total radiative transition rates \( (A_R) \). Using calculated lifetime values and total radiative transition rates one can calculate non-radiative transition rate \( A_{\text{NR}} \) (which includes relaxation by multiphonon emission and effective energy transfer rates arising from ion-ion interactions):

\[ A_{\text{NR}} = \frac{1}{\tau_R} - A_R. \]  

(7)

Then, the quantum efficiency of emission \( \eta \) is:

\[ \eta = \frac{A}{A_R + A_{\text{NR}}}. \]  

(8)

This quantity represents \( \eta \) ratio between the number of photons emitted by the europium(III) ion to the number of those absorbed.

The asymmetry ratio \( R \) can be considered as indicative of the asymmetry of the coordination environment around the europium(III) ion. Higher values of \( R \) indicate higher asymmetry around the trivalent europium ions [41,42]. \( \Omega_2 \) and \( R \) affirm similar physical information on the bonding nature between europium(III) and the surrounding anions. \( \Omega_2 \) parameter depends on the local environment around the europium(III) site and it is affected by the covariance between europium(III) and ligand anions, whereas \( \Omega_4 \) and \( \Omega_6 \) are related to the viscosity and rigidity of the host material in which the ions are situated. \( \Omega_4 \) intensity parameter could not be determined because \(^{5}D_0 \rightarrow ^{7}F_6\) emission in this sample couldn’t be detected due to the instrumental limitations.

3.2.2. Influence of annealing temperature on europium(III) emission

Judd-Ofelt calculations were used to analyse emission spectra of Y_{2}Hf_{2}O_{7} nanoparticles doped with 2 at.% of europium(III) that were prepared at 800, 1100, 1400 °C. Table 3 comprises values of Judd-Ofelt intensity parameters, experimental lifetime, radiative and non-radiative transition rates, quantum efficiencies and asymmetry ratios; their temperature dependences are depicted in Fig. 4.

For all annealing temperatures europium(III) emission was characterized with \( \Omega_2 > \Omega_4 \). Fig. 4a. According Kumar et al. [42] this trend confirms the coherence between europium(III) ions and ligands, as well as the asymmetry around europium(III) site. One can notice that \( \Omega_2 \), \( \Omega_4 \) and \( R \) (Fig. 4b) decrease with the annealing temperature increase. Both \( R \) and \( \Omega_2 \) reveal information on the short range structural ordering around europium(III); the higher the values of \( R \) and \( \Omega_2 \) the lower the symmetry around the europium(III) [43,44]. This result can be correlated with results of structural analyses (Table 1) which showed significant (an order of magnitude) decrease of microstrain in samples annealed at high temperatures.

Sample prepared at 800 °C has the largest values of radiative transition rate and quantum efficiency. At larger temperatures, 1100 and 1400 °C, radiative transition rates and quantum efficiencies decrease, Fig. 4c and d. Stronger and more efficient emission could be ascribed to the disrupted symmetry around europium(III) in sample prepared at 800 °C which has much larger microstrain and smaller particle size compared to the samples.
synthesized at higher temperatures. We should mention that the values of quantum efficiency are slightly underestimated, since calculation does not account $^5D_0 \rightarrow ^7F_{3,5,6}$ emissions. However, the trend of quantum efficiency change with annealing temperature is unaffected by this calculation deficiency.

### 3.2.3. Concentration dependence of europium(III) emission

Concentration effect on europium(III) emission is analysed from emission spectra of Y$_2$Hf$_2$O$_7$ nanoparticles prepared at 800°C with 1, 2, 4, 8 and 12 at.% of europium. Results of Judd-Ofelt analyses are presented in Table 4 and Fig. 5.

Judd-Ofelt intensity parameters and asymmetry ratio did not show significant variations with the change of europium(III) concentration, Fig. 5a and b. The highest quantum efficiency values of 69.5% and 68.5% are obtained for 1 and 2 at.% doping, respectively. Reduction of quantum efficiency with the concentration increase, Fig. 5d, is a result of the intensification of non-radiative transition rate, Fig. 5c, due to the stronger energy migration between the neighbouring europium(III) owing to reduced distances between ions when concentration is high [45–47].

### 3.2.4. Variations in europium(III) emission between hosts with different A$^{3+}$ cation: A$_2$Hf$_2$O$_7$ (A = Y, Gd, Lu)

Small differences of Y(III), Gd(III) and Lu(III) properties, in particular the ion radius values, provide slightly different local environments for dopant europium(III) ions. Emission spectra of Y$_2$Hf$_2$O$_7$, Gd$_2$Hf$_2$O$_7$ and Lu$_2$Hf$_2$O$_7$ samples prepared at 800°C with 1 at.% europium were analysed with Judd-Ofelt theory and the results are presented in Table 5 and Fig. 6.

The highest values of quantum efficiency (~76.5%), lifetime and $\Omega_2$ are found for Lu$_2$Hf$_2$O$_7$ host as a consequence of the largest intensity parameters; the lowest value of ~69% is obtained for Y$_2$Hf$_2$O$_7$.

### Table 3

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$\Omega_2$ ($10^{-20}$ cm$^2$)</th>
<th>$\Omega_4$ ($10^{-20}$ cm$^2$)</th>
<th>$\tau$ (μs)</th>
<th>$A_4$ (s$^{-1}$)</th>
<th>$A_{4\text{NR}}$ (s$^{-1}$)</th>
<th>$\eta$ (%)</th>
<th>$R$</th>
</tr>
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<tbody>
<tr>
<td>800</td>
<td>6.88</td>
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<td>1.54</td>
<td>444.61</td>
<td>204.73</td>
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<tr>
<td>1100</td>
<td>5.40</td>
<td>2.34</td>
<td>1.72</td>
<td>371.75</td>
<td>209.63</td>
<td>63.94</td>
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<tr>
<td>1400</td>
<td>3.84</td>
<td>1.64</td>
<td>1.67</td>
<td>285.06</td>
<td>313.47</td>
<td>47.60</td>
<td>2.37</td>
</tr>
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</table>

![Fig. 4](https://example.com/fig4.png)

Fig. 4. a) $\Omega_2$ (blue spheres) and $\Omega_4$ (red triangles) Judd-Ofelt intensity parameters, b) asymmetry ratio, c) radiative (black squares) and nonradiative transition rates (red circles), and d) quantum efficiency of europium(III) emission in Y$_2$Hf$_2$O$_7$ nanoparticles prepared at 800, 1100 and 1400 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
4. Conclusion

To conclude, the combustion synthesis method that utilize polyethylene glycol as a chelating agent and as a fuel can be used for preparation of nanoparticles of rare earth hafnate fluorites $A_2Hf_2O_7$ ($A = Y, Gd, Lu$). Nanoparticles of different sizes from 6 nm to 300 nm are obtained by varying annealing temperature from 800 °C to 1400 °C. Higher annealing temperatures reduce microstrain and enlarge crystallite size of samples but do not affect the size of unit cell. Europium(III) emission has the highest quantum efficiency in nanoparticles prepared at 800 °C with 1 to 2 at.% of europium. Also, quantum efficiencies of europium(III)

### Table 4

<table>
<thead>
<tr>
<th>Concentration (at%)</th>
<th>$\Omega_2 (10^{-20} \text{ cm}^2)$</th>
<th>$\Omega_4 (10^{-20} \text{ cm}^2)$</th>
<th>$\tau$ (ns)</th>
<th>$A_R (s^{-1})$</th>
<th>$A_{NR} (s^{-1})$</th>
<th>$\eta$ (%)</th>
<th>$R$</th>
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### Table 5

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<tr>
<th>Host</th>
<th>$\Omega_2 (10^{-20} \text{ cm}^2)$</th>
<th>$\Omega_4 (10^{-20} \text{ cm}^2)$</th>
<th>$\tau$ (ns)</th>
<th>$A_R (s^{-1})$</th>
<th>$A_{NR} (s^{-1})$</th>
<th>$\eta$ (%)</th>
<th>$R$</th>
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<tbody>
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<td>1.53</td>
<td>454.39</td>
<td>199.20</td>
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<td>$Gd_2Hf_2O_7$</td>
<td>7.68</td>
<td>3.77</td>
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<td>182.05</td>
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Fig. 5. a) $\Omega_2$ (blue spheres) and $\Omega_4$ (red triangles) Judd-Ofelt intensity parameters, b) asymmetric ratio, c) radiative (black squares) and nonradiative transition rates (red circles), and d) quantum efficiency of europium(III) emission from $Y_2Hf_2O_7$ nanoparticles prepared at 800 °C with 1, 2, 4, 8 and 12 at.% of europium. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
emission follow Lu$_2$Hf$_2$O$_7$ > Gd$_2$Hf$_2$O$_7$ > Y$_2$Hf$_2$O$_7$ trend.

Acknowledgment

The authors acknowledge the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project no 45020). The work of K. Smits was supported by Latvian National Research Programme IMIS2 (Grant No. 302/2012).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.optmat.2016.04.007.

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Please cite this article in press as: J. Papan, et al., Europium(III)-doped A$_2$Hf$_2$O$_7$ (A = Y, Gd, Lu) nanoparticles: Influence of annealing temperature, europium(III) concentration and host cation on the luminescent properties, Optical Materials (2016), http://dx.doi.org/10.1016/j.optmat.2016.04.007.


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