Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Composition Dependent Photoluminescence in Nanocrystalline $La_2Hf_{2-x}Zr_xO_7$:Eu Phosphor: Role of Chemical Twin Zr/Hf Environments Around Luminescent Center

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S1. CCT estimation:

The correlated colour temperatures (CCT) of LHZOE are also calculated using McCamy and Kelly approximation using equation S1[1, 2]:

$$CCT(x, y) = -449n^3 + 3525n^2 - 6823.3n + 5520.33 \quad \text{(S1)}$$

where $n = (x - x_e)/(y - y_e)$ is the inverse slope line, (x_e = 0.3320, y_e = 0.1858) is the "epicenter" which is close to the intersection point mentioned by Kelly.

S2. PLQY estimation:

The absolute value of the quantum yield (PLQY) is calculated by using an integrating sphere (Edinburgh, UK). For LHZO:Eu^{3+} phosphor, the PLQY was determined using the equation S2 as shown below.[3]

$$QY = \frac{number\ of\ photon\ emitted}{number\ of\ photon\ absorbed} = \frac{\int L\ (Eu)}{\int E\ (Reference) - \int E\ (Eu)} \quad \text{(S2)}$$

Where L (Eu) is the photoluminescence intensity of the phosphor (45 mg), E (reference) and E (Eu) are the excitation light intensities of the reference and the phosphor samples, respectively.

∫L (Eu) is the area under the curve of the photoluminescence spectrum of the phosphor sample and ∫E (Reference) and ∫E (Eu) are the areas under the excitation spectra of the reference and the phosphor sample.

S3. Judd-Ofelt Calculations:

The chemical environment effect on the luminescent properties of Eu^{3+} ions can be better understood through Judd-Ofelt theory analysis of the transition intensity parameters of the LHZOE NPs.

The determination of Ω_λ (λ = 2, 4, and 6) parameters from emission spectra are necessary, where the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ can be noted as follow:

$$A_{md} = \frac{64\pi^4 k_{md}^3}{3h\,(2J+1)} n^3 S_{md} \quad \text{(S3)}$$

Here, k_{md} represents the energy of the magnetic dipole in wavenumber and h is Planck's constant, 6.626×10^{-34} J·s. In addition, the variable n depicts the refractive index of the host LHZO as 1.99 and $2J' + 1$ is the degeneracy of the initial state (1 for $^5D_0$). Furthermore, S_{md} is a constant independent of the host and is equal to 9.6×10^{-42}.[4] The electric dipole transitions can be denoted by $^5D_0 \rightarrow {}^7F_J$ (J = 2, 4, and 6) transitions where the radiation rate can be stated as follows[5, 6]:

$$A_J = \frac{64\pi^4 e^2 k^3\, n\,(n^2+2)^2}{3h\,(2J+1)\qquad 9} \sum_{\lambda=2,4,6} \Omega_\lambda \left\langle \Psi J \| U^\lambda \| \Psi' J' \right\rangle^2$$

(S4)

In this equation, e is the electric charge, k is the transition energy of electric dipole transitions in cm^{-1}, Ω_λ is the intensity parameter, and $\left\langle \Psi J \| U^\lambda \| \Psi' J' \right\rangle^2$ values are the squared reduced matrix elements, whose values are 0.0032 and 0.0023 for J' =2 and 4, respectively[7]. In all the parameters of the equations, Gaussian units are used for ease of calculating. Therefore, the transition intensity ratio between electronic dipole and magnetic dipole can be written as follow:

$$\frac{\int I_J(k)dk}{\int I_{md}(k)dk} = \frac{A_J}{A_{md}} = \frac{e^2 k_j^3 (n^2+2)^2}{k_{md}^3 \quad 9n^2} \Omega_\lambda \langle \Psi J \| U^\lambda \| \Psi' J' \rangle^2$$

(S5)

This can be easily simplified as follow:

$$A_J = \frac{64\pi^4 e^2 k^3 \, n\,(n^2+2)^2}{3h\,(2J+1) \qquad 9} \Omega_\lambda \langle \Psi J \| U^\lambda \| \Psi' J' \rangle^2$$

(S6)

In equation 4, the value of $\frac{\int I_J(k)dk}{\int I_{md}(k)dk}$ can be acquired from the integral area of the emission spectra. In addition, Ω_λ can be determined from the calculated basis of the emission spectra. However, the Ω_6 intensity parameter is not included in this calculation due to the fact that $^5D_0 \rightarrow {}^7F_6$ transitions were not observed.

The internal quantum efficiency (IQE) of the $^5D_0$ level of Eu^{3+} ions in the LHZOE NPs can be deduced using the emission spectra and lifetimes of the former electronic transition level. We can correlate the lifetime (τ), radiative (A_R), and nonradiative (A_{NR}) rates through the following equation:

$$\frac{1}{\tau} = A_R + A_{NR} \qquad \text{(S7)}$$

Here the AR rate can be determined by adding over the radiative rates for each $^5D_0 \rightarrow {}^7F_J$ (J= 1-4), $\sum_{J=1-4} A_J$. Therefore, the IQE of the emitting $^5D_0$ level is written as

$$IQE = \frac{A_R}{A_R + A_{NR}} = \tau \sum_{J=1-4} A_J$$

(S8)

In this case, the radiative contribution can be calculated from the relative intensities of the $^5D_0 \rightarrow {}^7F_J$ (J = 1-4) transitions. The $^5D_0 \rightarrow {}^7F_{5,6}$ branching ratios $\left(\beta_J = \frac{A_J}{\sum A_J}\right)$ are neglected since both have poor relative intensity compare to the $^5D_0 \rightarrow {}^7F_{1-4}$ transitions.

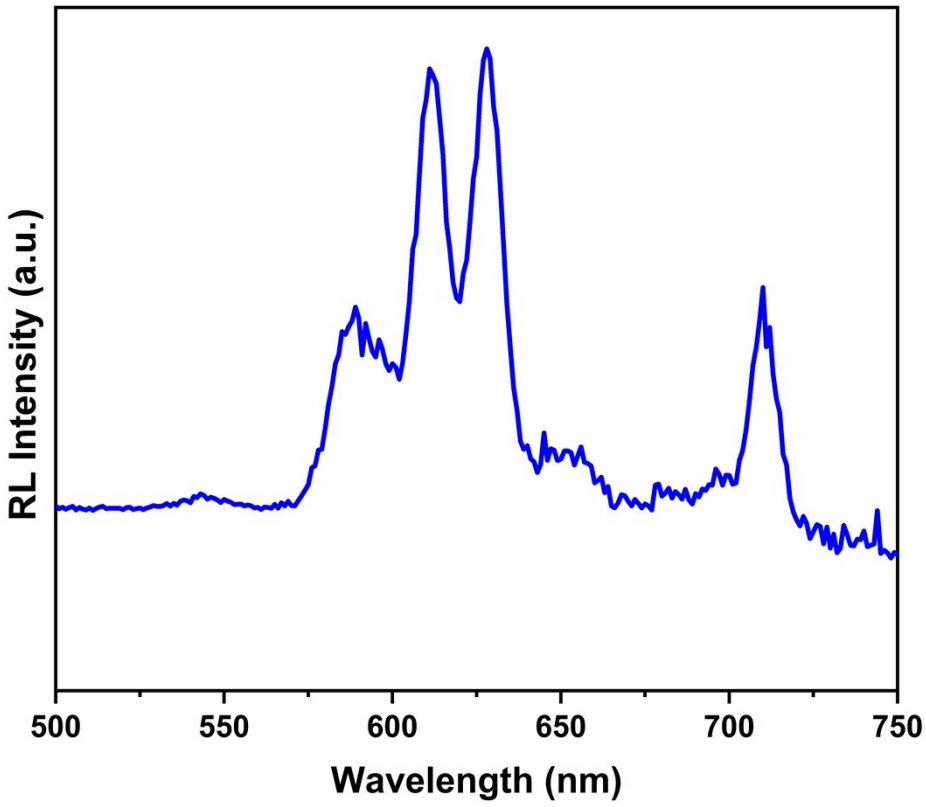

Figure S1: RL spectrum of for the representative Hf0.7-Zr1.3 LHZO NPs under X-ray excitation.

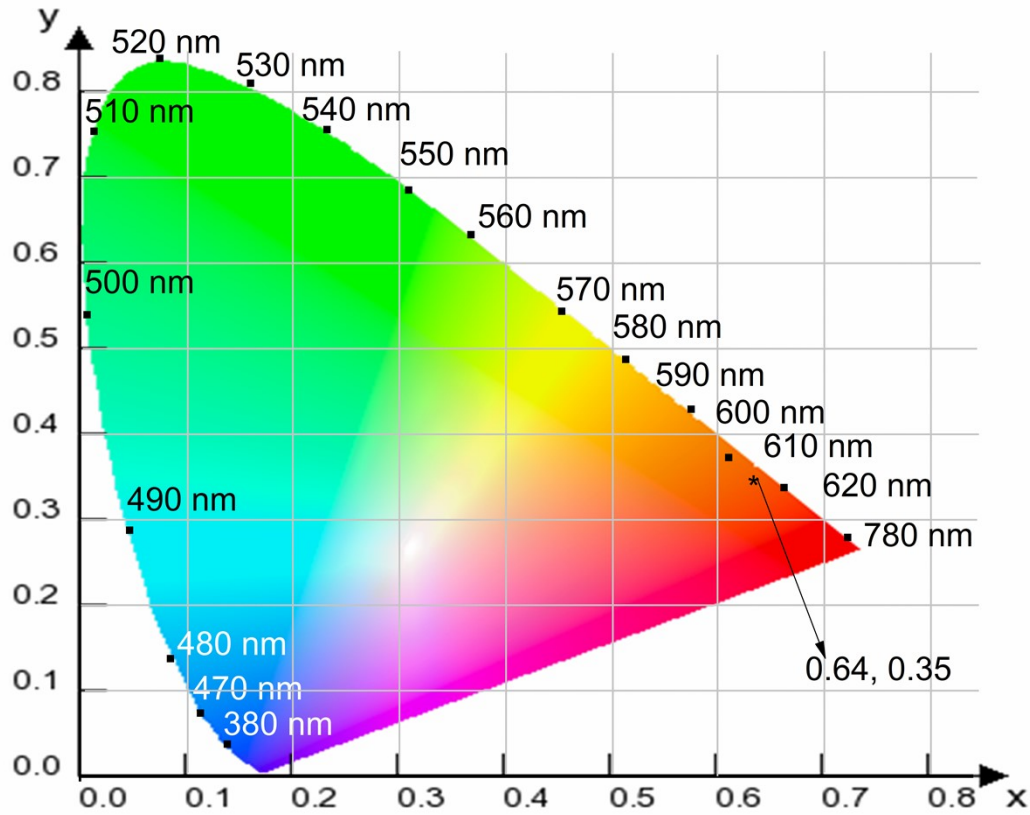

Figure S2: CIE index diagram for the representative Hf0.7-Zr1.3 LHZO NPs

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