

## Supporting Information

### **Temperature Dependent Quantum Cutting in Cubic BaGdF<sub>5</sub>:Eu<sup>3+</sup> Nanophosphors**

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**Chemicals:** 1-methylimidazolium (Alfa Aesar, 99%), Bromoethane (Himedia, 99%), Barium Acetate, [(CH<sub>3</sub>COO)<sub>2</sub>.Ba] (Himedia, 99%), Gadolinium Nitrate Hexahydrate, [Gd(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O] (Alfa Aesar, 99.9%), Europium Nitrate Pentahydrate, [Eu(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O] (Alfa Aesar, 99.9%), Ammonium Fluoride, [NH<sub>4</sub>F] (Himedia, 97%), Acetone, [CH<sub>3</sub>COCH<sub>3</sub>] (LobaChemie, 99.5%), Ethanol, [C<sub>2</sub>H<sub>5</sub>OH] (Merck, ACS grade), Methanol, [CH<sub>3</sub>OH] (LobaChemie), Deionized (DI) Water, [H<sub>2</sub>O] (CDH), Acetonitrile, [CH<sub>3</sub>CN] (LobaChemie).

**Synthesis of 1-Ethyl-3-methyl imidazolium bromide [C<sub>2</sub>mim]Br:** Modifying a literature procedure, 1-ethyl-3-methylimidazolium bromide [C<sub>2</sub>mim]Br was synthesized by incorporation of 12.4 ml bromoethane (Himedia 99%) and 10 m N-methylimidazole (Sigma Aldrich 99%) followed by refluxed at 40°C for 4 hours in an inert gas (Argon) atmosphere in a two neck round

bottom flask (250 ml).<sup>1</sup> After the reaction completion, the obtained product was washed with ethyl acetate and stirred for 1 hour. The obtained product was dried in vacuum for 12 hours to get a white solid crystal.

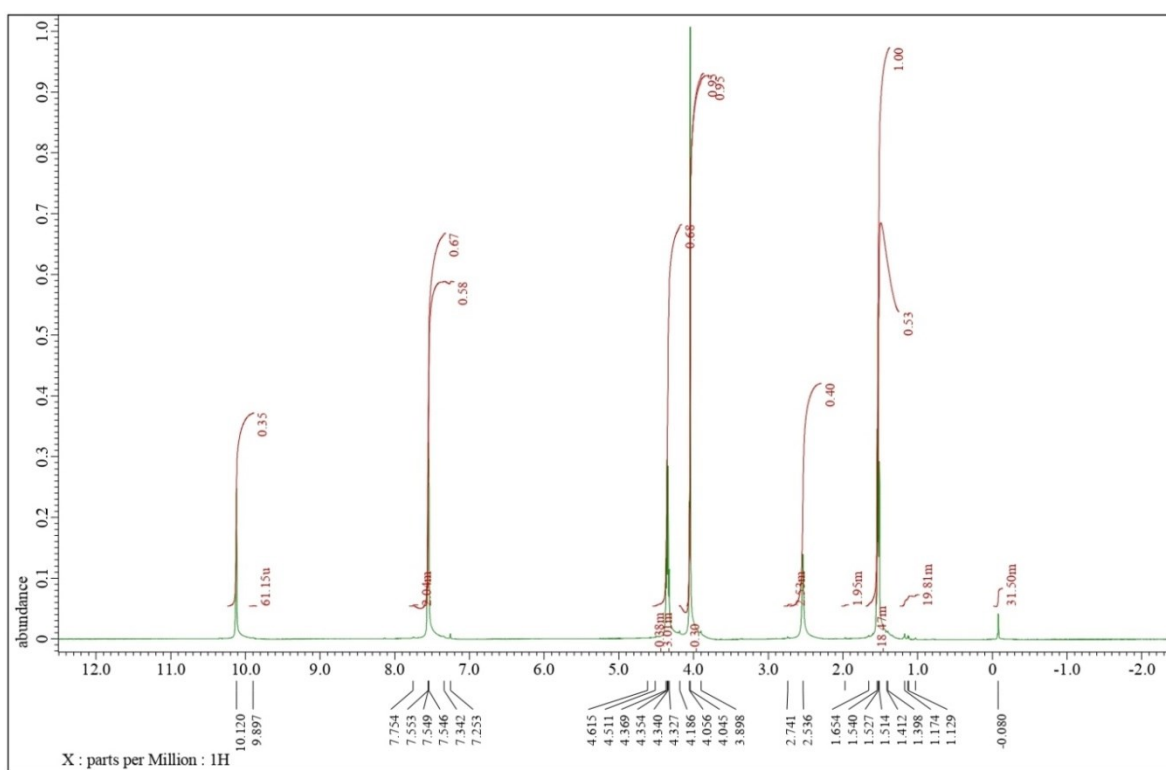
**NMR spectrum of 1-ethyl-3-methylimidazolium bromide ([C<sub>2</sub>mim]Br) ionic liquid:-**

<sup>1</sup>H NMR δ<sub>H</sub>/ppm (299K, 500MHz, CDCl<sub>3</sub>): δ 1.51-1.54 (3H, t, -CH<sub>3</sub>), 2.53 (3H, s, N-CH<sub>3</sub>)

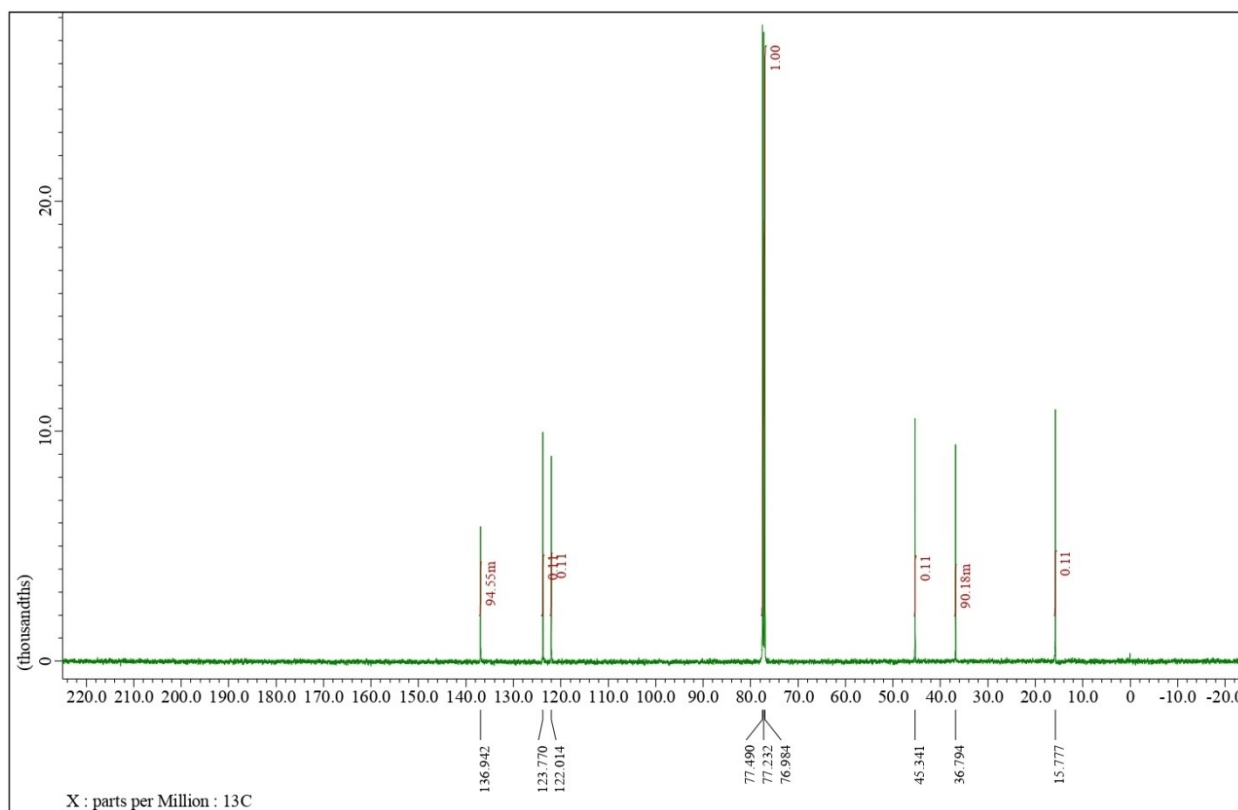
4.32-4.36 (2H, q, N-CH<sub>2</sub>-), 7.54-7.55 (1H, d, N-CH=), 10.12 (1H, s, N-CH-N).

<sup>13</sup>C NMR δ<sub>C</sub>/ppm (299K, 500MHz, CDCl<sub>3</sub>): δ 15.77 (-CH<sub>3</sub>), 36.79 (N-CH<sub>3</sub>), 45.34 (N-CH<sub>2</sub>),

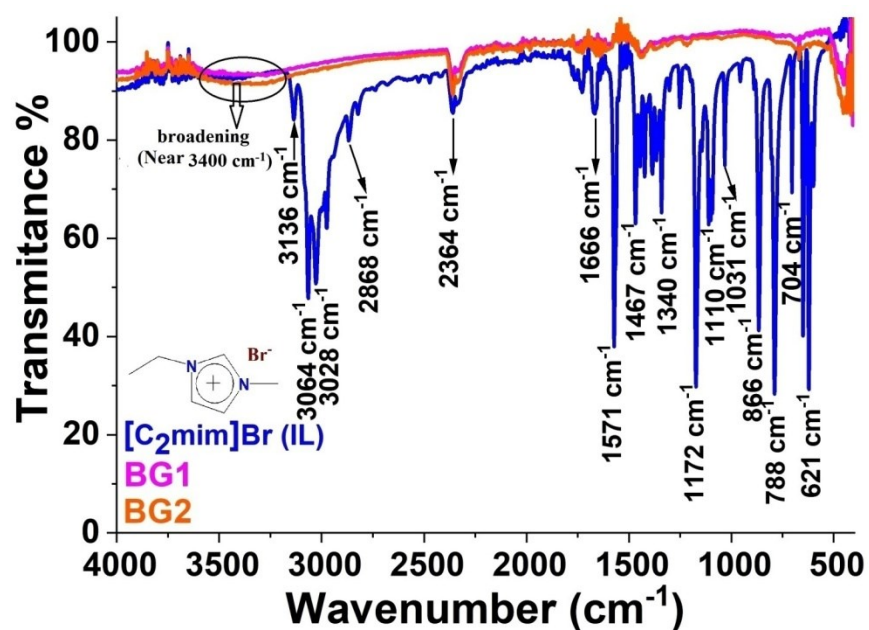
122.01 (N-C=), 123.77(N<sup>+</sup>-C=), 136.94 (N=C-N).



**Figure S1a.** <sup>1</sup>H NMR spectrum of as prepared 1-ethyl-3-methylimidazolium bromide [C<sub>2</sub>mim]Br ionic liquid.



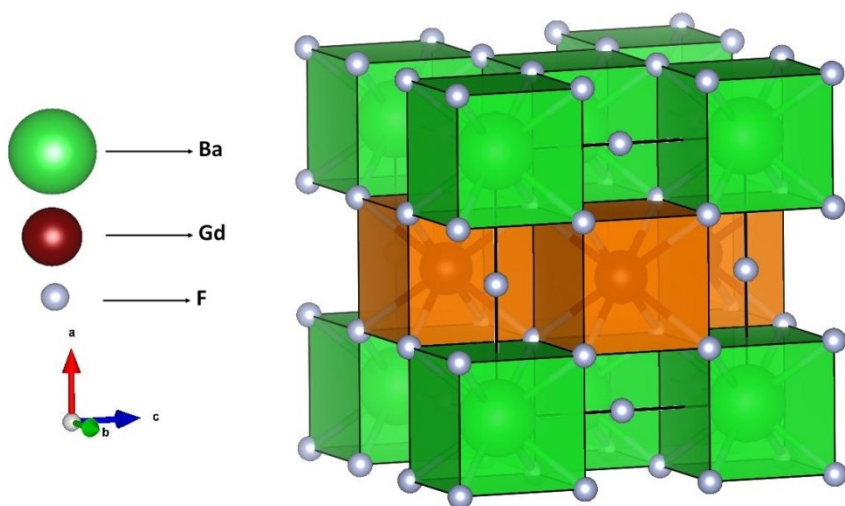
**Figure S1b.**  $^{13}\text{C}$  NMR spectrum of as prepared 1-ethyl-3-methylimidazolium bromide  $[\text{C}_2\text{mim}]\text{Br}$  ionic liquid.



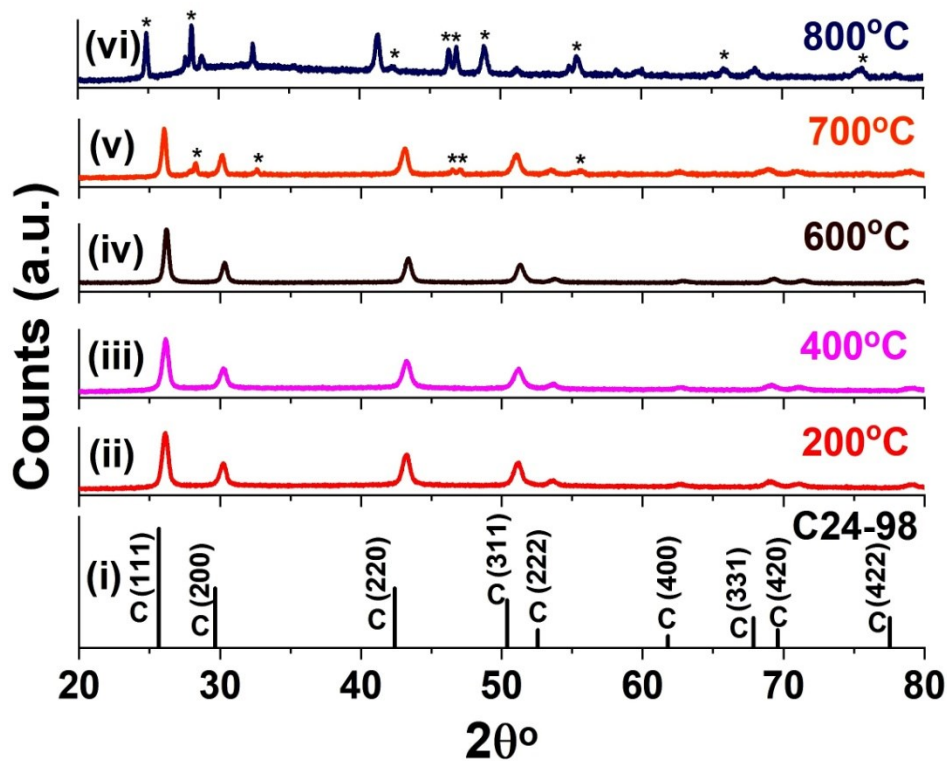
**Figure S2.** Comparative FTIR spectrum of  $[\text{C}_2\text{mim}]\text{Br}$  IL, BG1 and BG2 nanoparticles.

FTIR result indicates that (Figure S2) vibration bands in the range of 3700 to 3400  $\text{cm}^{-1}$  are assigned due to symmetric and asymmetric stretching vibrations of O-H of water molecules. The vibration frequencies of C(2)-H stretching vibration of imidazole ring system and stretching vibration of C-H bonds of alkyl chain length corresponding to 3136, 3064 and 3028  $\text{cm}^{-1}$  respectively. The imidazole ring skeleton stretching vibration is occurred at 1467  $\text{cm}^{-1}$  and 1172  $\text{cm}^{-1}$  ( $\text{CH}_2$  stretching). The vibration band at 1666  $\text{cm}^{-1}$  is observed due to stretching vibration of imidazole ring skeleton belongs to C=C. And the stretching vibrations of C-N bonds of imidazole ring system are assigned at 1031  $\text{cm}^{-1}$ .

In above FTIR spectrum, it is observed that stretching vibration frequencies of imidazole ring system and alkyl chain length are absent. It means as-prepared nanoparticles are free of the ionic liquid.



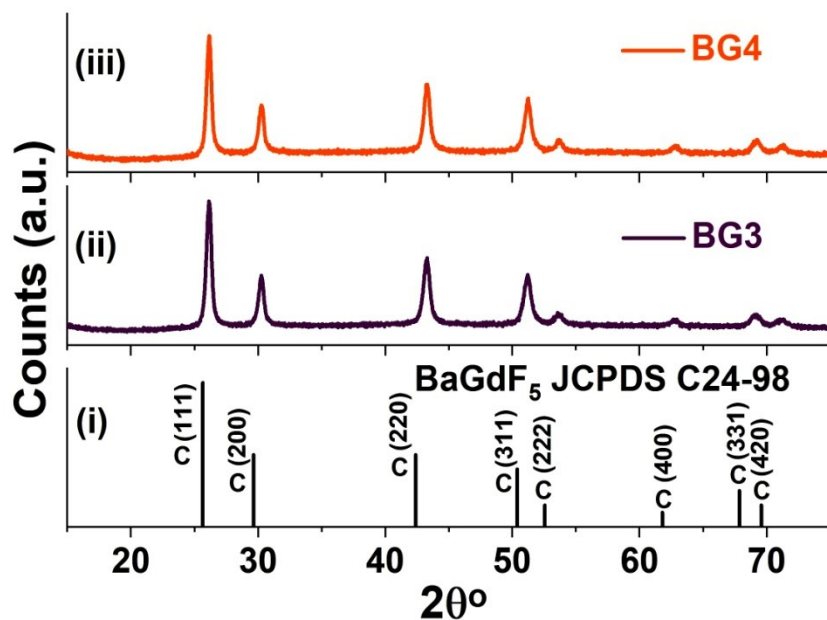
**Figure S3.** Crystal structure of  $\text{BaGdF}_5$ .



**Figure S4.** PXRD patterns of calcined BaGdF<sub>5</sub>:Eu<sup>3+</sup> (BG1) NPs at different temperature: (i) standard BaGdF<sub>5</sub> JCPDS C24-98, (ii) calcined at 200 °C, (iii) calcined at 400 °C, (iv) calcined at 600 °C, (v) calcined at 700 °C and calcined at 800 °C [\* indicates appearance of orthorhombic GdF<sub>3</sub> impurities (JCPDS card-49-804)].

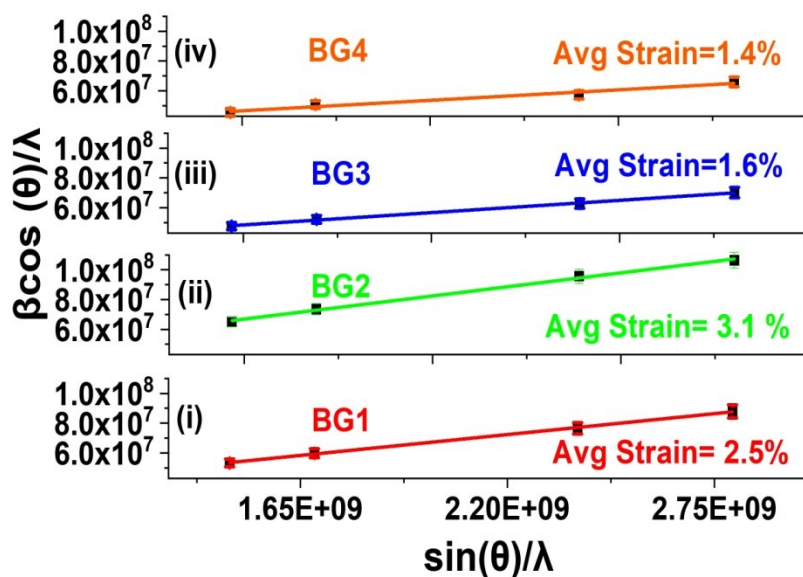
**Table S1.** Crystallite size, lattice strain and crystal phase of the as prepared Eu<sup>3+</sup> -doped BaGdF<sub>5</sub> nanomaterials.

Sample Code	Sample Name	IL (Y/N)	As-prepared	Crystal Size (nm)	Average lattice strain (%)	Crystal Phase	Lattice strain
BG1	BaGdF <sub>5</sub> :Eu	N	As-prepared	13.5	2.5	Cubic	Tensile
BG2	BaGdF <sub>5</sub> :Eu (1%)	Y	As-prepared	11.0	3.1	Cubic	Tensile
BG3	BaGdF <sub>5</sub> :Eu (2%)	Y	As-prepared	15.8	1.64	Cubic	Tensile
BG4	BaGdF <sub>5</sub> :Eu (5%)	Y	As-prepared	16.7	1.4	Cubic	Tensile



**Figure S5.** PXRD patterns of as-prepared  $\text{Eu}^{3+}$ -doped  $\text{BaGdF}_5$  NPs: (i) standard, (ii) 2%  $\text{Eu}^{3+}$  doped  $\text{BaGdF}_5$  NPs with IL (BG3) and (iii) 5%  $\text{Eu}^{3+}$  doped  $\text{BaGdF}_5$  NPs with IL (BG4).

**Lattice strain of the as-prepared  $\text{Eu}^{3+}$  ion doped  $\text{BaGdF}_5$ :-**

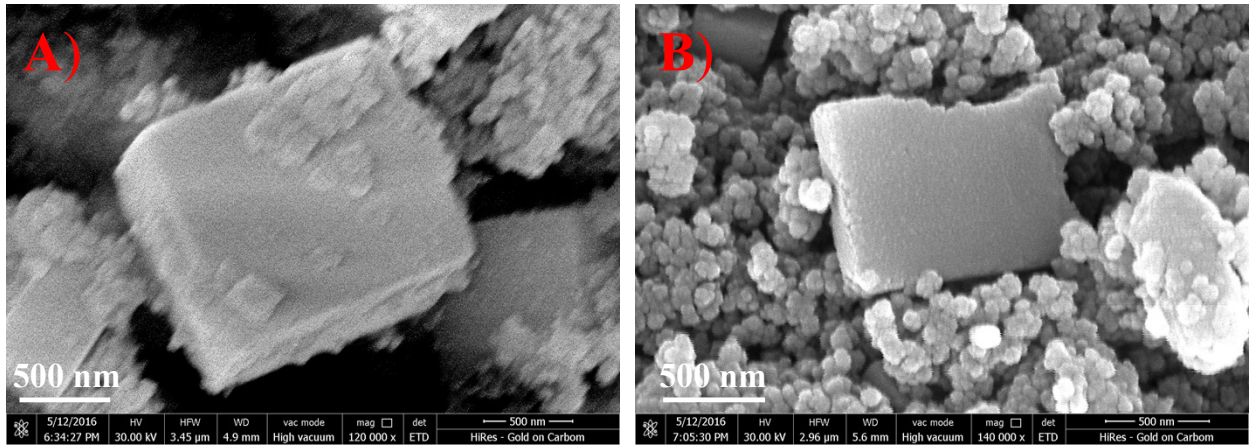


**Figure S6.** Lattice Strain of as-prepared  $\text{Eu}^{3+}$ -doped  $\text{BaGdF}_5$  nanocrystals prepared without IL (BG1) and with  $[\text{C}_2\text{mim}]\text{Br}$  IL [BG2, BG3 and BG4].

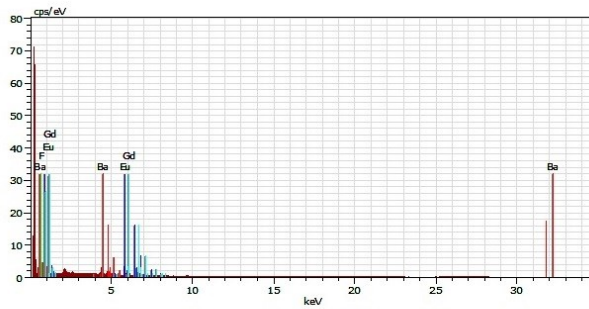
Commonly, the broadenings of the diffraction peaks depend upon lattice strain and crystallite size and lattice strain can be calculated according to the equation derived by Williamson and Hall<sup>2</sup>:

$$\beta \cos \theta / \lambda = 1/D + \eta \sin \theta / \lambda \quad (1)$$

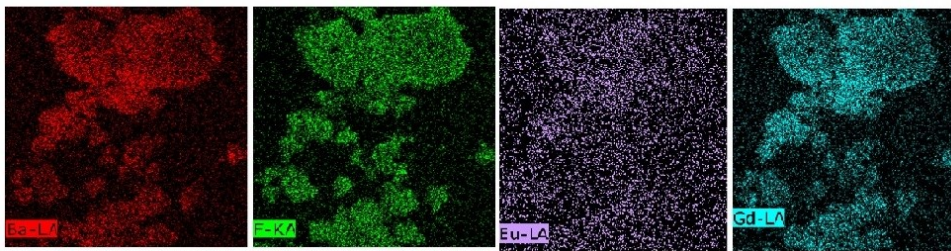
where  $\eta$  is the effective strain. When we are plotting  $\beta \cos \theta / \lambda$  against  $\sin \theta / \lambda$  the strain can be derived from the slope. The positive and negative magnitude of lattice strain indicates the tensile and compressive strain respectively.



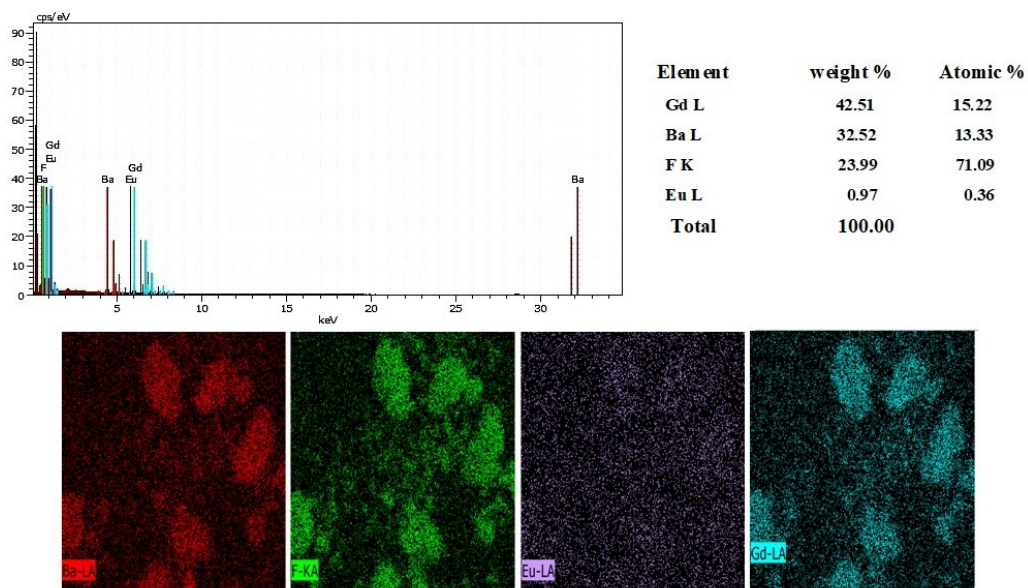
**Figure S7.** FESEM images of as-prepared 1%  $\text{Eu}^{3+}$  doped  $\text{BaGdF}_5$  (A) without IL and (B) with IL  $[\text{C}_2\text{mim}]\text{Br}$  respectively.



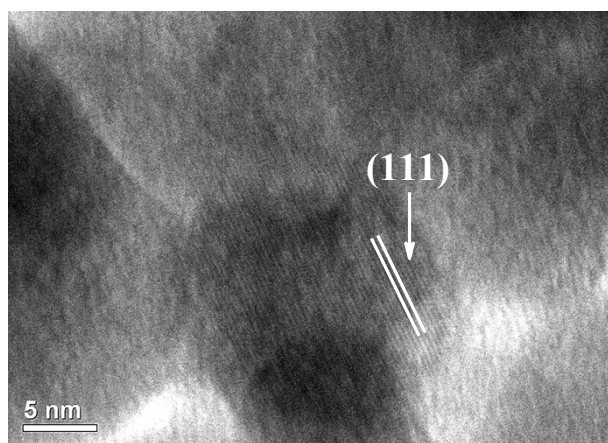
Element	weight %	Atomic %
Gd L	43.47	16.92
Ba L	34.59	15.42
FK	20.86	67.22
Eu L	1.07	0.4
<b>Total</b>	<b>100.00</b>	



**Figure S8.** EDX and elemental mapping of 1%  $\text{Eu}^{3+}$  -doped  $\text{BaGdF}_5$  nanomaterials without IL (BG1)

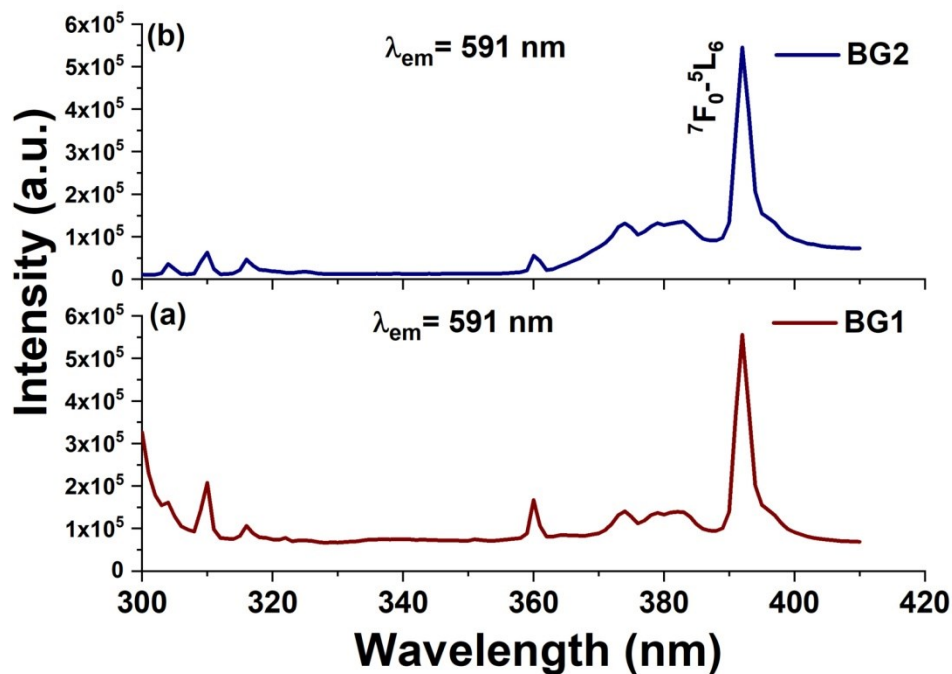


**Figure S9.** EDX and elemental mapping of 1%  $\text{Eu}^{3+}$  -doped  $\text{BaGdF}_5$  nanomaterials with IL (BG2).

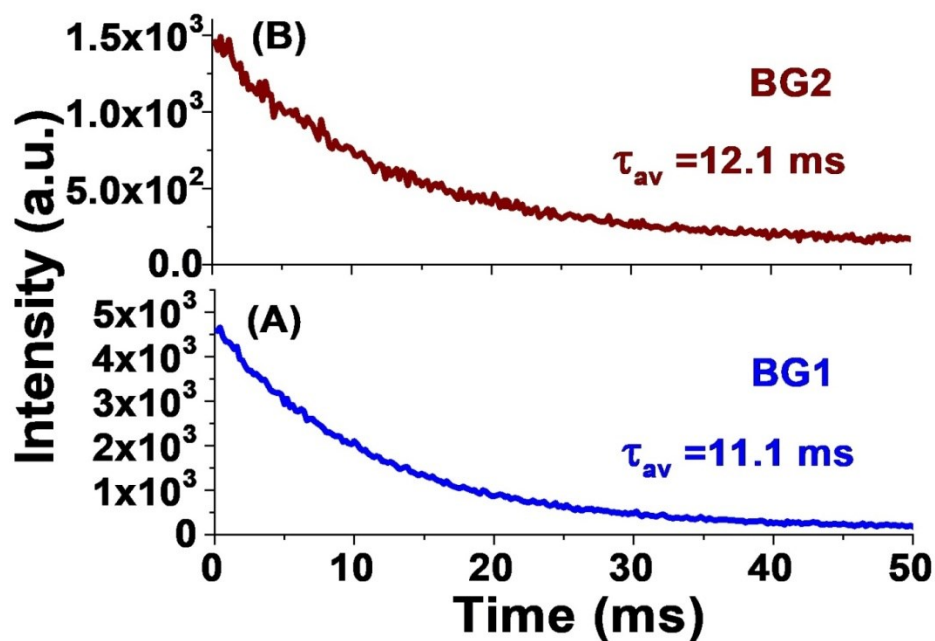


**Figure S10.** HRTEM image of 1%  $\text{Eu}^{3+}$  -doped  $\text{BaGdF}_5$  synthesized using without IL.

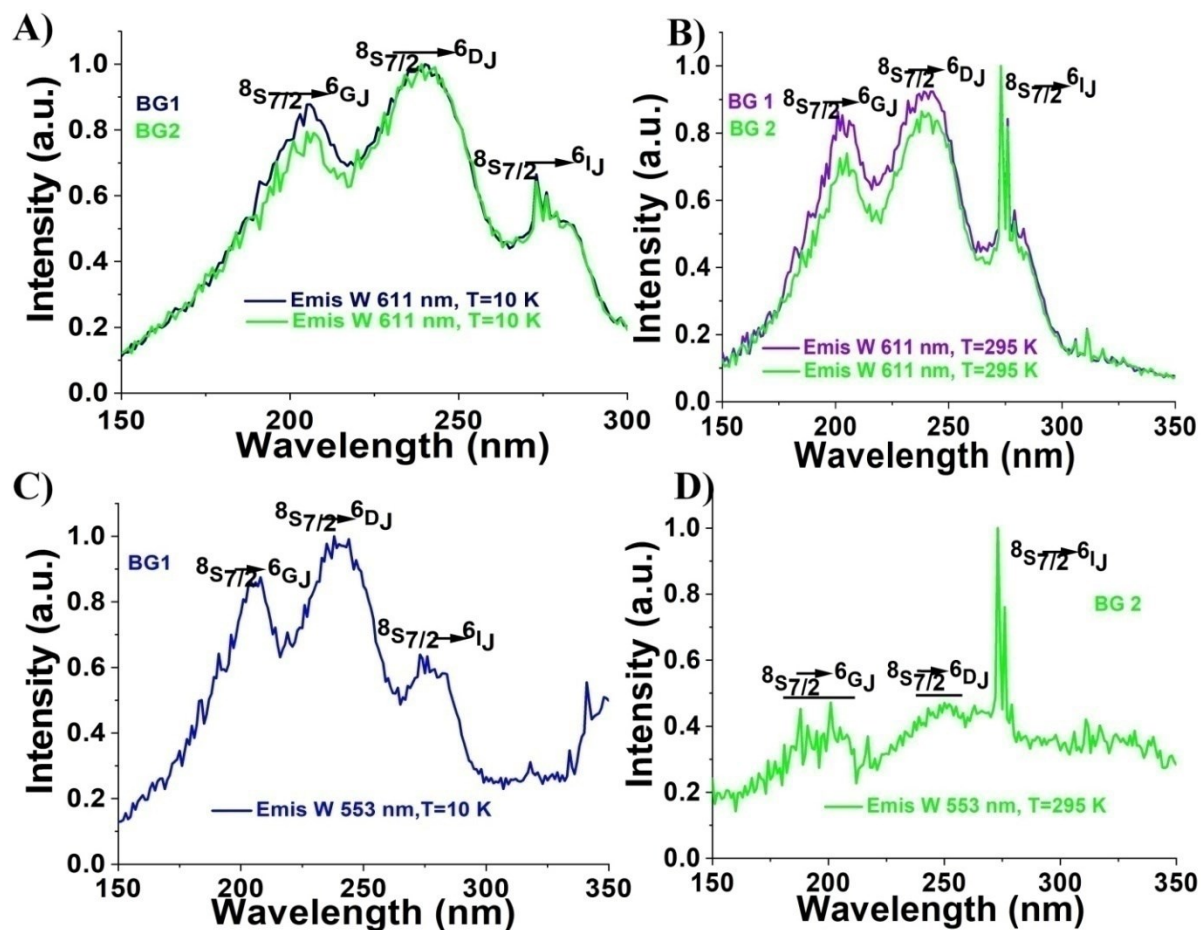




**Figure S11.** Photoluminescence excitation spectra of as-prepared BaGd<sub>5</sub>:Eu<sup>3+</sup>(1%) nanoparticles synthesized: (a) without IL (BG1) and (b) with IL (BG2).



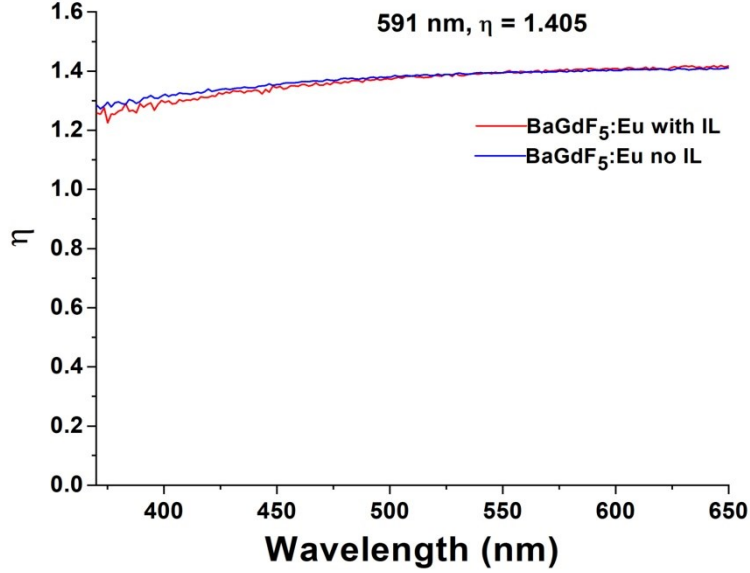
**Figure S12.** Decay time of 1% Eu<sup>3+</sup> -doped BaGdF<sub>5</sub> NPs synthesized: (A) without IL (BG1) and (B) with IL [C<sub>2</sub>mim]Br (BG2).



**Figure S13.** Excitation spectra of as-prepared 1%  $\text{Eu}^{3+}$ -doped  $\text{BaGdF}_5\text{NPs}$  (A) 10 K and (B) 295 K monitoring  $\lambda_{\text{em}} = 611$  nm; C-D) excitation spectra  $\text{Gd}^{3+}$  monitored at 553 nm without and with IL  $[\text{C}_2\text{mim}]\text{Br}$  at 10 K and 295 K.

**Table S2.** The  $I_e/I_m$  ratio of  $\text{Eu}^{3+}$ -doped  $\text{BaGdF}_5$  nanophosphors

Condition	Without IL ( $I_e/I_m$ )	With IL ( $I_e/I_m$ )
At RT, 202 nm	1.23	1.43
At RT, 273 nm	0.55	0.58
At RT, 393 nm	0.46	0.51
At 10 K, 202 nm	0.99	0.99
At 10 K, 273 nm	0.75	0.70



**Figure S14.** Refractive index of BaGdF<sub>5</sub>:Eu<sup>3+</sup> (1%) doped NPs at different wavelength.

### Calculation of Judd-Ofelt ( $\Omega_2$ ) Parameters and Quantum efficiency ( $\eta\%$ )

The J-O parameter ( $\Omega_2$ ) provides the information on the basis of intensities or nature of the hypersensitive transition of the Eu<sup>3+</sup> ions. The Judd-Ofelt parameters ( $\Omega_2$ ) were determined using the emission spectra of Eu<sup>3+</sup> ions resulting of <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>1</sub> magnetic dipole allowed and <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>2</sub> electric dipole allowed transitions and its value can be determined using equation 2.<sup>3</sup>

$$A = \frac{4e^2\omega^3}{3hc^3} \frac{1}{2J+1} \chi \sum \Omega_2 \langle {}^5D_0 \parallel U^{(2)} \parallel {}^7F_2 \rangle^2 \quad (2)$$

Where A is the coefficient of spontaneous emission,  $\omega$  is the angular frequency, e is the electronic charge, c is the velocity of light,  $\hbar$  is the Planck's constant,  $\chi$  is the Lorentz local field correction and it can be further expressed as  $\chi = \eta(\eta^2 + 2)^2/9$ , where  $\eta$  is the refractive index of the sample,  $\langle {}^5D_0 \parallel U^{(2)} \parallel {}^7F_2 \rangle^2$  is the squared reduced matrix elements and its value is independent of the chemical environment of the ion and it is 0.0039 for J=2. Since the magnetic dipole transition is relatively insensitive to the chemical environment around the Eu<sup>3+</sup> ion, so it can be regarded as a reference for the entire spectrum. The coefficient of spontaneous emission can be determined using the following equation.<sup>3</sup>

$$A_{0,J} = A_{01} (I_{0,J} / I_{01}) (\gamma_{01} / \gamma_{0,J}) \quad (3)$$

Where  $A_{01}$  is the Einstein's coefficient between  ${}^5D_0$ - ${}^7F_1$  levels and it can be determined using  $A_{01} = \eta^3 (A_{0-1})_{\text{vac}}$ ; where  $\eta$  is the refractive index of the sample and  $(A_{0-1})_{\text{vac}} = 14.65 \text{ s}^{-1}$ . Refractive index of  $\text{BaGdF}_5:\text{Eu}^{3+}$  is determined using Ellipsometer and is found to be 1.4049. However,  $\gamma_{01}$  and  $\gamma_{0J}$  are the energy barycentre of the  ${}^5D_0$ - ${}^7F_1$  and  ${}^5D_0$ - ${}^7F_1$  transitions, respectively.

Radiative ( $A_{\text{rad}}$ ), non-radiative ( $A_{\text{nrad}}$ ) transition and average decay time can be correlated by following expression<sup>3</sup>

$$A_{\text{tot}} = \frac{1}{\tau} = A_{\text{rad}} + A_{\text{nrad}} \quad (4)$$

Where  $A_{\text{rad}}$  can be determined using the following expression<sup>3</sup>

$$A_{\text{rad}} = A_{01} \frac{\gamma_{01}}{I_{01}} \sum_{J=0}^2 \frac{I_{0,J}}{\gamma_{0,J}} = \sum_J A_{0,J} \quad (5)$$

Quantum efficiency is the ratio of number of photons emitted to the number of photons absorbed by the  $\text{Eu}^{3+}$  ion and it is the balance between radiative and non-radiative processes, and it can be calculated by following equation<sup>3</sup>

$$\eta = \frac{A_{\text{rad}}}{A_{\text{rad}} + A_{\text{nrad}}} \quad (6)$$

## References

- 1 R. K. Sharma, Y. N. Chouryal, S. Chaudhari, J. Saravanakumar, S. R. Dey and P. Ghosh, *ACS Appl. Mater. Interfaces*, 2017, **9**, 11651–11661.
- 2 R. K. Sharma, S. Nigam, Y. N. Chouryal, S. Nema, S. P. Bera, Y. Bhargava and P. Ghosh, *ACS Appl. Nano Mater.*, 2019, **2**, 927–936.
- 3 P. Ghosh, A. Kar and A. Patra, *J. Appl. Phys.* 2010, **108**, 1–8.