Supporting Information

Influence of ionothermal synthesis using $BmimBF_4$ on nanophosphors $BaFBr:Eu^{2+}$ photoluminescence

Jacob Olchowka Hans Hagemann, Teresa Delgado, Claudia Wickleder **

S1. Experimental Section

Method for preparing nano $BaFBr:Eu^{2+}$: The samples were prepared under air using $BaBr_2$, $EuBr_2$ and $BmimBF_4$ as solvent and fluoride source. The ionic liquid purchased from Iolitec was used without any treatment. For $BaFBr:Eu^{2+}$, 0.15 g (5.10^{-4} mol) of $BaBr_2$ (Merck, 99.99%) and 0.003 g (10^{-6} mol) of $EuBr_2$ (Merck, 99.99%) were dissolved in a mixture of 3 mL of $BmimBF_4$ / 2 mL of absolute ethanol (ethanol which is miscible with $BmimBF_4$, was mainly used to lower the viscosity and improve the solubility of the bromides). The mixture was then placed in a typical ultrasound cleaning bath during 1h, and centrifuged to harvest the nanocrystalline powder. The sample was then washed several times with ethanol and water and dried at 80 °C during 2 h. All the reflection peaks of the synthesized compound could be indexed to the theoretical pattern of BaFBr. The doping concentration is too low to have a significant influence on XRD pattern and hence no shift of peak position could be observed due to the substitution of Ba by smaller Eu. (Figure S2)

Fourier Transformed Infrared (FTIR): FTIR experiments were performed with a Biorad Excalibur Instrument equipped with a portable Specac Golden Gate heatable ATR setup. IR spectra were recorded with a spectral resolution of 1 cm^{-1}, with 30 scans in the range 600 – 4000 cm^{-1}.

Photoluminescence measurements: The excitation and emission spectra were measured with a Fluorolog3-22 from Horiba Jobin Yvon, equipped with a water-cooled photo multiplier tube (PMT). All emission spectra were corrected for photomultiplier sensitivity, the excitation spectra for lamp intensity and both for the transmission of the monochromators.

X-ray diffraction (XDR): X-ray diffraction was performed using PaNalitycal Empyrean powder diffractometer with $K\alpha_1$ monochromator for measurements in reflection. The data collection was performed between 10 and 60° 2θ.

Raman: This Raman spectrum was taken with a Horiba Labram HR Evolution Raman microscope using 532 nm excitation with a 50x focusing lens.

Transmission Electron Microscopy (TEM): Samples were dispersed in ethanol and few drops of this dispersion were added on a carbon coated copper grid (Formar Carbon film, 200 Mesh). TEM images were taken with a Tecnai G2 Sphere with 100 keV electrons focused on the sample.

Photoluminescence decay measurements: Luminescence decay were recorded by photo-excitation of the samples at the appropriate wavelength (266 nm) with a Nd:YAG laser (Quantel Brilliant). For single wavelength decay curves, the luminescence was dispersed by a Spex 270M monochromator, and detected by a Hamamatsu R928 photomultiplier.

Time resolved spectroscopy measurements: They were performed with a laser excitation source set at 266 nm. A 370 nm cutoff filter was used to measure emission spectra The time resolved emission was collected using a photomultiplier and an oscilloscope in Boxcar mode.

Figure S2. Comparison between experimental (BaFBr: 2% Eu) and theoritical (BaFBr). The reference diagram was simulated using Diamond software from the CIF file with the PDF number: 01-070-0482 34-680 available on ICSD.

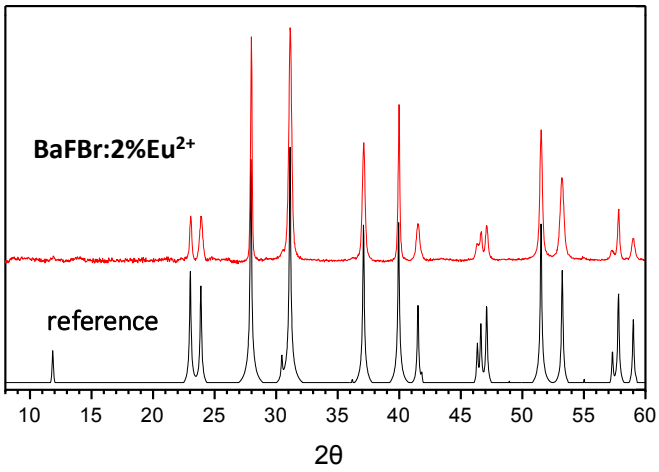
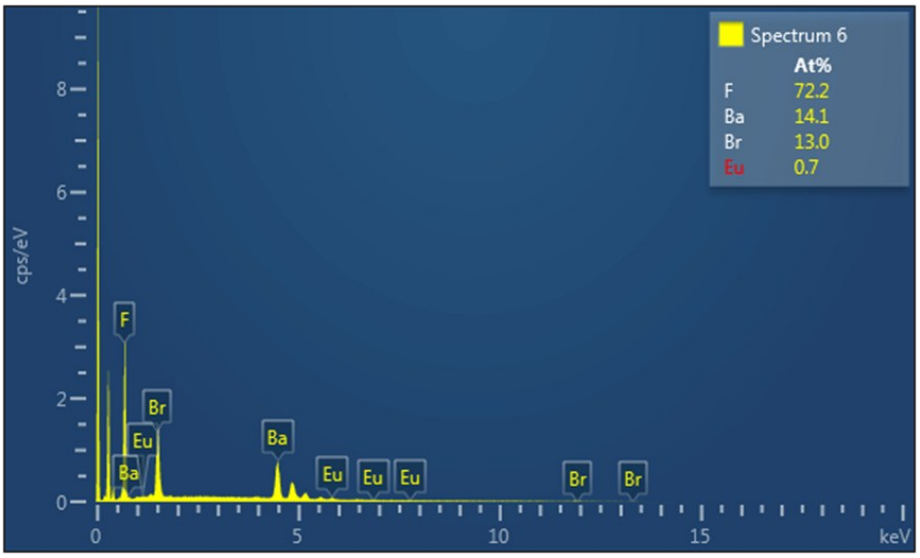
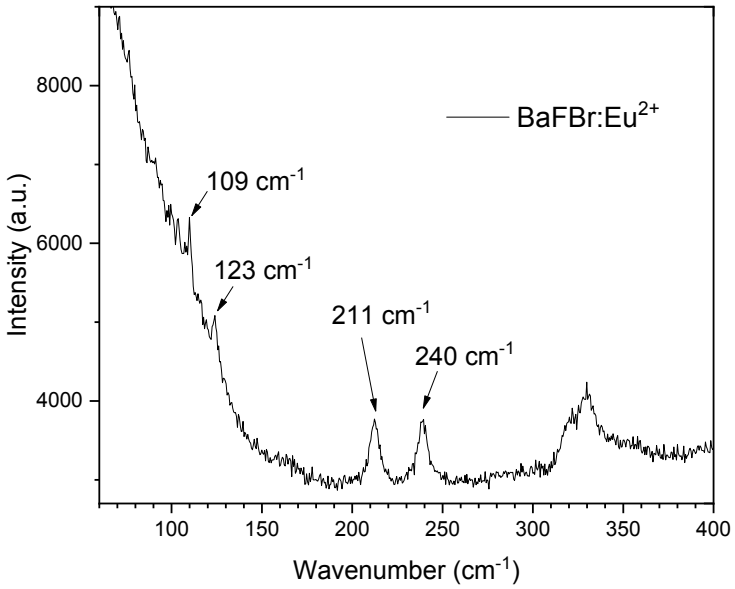


Figure S3. EDX analyses for BaFBr: 2% Eu^{2+}



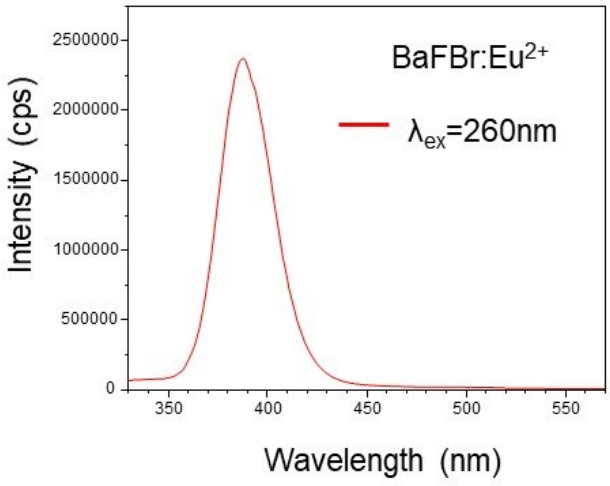
As expected by EDX analyses Ba, F, Br and Eu elements are detected. The high ratio of fluorine compared to Bromine and Barium confirms the presence of the protecting shell at BaFBr:Eu^{2+} surface and made of $BmimBF_4$. Moreover, we do not detect the presence of Oxygen, which usually appears at 0.525 eV (K-alpha). These results are in good agreement with the lifetime measurements and the oxygen-defect free material.

S4. Raman spectrum of BaFBr: 2% Eu^{2+}



At low frequencies, 4 well defined bands at 109, 123, 211 and 240 cm^{-1} are detected in perfect agreement with the literature data (103, 109, 123, 211, 238 cm^{-1}). Additional bands of organic origin that belong to the ionic liquid.

Figure S5. Room temperature photoluminescence emission with excitation wavelength set at



260nm.

Figure S6. Decay time measurements for BaFBr:Eu^{2+} with excitation set to 266 nm represented in a semi-logarithmic plot.

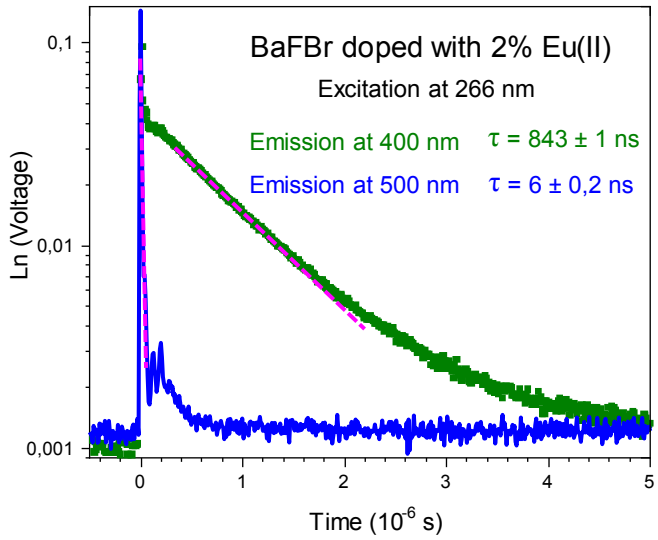
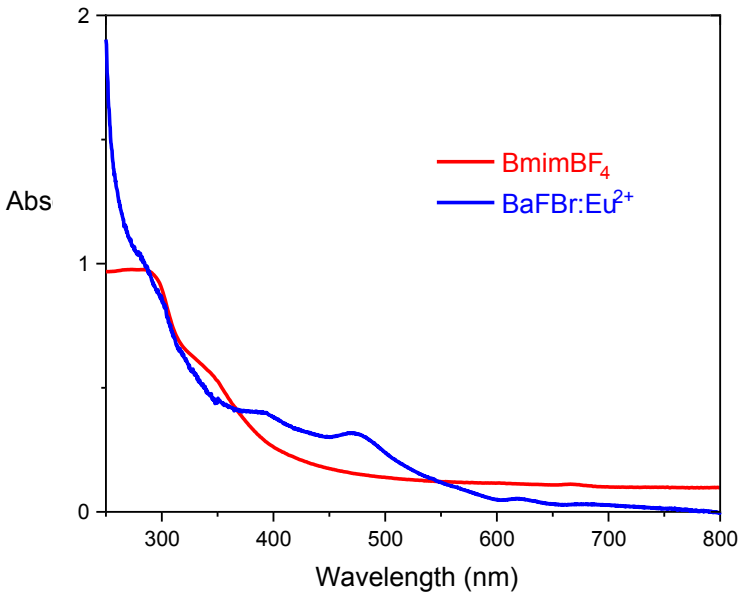


Figure S7. UV-vis absorption spectra of pure $BmimBF_4$ and BaFBr: Eu^{2+}



Bibliography:

[1] D. Nicollin and H. Bill, J. Phys. C Solid State Physics 11 (1978) 4803