Harvesting Light from BaHfO$_3$:Eu$^{3+}$ through Ultraviolet, X-ray and Heat Stimulation: An Optically Multifunctional Perovskite

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Experimental:

S1. Synthesis

Both BHO and BHOE were synthesized using high temperature solid-state diffusion method. The precursors used in the synthesis were, BaCO$_3$, Eu$_2$O$_3$, and HfO$_2$. The heating was carried out in two steps. Firstly at 900 °C for 5h to get rid of any unwanted residue and then finally at 1400 °C for 5hr. The dopant concentration was fixed at 2.0 mol %. For Eu$^{3+}$ doping, 1.0 mol % of Eu$_2$O$_3$ with respect BaCO$_3$ (2 mol% Eu with respect Ba) was mixed along with the BaCO$_3$ and HfO$_2$ and grounded before annealing.

S2. Sample Preparation for RL measurements

The handling of as such prepared powdered material is difficult and measurements often yield uncertainty and errors particularly when comparisons of different samples are made. To overcome this problem RL measurements were carried out on polytetrafluoroethylene (PTFE) embedded BaHfO$_3$ discs.$^1$ The discs were prepared by mixing BaHfO$_3$ powder with PTFE in ratio of 1:2. Subsequently, the combination was subjected to ball milling to ensure homogeneous mixing. This mixture was cold compacted into discs admeasuring 10 mm diameter and 0.3 mm thickness by applying pressure of about 5 ton. Each disc weighed 100 mg (34 mg phosphor and 66 mg PTFE). Finally, the discs were treated thermally at 380 °C for 1 h which lead to firm binding of entire matrix with increased mechanical strength and eliminated their brittleness. These discs offer ease of handling, ascertain consistency and geometrical reproducibility. All RL measurements reported in this communication were carried out on these discs.
S3. Instrumentation

For phase purity assessment, powder XRD measurements were carried out using a Proto-AXRD benchtop system using Cu Kα line ~ 1.5405 Å with the scan rate of 2°/min.

An Edinburgh make florescence spectrometer (model CD 920) was used for the photoluminescence measurements. Xenon flash lamp (µF2) of power-150 Watt was used as the excitation source. Both the emission and excitation spectra were recorded with a step of 1.0 nm. Emission and excitation spectra were recorded at lamp frequency of 100 Hz while emission lifetimes were recorded at lamp frequency of 10 Hz. Time-correlated single-photon counting (TCSPC) technique was used to record lifetime spectra.

For low temperature PL measurements, powder sample was transferred into an NMR glass tube (length of sample = 1.5 cm and length of NMR tube = 6 cm and its inner diameter = 5 mm). This NMR tube was dipped into liquid nitrogen and kept for 10 minutes so that sample attained thermal equilibrium with liquid nitrogen. Then, it was immediately transferred in a quartz 4 side transparent cuvette filled with glycerol, which was already kept at sample holder of photoluminescence instrument. Measurement was carried out immediately. In this, temperature was found to be 100 K ± 20 K. After allowing the sample to attain room temperature (in about 30 minutes), room temperature PL was again recorded.

Positron annihilation lifetime measurements were carried out using a lifetime spectrometer having a time resolution 265 ps. 15 µCi Carrier free $^{22}$Na deposited between two 8 micron polyimide films was the source of positrons. The source was immersed in the powder so that all positrons annihilate in the sample. All the lifetime spectra were analyzed using PALSFit\textsuperscript{2} incorporating correction for the positrons annihilating in the polyimide films used to deposit $^{22}$Na. The thermo-luminescence (TL) was measured using the Lexsyg research imaging TL-OSL-RF system. The program routine starts with the pre-heating upto 350°C at 5°C/s and cooling upto 50°C to bleach any filled traps. It was subsequently followed by the irradiation using $^{90}$Sr beta radiation source that provides a homogeneous irradiation field at a dose rate of about 0.1 Gy/s for 100 sec. Subsequently, TL was performed and the samples were heated upto 350°C at a rate of 5°C/s. Thermally stimulated emission was recorded using a Hamamatsu PMT with standard bi-alkaline cathode. After optimizing the intensity by using different optical filters, a filter having transmission window from 400 nm to 700 and peaking about 560 nm was used.
Radio-luminescence was measured using an X-ray tube operated at 40kV and 10 mA. The emission was recorded using an optical fiber and Avantes Spectrograph. The curve was corrected for the spectral sensitivity of fiber and spectrograph. The electron paramagnetic resonance (EPR) experiments were carried out using a Bruker EMX series spectrometer (EMM1843) at X-band frequencies with 100 kHz field modulation. The other experimental parameters were attenuation = 15dB, gain = $4 \times 10^4$, 5 scans. The ‘g’ values were evaluated relative to a 2, 2 diphenyl-1 picryl hydrazil (DPPH) sample with $g=2.0036$. X-ray photoelectron spectroscopy (XPS) measurements were acquired using 1253.6 eV Mg-K\(_\alpha\)source and DESA-150 electron analyzer (Staib Instruments, Germany). The binding-energy scale was calibrated to Au-4f\(_{7/2}\) line of 84.0 eV. The analyzer was operated at 40 eV pass energy and pressure was $\sim 7 \times 10^{-9}$ Torr. XPS spectra were analyzed with XPSPEAK 4.1 software.

**S4. Computational Details:**

The first-principles calculations within the framework of Density Functional Theory (DFT) have been performed using projector augmented wave (PAW) based electronic structure program, Vienna ab initio simulation package (VASP).\(^3\) The set of valence states for each element considered in the current study for the generation of pseudo potentials are: Ba (5s\(^2\)5p\(^6\)6s\(^2\): 10 valence electrons), Hf (5p\(^6\), 5d\(^3\) 6s\(^1\): 10 valence electrons), O (2s\(^2\)2p\(^4\): 6 valence electrons), Eu (6s\(^2\)5p\(^6\)5d\(^1\): 9 valence electrons). However, in the case of electronic structure calculations we have employed valence set of Eu (5s\(^2\)6s\(^2\)5p\(^6\)4f\(^7\): 17 electrons) for the construction of pseudo potentials. The generalized gradient approximations (GGA) type Perdew–Burke–Ernzerhof (PBE) functional has been employed throughout the calculations.\(^5\)\(^6\) The plane wave basis set with 600 eV kinetic energy cut off and $10^{-6}$eV energy convergence criteria for self-consistent iteration have been kept fixed for all DFT calculations. All the model structures have been optimized fully by imposing relaxation of both cell dimensions and ionic positions with $\Gamma$-centered k-point mesh of $6 \times 6 \times 6$ generated using Monkhorst and Pack scheme.\(^7\)

**S5. Color coordinated calculations:**

To identify the actual color of light emitted by IRMOF samples; color coordinate values using corrected emission spectra was calculated and displayed in Figure 9d. The chromaticity coordinates were evaluated adopting standard procedures as lay down by CIE. In general, the
color of any light source can be represented as an \((x, y)\) coordinate in the CIE color space. The chromatic coordinates \((x, y)\) can be calculated as follows:

\[
x = \frac{X}{X+Y+Z} \quad \text{and} \quad y = \frac{Y}{X+Y+Z}
\]

Where \(X = \int \bar{x}(\lambda)s(\lambda)d\lambda\), \(Y = \int \bar{y}(\lambda)s(\lambda)d\lambda\) and \(X = \int \bar{z}(\lambda)s(\lambda)d\lambda\). Here \(\bar{x}(\lambda), \bar{y}(\lambda)\) and \(\bar{z}(\lambda)\) are the CIE \(x\), \(y\), and \(z\) color matching functions, respectively. \(s(\lambda)\) is the spectrum of a light source. The dominant wavelength is defined as the single monochromatic wavelength that appears to be having same color as the light source. The dominant wavelength can be determined by drawing a straight line from one of the CIE white illuminants, through the \((x, y)\) coordinates to be measured, until the line intersects the outer locus of points along the spectral edge of the 1931 CIE chromatic diagram. The dominant wavelength is the wavelength of the intercept of the straight line and the outer edge of space.

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