Supporting Information

Electronic structure, colour-tunable emission and energy transfer in $Li_3Ba_2Y_3(WO_4)_8:Bi^{3+},Eu^{3+}$ phosphors for white light-emitting diodes

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Materials and synthesis

A series of phosphors including $Li_3Ba_2Y_3(WO_4)_8$ (abbreviated as LBYW), LBYW:xBi^{3+}(x = 2%, 4%, 6%, 8%, 10%), LBYW:yEu^{3+}(y = 2%, 4%, 6%, 8%, 10%) and LBYW:4%Bi^{3+},yEu^{3+}(y = 2%, 4%, 6%, 8%, 10%) were prepared by traditional high temperature solid state reaction method. For raw materials Li_2CO_3 (A.R. 99%), $BaCO_3$ (A.R. 99%), Y_2O_3 (A.R. 99%), WO_3(A.R. 99.99%), Bi_2O_3(A.R. 99.99%) and Eu_2O_3(A.R. 99.99%) were stoichiometric weighed and fully mixed in agate mortar, then the mixture was transferred to the Al_2O_3 crucible and pre-burned at 873 K for 1 h. After cooling, the powder was re-ground and sintered at 1173 K for 10 h. Eventually, it was naturally cooled to room temperature to obtain the final product for subsequent studies.

Measurements and characterization

The X-ray diffraction (XRD) analyses of the samples were conducted using a Cu-Kα source with settings of 40 kV and 40 mA (λ = 1.54178 Å) on a Rigaku/Max-3A x-ray diffractometer, covering a scan range from 5 to 80 degrees (2θ) at a rate of 20 degrees per minute. For detailed Rietveld structural refinement, scans were extended from 5 to 120 degrees at a slower rate of 1 degree per minute. The morphology and energy dispersive spectroscopy (EDS) of the samples were measured by Hitachi S-3400N scanning electron microscopy (SEM), and the element mapping was analyzed by TESCANCLARA Field emission scanning electron microscopy (FE-SEM). Diffuse reflectance spectra (UV-vis DRS) were obtained using a U-3310 UV-vis spectrophotometer, with $BaSO_4$ serving as the reference. Bi ions valence states were explored through X-ray photoelectron spectroscopy (XPS) on a Thermo Scientific AXIS SUPRA, utilizing a monochromatic Al Kα radiation source. Photoluminescence (PL) emission and excitation (PLE) spectra, along with decay curves were recorded on an Edinburgh Instruments FLS 980 time-resolved steady-state fluorescence spectrometer, equipped with Xe/nF/μF lamps. Temperature-dependent emission spectra were captured using an Edinburgh FLS 1000 spectrometer, supplemented with an Oxford temperature controller. CIE coordinates were calculated based on emission spectra and according to the CIE1931 colorimetric system. The prepared white LED

device was assembled by coating a mixture of synthesized LBYW:4%Bi^{3+},4%Eu^{3+} phosphor and commercial $BaMgAl_{10}O_{17}:Eu^{2+}$ blue phosphor (20:1 mass ratio) onto a 365 nm UV chip. The device's performance was evaluated using an OHSP-350M LED Fast-Scan Spectrophotometer (350-1050 nm), produced by Hangzhou Hopoo Light & Color Technology.

DFT calculation

First-principles calculations based on Plane-wave pseudopotential density functional theory (DFT) were performed on the substrate of LBYW and Bi^{3+} single-doped and Bi^{3+},Eu^{3+} co-doped materials. The geometric optimization, electronic structure and state density were calculated using the generalized gradient correction PBE function. A 4×2×1 k-point grid in the Brillouin zone was used under the GAMMMER scheme. The kinetic energy cutoff and self-consistent field tolerance are set to 500 eV and 1×10^{-4} eV $atom^{-1}$, and the force received by each atom is less than 0.05 eV/Å. In addition, the electronic structures of Bi^{3+} single-doped and Bi^{3+},Eu^{3+} co-doped $Li_3Ba_2Y_3(WO_4)_8$ have been studied using PBE and PBE U with different U values. It is found that when the U values of Y, W and Eu are 2.0, 3.6 and 6.0 respectively, a good agreement can be achieved with experimental results.

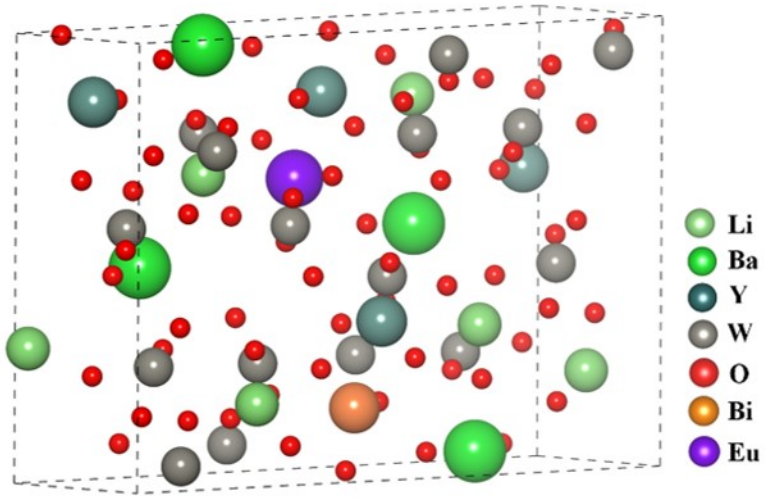

Figure S1. LBYW matrix model doped with $Bi^{3+}$and Bi^{3+}/Eu^{3+}.

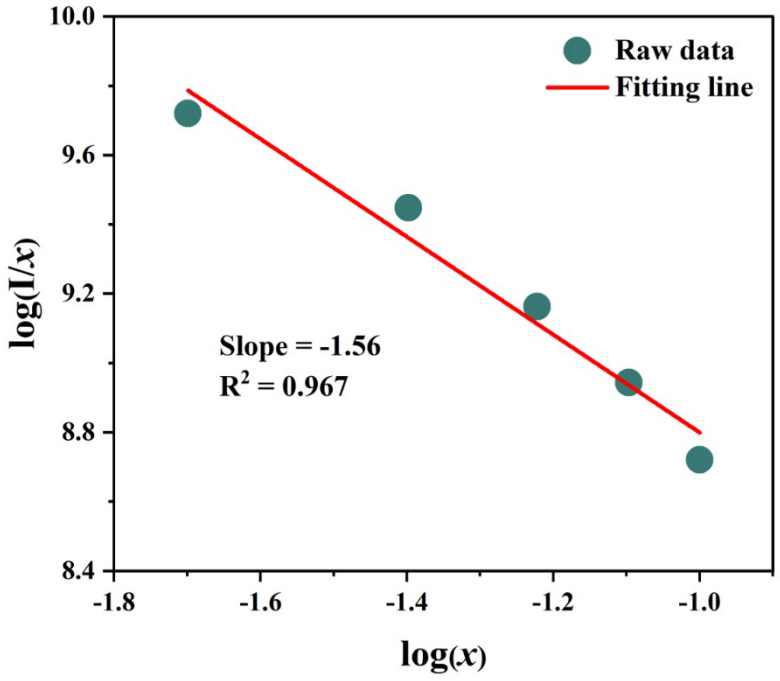

Figure S2. The plot of log (I/x) versus log (x) for LBYW:$x$$Bi^{3+}$ phosphors.

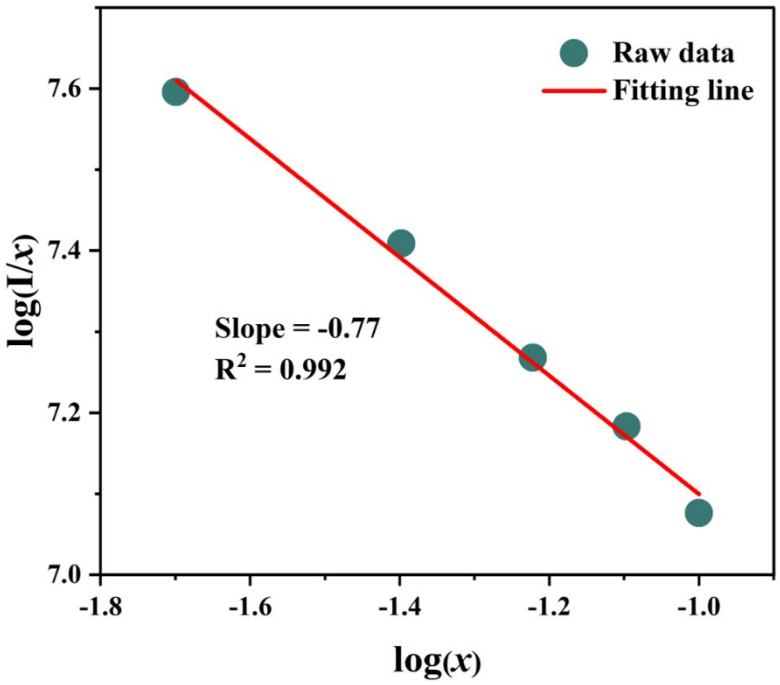

Figure S3. The plot of log (I/x) versus log (x) for LBYW:yEu^{3+} phosphors.

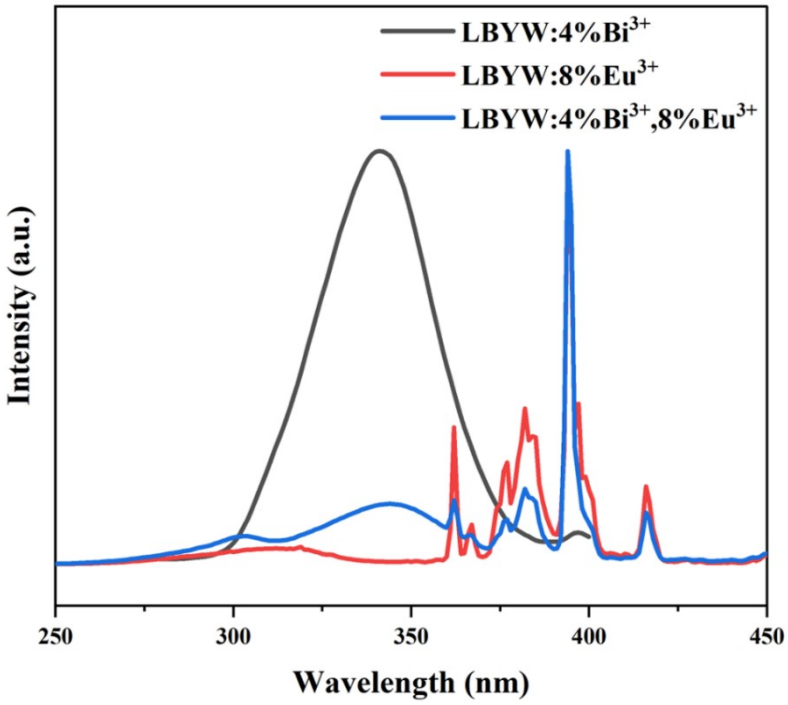

Figure S4. Excitation spectra of LBYW:4%Bi^{3+} (λ_{em} = 553 nm), LBYW:8%Eu^{3+}(λ_{em} = 614 nm) and LBYW:4%Bi^{3+},8%Eu^{3+}(λ_{em} = 614 nm).

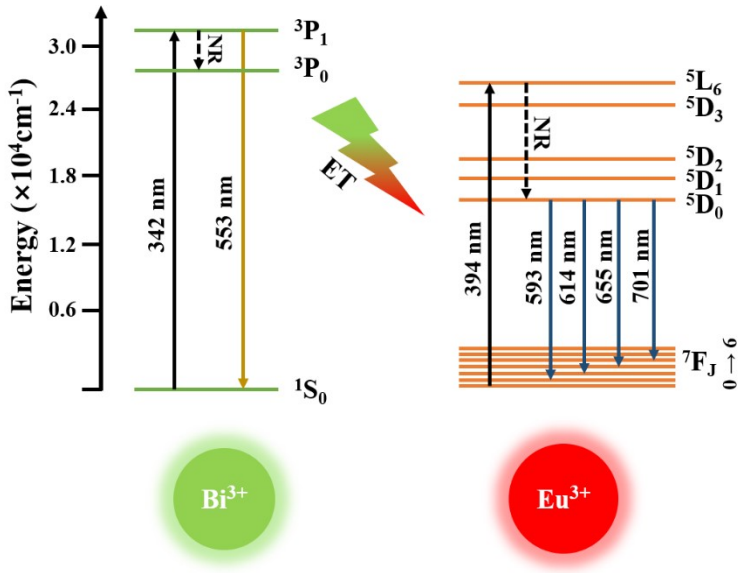

Figure S5. Schematic diagram of the Bi^{3+}→Eu^{3+} ET of LBYW:Bi^{3+},Eu^{3+} phosphors.

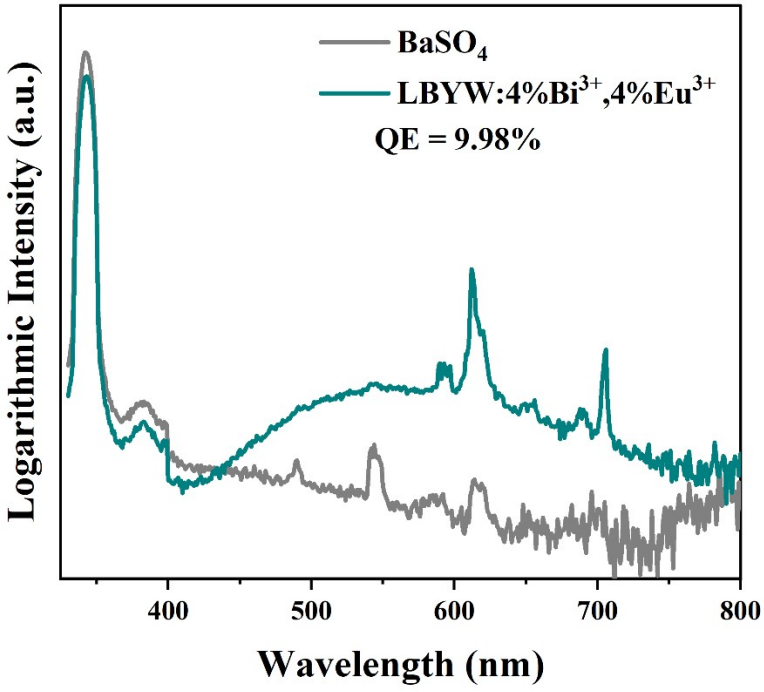

Figure S6. Quantum efficiency of LBYW:4%Bi^{3+},4%Eu^{3+} phosphor.

Table S1. Rietveld refinement and lattice parameters of LBYW:4%Bi^{3+} and LBYW:4%Bi^{3+},4%Eu^{3+} phosphors.

Formula	LBYW:4%Bi^{3+}	LBYW:4%Bi^{3+},4%Eu^{3+}
Space group	C2/c	C2/c
a (Å)	5.1775	5.1803
b (Å)	12.664	12.673
c (Å)	19.140	19.160
alpha(°)	90.000	90.000
beta(°)	92.142	92.160
gama(°)	90.000	90.000
units,Z	2	2
V ($Å^3$)	1254.16	1256.27
R_{wp} (%)	9.03	9.93
R_p(%)	5.34	5.91
χ^2	1.45	1.43

Table S2. The CIE coordinates of the LBYW:4%Bi^{3+},*y*Eu^{3+}(*y* = 0, 2%, 4%, 6%, 8%, 10%) phosphors.

LBYW:4%Bi^{3+},*y*Eu^{3+}	(*x*, *y*)
y = 0	(0.3731, 0.4684)
y = 2%	(0.4256, 0.4412)
y = 4%	(0.4661, 0.4247)
y = 6%	(0.4848, 0.4152)
y = 8%	(0.4920, 0.4087)
y = 10%	(0.5042, 0.4062)