Highly Efficient Blue-emitting Phosphor of $Sr[B_8O_{11}(OH)_4]:Eu^{2+}$ Prepared by Self-reduction Method

Pan Liang[a, b], Wen-Li Lian[a] and Zhi-Hong Liu[a]*

[a] *Key Laboratory for Macromolecular Science of Shaanxi Province, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, People's Republic of China; E-mail: liuzh@snnu.edu.cn.*

[b] *School of Chemistry & Chemical Engineering, Shaanxi Xueqian Normal University, Xi'an 710100, PR China*

Experimental section

Preparation. The $Sr[B_8O_{11}(OH)_4]:Eu$ powders were prepared by using a medium-high temperature boric acid melting method. The stoichiometric amounts of $SrCl_2•6H_2O$(Aladdin, 99.5%), H_3BO_3(Aladdin, 99.5%) and Eu_2O_3(Aladdin, 99.99%) were weighed and ground in an agate mortar. The obtained mixtures were then transferred into platinum crucibles and sealed in a hastelloy flange autoclave, and then the autoclave was treated in muffle furnace at 350 °C for 12 h. After cooling to room temperature, the products were obtained by filtering, washing with deionized hot water several times and drying at 60 °C for 12 h.

For comparison, blue-emitting phosphor of $BaMgAl_{10}O_{17}:Eu^{2+}$ ($BAM:Eu^{2+}$) was used from a commercial available product(Shenzhen looking long technology co., LTD).

Characterization. The crystal structure and phase purity of the as-prepared samples were characterized by X-ray powder diffraction (XRD) (Bruker D8 Advance, operating at 40 kV and 30 mA, with Cu target). XRD Rietveld profile refinements of the structural models and texture analysis were performed with the use of Fullprof software.[1] The morphologies of the samples were inspected using a field emission scanning electron microscope (FE-SEM, 8020, Hitachi). The thermal analysis was measured by TGA/DSC 3+(Mettler Instrument) under a N_2 atmosphere with heating rate of 10 $K•min^{-1}$. The X-ray photoelectron spectroscopy (XPS) spectra of phosphors were measured by a XPS spectrometer (AXIS ULTRA, Kratos Analytical Ltd.). The photoluminescence excitation (PLE) and emission (PL) spectra were measured by a fluorescence spectrometer (F-7000, Hitachi.) equipped with a 150 W xenon lamp as the excitation source. The high-temperature PL was measured by a fluorescence spectrophotometer (F-4600, HITACHI, Japan) equipped with a heating device. The decay curve was collected by FLS1000 Edinburgh Analytical Instrument apparatus equipped with an nF900H high-energy flash lamp as the excitation sources. The photoluminescence quantum yield (QY) was measured by an absolute PL quantum yield measurement system C9920-02G (Hamamatsu photonics K.K., Japan) using an integrating sphere. The EL properties of the samples were obtained using a HP 900 (Hopoo instrument, China) instrument.

Calculation Method

We have employed the Vienna Ab Initio Package (VASP)[2-3] to perform all the density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the PBE[4] formulation. We have chosen the projected augmented wave (PAW) potentials[5-6] to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400 eV. Partial occupancies of the

Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10^{-5} eV. A geometry optimization was considered convergent when the force change was smaller than 0.02 eV/Å.

The equilibrium lattice constants of monoclinic $Sr[B_8O_{11}(OH)_4]$ were optimized, when using a 5×4×4 Monkhorst-Pack k-point grid for Brillouin zone sampling. All the electronic properties were calculated by the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE06).[7] In this approach, the long-range exchange potential and the correlation potential are calculated with the PBE functional, while the short-range exchange potential is calculated by mixing a fraction of nonlocal Hartree–Fock exchange with PBE. The screening and mixing parameter are fixed at 10 Å and 0.25, respectively.

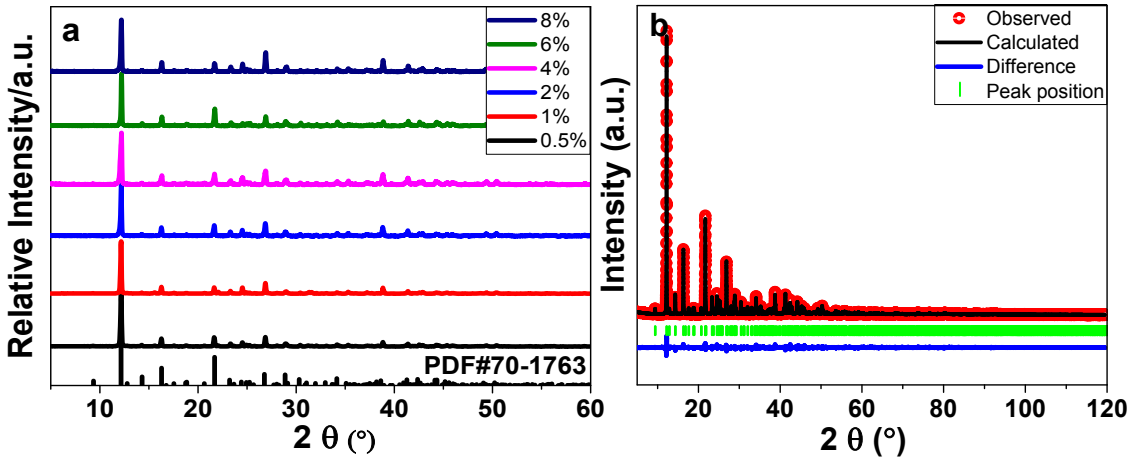

Figure S1. (a) XRD patterns of SBH:xEu^{2+}(0.5% ≤ x ≤ 8%), and standard patterns of PDF card No. 70-1763 for $Sr[B_8O_{11}(OH)_4]$; (b) Rietveld refinement XRD patterns of SBH. The measured data, fitting data, and their difference are depicted with red circles, black solid line, and blue solid line, respectively. The green short vertical lines show the positions of Bragg reflections of the fitting XRD patterns.

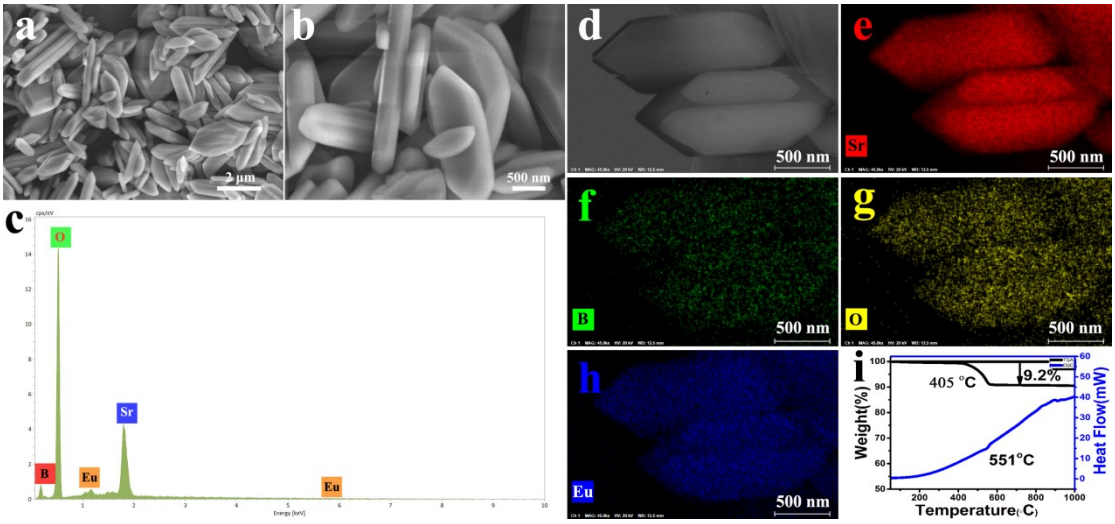

Figure S2. (a, b, and d) SEM images, (c) EDS pattern, (e, f, g, and h) corresponding element mapping images and (i)TG-DSC of SBH:Eu^{2+}.

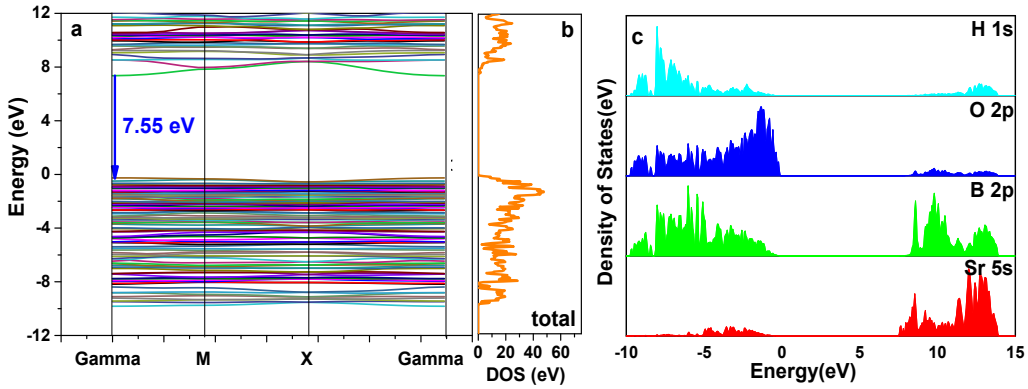

Figure S3. The energy band structure, total and partial density of states of SBH calculated based on the HSE06 functional.

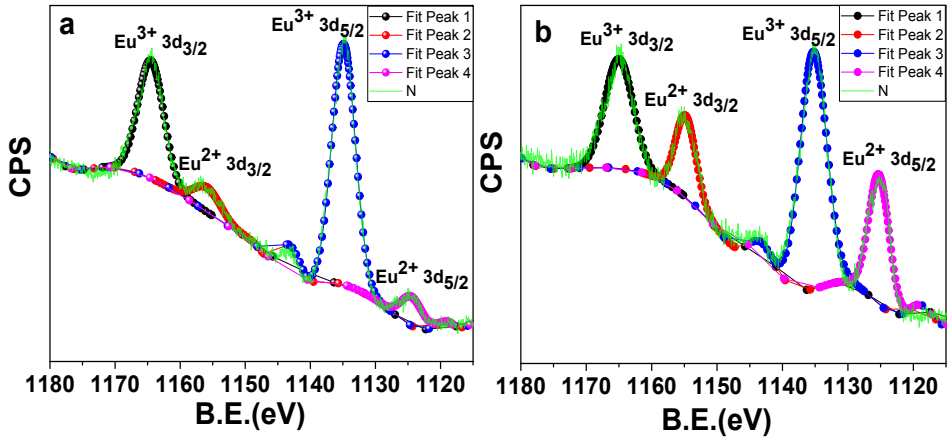

Figure S4. (a) High-resolution XPS spectra and (b) the ion sputter depth profiling high-resolution XPS of Eu $3d_{3/2}$ and Eu $3d_{5/2}$ in SBH:Eu^{2+}.

Table S1. Structure Refinement Parameters Obtained through Rietveld Refinement of Powder Diffraction Data of $Sr[B_8O_{11}(OH)_4]$

Parameter	**Value**
Formula	$Sr[B_8O_{11}(OH)_4]$
Crystal system	monoclinic
Space group, Z	$P\,2_1$, 2
a (Å)	9.91832
b (Å)	8.17151
c (Å)	7.62265
β	108.3540
Volume	586.370 $Å^{-3}$
R_p	5.99%
R_{wp}	7.7%
R_{exp}	3.49%
Chi^2	2.21%

Table S2. Refined Atom Positions, Occupancies and Thermal Parameters of $Sr[B_8O_{11}(OH)_4]$ from the Rietveld Refinement of X-ray Powder Diffraction Data

Atom	x	y	z	Occ	U
Sr1	0.27985	0.08812	0.11312	1.000	0.054
O1	0.77829	0.11000	0.05078	1.000	0.019
O2	0.52074	0.10281	0.09437	1.000	0.019
O3	0.59618	0.34699	0.02365	1.000	0.019
O4	0.00318	0.10615	0.04793	1.000	0.019
O5	0.31464	0.58208	0.29850	1.000	0.019
O6	0.20502	0.11668	0.42187	1.000	0.065
O7	0.13917	0.40753	0.10716	1.000	0.019
O8	0.57960	0.60067	0.30568	1.000	0.019
O9	0.47905	0.12145	0.42346	1.000	0.065
O10	0.38606	0.39260	0.06189	1.000	0.019
O11	0.72119	0.20262	0.30337	1.000	0.019
O12	0.94083	0.18622	0.30240	1.000	0.019

O13	0.09588	0.65102	0.39871	1.000	0.065
O14	0.79896	0.58390	0.25957	1.000	0.065
O15	0.90513	0.35115	0.03220	1.000	0.019
B1	0.48221	0.58735	0.38690	1.000	0.016
B2	0.02187	0.45107	0.04335	1.000	0.016
B3	0.27078	0.48578	0.08705	1.000	0.016
B4	0.48823	0.45739	0.00673	1.000	0.016
B5	0.65271	0.16985	0.09979	1.000	0.016
B6	0.91051	0.17110	0.11214	1.000	0.016
B7	0.72566	0.60263	0.39307	1.000	0.016
B8	0.87751	0.20356	0.41107	1.000	0.016

Table S3 The QY and fwhm of SBH:6%Eu^{2+} and some other blue emitting phosphor obtained by different authors

structure	**QY**	**fwhm**	**Reference in manuscript**
$RbNa_3(Li_3SiO_4)_4:Eu^{2+}$	53%	22.4 nm	4
$BaAl_{12}O_{19}:Eu^{2+}$	90%	52 nm	13
$BaMgAl_{10}O_{17}:Eu^{2+}$	92.4%	51.7 nm	5
$Sr_5(PO_4)_3Cl$: Eu^{2+}	80.5%	~40 nm	14
$NaMgBO_3:Ce^{3+}$	93%	102 nm	24
SBH:6%Eu^{2+}	99.0%	33.5 nm	This work

References

1. J. Rodríguez Carvajal, *Physica B: Condensed Matter*, 1993, **192**, 55.
2. G. Kresse and J. Furthmüller, *Computational Materials Science*, 1996, **6**, 15.
3. G. Kresse and J. Furthmüller, *Physical Review B*, 1996, **54**, 11169.
4. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1996, **77**, 3865.
5. G. Kresse and D. Joubert, *Physical Review B*, 1999, **59**, 1758.
6. P. E. Blöchl, *Physical Review B*, 1994, **50**, 17953.
7. J. Heyd, G. E. Scuseria and M. Ernzerhof, *The Journal of Chemical Physics*, 2003, **118**, 8207.