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Structure, Luminescence Property, and Valence-induced Spectral Behavior in a Bismuth-activated Garnet Phosphor

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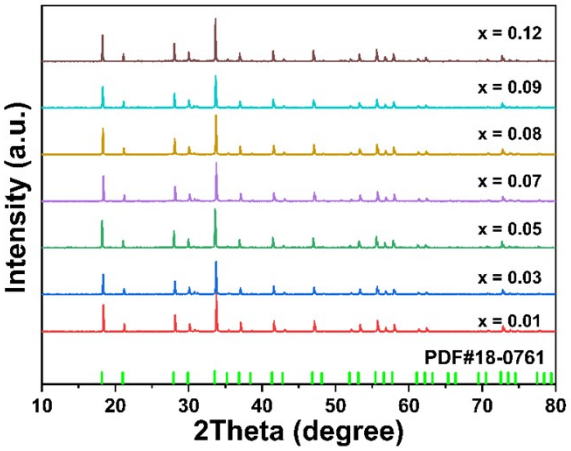

Figure S1. the XRD patterns of the LSAS:xBi^{3+} ($0.01 \leq x \leq 0.12$) samples; the standard card of $Lu_3Al_5O_{12}$ (PDF #18-0761) are shown as a reference.

Table S1. Crystallographic data for LSAS

Formula	$Lu_2SrAl_4SiO_{12}$
Crystal system	Cubic
Space group	Iad（No.230）
Lattice parameters	
$a = b = c$ (Å)	11.88705(0)
$\alpha = \beta = \gamma$ (°)	90
Cell volume (Å^3)	1276.67(1)
Z	16
R-factors	
R_{wp}	0.1037
R_p	0.0805
χ^2	2.131

Table S2. Atomic coordinates and isotropic displacement parameters for LSAS

Atom	Wyckoff	S.O.F	*x*	*y*	*z*	Uiso
Al1	16a	1	0	0	0	0.0246
Al2	24d	0.667	3/8	0	1/4	0.0077
Lu1	24c	0.667	0	3/4	1/8	0.0014
O1	96h	1	-0.0299(8)	0.0516(5)	0.1485(7)	0.0262
Sr1	24c	0.333	0	3/4	1/8	0.0149(13)
Si1	24d	0.333	3/8	0	1/4	0.1276

Table S3. Bond distance from Rietveld refinement of LSAS

Bond	Distance(Å)	Bond	Distance(Å)
Al1-O	1.900(77)×6	Lu-O	2.2825(41)×4
Al2-O	1.7600(20)×4	Lu-O	2.3976(81)×4
Sr-O	2.2825(41)×4	Sr-O	2.3976(81)×4
Si-O	1.7600(20)×4		

Table S4. Bond valence calculate from Rietveld refinement of LSAS

Bond type	R_0	*B*	*V*
Lu-O	1.971	0.37	2.9860
Sr-O	2.090	0.37	4.1188

$$V_i = \sum_j V_{ij} \quad \text{(S1)}$$

$$V_{ij} = exp\left(\frac{R_0 - R_{ij}}{b}\right) \quad \text{(S2)}$$

Where V_i represents the sum of all valences of the cation i in the crystal structure, V_{ij} corresponds to the bond valence between the cation i and its coordinating anion j, R_{ij} represents the distance between the ij bonds (values are obtained from the refinement and listed in Table S3), and R_0 is different for the cation, the value of b is a constant of 0.37.[1]

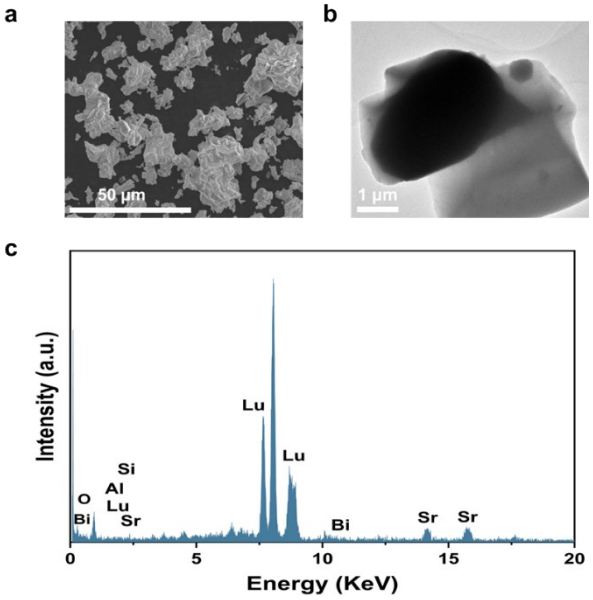

Figure S2. (a) the SEM image; (b) TEM image; (c) EDS spectrum of the LSAS: Bi^{3+} phosphor

$$I(t) = A_0 + A_1\exp\left(-\frac{t}{\tau_1}\right) + A_2\exp\left(-\frac{t}{\tau_2}\right) \quad \text{(S3)}$$

where I (t) represent the luminescence intensity at time t, A_0 is the background luminescence intensity, A_1 and A_2 are constants; τ_1 and τ_2 are the decay times, respectively.[2]

Figure S3.

Table S5. The emission peak, FWHM, lifetime of LSAS:$x$$Bi^{3+}$ phosphors

Bi^{3+} concentration (x)	Emission peak (nm)	FWHM (nm)	Lifetime (ns)
0.01	459	136.67	446.06
0.03	449	136.28	442.42
0.05	450	107.41	439.89
0.07	451	106.96	433.62
0.08	456	109.1	428.76
0.09	456	109.6	408.97
0.12	453	108.7	383.35

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad \text{(S4)}$$

$$\alpha = \frac{(1-R)^2}{2R} \quad \text{(S5)}$$

Where α represents the absorption coefficient, $h\nu$ is the incident photon energy. A is a constant. n equals 1/2 and 2 for indirect bandgap and direct bandgap, respectively. In this case, the value of n is 1/2. R is the reflectivity.[3]

$$MMCT\ (Bi^{3+}, cm^{-1}) = k_{CN'}[X_{CN}(Bi^{3+}) - \alpha_{CN'}^{CN}\frac{X_{CN'}(M^{n+})}{d}] \quad \text{(S6)}$$

where $k_{CN'}$ is a constant that is dependent on CN′ (the coordination numbers for the Bi^{3+} site (CN) and for the Mn^{+} site (CN′)), $X_{CN}(Bi^{3+})$ the electronegativity (EN) of Bi^{3+}, and $\alpha_{CN'}^{CN}$ an adjustable parameter that is dependent on CN and CN′. $X_{CN'}(M^{n+})$ is the electronegativity of the metal cations. The term d represents the shortest Bi^{3+}–Mn+ interatomic distances in the host lattices.

$$d = d_{host} + \frac{1}{2}[r(Bi^{3+}) - r(host)] \quad \text{(S7)}$$

Where d_{host} is the shortest distances between the Mn+ site(s) and the cation site(s) available for Bi^{3+}, $r(Bi^{3+})$ is the ionic radius of the Bi^{3+} ion and r(host) is the ionic radius of the host cation that is substituted to Bi^{3+}.

$X_{CN}(Bi^{3+})$ can be calculated for any value of CN, following the procedure given in Li and Xue:[4]

$$X_{CN}(Bi^{3+}) = \frac{0.105n^*}{r(Bi^{3+})}\sqrt{\frac{I_m}{13.6}} + 0.863 \quad \text{(S8)}$$

where n* is the effective principal quantum number (4.36), and I_m is the ultimate ionization energy (25.56 eV). The $k_{CN'}$ values were calculated as 70 000/$X_{CN}(Bi^{3+})$ for CN′ = 4 and 55 000/$X_{CN}(Bi^{3+})$ for CN′ > 4. The $\alpha_{CN'}^{CN}$ values were then obtained as 52 000/k_{CN} for CN = 4 and as 45 500/$k_{CN'}$ for CN′ > 4. [5]

In this work, the empirical equation for metal-to-metal charge-transfer (MMCT) state of Bi^{3+} doped $Lu_2SrAl_4SiO_{12}$ phosphor can be defined as:

$$MMCT\ (Bi^{3+}, cm^{-1}) = 55000 - 45500\frac{X_{CN'}(Lu^{3+})}{d}] \quad \text{(S9)}$$

$X_{CN'}(Lu^{3+})$=1.425, d=3.731Å, MMCT(Bi^{3+}) = 37621.95 cm^{-1}.

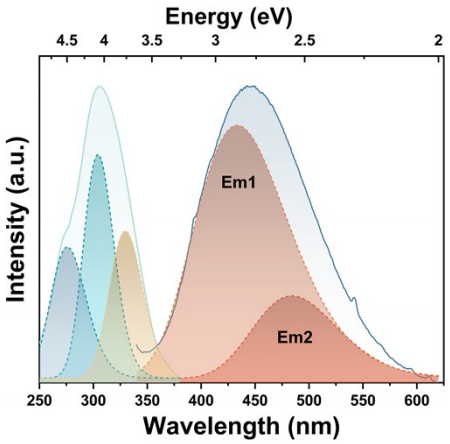

Figure S3. Gaussian fitting for PL and PLE spectra of LSAS: 8%Bi^{3+}.

$$L(\text{Å}) = 250\left(\frac{A}{\rho}\right)\left(\frac{E}{\sqrt{Z}}\right)^{n}, n = \frac{1.2}{1 - 0.29\lg Z} \qquad (S10)\#$$

where A is the atomic or molecular weight of the material, ρ is the bulk density, Z is the atomic number or the number of electrons per molecule in the case compounds, and E is the accelerating voltage (kV). For LSAS, Z = 144, A = 765.63, ρ = 6.73 g/cm^{-3}. So according to the above empirical formula, the estimated electron penetration depth at different accelerating voltage showed in table S5.[6]

Table S6. The estimated electron penetration depth for LSAS:Bi^{3+} phosphor

Accelerating voltage (kV)	Penetration depth (nm)
2	9.01
4	83.8
6	307.8
8	774.6
10	1584.6
12	2844.1
14	4663.4
15	5818.7

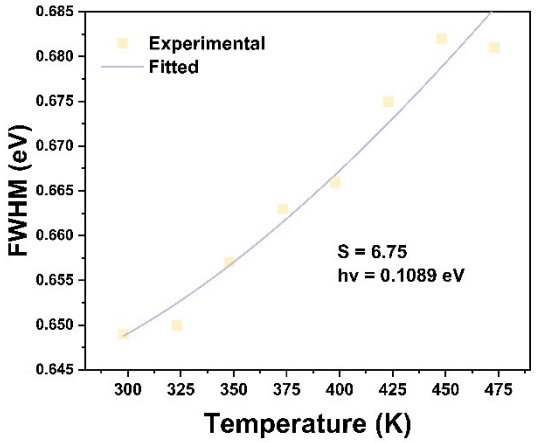

Figure S4. Huang–Rhys factor (S) and the phonon energy (hv) obtained through fitting the relationship between FWHM (eV) and *T* (K).

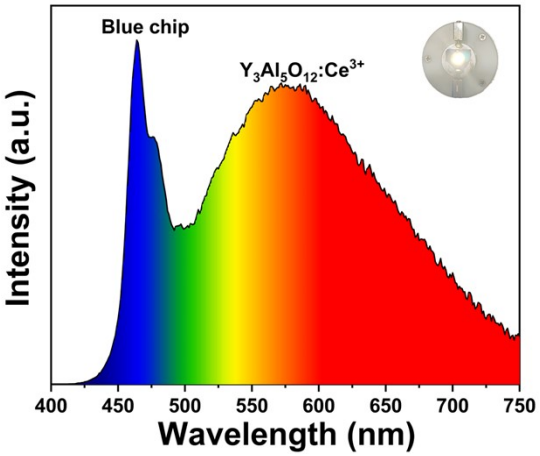

Figure S5. electroluminescence spectrum of the WLED device combing blue LED chip with $Y_3Al_5O_{12}$: Ce^{3+}

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