Unraveling the Origin of the Broadband Yellow Emission in Bi^{3+}-doped $LuXnGaO_4$ (Xn = Mg, Zn) Phosphors

Wanying Geng,[a] Xufeng Zhou,[a] Jianyan Ding[b] and Quansheng Wu *[b]

[a] *College of Materials Science and Engineering, Liaocheng University, Liaocheng, Shandong, 252000, China*

[b] *College of Chemistry & Materials Science, Longyan University, Longyan, Fujian, 364000, China*

***Address correspondence to E-mail**: *wuqsh1989@qq.com*

Experiment section

Material and preparation

A series of samples of $LuXnGaO_4$:$x$$Bi^{3+}$ (Xn = Mg, Zn) (x = 0, 0.0015, 0.003, 0.0045, 0.006, 0.0075 and 0.009) were synthesized by high temperature solid-state reaction method. The raw materials are Lu_2O_3 (≥99.0%, Aladdin), $MgCO_3$ (≥99.5%, Aladdin), $ZnCO_3$ (≥99.5%, Aladdin), Ga_2O_3 (99.5%, Aladdin), Bi_2O_3 (99.99%, Aladdin) were homogeneously mixed and finely ground in an agate mortar containing ethanol as the dispersing medium. H_3BO_3 (Sinopharm Chemical) was used as a fluxing solvent with a mass faction of 5, after which they were dried and packed in aluminum oxide crucibles. The powder mixture was sintered in a high-temperature tube furnace at 1350°C for 4 h under air atmosphere and the heating rate was 10°C/min. The resulting samples after cooling were reground into powder for further characterization analysis.

Measurements and characterization

All the measurements were conducted at room temperature. The X-ray powder diffraction (XRD) (D2 PHASER X-ray Diffractometer, Germany) with a graphite monochromator using Cu Kα radiation (λ = 1.54056 A), operating at 30 kV and 15 mA was employed to identify the phase formation and crystal structure of the samples. The Rietveld method was employed to perform the structure refinement by the program of the General Structure Analysis System. The band structure for the sample was

calculated with density functional theory and performed with the Cambridge Serial Total Energy Package code. The theoretical basis of density was used for local-density approximation. The photoluminescence (PL) and PL excitation (PLE) spectra were obtained using a FLS-920T fluorescence spectropho-tometer equipped with a 450 W Xe light source and double excitation monochromators. The luminescence intensities of the samples depending on the temperature were carried out using an aluminum plaque with cartridge heaters; the temperature was measured by thermocouples inside the plaque and controlled by a standard TAP-02 high temperature fluorescence controller. The diffusion reflectance spectra (DRS) were measured on an UV−vis spectrophotometer (PE Lambda 950). The powder morphology was investigated using scanning electron microscopy (SEM; S-3400, Hitachi, Japan).

The band structure for the sample was calculated with density functional theory and performed with the Cambridge Serial Total Energy Package (CASTEP) code. The theoretical basis of density was used for local-density approximation (LDA).

The bandgap is calculated by the following equations:

$$(\alpha hv)^n = A(hv - E_g) \quad (1)$$

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

Where α is the absorption coefficient, hv is the incident photo energy, A is a constant, and n = 1/2 for direct bandgap.

Table S1 Unit cell data of $LuXnGaO_4:Bi^{3+}$

	$LuMgGaO_4$	$LuMgGaO_4:Bi^{3+}$	$LuZnGaO_4$	$LuZnGaO_4:Bi^{3+}$
Crystal system	trigonal	trigonal	trigonal	trigonal
Space-group	R -3 m (166)	R -3 m (166)	R -3 m (166)	R -3 m (166)
Cell parameters (Å)	a=3.3880(1),	a=3.3890(2)	a=3.3984(0),	3.3986(0)
	c=25.2146(5)	25.2217(18)	c=25.2214(6)	25.2216(6)
Cell volume ($Å^3$)	250.65 (1)	250.87(4)	252.27(1)	252.29(1)
Z	3	3	3	3

Calc. density (g/cm^3)	6.61768	6.61196	7.38625	7.38567

Table S2 Atomic parameters of $LuMgGaO_4$

Atom	Wyck.	S.O.F.	x/a	y/b	z/c	U [Å^2]
Lu1	3a	1	0	0	0	0.0198
Mg1	6c	0.5	0	0	0.2177(3)	0.6281
Ga1	6c	0.5	0	0	0.2177(3)	0.0048
O1	6c	1	0	0	0.2954(1)	0.0056
O2	6c	1	0	0	0.1303(5)	0.0329

Table S3 Atomic parameters of $LuMgGaO_4:Bi^{3+}$

Atom	Wyck.	S.O.F.	x/a	y/b	z/c	U [Å^2]
Lu1	3a	0.997	0	0	0	0.0238
Bi1	3a	0.003	0	0	0	0.0257
Mg1	6c	0.5	0	0	0.2205(6)	0.0355
Ga1	6c	0.5	0	0	0.2205(6)	0.0146
O1	6c	1	0	0	0.2923(6)	0.0016
O2	6c	1	0	0	0.1274(6)	0.0837

Table S4 Atomic parameters of $LuZnGaO_4$

Atom	Wyck.	S.O.F.	x/a	y/b	z/c	U [Å^2]
Lu1	3a	1	0	0	0	0.0198
Zn1	6c	0.5	0	0	0.2155(1)	0.0503
Ga1	6c	0.5	0	0	0.2155(1)	0.0165
O1	6c	1	0	0	0.2912(6)	0.0216

O2	6c	1	0	0	0.1258(5)	-0.0147

Table S5 Atomic parameters of $LuZnGaO_4:Bi^{3+}$

Atom	Wyck.	S.O.F.	x/a	y/b	z/c	U [Å^2]
Lu1	3a	0.997	0	0	0	0.0093
Bi1	3a	0.003	0	0	0	0.0087
Zn1	6c	0.5	0	0	0.2198(6)	0.0489
Ga1	6c	0.5	0	0	0.2198(6)	0.0146
O1	6c	1	0	0	0.2918(2)	0.0107
O2	6c	1	0	0	0.1352(2)	0.0029

Table S6 Bond length (d) data of $LuMgGaO_4$ obtained from Rietveld refinement.

Atom1	Atom2	Conut	d (Å)
Lu	O1	6×	2.1773
	Mg/Ga	6×	3.5098
	Lu	6×	3.3880
Mg/Ga	O1	1×	1.9579
	O2	3×	1.9914
	O2	1×	2.2033

Table S7 Bond length (d) data of $LuZnGaO_4$ obtained from Rietveld refinement.

Atom1	Atom2	Conut	d (Å)
Lu	O1	6×	2.2303
	Mg/Ga	6×	3.5612
	Lu	6×	3.3984
	O1	1×	1.9115

Zn/Ga	O2	3×	1.9725
	O2	1×	2.2611

Table S8 Values of each parameter for the calculation of Bi^{3+} pairs energy

	χ_{CN}	k_{CN}	α_{CN}	d_{host}	r(Bi^{3+})	r(X)	r(X')
LMGO	1.4	65857	2.518	3.3880	1.03	0.861	0.861
LZGO	1.4	65857	2.518	3.3984	1.03	0.861	0.861

Table S9 Values of each parameter for the calculation of E_{sp} energy

	E_A	K	α	f_c(M–Xi)	α(M–Xi)	Q(Xi)	Q(M)	h_e	N(M)
LMGO	9.41	0.555	0.24	0.076	0.482	2.29	3.44	1.153	6
LZGO	9.41	0.555	0.24	0.094	0.567	1.99	2.98	1.123	6
	N(M-Xi)	N(Xi)	N(Xi-M)	Z	ω(M)	ω(A)	BVP(M)	d(M-Xi)	d(A-Xi)
LMGO	6	4	3	3	3	6	1.971	2.1773	1.9579
LZGO	6	4	3	3	3	6	1.971	2.2303	1.9115

Table S10 Precise values of each parameter for the calculation of MMCT energy

		x(Lu^{3+})	x(Ga^{3+})	d_{host}	r(Bi^{3+})	r(host)	d_{corr}
LMGO	Bi^{3+}-Lu^{3+}	1.431	/	3.3880	1.03	0.861	3.4725
	Bi^{3+}-Ga^{3+}	/	1.652	3.5098	1.03	0.861	3.5943
LZGO	Bi^{3+}-Lu^{3+}	1.431	/	3.3984	1.03	0.861	3.4829

	Bi^{3+}-Ga^{3+}	/	1.652	3.5612	1.03	0.861	3.6457
	Bi^{3+}-Zn^{2+}	/	1.371	3.5612	1.03	0.861	3.6457

Table S11 Values of the parameters specific to $LuXnGaO_4$:Bi^{3+} (Xn = Zn, Mg) for the calculations of the critical distance.

	x_c	V (Å^3)	Z
LMGO	0.0060	250.65 (1)	21
LZGO	0.0045	252.27(1)	21

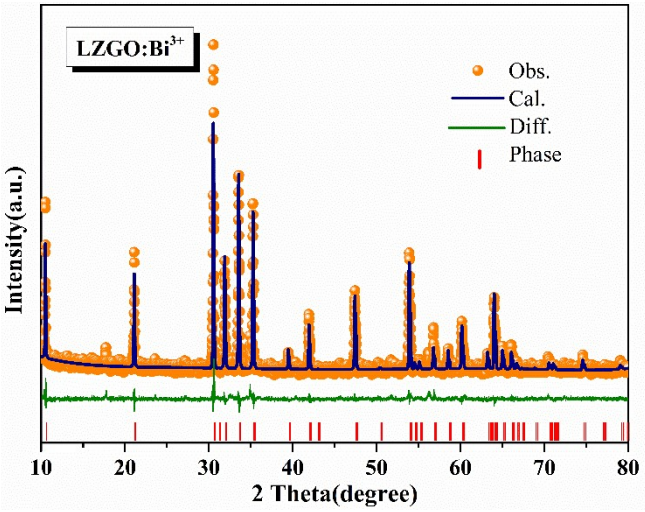

Fig. S1 Refinement pattern of LZGO:Bi^{3+}.

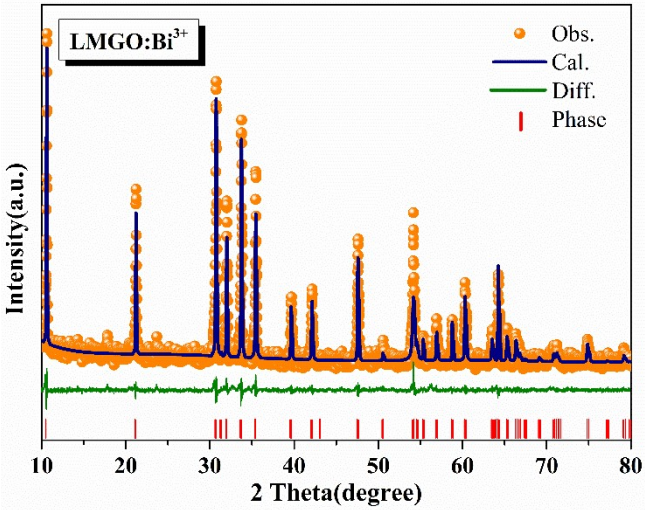

Fig. S2 Refinement pattern of LMGO:Bi^{3+}.

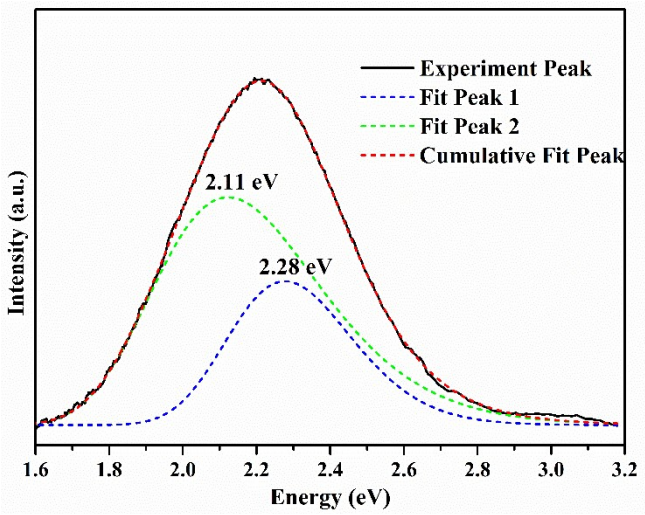

Fig. S3 Gaussian fitting of the emission spectrum of LZGO:Bi^{3+}.

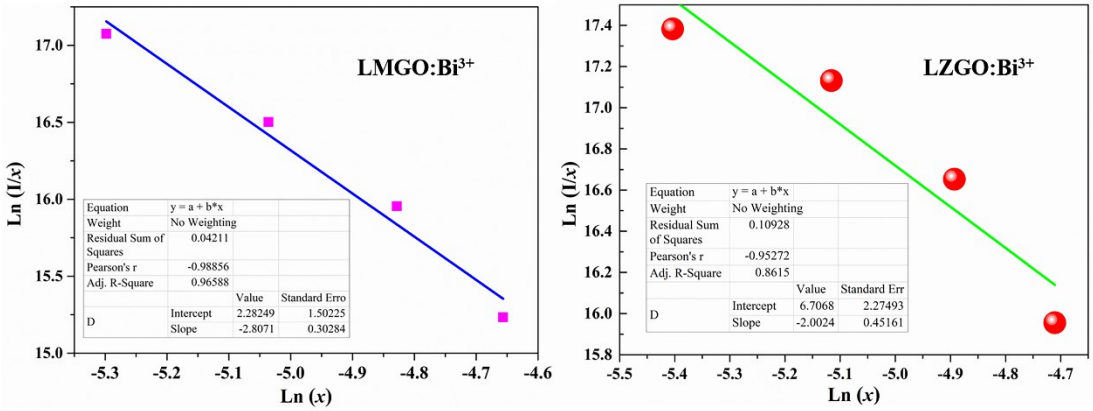

Fig. S4 Relationship between Ln (I/x) and Ln (x) for $LuXnGaO_4$:Bi^{3+} (Xn = Zn, Mg).