Full Color Luminescence Tuning in Bi^{3+}/Eu^{3+}-Doped $LiCa_3MgV_3O_{12}$ Garnet Phosphors Based on Local Lattice Distortion and Multiple Energy Transfers

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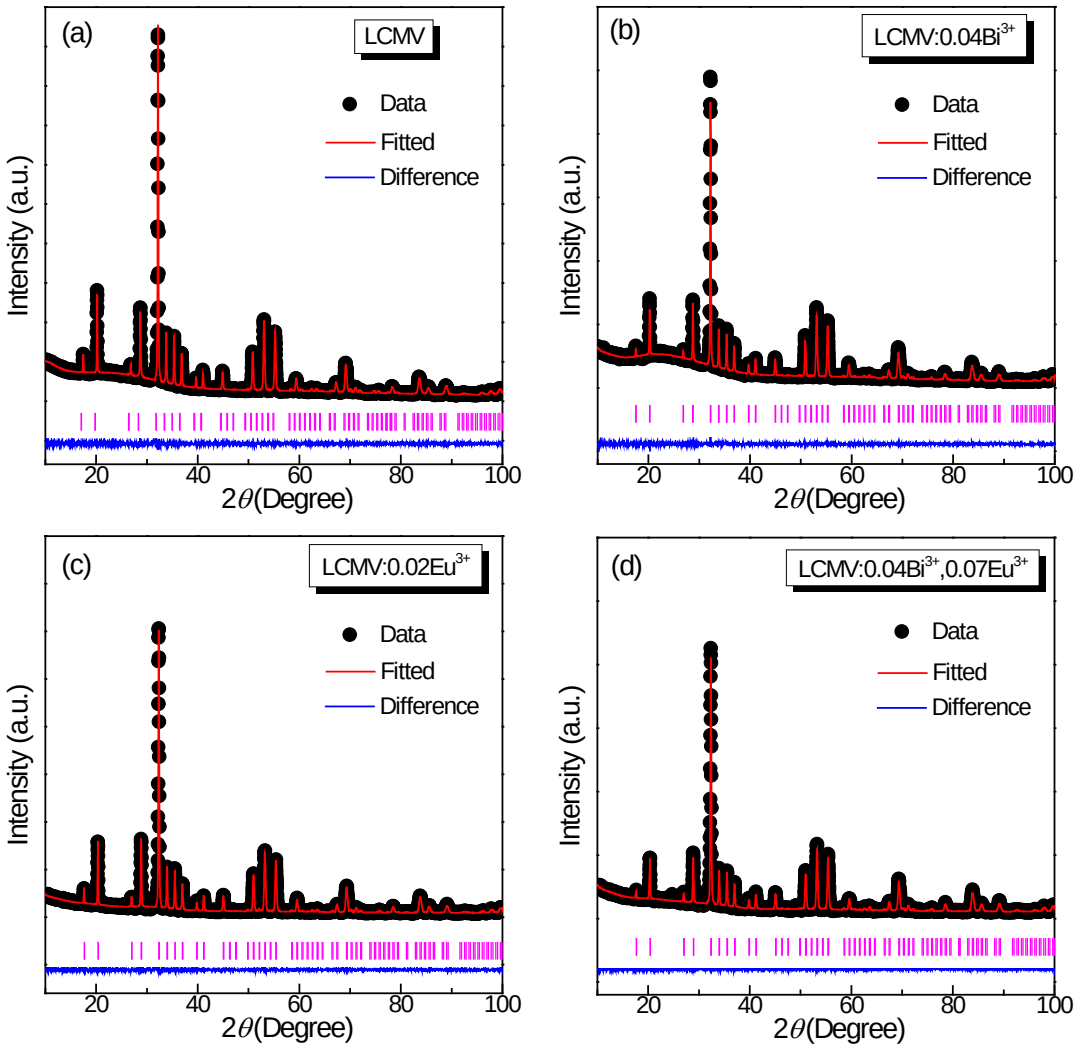

Figure S1. Data (black dots) and fitted (red line) powder XRD patterns as well as difference profile (blue line) for Rietveld analysis of LCMV:xBi^{3+},yEu^{3+}: (a) x = 0, y = 0 (b) x = 0.04, y = 0 (c) x = 0, y = 0.02 (d) x = 0.04, y = 0.07. The short vertical lines show the positions of Bragg reflections of the fitted patterns.

Table S1. Main refinement parameters of the LCMV:xBi^{3+},yEu^{3+} (x = 0-0.10; y = 0-0.07) samples.

x (y = 0)	Cell parameters, Å	Cell volume, Å^3	R_{wp}, R_p, %, χ^2
x = 0	$a = b = c$ =12.439(4) $\alpha = \beta = \gamma$= 90°	1924.5(10)	4.45, 3.36, 2.012
x = 0.01	$a = b = c$ = 12.4535(4) $\alpha = \beta = \gamma$= 90°	1931.39(10)	4.25, 3.28,1.668
x = 0.02	$a = b = c$ = 12.4566(17) $\alpha = \beta = \gamma$ = 90°	1932.84(5)	4.95, 3.68, 2.333
x = 0.03	$a = b = c$ = 12.4549(18) $\alpha = \beta = \gamma$ = 90°	1932.07(5)	6.08, 4.49, 2.019
x = 0.04	$a = b = c$ = 12.4457(27) $\alpha = \beta = \gamma$ = 90°	1927.78(7)	4.73, 3.67, 1.611
x = 0.05	$a = b = c$ = 12.4518(31) $\alpha = \beta = \gamma$ = 90°	1930.60(8)	5.35, 3.99, 1.723
x = 0.06	$a = b = c$ =12.4508(27) $\alpha = \beta = \gamma$ = 90°	1930.17(7)	6.00, 4.41, 2.114
x = 0.08	$a = b = c$ = 12.4535(27) $\alpha = \beta = \gamma$ = 90°	1931.39(7)	6.32, 4.63, 2.280
x = 0.10	$a = b = c$ =12.4496(26) $\alpha = \beta = \gamma$ = 90°	1929.59(7)	6.12, 4.65, 2.164
x = 0 y = 0.02	$a = b = c$ =12.4565(4) $\alpha = \beta = \gamma$ = 90°	1932.78(10)	7.19, 5.07, 2.788
x = 0.04 y = 0.04	$a = b = c$ =12.4497(28) $\alpha = \beta = \gamma$ = 90°	1929.65(8)	6.56, 4.62, 2.413
x = 0.04 y = 0.07	$a = b = c$ = 12.4489(4) $\alpha = \beta = \gamma$ = 90°	1929.28(10)	6.55, 4.68, 2.443

Table S2. Final refined structure parameters of $LiCa_3MgV_3O_{12}$ and $LiCa_{2.96}MgV_3O_{12}$:0.04Bi^{3+} derived from the GSAS refinement of XRD data.

Atom	Wyckoff position	X	Y	Z	Frac.	*Uiso*
$LiCa_3MgV_3O_{12}$						
Ca1	24*c*	0.375000	0.500000	0.250000	0.779(6)	0.03
Li1	16*a*	0.375000	0.500000	0.250000	0.3333	0.03
Mg1	16*a*	0.500000	0.500000	0.000000	0.514(19)	1.4(6)
V1	24*d*	0.625000	0.500000	0.250000	1.0000	0.03
O1	96*h*	0.5334(4)	0.5552(4)	0.16276(23)	1.150(14)	1.00(21)
Cell parameters: $a = b = c$ = 12.439(4) Å, $\alpha = \beta = \gamma = 90°$ V =1924.5(10) Å^3, z = 8 Space group: $Ia\bar{3}d$ *(230)* Reliability factor: R_{wp}= 4.45%, R_p= 3.36%, and χ^2 = 2.012						
$LiCa_{2.96}MgV_3O_{12}$:0.04Bi^{3+},0.04Eu^{3+}						
Ca1	24*c*	0.375000	0.500000	0.250000	0.899(35)	3.5(4)
Li1	16*a*	0.375000	0.500000	0.250000	0.3333	0.03
Mg1	16*a*	0.500000	0.500000	0.000000	0.85(6)	4.2(7)
V1	24*d*	0.625000	0.500000	0.250000	1.13(5)	1.96(33)
O1	96*h*	0.5316(28)	0.55293(24)	0.15710(28)	1.0000	3.0(6)
Cell parameters: $a = b = c$ =12.44973(28) Å, $\alpha = \beta = \gamma = 90°$ V =1929.65(8)Å^3, z = 8 Space group: $Ia\bar{3}d$ *(230)* Reliability factor: R_{wp}= 6.56%, R_p= 4.62%, and χ^2 = 2.413						

Table S3. Selected interatomic distances in LCMV:xBi^{3+},yEu^{3+} (x = 0-0.10, y = 0-0.04) samples.

x = 0, y = 0		x = 0.02, y = 0		x = 0.04, y = 0		x = 0.06, y = 0	
Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Ca1-O1	2.427	Ca1-O1	2.436	Ca1-O1	2.475	Ca1-O1	2.479
Mg1-O1	2.178	Mg1-O1	2.170	Mg1-O1	2.105	Mg1-O1	2.088
V1-O1	1.717	V1-O1	1.718	V1-O1	1.736	V1-O1	1.742

x = 0.10, y = 0		x = 0, y = 0.02		x = 0.04, y = 0.04	
Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Ca1-O1	2.480	Ca1-O1	2.475	Ca1-O1	2.480
Mg1-O1	2.076	Mg1-O1	2.078	Mg1-O1	2.118
V1-O1	1.752	V1-O1	1.741	V1-O1	1.715

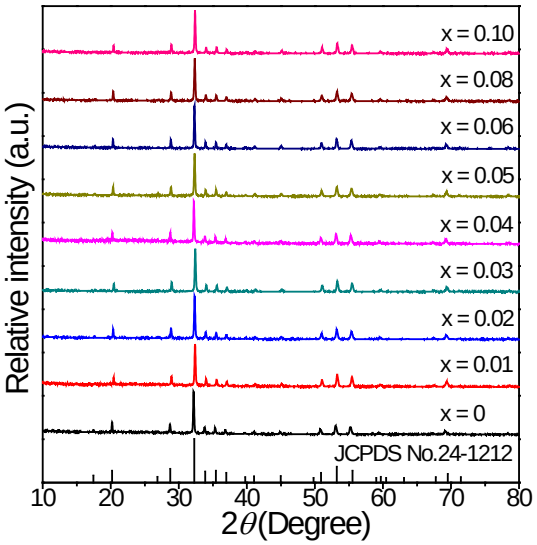

Figure S2. The typical XRD patterns at 2θ = 10°-80° of LCMV:xBi^{3+} (x = 0-0.10) samples. The standard data of $LiCa_3MgV_3O_{12}$ (JCPDS No.24-1212) is shown as a reference.

Table S4. The emission wavelengths, fwhms and internal quantum yields (IQYs) of LCMV:xBi^{3+} (x = 0-0.10) samples monitored at different excitation wavelengths.

x	λ_{em}/nm	fwhm /nm	EM1/nm	fwhm /nm	EM2/nm	fwhm /nm	IQYs (%)
0	480	100.50	474	76.42	533	113.66	37.8
0.01	488	110.06	477	79.74	549	123.30	26.5
0.02	503	122.48	480	81.31	557	126.84	42.1
0.03	513	129.37	480	81.75	560	128.89	42.5
0.04	539	137.11	485	84.68	565	130.84	42.3
0.05	548	136.84	488	86.02	567	130.15	41.4
0.06	556	137.36	494	91.28	569	130.03	43.9
0.08	557	137.79	504	98.85	573	128.97	35.1
0.10	562	134.22	536	115.30	583	130.95	28.9

Table S5. The lifetimes of LCMV:xBi^{3+} (x = 0-0.10) samples monitored at different excitation and emission wavelengths.

x	λ_{ex}/nm	λ_{em}/nm	τ_1/μs	A_1	τ_2/μs	A_2	τ*/μs
0	330	480	12.255	15702	23.305	4453.7	16.13
0.01	322	488	20.788	6411.4	11.310	14235	15.60
0.02	324	503	11.232	16517	20.971	4508.4	14.52
0.03	324	513	26.296	1398.5	12.671	19000	13.20
0.04	335	539	13.204	10542	13.204	10542	13.07
0.05	336	548	13.075	10499	13.075	10499	13.05
0.06	337	556	13.053	10734	13.053	10734	12.21
0.08	339	557	12.215	11055	12.215	11055	11.91
0.10	340	562	11.907	11065	11.908	11065	11.23

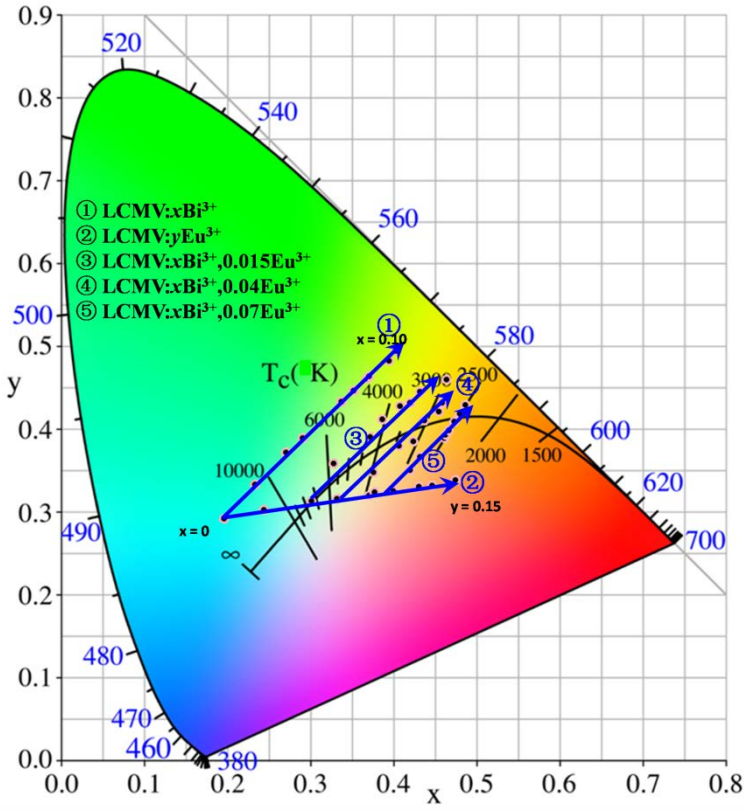

Figure S3. The CIE color coordinates diagram of LCMV:xBi^{3+},yEu^{3+} (x = 0-0.10, y = 0-0.15) samples excited under different UV wavelengths (320-340 nm).