Full-Visible-Spectrum Lighting Realized by a Novel Eu^{2+}-Doped

Nitride-Based Cyan-Emitting Phosphor

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Supporting Information

Material synthesis

The $Ca_2BN_2Cl:Eu^{2+}$ samples were prepared by high-temperature solid-phase reaction. The raw materials are Eu_2O_3 (99.99%), $CaCl_2$ (analytical reagent), BN (99%), Ca_3N_2 (99%). First, the raw materials were weighed in stoichiometric ratios and then ground in an agate mortar. The grinding process was carried out in a glove box filled with 99.99% high-purity nitrogen. Second, the ground powders were put into an alumina crucible, and then transferred to a vacuumized high-temperature muffle furnace. High-purity nitrogen and hydrogen ($95\%N_2/5\%H_2$) are introduced into the high-temperature muffle furnace. Finally, the temperature is increased to 1100℃ at a rate of 5℃ per minute, and the temperature is kept for 4 hours. After sintering, the bulk samples were obtained and reground into powders in a porcelain mortar for further analysis.

Measurements and characterization

The phase purity and crystal structure of the $Ca_2BN_2Cl: xEu^{2+}$ phosphor was characterized by powder X-ray diffraction (PXRD), which measurement angle range was 10-80°, the measurement step length was 0.03°. The crystal structure of the Ca_2BN_2Cl was refined through using the general structure analysis system software (GSAS) [18]. The electronic structure of the Ca_2BN_2Cl was analyzed through using the basic theory of the generalized gradient approximation (GGA) based on density functional theory (DFT).

The sample of Ca_2BN_2Cl photoluminescence excitation (PLE) and photoluminescence (PL) spectra, fluorescence decay curves, time-resolved photoluminescence (TRPL) and temperature-dependent spectra were recorded by using an FS5 fluorescence spectrometer. The morphology characterized and elemental mapping information was obtained using X-ray spectroscopy (EDX) and scanning electron (SEM, S-340, Hitachi, Japan) respectively.

Table S1. Crystal data on the Ca_2BN_2Cl acquired via Rietveld refinement.

Formula	Ca_2BN_2Cl
Space group	Pnma (62)
Cell	a = 11.6576(1) Å, b = 3.891(1) Å
parameters	c = 8.965(1) Å
Cell volume	$V = 406.65(11)$ Å^3
Z	4

Atom	x/a	y/b	z/c	Wyck.	Occupancy rate
Ca1	0.0896	1/4	0.6090	4c	1
Ca2	0.6697	1/4	0.4503	4c	1
Cl1	0.4388	1/4	0.3474	4c	1
N1	0.2865	1/4	0.6846	4c	1
N2	0.8776	1/4	0.5434	4c	1
B1	0.3353	1/4	0.8189	4c	1

Table S2. Value of R_i for Ca_1/Eu_1 and Ca_2/Eu_2.

Ca_1/Eu_1		Ca_2/Eu_2	
N_1	2.408 Å	N_1	2.347 Å
N_2	2.393 Å	N_2	2.564 Å
N_3	2.408 Å	N_3	2.347 Å
N_4	2.540 Å	Cl_1	2.945 Å

Cl_1	2.909 Å	Cl_2	2.845 Å
Cl_2	2.909 Å	Cl_3	2.945 Å
Av bond	2.5945 Å	Av bond	2.6655 Å

Table S3 PL properties of Ce^{3+}/Eu^{2+} doped cyan phosphor.

Phosphor	Synthesis	FWHM/nm	TQ(150 °C)	Reference
$Ca_2YHf_2Al_3O_{12}:Ce^{3+}$	1600°C	100	64.5%	32
$Lu_4SiAlO_8N: Ce^{3+}$	1400°C	120	50%	33
$Li_2CaSiO_4:Eu^{2+}$	800°C	37	60%	34
$K_2ZrSi_3O_9:Eu^{2+}$	800°C	57	65%	35
$Al_9O_3N_7:Eu^{2+}$	1950°C	67	86%	36
$YScSi_4N_6C: Ce^{3+}$	2000°C	89	48%	37
$Ca_2BN_2Cl:Eu^{2+}$	1100°C	121	60%	this work

Some formulas used in this article:

As exhibited in Fig. 3 (d) inset, the band gap value of Ca_2BN_2Cl can be attained by the Kubelka–Munk method: [21]

$$F(R) = \frac{(1-R)^2}{2R} \qquad (1)$$

$$[F(R)h\upsilon]^2 = \kappa(h\upsilon - E_g) \qquad (2)$$

where R represents the reflectance measured in DRS, $h\upsilon$ is the incident photon energy, and κ is a constant. As described in Fig. 3 (d), the experimental band-gap value of Ca_2BN_2Cl is 3.99 eV.

As afforded in Fig. 4 (d), the connection of Ln (I/x) and Ln (x) of the Ca_2BN_2Cl can be attained by the Van Uitert and Dexter method: [23-24]

$$I/x = K[1 + \beta(x)^{\frac{\theta}{3}}]^{-1} \qquad (3)$$

where I corresponds to the emission intensity, x represents the content of the activator ions, β and K are constants, and θ = 6, 8 and 10 refer to dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions, respectively. The relationship of Ln (I/x) on Ln (x) was fitted with a linear function and the slope of the fitted linear was about 1.50, as exhibited in Fig. 4 (d). The value of θ is calculated to be 4.5 closing to 6, implying that concentration quenching is caused by the dipole-dipole interaction.

As depicted in Fig. 5 (a), the average lifetime of Ca_2BN_2Cl: Eu^{2+} can be calculated by the below equation: [25]

$$\tau = \frac{(A_1\tau_1^2 + A_2\tau_2^2)}{(A_1\tau_1 + A_2\tau_2)} \qquad (4)$$

where A_1 and A_2 are the constants; τ_1 and τ_2 refers to the short and long lifetime, respectively. Therefore, the average lifetime τ of Ca_2BN_2Cl: xEu^{2+} ($0.01 \leq x \leq 0.05$) can be received through the above formula, which is calculated to be about 567.6, 565.3, 551.9, 550.8 and 542.8 ns.

As displayed in Fig. 6 (a) inset, the thermal activation energy of sample is calculated by the following equation: [26]

$$I_T = \frac{I_0}{[1 + Aexp\left(\frac{-\Delta E}{kT}\right)]} \qquad (5)$$

where I_o and I_T are the emission intensity at initial temperature and a temperature T, respectively; ΔE represents the thermal activation energy; k and A are constants. According to the above formula, the thermal activation energy of Ca_2BN_2Cl: Eu^{2+} was calculated to be 0.2179 eV.