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Full spectral light-emitting diodes based on a new efficient zirconium silicates green phosphor for health lighting

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Experiment section

Material and preparation

A series of samples of $Rb_2ZrSi_2O_7$:xEu^{2+} ($0 \leq x \leq 6\%$) were synthesized by high temperature solid-state reaction method. The raw materials are Rb_2CO_3 (≥99.0%, Aladdin), ZrO_2 (99%, Aladdin), SiO_2 (99.5%, Aladdin), Eu_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 1200°C for 4 h under reducing 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

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 (GSAS). The band structure

for the sample was calculated with density functional theory (DFT) and performed with the Cambridge Serial Total Energy Package (CASTEP) code. The theoretical basis of density was used for local-density approximation (LDA). 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 CL measurements were performed on a modified Mp-Micro-S instrument (Horiba Jobin Yvon, Paris, France) attached to the SEM (Hitachi, S3400).

The $Rb_2ZrSi_2O_7$'s 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 indirect bandgap.

The decay curves were fitted by a second-order exponential decay curve using the following biexponential equation:

$$I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (3)$$

where I is the luminescence intensity, A1 and A2 are fitting constants, t is the time, and t1 and t2 are short and long lifetimes for exponential components, respectively. Therefore, the average lifetime was obtained by the formula as follows:

$$\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2) \quad (4)$$

According to the report of Van Uiter and Dexter, the emission intensity per activators can be expressed by the following equation:

$$I/x = K[1+\beta(x)^{\theta/3}]^{-1} \quad (5)$$

where I/x is the emission intensity of per ions, K and β are constants for the same

excitation condition for RZSO, where θ = 6, 8 and 10 correspond to dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions, respectively.

Tabla S1 Phase data of $Rb_2ZrSi_2O_7$

Formula sum: $Rb_2ZrSi_2O_7$
Formula weight: 430.32 g/mol
Crystal system: monoclinic
Space-group: P 1 1 21/b (14)
Cell parameters: a=9.7156(15) Å b=14.3237(20) Å c=5.6093(6) Å γ=116.885(9)°
Cell ratio: a/b=0.6783 b/c=2.5536 c/a=0.5773
Cell volume: 696.24(10) $Å^3$
Z: 4
Calc. density 4.10504 g/cm^3
Pearson code: mP48
Formula type: NO2P2Q7
Wyckoff sequence: e12

Table S2 Atomic parameters of $Rb_2ZrSi_2O_7$

Atom	Wyck.	x/a	y/b	z/c	U [$Å^2$]
Rb1	4e	0.03580	0.42890	0.26500	0.0095
Rb2	4e	0.47190	0.59180	0.26130	0.0707
Zr1	4e	0.24100	0.24190	0.25710	0.0229
Si1	4e	0.17980	0.37140	0.74740	-0.0073
Si2	4e	0.33230	0.11050	0.73850	-0.0102
O1	4e	0.00400	0.66100	0.26400	0.2851
O2	4e	0.30670	0.51000	0.78100	-0.0054
O3	4e	0.48100	0.32100	0.23100	-0.0729
O4	4e	0.22100	0.32100	0.46100	0.0663
O5	4e	0.19100	0.31020	0.92550	-0.0628
O6	4e	0.25100	0.10950	0.00910	-0.0610
O7	4e	0.26100	0.14300	0.53600	-0.0899

Table S3 Bond length data of Rb-O

type	bond length (Å)	type	bond length (Å)
Rb1-O1	3.1878(3)	Rb2-O2	3.0833(3)
Rb1-O1	2.8875(3)	Rb2-O2	3.1058(4)
Rb1-O4	3.0578(4)	Rb2-O3	2.9796(3)
Rb1-O6	2.7888(4)	Rb2-O3	3.0566(3)
Rb1-O6	2.9250(4)	Rb2-O4	3.0852(4)
Rb1-O7	2.8879(4)	Rb2-O5	3.1043(5)
-	-	Rb2-O6	2.6117(3)
-	-	Rb2-O7	2.9793(3)
Average	2.9558	Average	3.0007

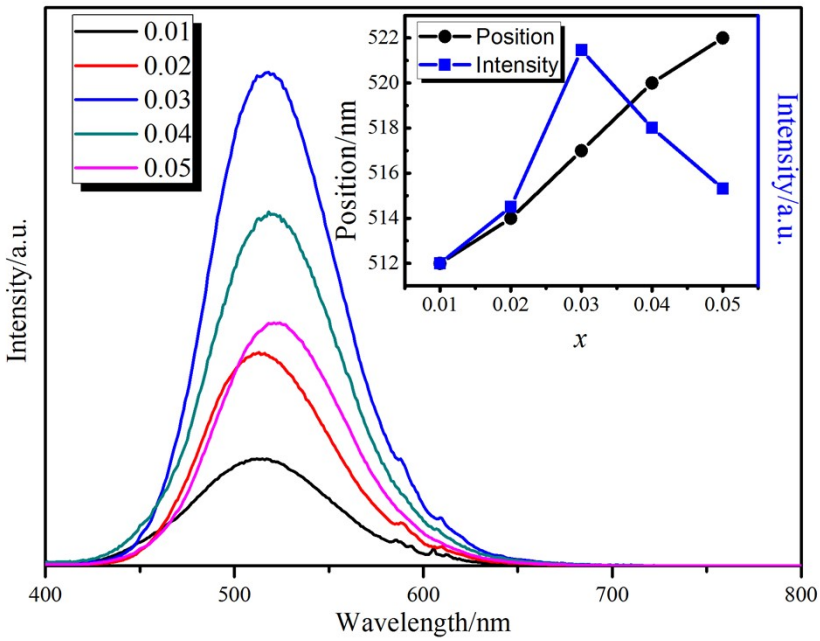

Fig. S1 emission spectra of $Rb_2ZrSi_2O_7$:$x$$Eu^{2+}$ (x=0.01-0.05)

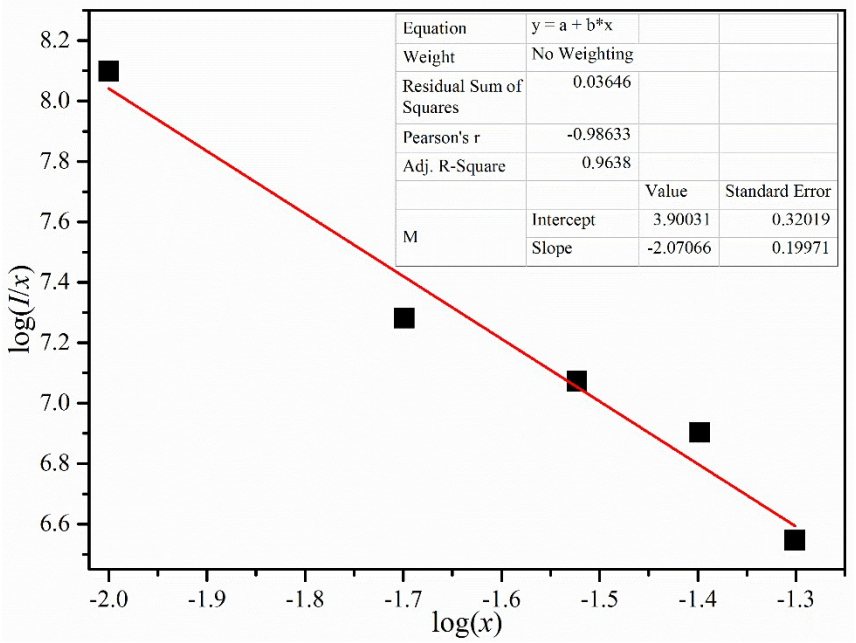

Fig. 2 Relationship of log(I/x) and log(x)

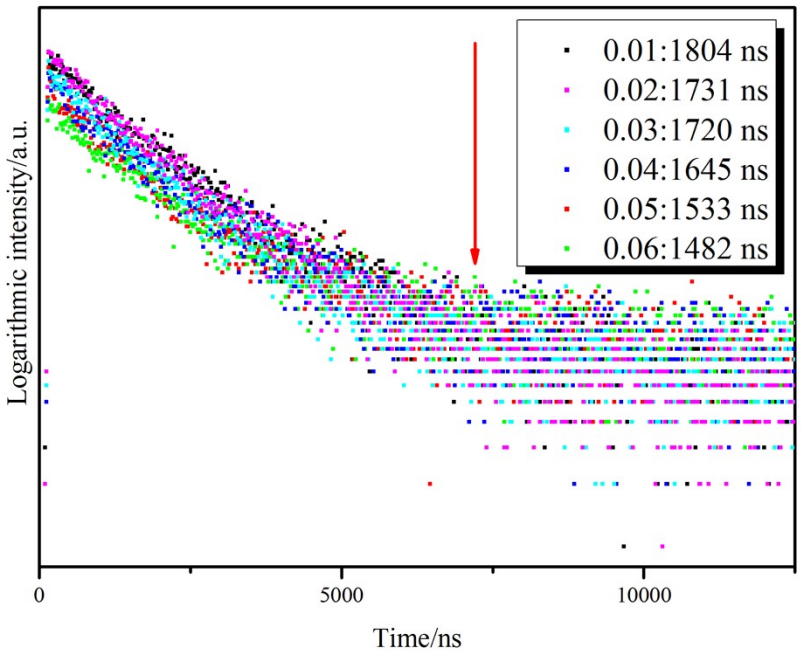

Fig. S3 Decay curves of $Rb_2ZrSi_2O_7$:$x$$Eu^{2+}$ (x=0.01-0.06)

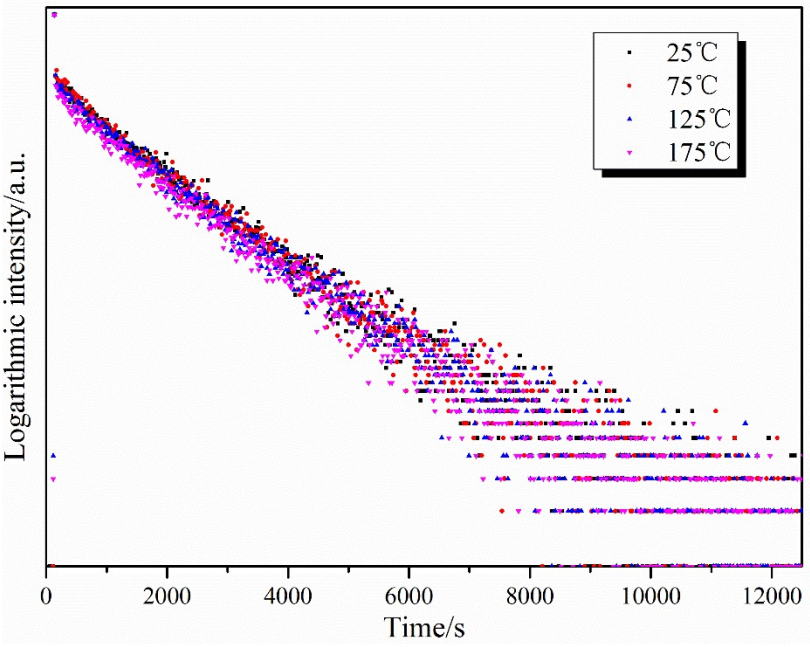

Fig. S4 Temperature-dependent decay curves of $Rb_2ZrSi_2O_7$:0.03Eu^{2+}