Supporting Information Available

Breakdown of the geometry restriction of crystallographic site on the valence state of Eu in $CaGdAlO_4$: realization of white emission from Eu singly-doped phosphors

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Experimental Section

Materials: Gd_2O_3, Eu_2O_3 (99.999%) was purchased from Science and Technology Parent Company of Changchun Institute of Applied Chemistry. Al_2O_3 and SiO_2 and $CaCO_3$ were purchased from Sigma-Aldrich.

Preparation: $Ca_{0.99+x}Gd_{1-x}Al_{1-x}Si_xO_4$: $Eu_{0.01}$ (x = 0-0.25) powder samples were prepared by conventional high temperature solid state reaction process. Firstly, the stoichiometric amount of raw materials was thoroughly mixed by grinding in an agate mortar for 45 min for a good mixing. The mixture was then transferred into crucibles and calcined at 1200 ^oC for 6 h under a reducing atmosphere of N_2 (90%) and H_2 (10%). After that, the sample was reground in a mortar followed by sintering under a reducing atmosphere of N_2 (90%) and H_2 (10%) at 1500-1600 ^oC for 6 h, yielding the resulting samples. The material of the crucible is alumina.

Characterization: The X-ray diffraction (XRD) measurements were performed on a D8 Focus diffractometer in the 2θ range from 20° to 100° operating at 40 kV and 40 mA with graphite-monochromatized Cu $K\alpha$ radiation (λ = 0.15405 nm). The Rietveld analysis of the XRD was done using the General Structure Analysis System (GSAS) program. Raman spectrum was collected using a micro-Raman spectrometer with a laser of 532 nm wavelength. The photoluminescence (PL) measurements were recorded with a Hitachi F-7000 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. Photoluminescence absolute quantum yields (QY) were measured by an absolute PL quantum yield measurement system (C9920-02, Hamamatsu Photonics K. K., Japan). Time-resolved photoluminescence spectra and luminescence decay curves were obtained from a Lecroy Wave Runner 6100 Digital Oscilloscope (1GHz) (pulse width = 4 ns, gate = 50 ns) as the excitation source (Continuum Sunlite OPO). All the measurements were performed at room temperature (RT).

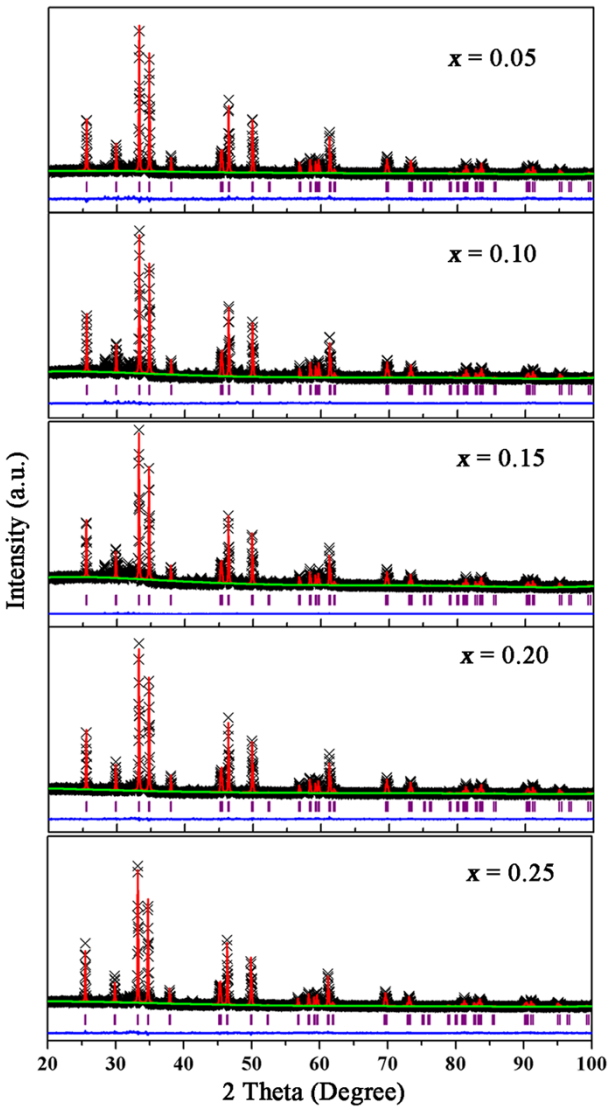

Fig. S1 The Rietveld refinement to XRD patterns for $Ca_{0.99+x}Gd_{1-x}Al_{1-x}Si_xO_4$: $Eu_{0.01}$ (x = 0.05-0.25), respectively.

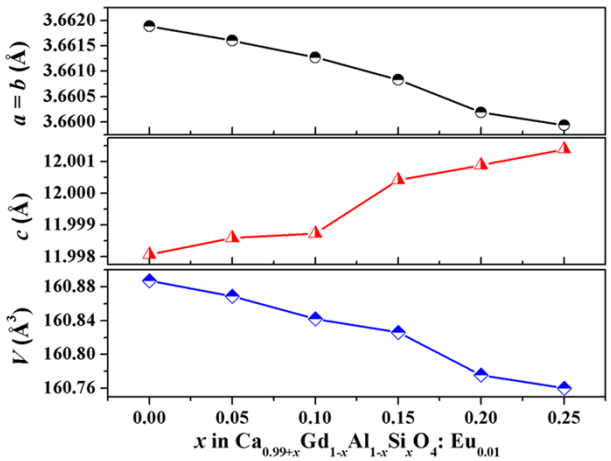

Fig. S2 Unit cell parameters of $Ca_{0.99+x}Gd_{1-x}Al_{1-x}Si_xO_4$: $Eu_{0.01}$ (x = 0-0.25) obtained from Rietveld refinement, reflecting the effects of the Si^{4+}-Ca^{2+} incorporation.

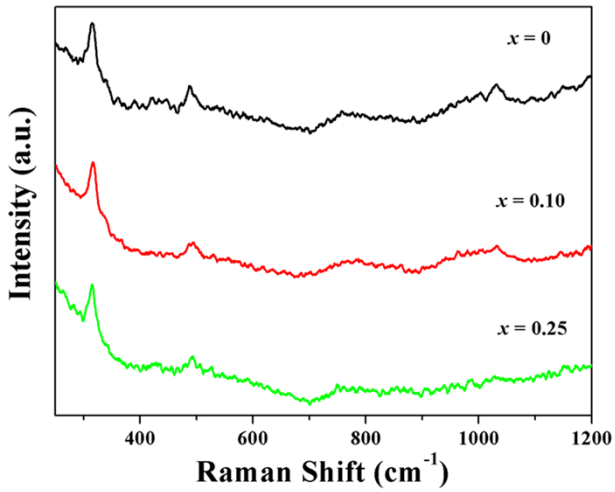

Fig. S3 The Raman spectra of $Ca_{0.99+x}Gd_{1-x}Al_{1-x}Si_xO_4$: $Eu_{0.01}$ (x = 0, 0.10 and 0.25) samples.

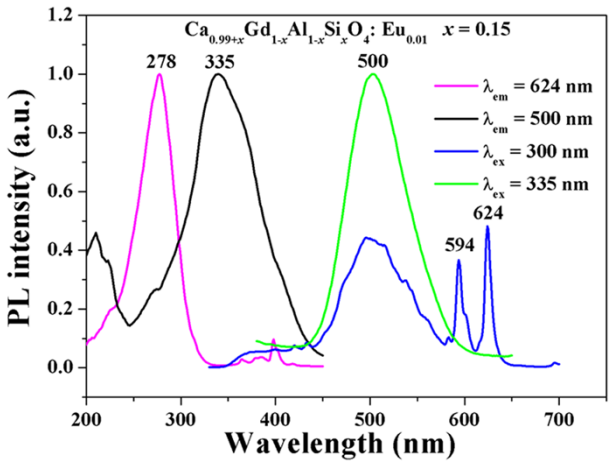

Fig. S4 The PLE and PL spectra $Ca_{0.99+x}Gd_{1-x}Al_{1-x}Si_xO_4$: $Eu_{0.01}$ (x = 0.15) sample.

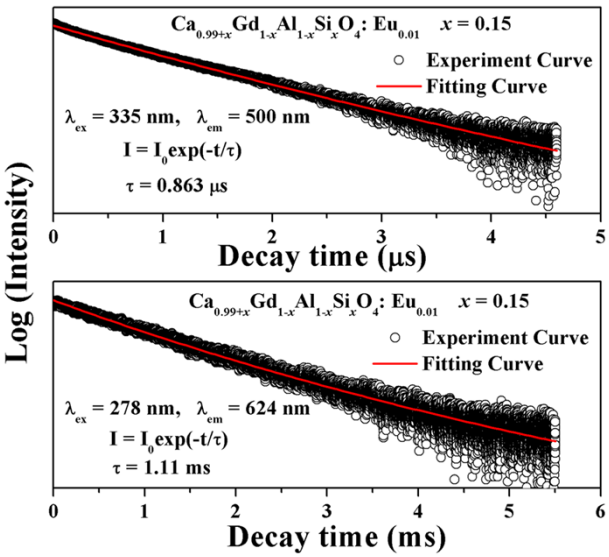

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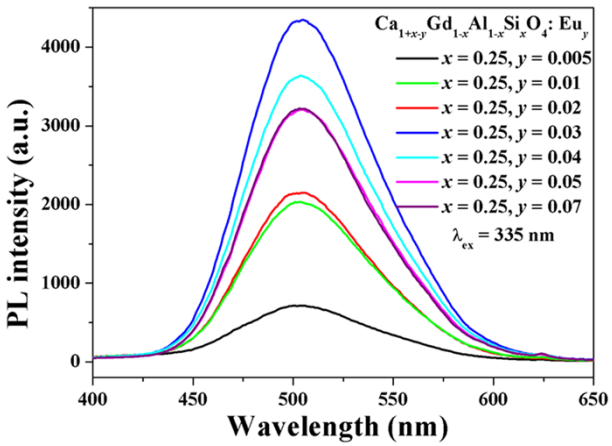
Fig. S5 Decay curves of (a) Eu^{2+}: λ_{ex} = 335 nm, λ_{em} = 500 nm; (b) Eu^{3+}: λ_{ex} = 278 nm, λ_{em} = 624 nm of $Ca_{0.99+x}Gd_{1-x}Al_{1-x}Si_xO_4$: $Eu_{0.01}$ (x = 0.15) sample.



5 **Fig. S6** The influence of doping concentration of Eu ions on the emission intensity of the obtained $Ca_{1+x-y}Gd_{1-x}Al_{1-x}Si_xO_4$: Eu_y (x = 0.25, y = 0.005-0.07) phosphors, λ_{ex} = 335 nm.

Table S1. Crystallographic data of $CaGdAlO_4$: $0.01Eu^{3+}$, as determined by the Rietveld refinement of power XRD data at room temperature.

atom	site	*x*	*y*	*z*	Occupancy
Ca1	4*e*	0.0000	0.0000	0.3591	0.495
Gd1	4*e*	0.0000	0.0000	0.3591	0.500
Al1	2*a*	0.0000	0.0000	0.0000	1.000
O1	4*c*	0.0000	0.5000	0.0000	1.000
O2	4*e*	0.0000	0.0000	0.1693	1.000
Eu1	4*e*	0.0000	0.0000	0.3591	0.005

Tetragonal crystal system, space group: *I*4/*mmm* (No. 139), $Z = 2$, $a = b = 3.66189$ Å, $c = 11.99807$ Å, $V = 160.89$ Å^3, $\alpha = \beta = \gamma = 90°$， $R_p = 2.34\%$, $R_{wp} = 3.29\%$.

Table S2. Crystallographic data and reliability factor of $Ca_{0.99+x}Gd_{1-x}Al_{1-x}Si_xO_4$: $Eu_{0.01}$ (x = 0.05-0.25) samples.

x	x = 0.05	x = 0.10	x = 0.15	x = 0.20	x = 0.25
$a = b$ (Å)	3.6616	3.66127	3.66083	3.66019	3.65994
c (Å)	11.99859	11.99873	12.00043	12.00089	12.00139
V (Å^3)	160.87	160.84	160.83	160.78	160.76
R_p	2.19%	2.71%	2.78%	2.18%	2.38%
R_{wp}	2.98%	3.87%	4.00%	2.94%	3.31%

5

Table S3. Luminescence properties of $Ca_{0.99+x}Gd_{1-x}Al_{1-x}Si_xO_4$: $Eu_{0.01}$ (x = 0-0.25) samples.

x	$\tau(Eu^{3+}$, ms)	$\tau(Eu^{2+}$, μs)	QY (%) λ_{ex} = 300 nm	QY (%) λ_{ex} = 335 nm	I_{02}/I_{01} ratios (Eu^{3+})
0	1.11	--	12.0	--	1.26
0.05	1.11	0.678	13.4	20.2	1.22
0.10	1.10	0.734	15.8	24.6	1.18
0.15	1.11	0.863	19.7	28.7	1.16
0.20	1.11	0.737	20.2	31.5	1.17
0.25	1.12	0.686	22.0	35.7	1.15