Constructing Sensitive Luminescent Thermometers via Energy Transfer in Ce^{3+} and Eu^{2+} Co-Doped $Ca_8Mg_3Al_2Si_7O_{28}$ Phosphors

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Part A. The details of samples preparations and characterizations

Preparation. The analytic reagents $CaCO_3$, MgO, Al_2O_3, SiO_2, Na_2CO_3 and 99.99% pure rare-earth oxides CeO_2 and Eu_2O_3 were used as starting materials and weighed with the nominal formulas $Ca_{8-2x-y}Ce_xNa_xEu_yMg_3Al_2Si_7O_{28}$ for Ce^{3+} and Eu^{2+} doped samples. The mixtures were ground thoroughly in an agate mortar, and then moved to alumina crucibles. Ce^{3+} and Eu^{2+} doped $Ca_8Mg_3Al_2Si_7O_{28}$ samples were pre-fired at 973 K in air atmosphere for 4 h, and annealed at 1593 K for 6 h in CO ambience which was produced from the incomplete combustion of carbon at high temperature. Eu^{3+} doped $Ca_8Mg_3Al_2Si_7O_{28}$ sample were weighed with nominal formulas $Ca_{7.98}Eu_{0.01}Na_{0.01}Mg_3Al_2Si_7O_{28}$, and annealed in air atmosphere in the whole preparation. After cooling down to room temperature, the final products were ground into powders for subsequent analyses.

Characterizations. The phase purity of the synthetic samples was estimated by powder X-ray diffraction (P-XRD) on a Rigaku D-MAX 2200 VPC X-ray diffractometer of Cu Kα (λ = 1.5418 Å) radiation at 40 kV and 26 mA. The P-XRD data for refinement was collected with the 2θ range from 5° to 110° and 2θ step of 0.02° on a Bruker D8 advanced X-ray diffractometer with a wavelength of 1.54056 Å Cu Kα radiation at 40 kV and 40 mA. Temperature-dependent P-XRD data were also recorded on the Bruker D8 advanced X-ray diffractometer. The Rietveld refinement is performed using the TOPAS - Academic program.[1] The Raman spectra of 77−500 K were measured on an inVia Qontor confocal microscopic Raman spectrometer under the laser excitation of 532 nm. The exact Ce/Eu contents in samples were measured on an Agilent ICP-OES 730. The photoluminescence quantum yields (PLQYs) were recorded by integrated sphere, which was attached in the FLS1000 spectrofluorometer.

The excitation and emission spectra in the VUV-UV range were recorded on the 4B8 beamline of the Beijing Synchrotron Radiation Facility (BSRF).[2] The UV-vis excitation and emission spectra as well as the luminescence decay curves at room temperature (RT) were recorded on an Edinburgh FLS 1000 model spectrometer which was a combined fluorescence lifetime and steady-state, equipped with a cooled housing (-20 ^{o}C) photomultiplier PMT-900. The 450 W Xenon lamp was used as the excitation source of steady-state excitation and emission spectra. A 150 W nF900 lamp with a pulse width of 1 ns and pulse repetition rate of 40 kHz was used for the measurements of decay curves. The temperature-dependent spectral measurements in the 77−500 K range were performed by mounting the samples in an Oxford cryostat. The emission spectra of 20−450 K were measured in an Edinburgh FLS 920 model spectrometer and an Oxford cryostat with a closed cycle liquid helium apparatus.

References

1 A. A. Coelho. TOPAS Academic, Ver. 4; Coelho Software: 666 Brisbane, Australia, 2007.

2 Y. Tao, Y. Huang, Z. Gao, H. Zhuang, A. Zhou, Y. Tan, D. Li, S. Sun. Developing VUV Spectroscopy for Protein Folding and Material Luminescence on Beamline 4B8 at the Beijing Synchrotron Radiation Facility. *J. Synchrot. Radiat*. 2009, **16**, 857-863.

Part B. Tables and Figures

Table S1. Final Refined Structural Parameters of $Ca_8Mg_3Al_2Si_7O_{28}$ Host [h].

Atom	Site	x	y	z	Occ.	B_{iso}
Ca	4e	0.3382	0.1618	0.5094	1	1.43(5)
Al1	2a	0	0	0	0.25	0.90(9)
Mg	2a	0	0	0	0.75	0.90(9)
Al2	4e	0.1413	0.3587	0.9620	0.125	1.50(0)
Si	4e	0.1413	0.3587	0.9620	0.875	1.50(0)
O1	2c	1/2	0	0.1602	1	1.31(3)
O2	4e	0.1419	0.3581	0.2735	1	1.49(9)
O3	8f	0.0839	0.1711	0.8221	1	1.65(7)

[h] $Ca_8Mg_3Al_2Si_7O_{28}$ belongs to tetragonal symmetry with space group $P\bar{4}2_1m$ (113) and lattice parameters $a = b = 7.7773(6)$ Å, $c = 5.0159(4)$ Å, $Z = 1$, $V = 303.39(4)$ Å^3.

Table S2. CIE Chromaticity Coordinates (X, Y) of Emission Spectra (λ_{ex} = 340 nm; RT) of $Ca_{7.98-y}Ce_{0.01}Na_{0.01}Eu_yMg_3Al_2Si_7O_{28}$ (y = 0−0.09) Samples.

Concentration (y)	Chromaticity Coordinates (X, Y)
0	(0.157, 0.049)
0.01	(0.271, 0.365)
0.03	(0.333, 0.528)
0.05	(0.349, 0.565)
0.07	(0.358, 0.578)
0.09	(0.359, 0.578)

Table S3. The Detected Content of Ce and Eu in $Ca_{7.98-y}Ce_{0.01}Na_{0.01}Eu_yMg_3Al_2Si_7O_{28}$ (y = 0.03, 0.05, and 0.09) Samples [i].

Sample	$n(Ce^{3+})$ (mg/ Kg)	$n(Eu^{2+})$ (mg/ Kg)
$Ca_{7.97}Ce_{0.01}Na_{0.01}Eu_{0.01}Mg_3Al_2Si_7O_{28}$	1512.8	1882.9
$Ca_{7.95}Ce_{0.01}Na_{0.01}Eu_{0.03}Mg_3Al_2Si_7O_{28}$	1835.0	4193.0
$Ca_{7.93}Ce_{0.01}Na_{0.01}Eu_{0.05}Mg_3Al_2Si_7O_{28}$	1506.6	6743.7
$Ca_{7.91}Ce_{0.01}Na_{0.01}Eu_{0.07}Mg_3Al_2Si_7O_{28}$	1892.1	10159.5
$Ca_{7.89}Ce_{0.01}Na_{0.01}Eu_{0.09}Mg_3Al_2Si_7O_{28}$	2023.0	12545.8

[i] The density of Ca_8 $Mg_3Al_2Si_7O_{28}$ is 2.9885 g/cm^{-3}.

Table S4. Fitting Parameters via Inokuti-Hirayama Model for $Ca_{7.98-y}Ce_{0.01}Na_{0.01}Eu_yMg_3Al_2Si_7O_{28}$ (y = 0.03, 0.05, 0.07 and 0.09) Samples.

y	n_a (m^{-3})	C_{DA} (m^6/s)	R_{adj}^2
0.03	9.35×10^{24}	3.59×10^{-45}	99.4%
0.05	1.67×10^{25}	4.16×10^{-45}	99.1%
0.07	2.54×10^{25}	3.97×10^{-45}	98.1%
0.09	3.92×10^{25}	4.08×10^{-45}	97.7%

Table S5. Fitting Parameters via Yokota-Tanimoto Model for $Ca_{7.98-y}Ce_{0.01}Na_{0.01}Eu_yMg_3Al_2Si_7O_{28}$ (y = 0.03, 0.05, and 0.09) Samples.

y	n_a (m^{-3})	C_{DA} (m^6/s)	C_{DD} (m^6/s)	D	R_{adj}^2
0.03	9.39×10^{24}	3.46×10^{-46}	6.15×10^{-47}	5.53×10^{-21}	99.5%
0.05	1.61×10^{25}	4.80×10^{-46}	6.21×10^{-47}	5.58×10^{-21}	99.2%
0.09	4.10×10^{25}	4.23×10^{-46}	6.27×10^{-47}	5.64×10^{-21}	98.1%

Table S6. Lifetime of Ce^{3+} and Energy Transfer Efficiency (η) from Ce^{3+} to Eu^{2+} in $Ca_{7.98-y}Ce_{0.01}Na_{0.01}Eu_yMg_3Al_2Si_7O_{28}$ Samples at RT.

y	$\tau(Ce^{3+})$ (ns)	η (%)[j]
0.01	30.1	6.42
0.03	23.6	26.6

0.05	18.3	43.2
0.07	15.1	53.2
0.09	13.8	57.1

[j] $\eta = 100◊(1-\tau(Ce^{3+})/\tau_0)$, where τ_0 is the lifetime of isolated Ce^{3+} in $Ca_8Mg_3Al_2Si_7O_{28}$, and is about 32.2 ns.

Table S7. CIE Chromaticity Coordinates (X, Y) of Emission Spectra (λ_{ex} = 320 nm) of $Ca_{7.97}Ce_{0.01}Na_{0.01}Eu_{0.01}Mg_3Al_2Si_7O_{28}$ Samples at 77−500 K.

Temperature (K)	Chromaticity Coordinates (X, Y)	Temperature (K)	Chromaticity Coordinates (X, Y)
77	(0.368, 0.532)	300	(0.336, 0.507)
100	(0.367, 0.531)	325	(0.329, 0.497)
125	(0.365, 0.531)	350	(0.321, 0.482)
150	(0.363, 0.531)	375	(0.312, 0.466)
175	(0.360, 0.529)	400	(0.304, 0.447)
200	(0.355, 0.526)	425	(0.295, 0.426)
225	(0.350, 0.522)	450	(0.284, 0.399)
250	(0.346, 0.519)	475	(0.275, 0.365)
275	(0.341, 0.513)	500	(0.260, 0.331)

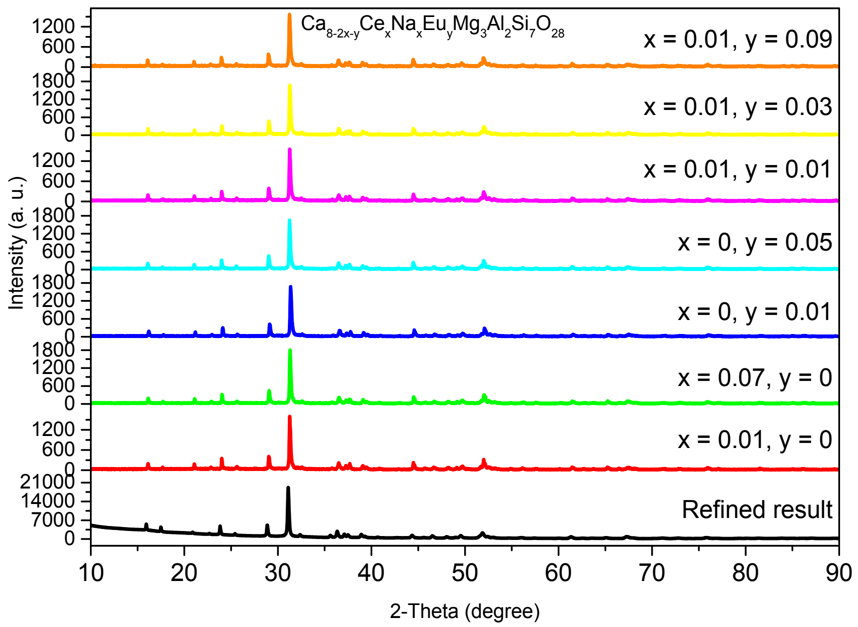


Fig. S1 Representative P-XRD patterns of $Ca_{8-2x-y}Ce_xNa_xEu_yMg_3Al_2Si_7O_{28}$ (x = 0, 0.01 and 0.07; y = 0−0.09) samples and corresponding refined result.

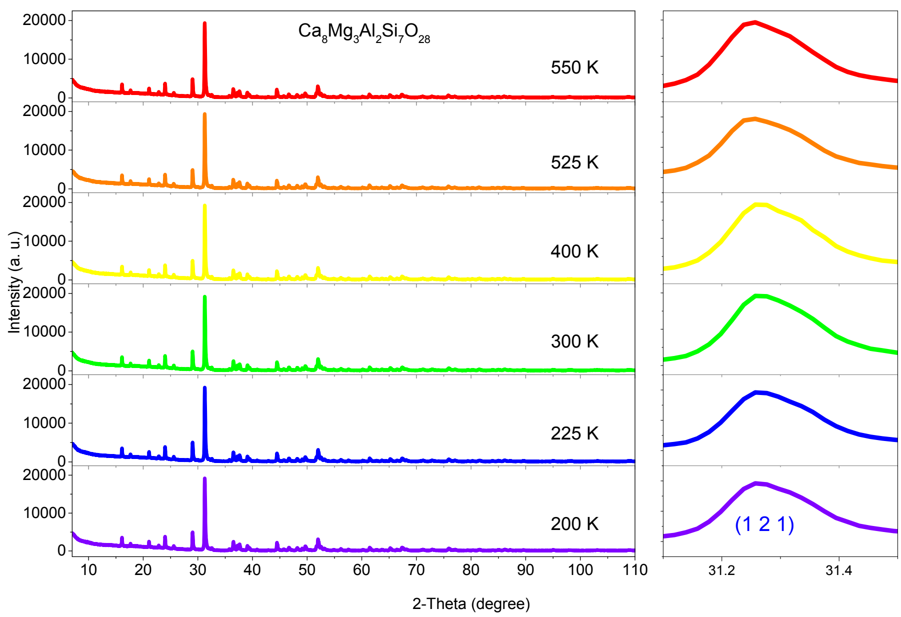


Fig. S2 Temperature-dependent P-XRD data of synthesized $Ca_8Mg_3Al_2Si_7O_{28}$ sample and magnified P-XRD patterns of 31.1−31.5° (2-theta) range.

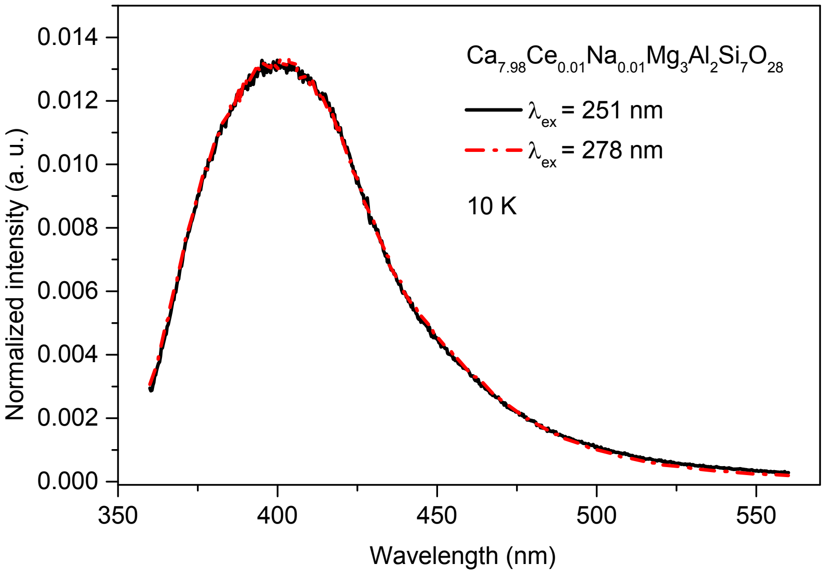


Fig. S3 Normalized synchrotron radiation emission (λ_{ex} = 251 and 278 nm; 10 K) spectra of $Ca_{7.98}Ce_{0.01}Na_{0.01}Mg_3Al_2Si_7O_{28}$ sample.

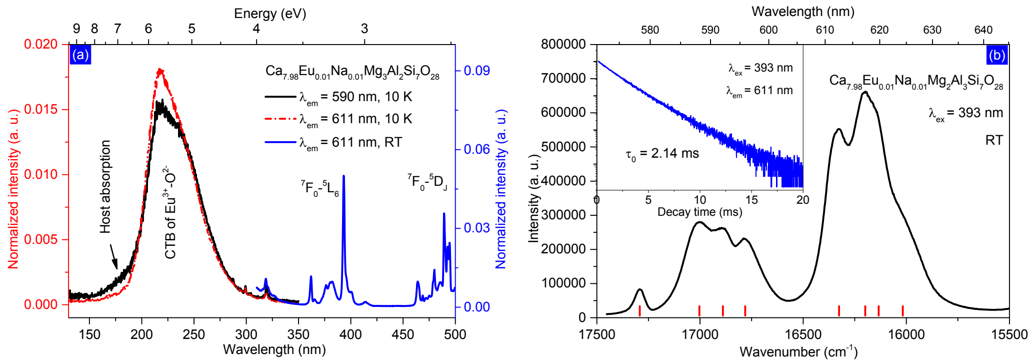


Fig. S4 (a) Normalized synchrotron radiation VUV-UV excitation (λ_{em} = 590 and 611 nm; 10 K) and normalized lab UV-vis excitation (λ_{em} = 611 nm; RT) spectra of $Ca_{7.98}Eu_{0.01}Na_{0.01}Mg_3Al_2Si_7O_{28}$ sample; (b) emission spectrum (λ_{ex} = 393 nm; RT) of $Ca_{7.98}Eu_{0.01}Na_{0.01}Mg_3Al_2Si_7O_{28}$ sample; the inset shows decay curve (λ_{ex} = 393 nm, λ_{em} = 611 nm; RT) of $Ca_{7.98}Eu_{0.01}Na_{0.01}Mg_3Al_2Si_7O_{28}$ sample.

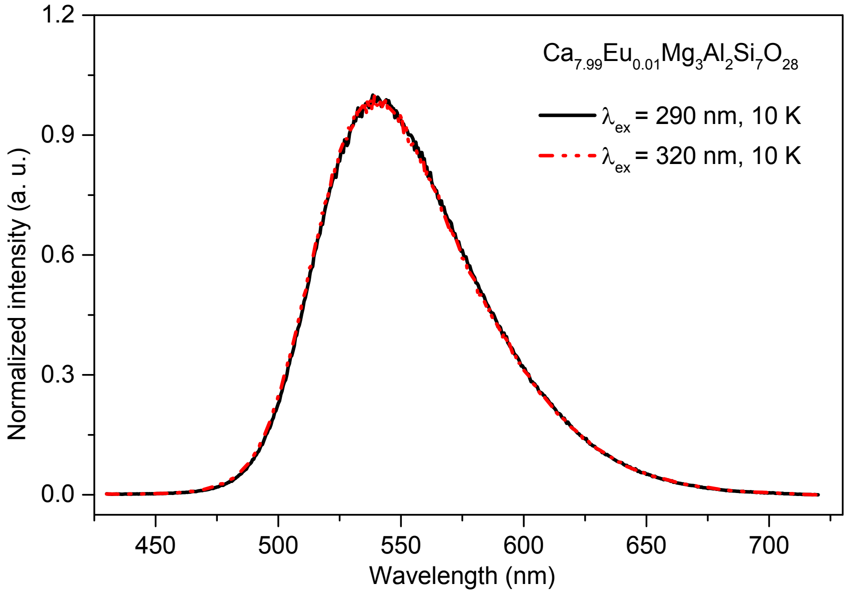


Fig. S5 Highest-height normalized emission (λ_{ex} = 290 and 320 nm; 10 K) spectra of $Ca_{7.99}Eu_{0.01}Mg_3Al_2Si_7O_{28}$ sample under the excitation of synchrotron radiation VUV-UV beamline.

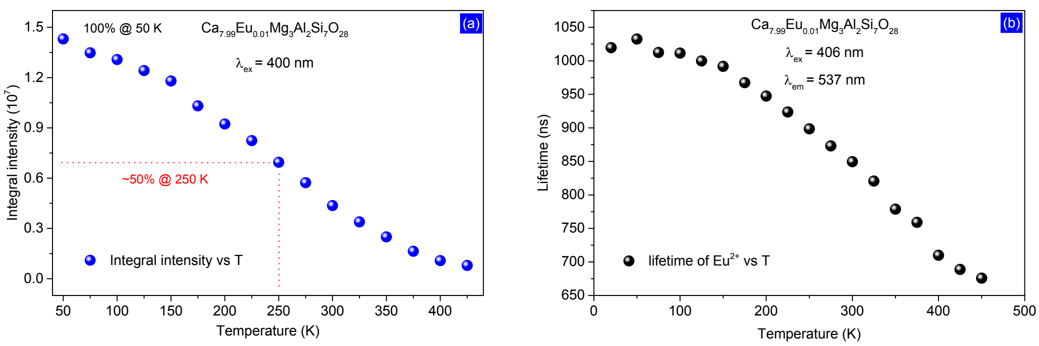


Fig. S6 Integral intensity (a, λ_{ex} = 400 nm) and lifetime (b, λ_{ex} = 406 nm, λ_{em} = 537 nm) of Eu^{2+} emission as a function of temperature in $Ca_{7.99}Eu_{0.01}Mg_3Al_2Si_7O_{28}$ sample.

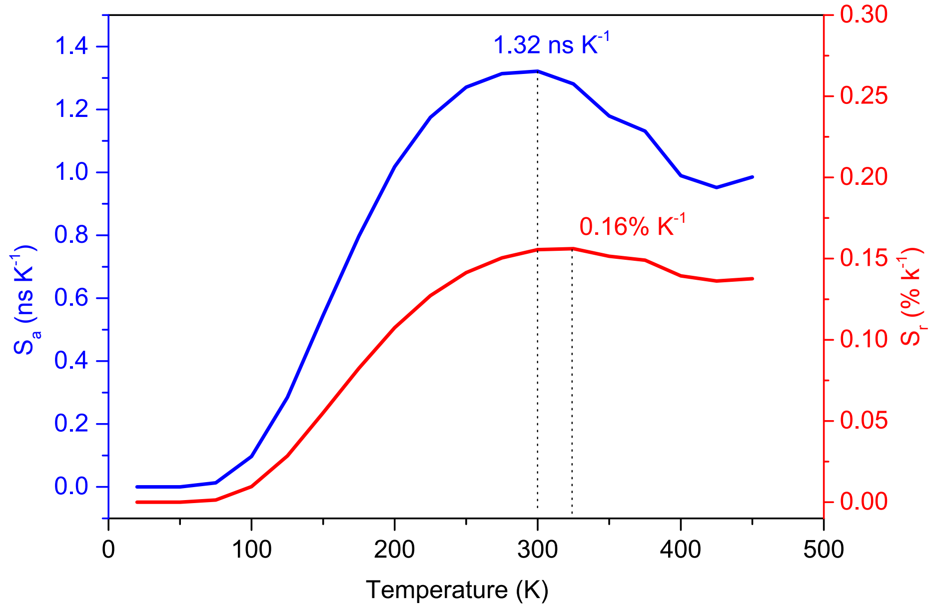
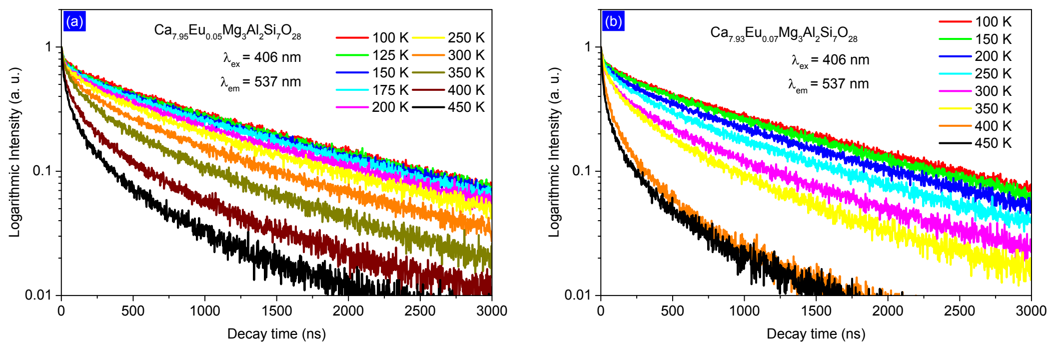


Fig. S7 Temperature sensitivities S_a and S_r values of phosphor $Ca_{7.99}Eu_{0.01}Mg_3Al_2Si_7O_{28}$ in the temperature range of 50−450 K.

$$S_a = \left|\frac{\partial(\tau)}{\partial(T)}\right| = \frac{E_a}{k_BT^2}\tau^2k_1\exp\left(\frac{-E_a}{k_BT}\right) \tag{S1}$$

$$S_r = \left|\frac{\partial(\tau)}{\tau\partial(T)}\right| \times 100\% = \frac{E_a}{k_BT^2}\tau k_1\exp\left(\frac{-E_a}{k_BT}\right) \times 100\% \tag{S2}$$



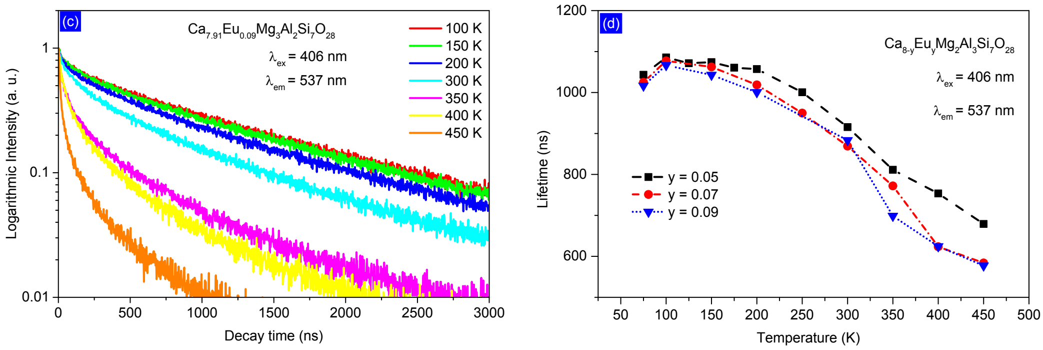


Fig. S8 (a, b, c) Temperature-dependent decay curves (λ_{ex} = 406 nm, λ_{em} = 537 nm) of $Ca_{8-y}Eu_yMg_3Al_2Si_7O_{28}$ (a, y = 0.05; b, y = 0.07; c, y = 0.09) samples at 100−450 K; (d) temperature-dependent lifetime of Eu^{2+} in $Ca_{8-y}Eu_yMg_3Al_2Si_7O_{28}$ samples.

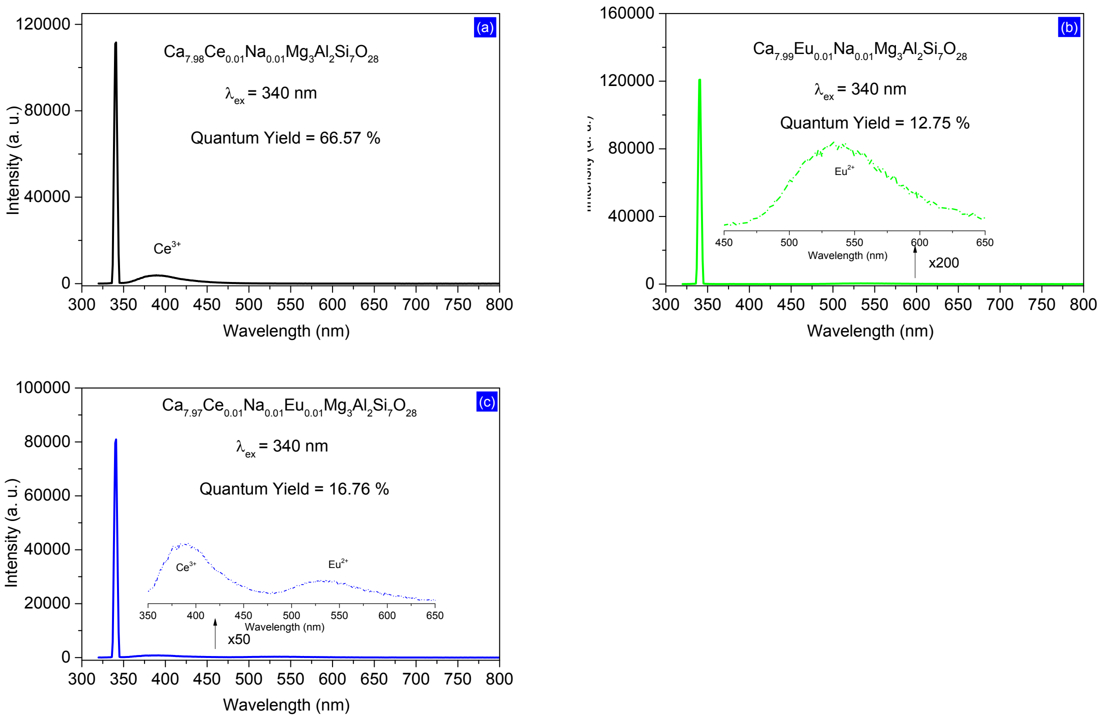


Fig. S9 Emission spectra of $Ca_{7.98}Ce_{0.01}Na_{0.01}Mg_3Al_2Si_7O_{28}$ (a), $Ca_{7.99}Eu_{0.01}Mg_3Al_2Si_7O_{28}$ (b), and $Ca_{7.97}Ce_{0.01}Na_{0.01}Eu_{0.01}Mg_3Al_2Si_7O_{28}$ (c) samples under the excitation at 340 nm in the integrated sphere.

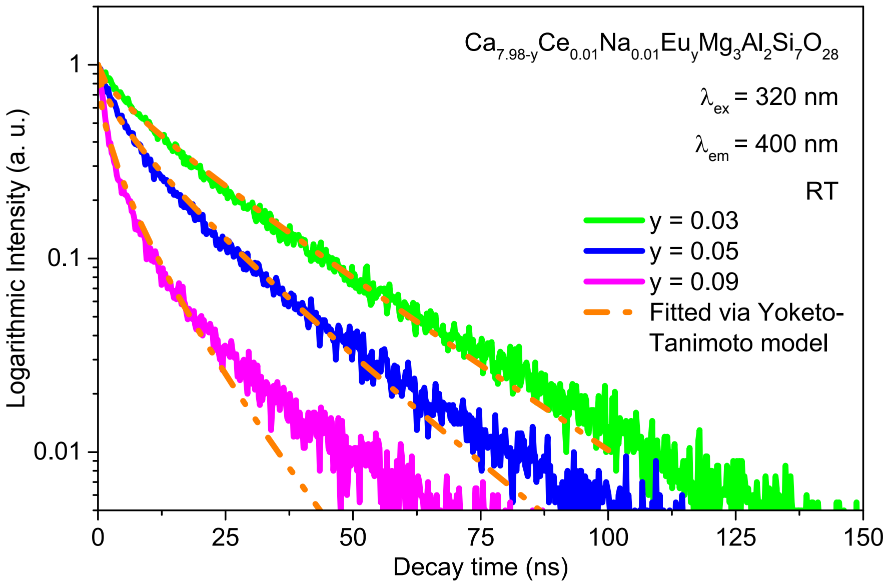


Fig. S10 Decay curves (λ_{ex} = 320 nm, λ_{em} = 400 nm; RT) of $Ca_{7.98-y}Ce_{0.01}Na_{0.01}Eu_yMg_3Al_2Si_7O_{28}$ (y = 0.03, 0.05, and 0.09) samples and corresponding fitting results via Yokota-Tanimoto model.

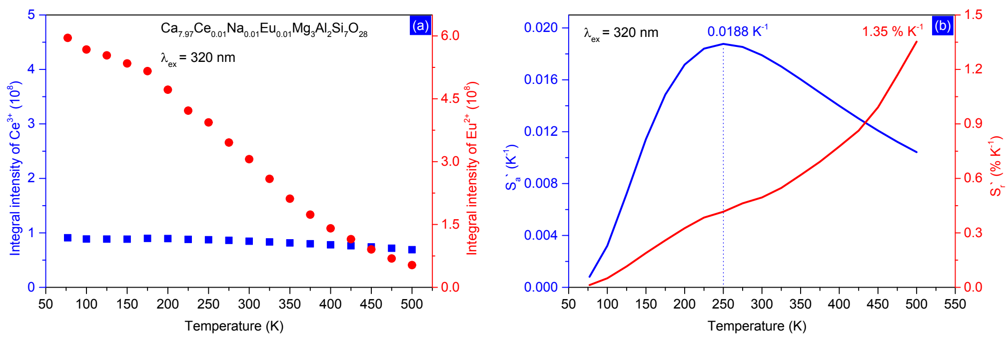


Fig. S11 (a) Integral intensities of Ce^{3+} (350−460 nm) and Eu^{2+} (460−680 nm) in $Ca_{7.97}Ce_{0.01}Na_{0.01}Eu_{0.01}Mg_3Al_2Si_7O_{28}$ at 77−500 K; (b) temperature sensitivities S_a\` and $S_r$\` values of phosphor $Ca_{7.97}Ce_{0.01}Na_{0.01}Eu_{0.01}Mg_3Al_2Si_7O_{28}$ at 77−500 K under the excitation at 320 nm.

$$S_a^{`} = \left|\frac{\partial(FIR)}{\partial(T)}\right| = \frac{D \cdot P \cdot \Delta E}{k_B T^2} \cdot \exp\left(\frac{-\Delta E}{k_B T}\right) \cdot \left[1 + P \cdot \exp\left(\frac{-\Delta E}{k_B T}\right)\right]^{-2}$$

(S3)

$$S_r^{`} = \left| \frac{\partial(FIR)}{FIR\partial(T)} \right| \times 100\% \tag{S4}$$

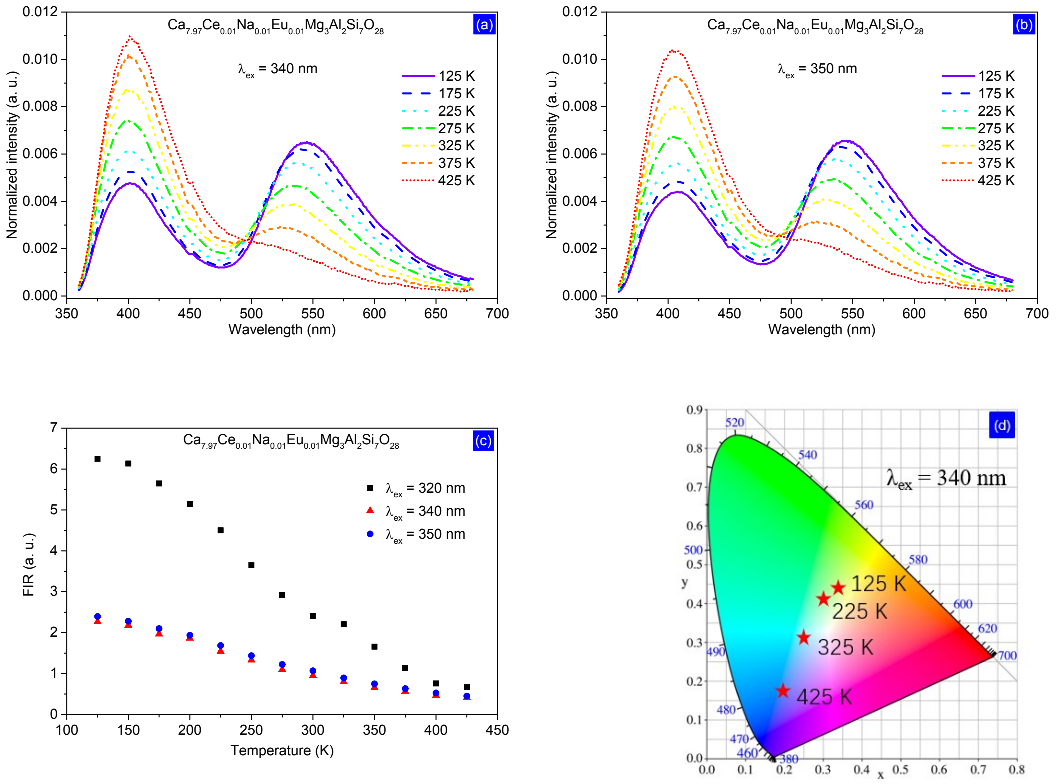


Fig. S12 (a, b) Temperature-dependent normalized emission spectra (a, λ_{ex} = 340 nm; b, λ_{ex} = 350 nm) of $Ca_{7.97}Ce_{0.01}Na_{0.01}Eu_{0.01}Mg_3Al_2Si_7O_{28}$; (c) temperature-dependent FIR values of $Ca_{7.97}Ce_{0.01}Na_{0.01}Eu_{0.01}Mg_3Al_2Si_7O_{28}$ sample with excitations at 320, 340 and 350 nm; (d) CIE chromaticity coordinates (125−425 K) of $Ca_{7.97}Ce_{0.01}Na_{0.01}Eu_{0.01}Mg_3Al_2Si_7O_{28}$ sample with excitation at 340 nm.