

Supporting Information

Structure, Luminescence of Eu^{2+} and Eu^{3+} in $\text{CaMgSi}_2\text{O}_6$ and Their Co-Existence for Excitation-Wavelength / Temperature

Driven Colour Evolution

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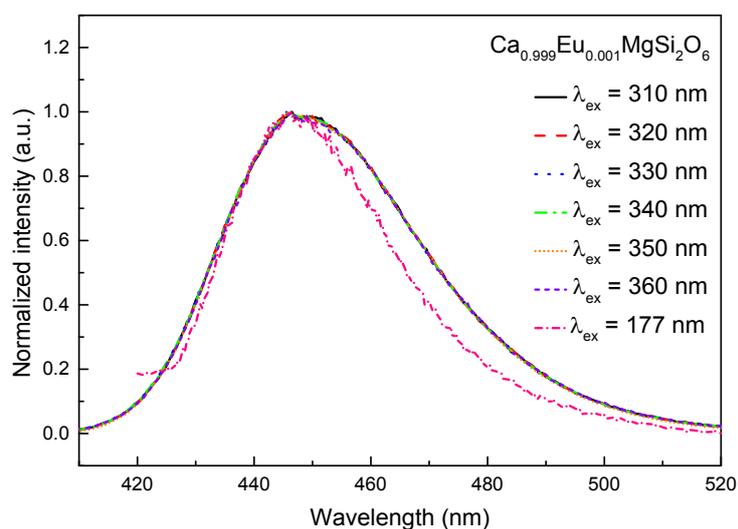


Figure S1. The highest-height normalized emission spectra ($\lambda_{\text{ex}} = 310, 320, 330, 340, 350$ and 360 nm, RT; $\lambda_{\text{ex}} = 177$ nm, 10 K) of $\text{Ca}_{0.999}\text{Eu}_{0.001}\text{MgSi}_2\text{O}_6$.

The emission curve under 177 nm excitation in **Figure S1** is recorded in BSRF at 10 K, and other spectra are recorded at RT using our lab spectrometer Edinburgh FLS 1000. The slight difference is due to the different measurement conditions (facilities and temperature).

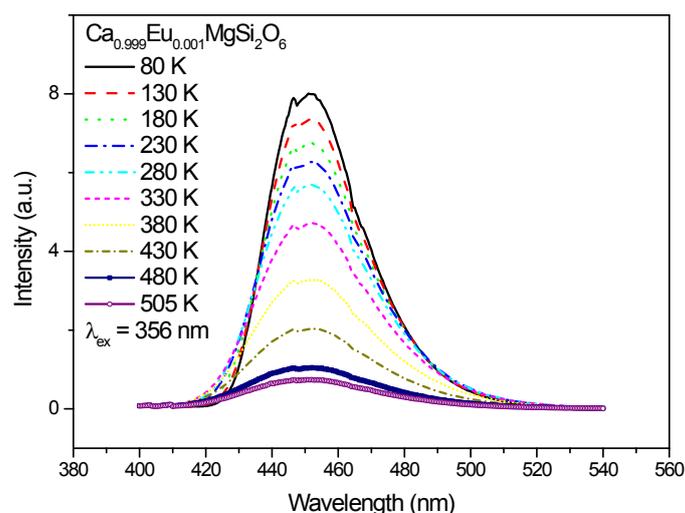


Figure S2. The emission spectra ($\lambda_{\text{ex}} = 356 \text{ nm}$) of the sample $\text{Ca}_{0.999}\text{Eu}_{0.001}\text{MgSi}_2\text{O}_6$ at temperatures from 80 to 505 K.

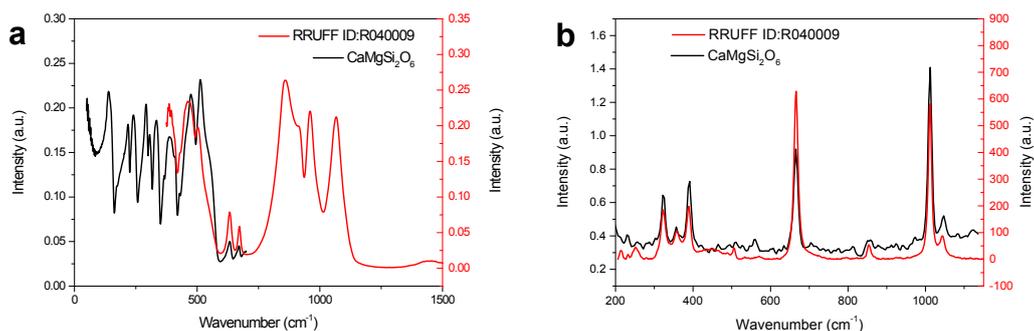


Figure S3. Synchrotron radiation infrared reflectance spectrum, Raman spectrum and the RRUFF standard pattern.

Figure S3 shows the synchrotron radiation infrared reflectance spectrum of $\text{CaMgSi}_2\text{O}_6$ measured at the National Synchrotron Radiation Laboratory, Raman spectrum collected by a Renishaw Via laser micro-Raman spectrometer and the RRUFF standard pattern.

In the infrared reflectance spectra, a series of bands from 50 to 1500 cm^{-1} are shown, which is in good agreement with the standard pattern at 400-700 cm^{-1} . In the Raman spectrum, major bands in $\text{CaMgSi}_2\text{O}_6$ overlap to the bands of RRUFF standard pattern. Bands below 500 cm^{-1} generally ascribed to non-tetrahedral cation and oxygen stretching of Ca-O and Mg-O bands, which is close to the fitted phonon energy (361 cm^{-1}).

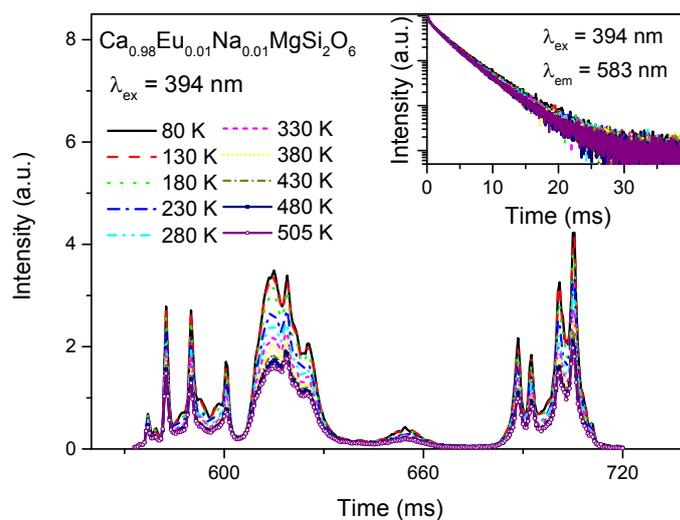


Figure S4. Temperature-dependent emission spectra ($\lambda_{\text{ex}} = 394$ nm) and decay curves ($\lambda_{\text{ex}} = 394$ nm, $\lambda_{\text{em}} = 583$ nm) of $\text{Ca}_{0.98}\text{Eu}_{0.01}\text{Na}_{0.01}\text{MgSi}_2\text{O}_6$ sample in the temperature range of 80-505 K.

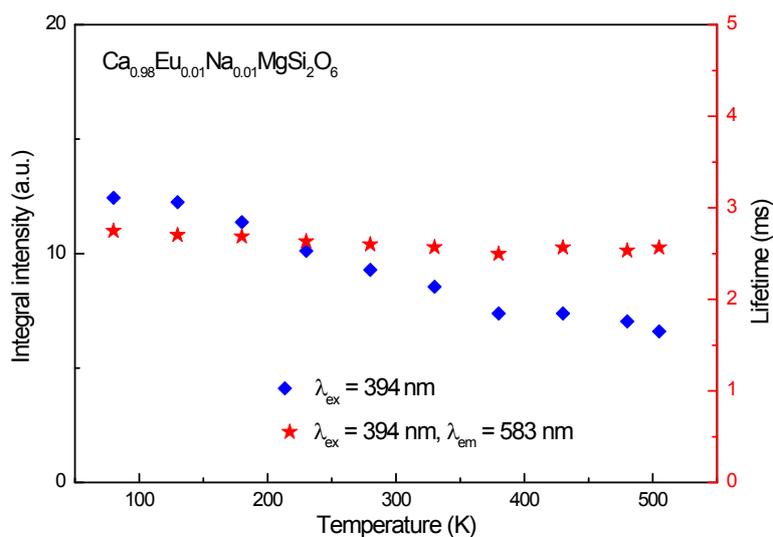


Figure S5. Temperature-dependent emission intensities and lifetime values of Eu^{3+} emissions in the temperature range of 80-505 K.

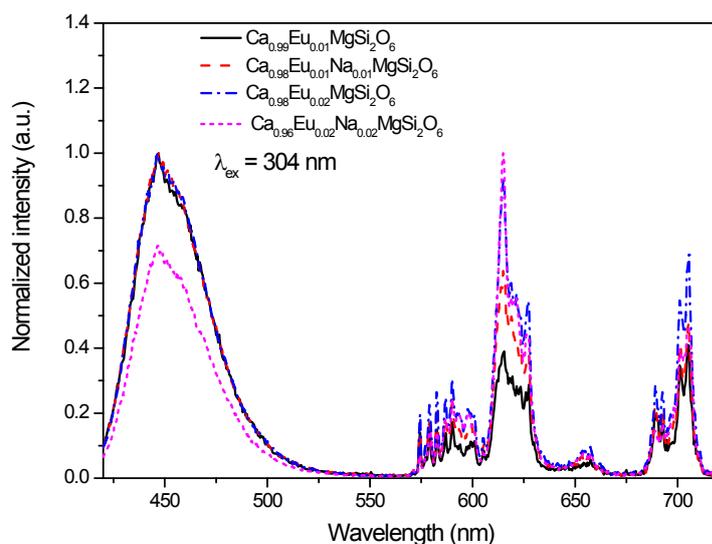


Figure S6. The highest-height normalized emission spectra ($\lambda_{\text{ex}} = 304$ nm, RT) of the samples $\text{Ca}_{1-x}\text{Eu}_x\text{MgSi}_2\text{O}_6$ and $\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MgSi}_2\text{O}_6$ ($x = 0.01, 0.02$).

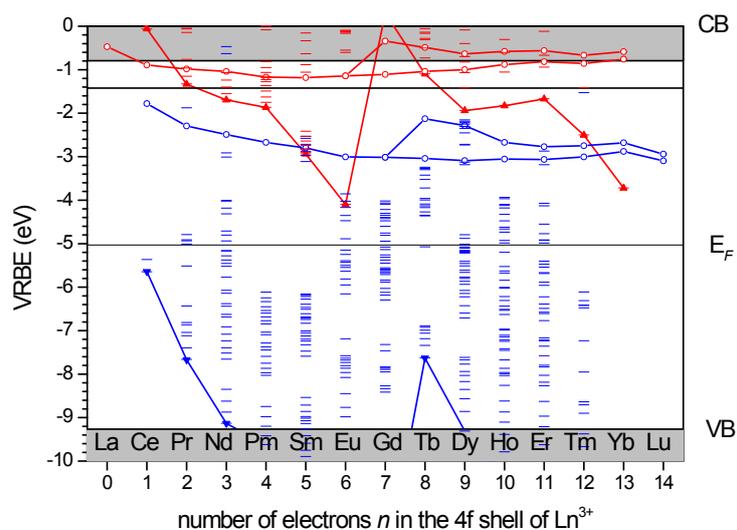


Figure S7. The VRBE scheme for all lanthanide 4f and 5d states in $\text{CaMgSi}_2\text{O}_6$. The blue curves connect the lowest 4f/5d states of the trivalent lanthanides and the red curves relate to those of the divalent lanthanides. The solid and hollow symbols stand for the 4f and 5d states, respectively.

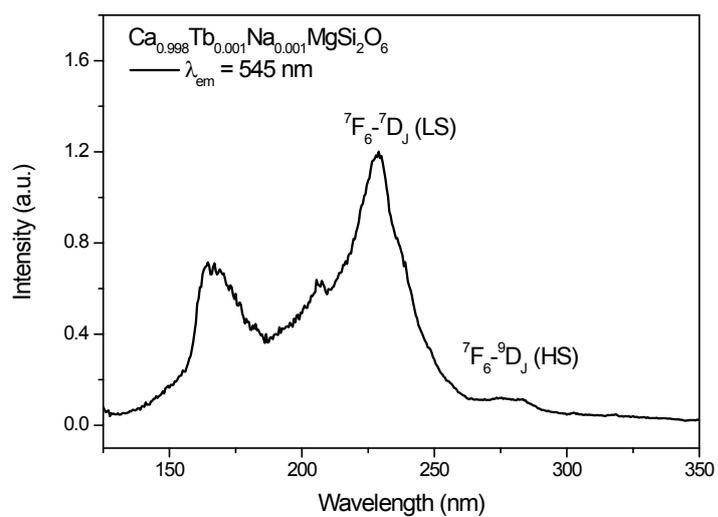


Figure S8. The excitation spectrum of $\text{Ca}_{0.998}\text{Tb}_{0.001}\text{Na}_{0.001}\text{MgSi}_2\text{O}_6$ ($\lambda_{\text{em}} = 545 \text{ nm}$) sample at 10 K. The slight shift of the host absorption band with that in **Figure 2** may be the influence of the spin-allowed f-d transitions of Tb^{3+} .