Supplementary Information

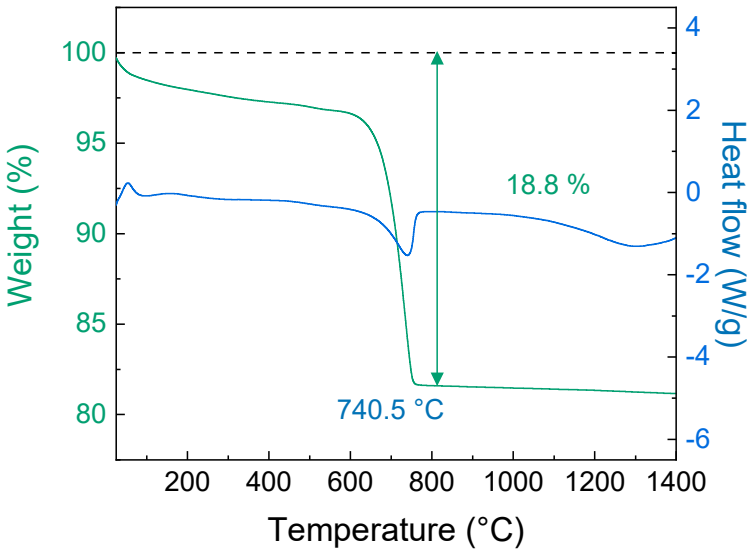

Figure S1. Thermogravimetric analysis (TGA, green line) and differential scanning calorimetry (DSC, blue line) curves of Ga-Substituted Eu-doped $CaYAlO_4$ (CYAGO:Eu) sample for a temperature range of 25–1200 °C with a heating rate of 10 °C/min. Significant weight loss and exothermic process are observed at about 740.5 °C, which is attributed to the decomposition of $CaCO_3$ [62-64].

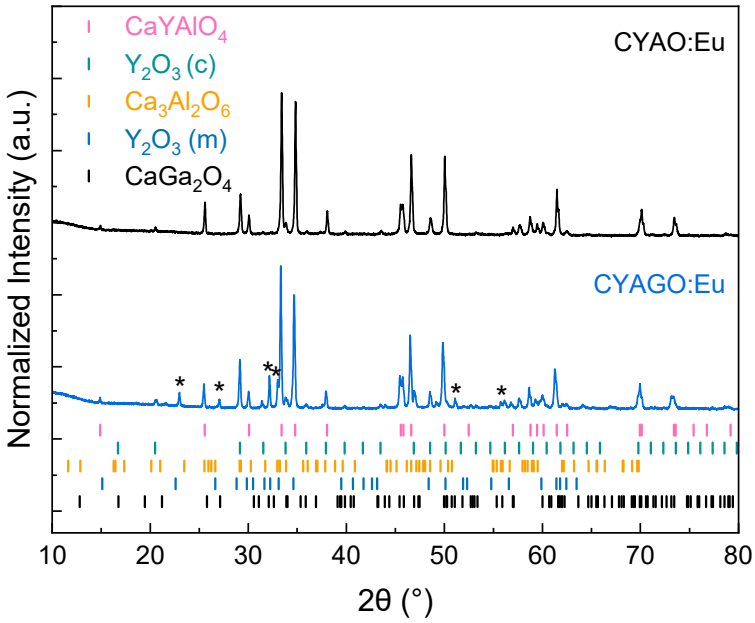

Figure S2. X-ray diffraction (XRD) patterns of Eu-doped $CaYAlO_4$ (CYAO:Eu) (solid black line) and Ga-substituted Eu-doped $CaYAlO_4$ (CYAGO:Eu) (solid blue line) samples synthesized at 1190 °C. The pink, green, orange, blue, and black bars indicate the standard XRD peak positions of $CaYAlO_4$, cubic Y_2O_3, $Ca_3Al_2O_6$, monoclinic Y_2O_3, and $CaGa_2O_4$, respectively (JCPDS Nos. 81-0742, 41-1105, 32-0148, 44-0399, and 88-2478, respectively). We note that the residue or formation of the Y_2O_3 phase appears inevitable in literature [20, 65], which is consistent with our results. Some of the peaks (marked by the asterisks) could not be definitively identified, but we have speculated that the peaks correspond to $Ca_3Al_2O_6$ and/or monoclinic Y_2O_3 phases within all possible phases (*i.e.*, the combination of Ca, Y, Al, Ga, Eu, and O) in the Inorganic Crystal Structure Database (ICSD) after our thorough inspection. In the peak searching using Highscore software (Malvern Panalytical), the $CaGa_2O_4$ phase gives the best score (=17/100), but it is unlikely considering its relative peak intensities.

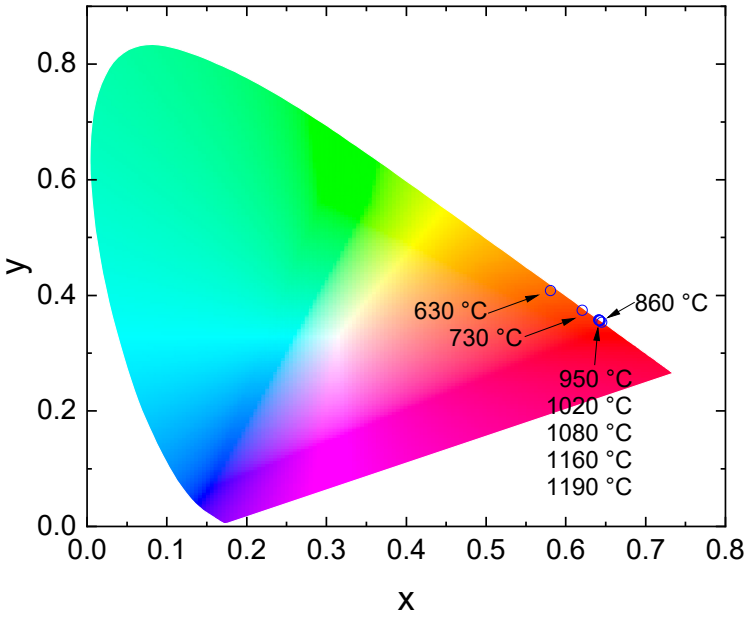

Figure S3. International Commission on Illumination (CIE) chromaticity diagram of the Ga-substituted Eu-doped $CaYAlO_4$ (CYAGO:Eu) samples synthesized at different temperatures under 277 nm excitation.

Table S1. International Commission on Illumination (CIE) chromaticity coordinates (x, y) of the Ga-substituted Eu-doped $CaYAlO_4$ (CYAGO:Eu) samples synthesized at different temperatures under 277 nm excitation.

Syn. Temp. (°C)	x	y
630	0.581	0.408
730	0.621	0.374
860	0.641	0.357
950	0.645	0.354
1020	0.643	0.356
1080	0.643	0.357
1160	0.642	0.357
1190	0.642	0.357

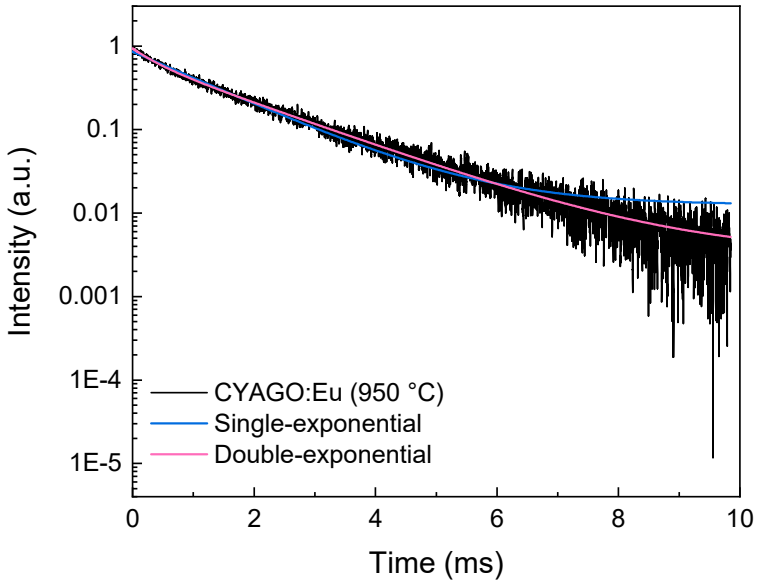

Figure S4. Decay curve of a Ga-substituted Eu-doped $CaYAlO_4$ (CYAGO:Eu) sample synthesized at 950 °C. The blue and pink solid lines indicate the single and double-exponential fits, respectively (see the main text). The single-exponential model is unsuitable for reflecting the decay curve of the CYAGO:Eu synthesized at 950 °C.

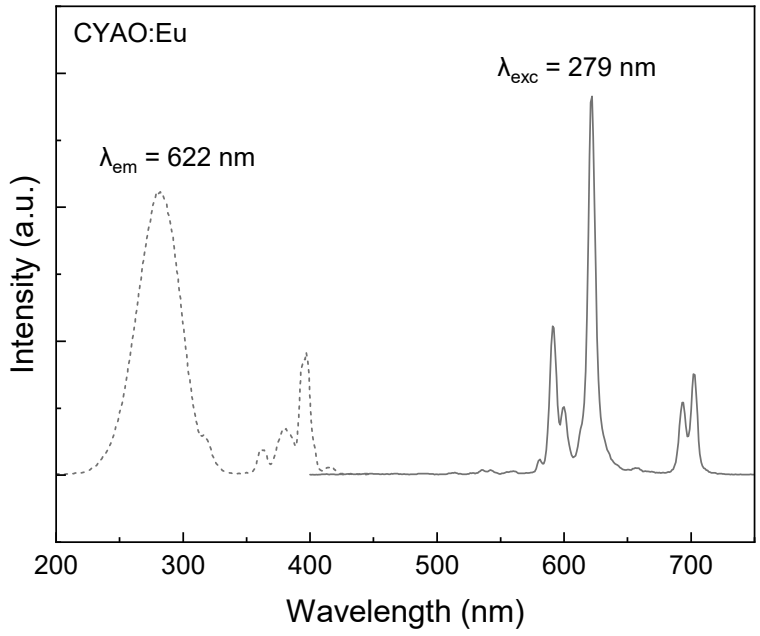

Figure S5. Photoluminescence (PL) and PL excitation (PLE) spectra of an Eu-doped $CaYAlO_4$ (CYAO:Eu) sample synthesized at 1190 °C. The PLE spectrum (dotted line) was monitored at λ_{em} = 622 nm, and the PL spectrum (solid line) was measured under 279 nm excitation (λ_{exc}).

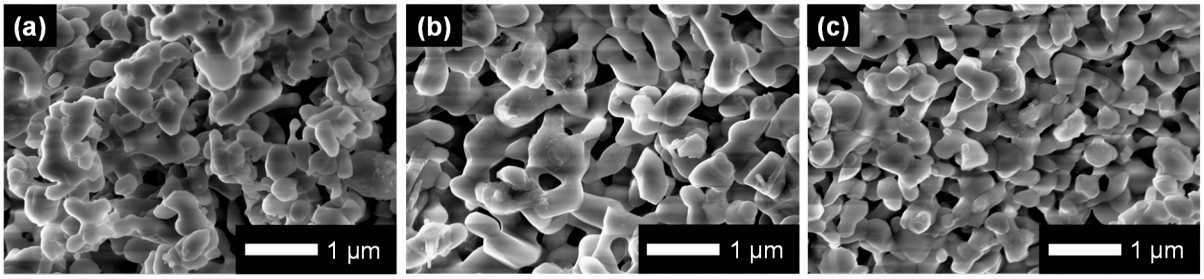

Figure S6. Field emission scanning electron microscopy (FE-SEM) images of Ga-substituted $CaYAlO_4$:Eu synthesized at (a) 1080 °C, (b) 1190 °C, and (c) $CaYAlO_4$:Eu synthesized at 1190 °C.

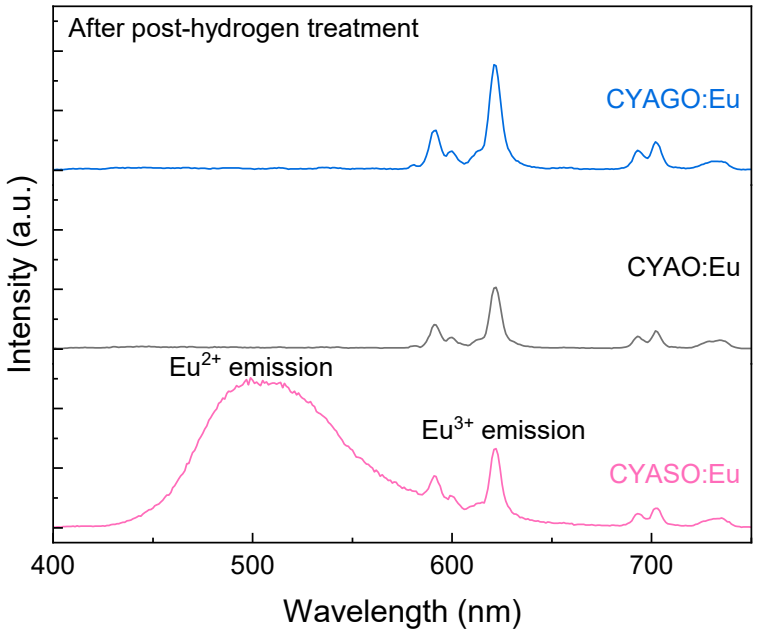

Figure S7. Photoluminescence (PL) spectra under 365 nm excitation of a Ga-substituted Eu-doped $CaYAlO_4$ (CYAGO:Eu, blue), pure Eu-doped $CaYAlO_4$ (CYAO:Eu, black), and Si-substituted Eu-doped $CaYAlO_4$ (CYASO:Eu, pink) samples after post-hydrogen treatment at 800 °C. The excitation wavelength of 365 nm is chosen to see the emissions from both Eu^{2+} and Eu^{3+} simultaneously. The Eu^{2+} emission is only observed in the CYASO:Eu sample.

[Sample preparation – Si-substituted $CaYAlO_4$:Eu (CYASO:Eu)]

For comparative analysis, we specially prepared Si-substituted $CaYAlO_4$:Eu (CYASO:Eu) sample in this study. The ratio of Ca and Y was adjusted to resolve the charge imbalance due to the substitution of Si^{4+} for Al^{3+}. $Ca_{0.95+x}Y_{1-x}Al_{1-x}Si_xO_4:Eu_{0.05}$ (x=0.2) were fabricated through a conventional solid-state method with stoichiometric amounts of Al_2O_3 (extra pure, Hayashi Pure Chemical Ltd.), SiO_2 (99.95%, Cerac Specialty Inorganic), $CaCO_3$ (99.5%, Junsei Chemical Ltd.), Y_2O_3 (99.99%, Sigma Aldrich), and Eu_2O_3 (99.99%, Alfa aesar) [1]. The mixture of the raw materials was subjected to a planetary ball milling process using zirconia balls and heated in a tube furnace at 1190 °C for 6 hours under dehydrated air. Basically, we followed the same synthesis condition used for preparing the CYAGO:Eu sample in the main text. In x-ray diffraction measurement, the CYASO:Eu sample exhibits the typical diffraction pattern of CYAO with some minor peaks corresponding to the Y_2O_3 phase, which is similar to the CYAGO:Eu.

Post-hydrogen treatments were performed under H_2/Ar (2:8) (flow rate: 0.15 L/min) for 3 h at 800 °C. Before the post-hydrogen treatment, the CYASO:Eu exhibited only Eu^{3+} (red) emission, but additional Eu^{2+} emission emerged after the post-hydrogen treatment, which is consistent with the previous report [31].