Electronic Supplementary information

Synthesis of Red-emitting Nanocrystalline Phosphor $CaAlSiN_3:Eu^{2+}$ Derived from Element Constituents

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Experimental Section

Synthesis of $CaAlSiN_3:Eu^{2+}$ ($CASN:Eu^{2+}$) using Autoclaves. All operation and handling in the synthesis were conducted under an inert atmosphere in order to prevent the oxygen contamination of air-sensitive chemicals. In addiiton, specially devised autoclaves with vacuum, ammonia and gas pressure lines was used to degas or fill the ammonia liquid into reactor vessel. Synthesis of $CASN:Eu^{2+}$ were performed via ammonotheraml method under the supercritical condition. Respective elemental constituents of Ca (99.0%, Aldrich), Al (91.0%, Aldrich), Si(Aldrich, 99.0%), and Eu (KoJundo chemical, 99.9%) were weighed based on the molecular ratio of Ca (0.238g; 5.9 mmol): Al (0.168g; 6.2 mmol): Si (0.175g; 6.2 mmol): Eu (0.047; 0.3 mmol)= 0.95: 1.00: 1.00: 0.05. The ratio of each component could be changed easily and deliberately at a weighting step. Thereafter, these are mixed with a mineralizer of NaN_3 (99%, Alfa Aesar) with the molar ratio of Na/(Ca+Eu), varing from 0.5 to 8. These chemicals were loaded into nickel alloy tube basket with outer diameter in 4 mm, thickness in 1 mm and length in 15 cm. The tube was loaded into a vertically positioned autoclaves with deep hole (inner diameter in 2 cm and length in 20 cm). And then, reaction vessel are filled with anhydrous liquid ammonia (99.999%, Jung-ang Gas, Korea). Two thermocouplers were fixed to the surface of the autoclaves at the position of both top and bottom. Autoclaves consisted of two parts which are lower part (reaction vessel) and upper part (pressure gauge system containing ammonia and vacuum line). Upper part of pressure gauge system was connected to outer pressure gauge to measure the pressure of reaction vessel. The autoclaves was first heated up to 400 °C at increasing temperature rate of 0.44 °C/min, and held for 24- 48 hours for metals to be converted to metal amide (ammonometallats). Thereafter, the reation temperature was increased up to 580 °C at increasing rate of 0.1°C/min and maintained for 10- 30 days at that reaction temperature in order for $CASN:Eu^{2+}$ to nucleate and grow. The pressure measured in experement was ranged from 1000 to 2000 bar according to added amount of mineralizer and liquid ammonia. After the autoclaves was cooled to room temperature, the gaseous ammonia filled in autoclaves was removed by releasing valve and

autoclaves was finally opened. The basket loaded in autoclaves was taken out from the reaction vessel, and sample in basket was analyzed for characterization.

Washing treatment. Sample in basket was washed with mixed ethanol and water for 3- 4 times in order to remove the minealizer and unreacted sodium ammonometallates. *At this step, handling should be conducted very carefully because these are so reactive toward water or oxygen, resulting in the formation of gas or sparkling.* For acid treatment, sample was stirred in round bottom flask contating 1M HCl for the designated time. After washing, the sample was dried in oven at 80 °C for overnight for further characteriztion.

Characterizations. The morphology and size of the samples were examined with a scanning electron microscope (FE-SEM, Tescan Mira 3 LMU FEG) operated at 10 kV. Composition of sample was analyzed by EDX analysis using Energy Dispersice X-ray Spectrometer (EDX, Bruker, Quantax 200). The X-ray diffraction XRD analysis was conducted by using XRD diffractometer (XRD, Rigaku D/Max-2200V) in a 2θ range from 10 to 70 using Cu Kα radiation (λ = 1.5405 Å). The room-temperature photoluminescence (PL) excitation and emission spectra was measured by PSI instruments equipped with DarsaPro 5000, equipped with 500W Xenon lamp.

Pressure-Temperature relationship. In order to synthesize CASN:Eu^{2+} under the supercritical fluid ammonia solution, it is requried to understand the relatonship of pressure-temperature in system with a function of time. Ammonia have critical pressure of 112.8 bar and temperature of 132.4 °C. It has been reported that P-V-T (pressure-volume-temperature) relationship of pure ammonia show that linear relationship between temperature and pressure maintained below or above critical point with a different slope. P-T relationship shown in Fig. S7, ESI. indicates the sodium amide-ammonia system contatining pure elements of Ca, Al, Si, and Eu. As increasing the temperature of vessel, the pressure linearly increased with a lower slope. However, betwen 200- 250 °C, the slope of pressure become sharper because sodium azide decomposed to sodium and nitrogen and generated sodium metal reacted with ammonia to make sodium amide, nitrogen, and hydrogen as following:

$2NaN_3 \rightarrow 2Na + 3N_2$ (1)

$2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$ (2)

The pressure was increased up to 500 °C and at this point the pressure increased drastically again due to the decomposition of ammonia to nitrogen and hyrogen: $2NH_3 \rightarrow N_2 + 3H_2$. Above 500 °C, the hydrogen produced from the decomposition of ammonia start to leak from the reaction vessel and pressure decrasesed slighly. After turning off the electrical furnace, the pressure naturally decreased with decreasing temperature.

Calculation of the conversion yield. We calculated the conversion yield for the sample after washing treatment with water and ethanol several times after assuming that the synthesized products is only composed of CASN:Eu^{2+}. The apporximate conversion yield was calculated, based on the conversion ratio of final number of molecules of CASN:Eu^{2+} to the initial number of molecules of Si (6.2 mmol). The final number of molecules of products was calculated by diving the weight of products by molecular weight (M.W) of $Ca_{0.95}Al_{0.54}Si_{1.38}N_3:Eu_{0.05}^{2+}$ (141.02g·mol^{-1}). The conversion yield were denoted in Fig. S6, ESI.

Reaction: $0.95Ca + 1.00Al + 1.00Si + 0.05Eu + NaN_3 \rightarrow Ca_{0.95}Al_{0.54}Si_{1.38}N_3:Eu_{0.05}^{2+}$

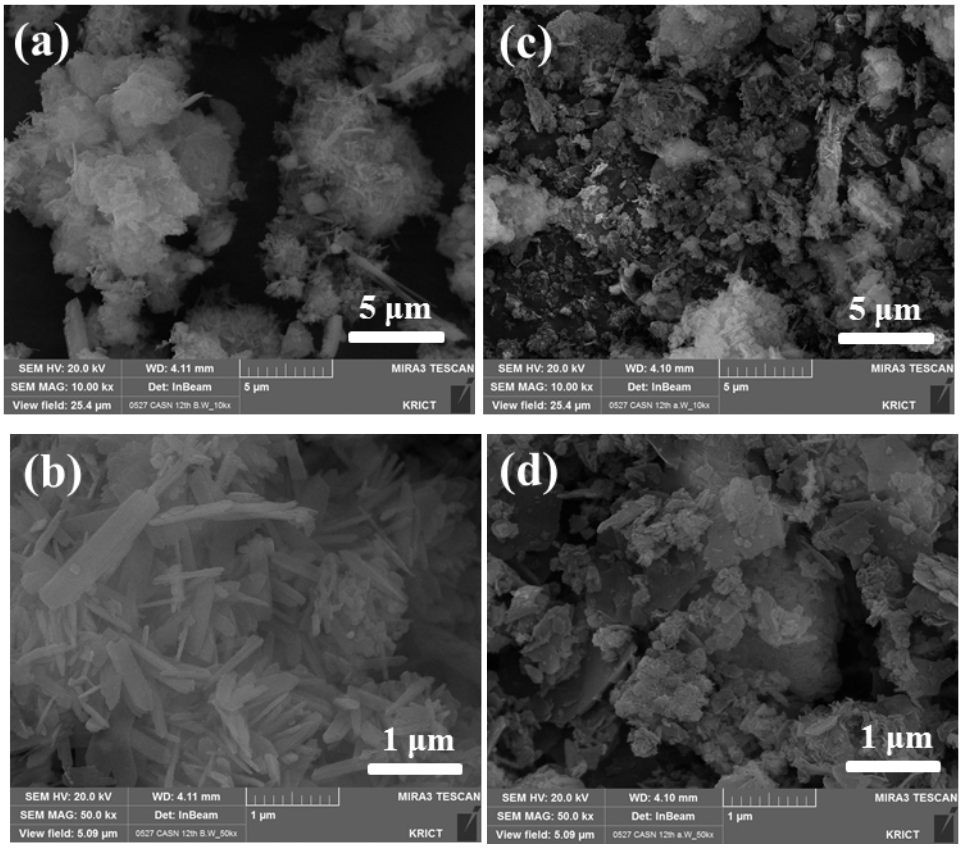

Fig. S1 SEM images of the intermediate sample collected at 500 °C for 50 hours: (a, b) before washing treatment and (c, d) sample after washing treatment with water and ethanol several times.

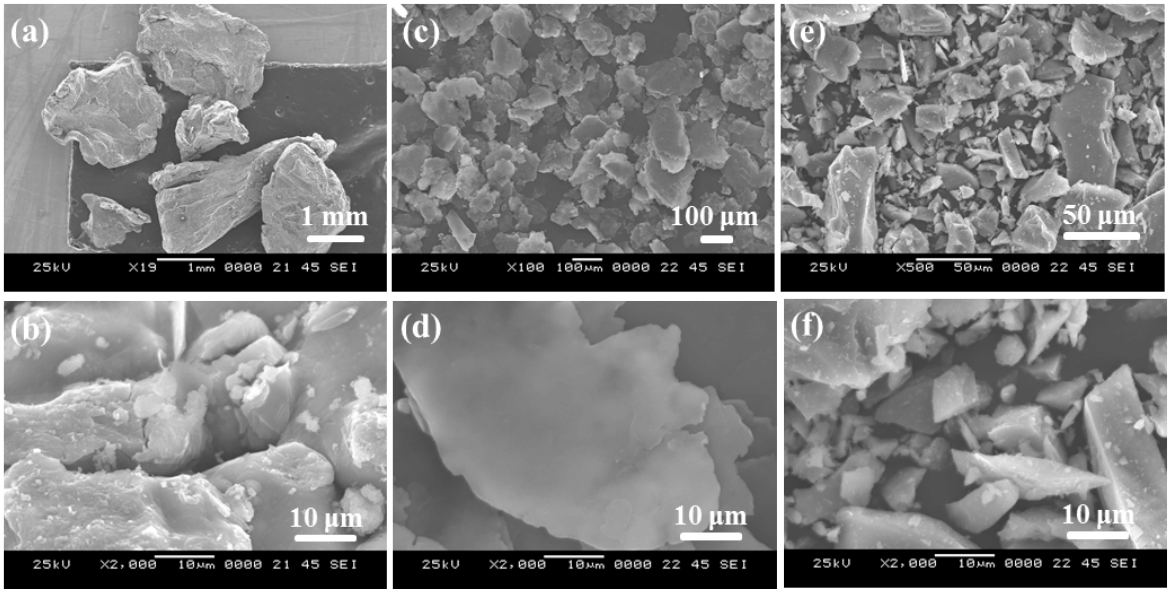

Fig. S2 SEM images of the starting elements of (a, b) calcium (Ca) , (c, d) aluminum (Al) , and (e, f) silicon (Si). Calcium with granule size and, silicon and aluminum with powder size were used.

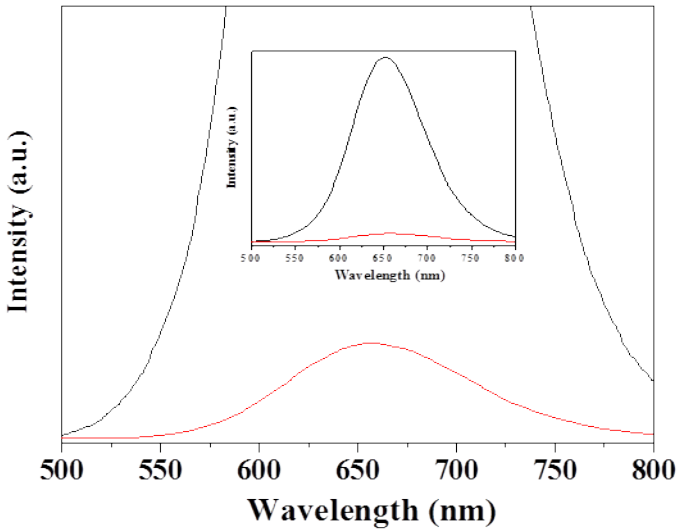

Fig. S3. Comparions of PL emission intensity of $CaAlSiN_3:Eu^{2+}$ prepared by an ammonthermal method at 580 °C (red) and a converntional method of carbon-thermal reduction and nitridation at 1600 °C (black); inset shows the whole intensity.

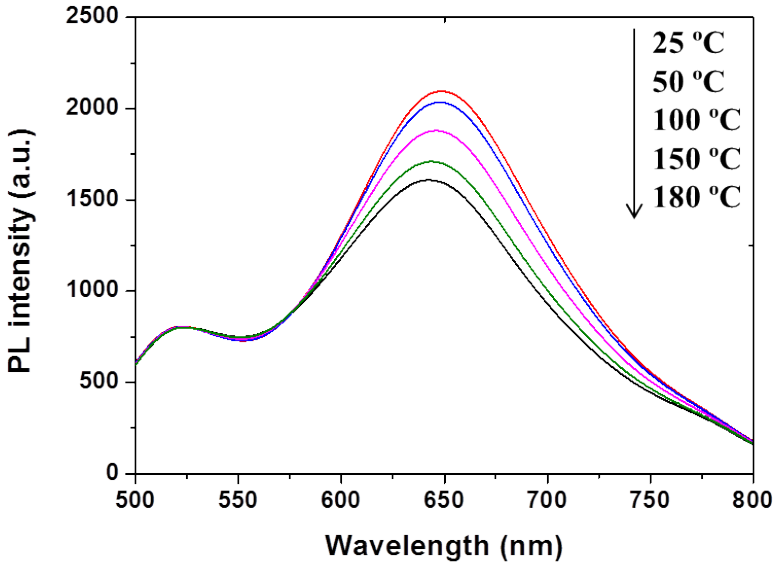

Fig. S4 Temperature-dependant PL emission spectra of $CaAlSiN_3:Eu^{2+}$ at various heating temperature from room temeprature to 180 ºC. The peak below 525 nm are not originated from the emission of $CaAlSiN_3:Eu^{2+}$ but from the line smoothing process.

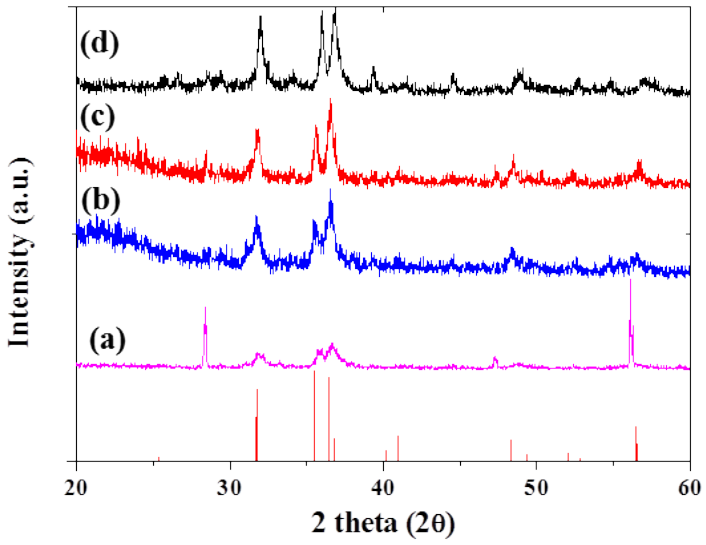

Fig. S5 XRD patterns of $CaAlSiN_3:Eu^{2+}$ under the reaction at 580 ºC for 10 days with changing the amount of mineralizer of NaN_3 at a moleculaarr ratio of Na/(Ca+Eu) of (a) 0.5, (b) 1, (c) 2, and (d) 8. Amorphous peaks around 2θ= 20- 25° are attributed to glass peaks.

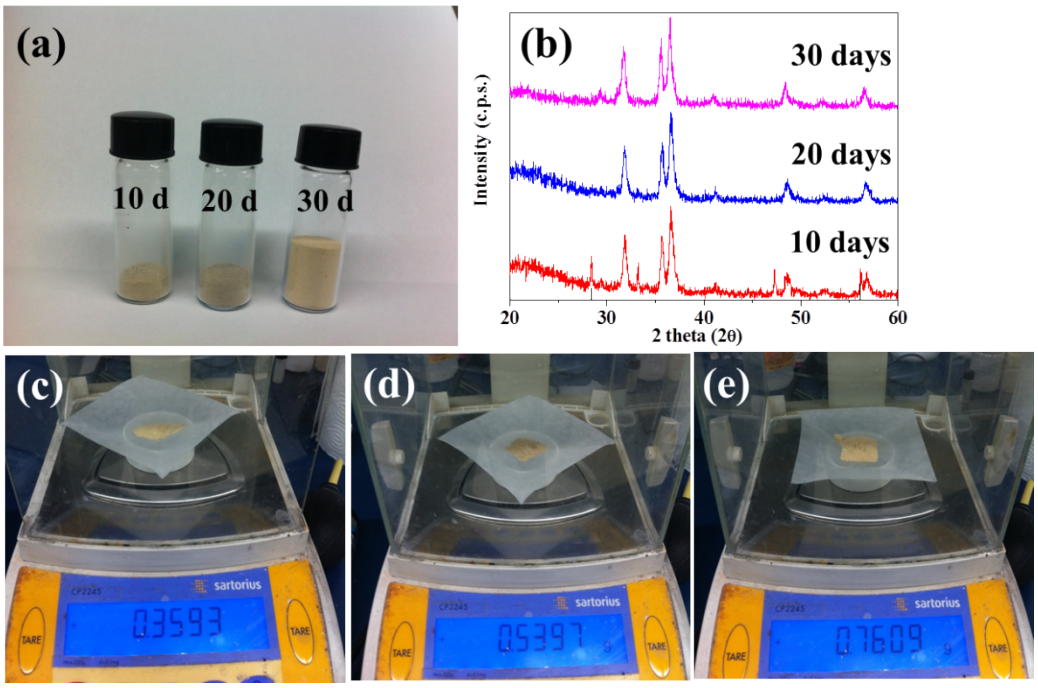

Fig. S6. Converision yield of $CaAlSiN_3:Eu^{2+}$ prepared at 580 °C with a function of time from 10-30 days: (a) a picture of synthesized products, (b) XRD patterns change, (c) weight of product for 10 days (0.3593g; conversion yield: 40.1 %), (d) for 20 days (0.5397 g; 61.4 %), and (e) for 30 days (0.7609 g; 86.5 %), respectively. The conversion yields were calculated based on the molecualr ratio between the number of molecules of synthesized $CaAlSiN_3:Eu^{2+}$ applying the theoretical molecular weight of $Ca_{0.95}Al_{0.54}Si_{1.38}N_3:Eu_{0.05}$ (M.W= 141.0107 $g \cdot mol^{-1}$) and the number of moleculess of initially added Si.

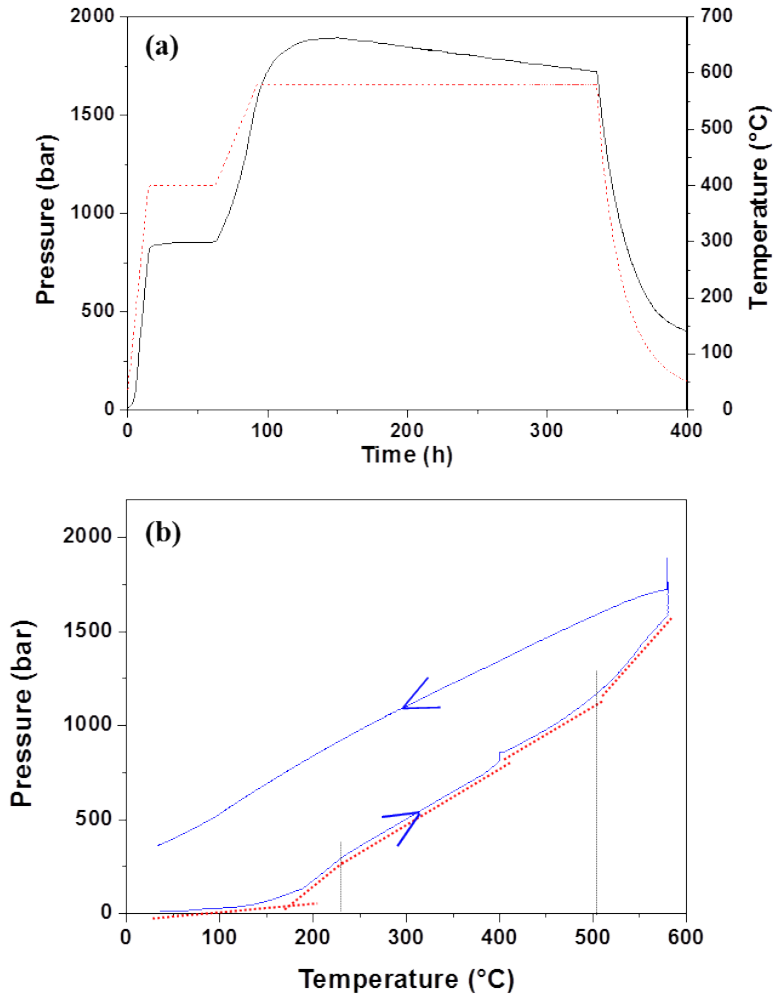

Fig. S7 (a) pressure and temperature curve as a function of reaction time (solid line: gas pressure and dotted line: reaction temperature), (b) pressure-temperature relationship curve and arrow showed the pathway of pressure with a function of temperature; pressure reached maximum around 1900 bar and decreased slightly due to the leakage of hydrogen gas.

Table. 1 EDS analysis of $CaAlSiN_3:Eu^{2+}$ with various treatment conditions. Atomic concentraiton of samples before washing, after washing, and after treatment with 1M HCl for 5 min and 20 min were measured, respecitively. After washing, sodium concentration was decreased significantly compared with the sample before washing, and after treatment with acid, oxygen content was reduced drastically.

Element	Atomic Number	Series	Before washing (at %)	After washing (at %)	After treated with 1M HCl for 5 min (at %)	After treatment with 1M HCl for 20 min (at %)
Ca	20	K-series	8.33	9.55	9.23	9.32
Al	13	K-series	11.69	11.32	10.94	11.44
Si	14	K-series	6.63	11.29	16.35	16.76
Eu	63	L-series	0.43	0.65	0.41	0.4
Na	11	K-series	11.41	3.13	4.68	5.17
N	7	K-series	24.96	24.78	42.91	41.25
O	8	K-series	36.54	39.28	15.48	15.66
			99.99	100	100	100
Chemical formula			$Ca_{1.26}Al_{1.76}Si_{1.00}Eu_{0.06}N_{3.76}O_{5.51}$	$Ca_{0.85}Al_{1.00}Si_{1.00}Eu_{0.06}N_{2.19}O_{3.48}$	$Ca_{0.56}Al_{0.67}Si_{1.00}Eu_{0.03}N_{2.62}O_{0.94}$	$Ca_{0.56}Al_{0.68}Si_{1.00}Eu_{0.02}N_{2.46}O_{0.93}$