

Supporting information

A thermal-sensitizing phosphor

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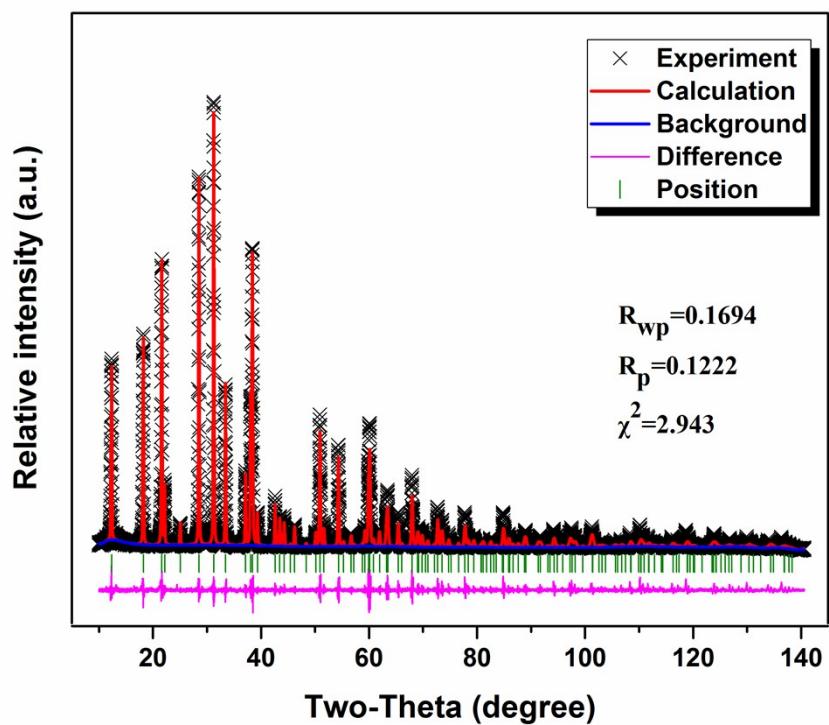


Figure S1, the Rietveld refinement of the $\text{Na}_2\text{CaGe}_6\text{O}_{14}$ host.

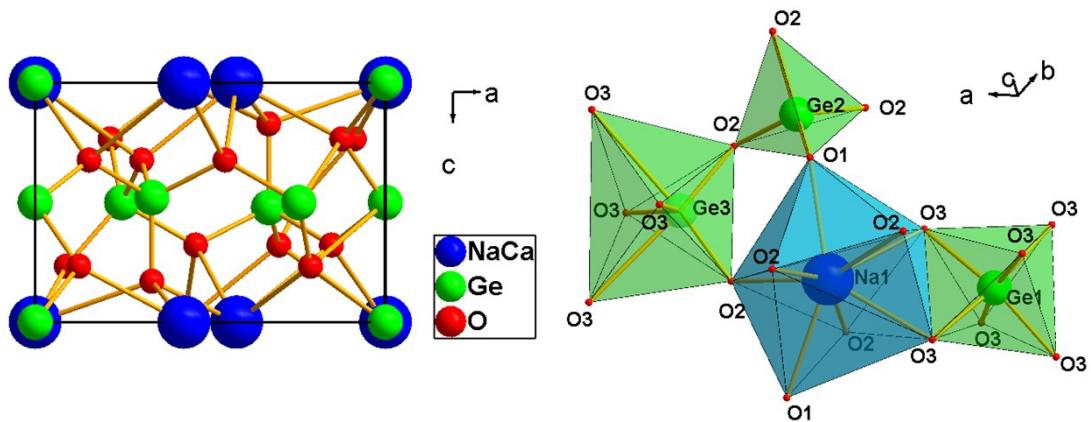


Figure S2a, the crystal structure of the $\text{Na}_2\text{CaGe}_6\text{O}_{14}$ host and the coordination environment of the $\text{Na}^+/\text{Ca}^{2+}$, and Ge^{4+} sites.

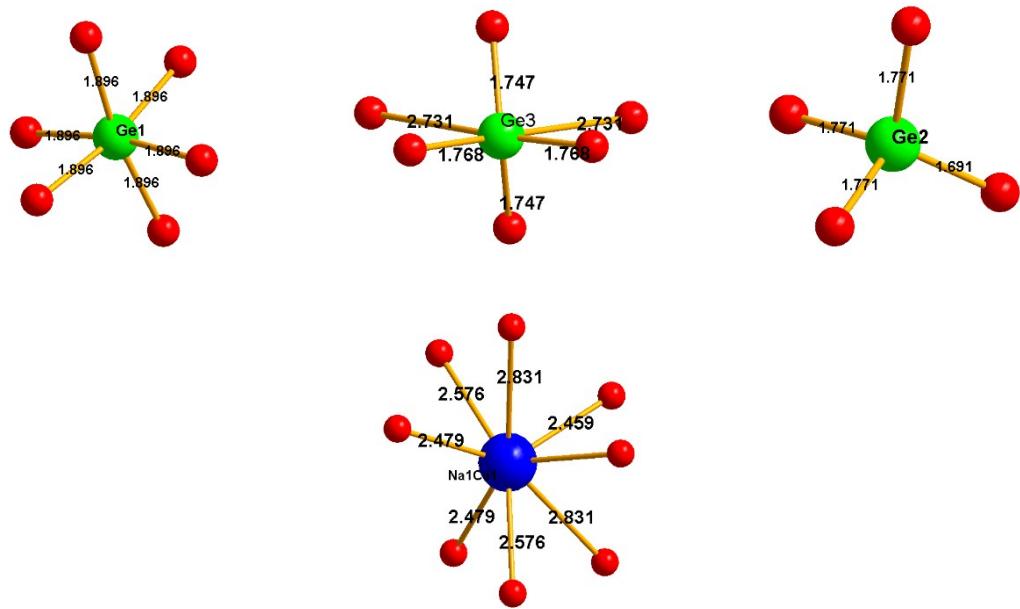


Figure S2b, the distances of the Na–O bonds, Lu–O bonds and Ge–O bonds.

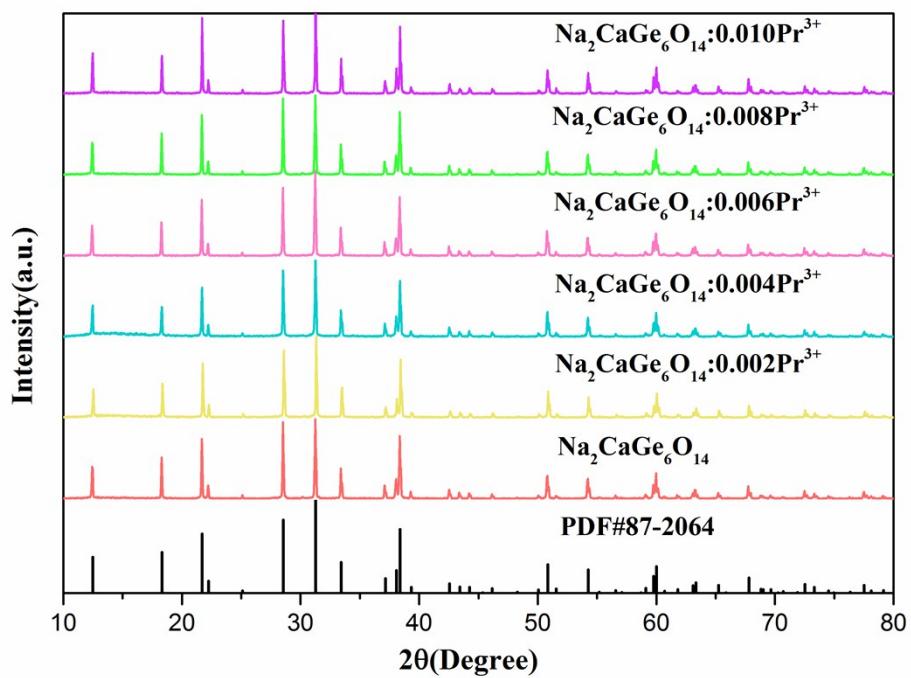


Figure S3, the XRD patterns of the $\text{Na}_2\text{CaGe}_6\text{O}_{14}:x\text{Pr}^{3+}$ samples with the different Pr^{3+} doping contents.

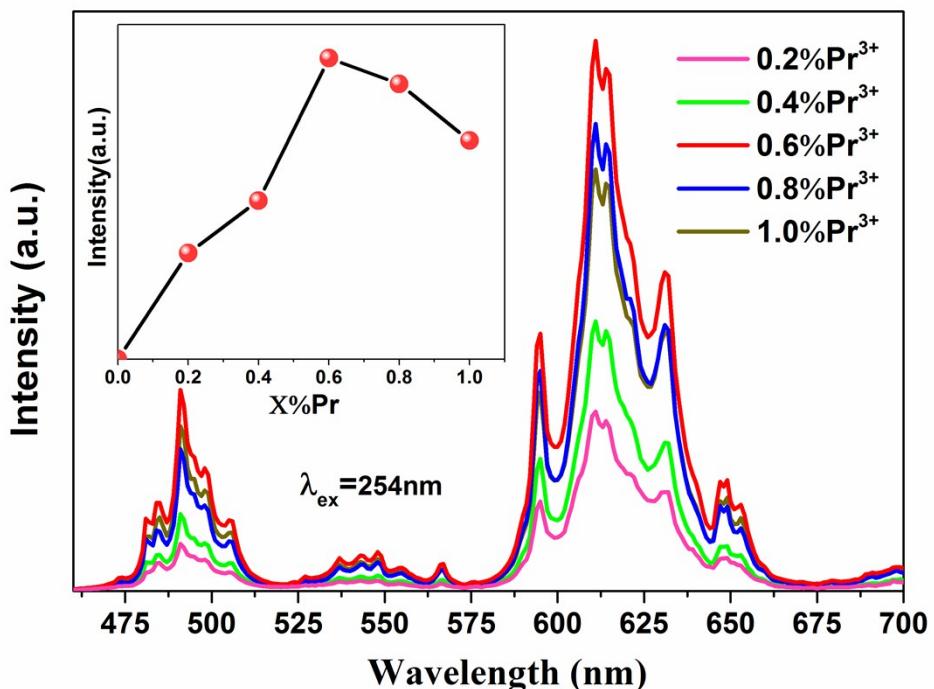


Figure S4, the PL emission spectra of the $\text{Na}_2\text{CaGe}_6\text{O}_{14}:x\text{Pr}^{3+}$ samples with the different Pr^{3+} doping contents under 254 nm excitation, and the emission intensity of the samples as a function of the Pr^{3+} contents (inset).

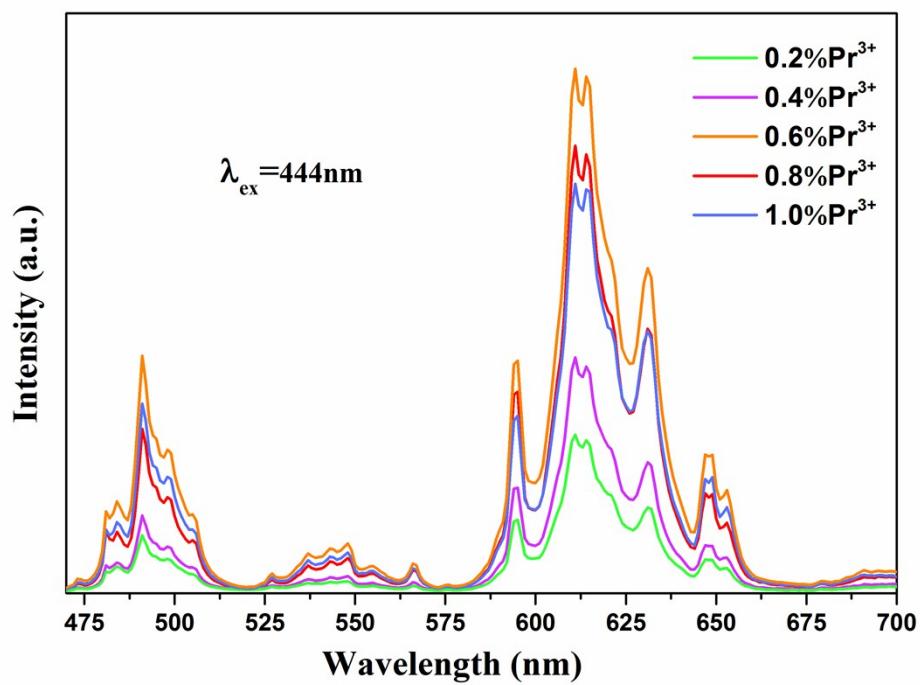


Figure S5, the PL emission spectra of the $\text{Na}_2\text{CaGe}_6\text{O}_{14}:x\text{Pr}^{3+}$ samples with the different Pr³⁺ doping contents under 444 nm excitation.

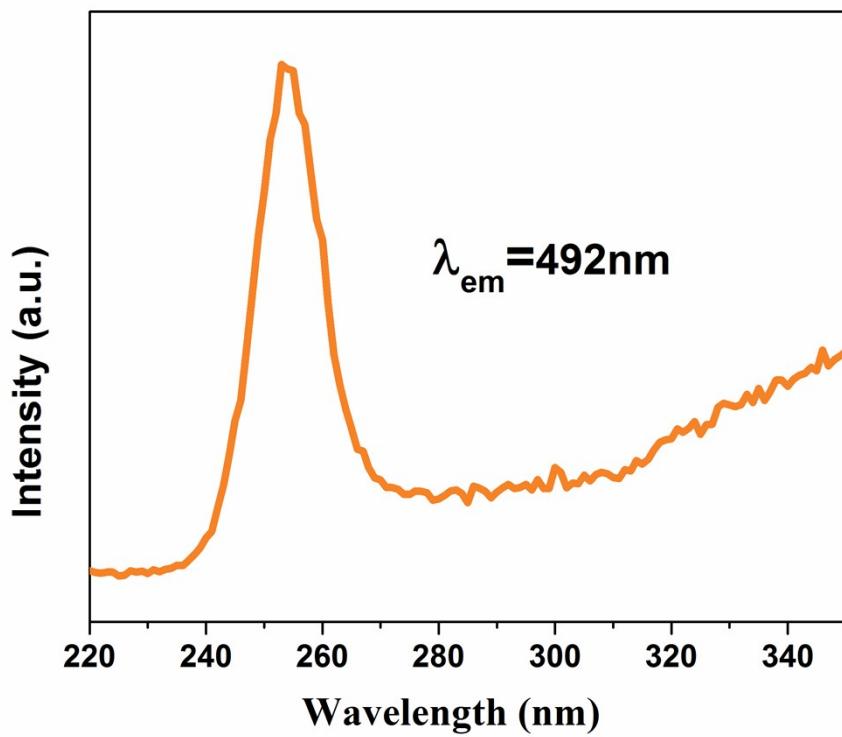


Figure S6, the PL excitation spectrum of the typical $\text{Na}_2\text{CaGe}_6\text{O}_{14}:0.6\text{mol}\%\text{Pr}^{3+}$ sample monitored at 492 nm.

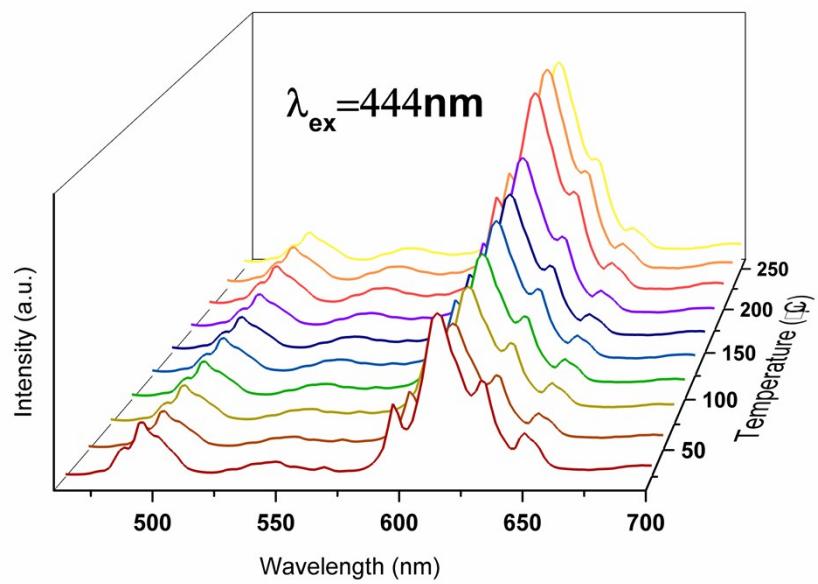


Figure S7a, the PL emission spectra excited at 444 nm of the typical $\text{Na}_2\text{CaGe}_6\text{O}_{14}:0.6\text{mol}\%\text{Pr}^{3+}$ sample at different temperature.

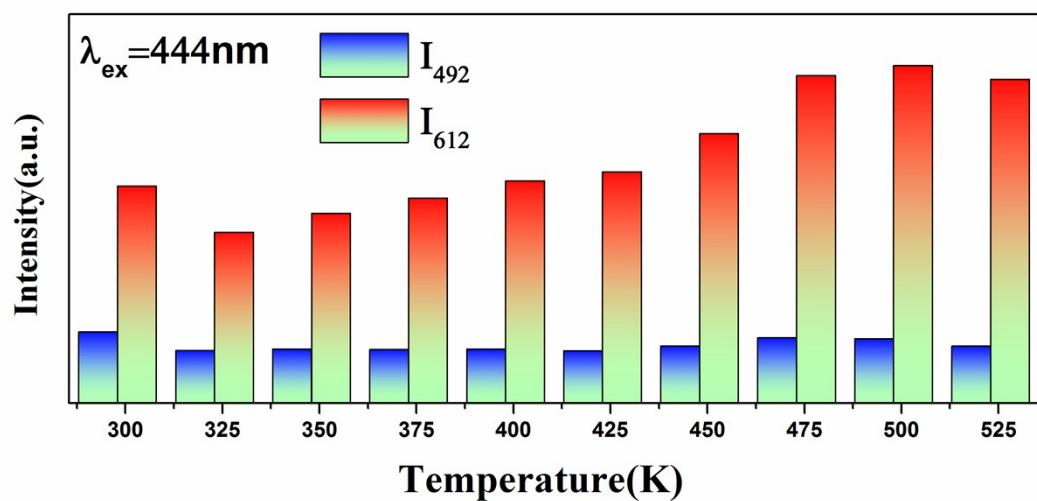


Figure S7b, the PL emission intensity excited at 444 nm of the typical $\text{Na}_2\text{CaGe}_6\text{O}_{14}:0.6\text{mol}\%\text{Pr}^{3+}$ sample at different temperature.

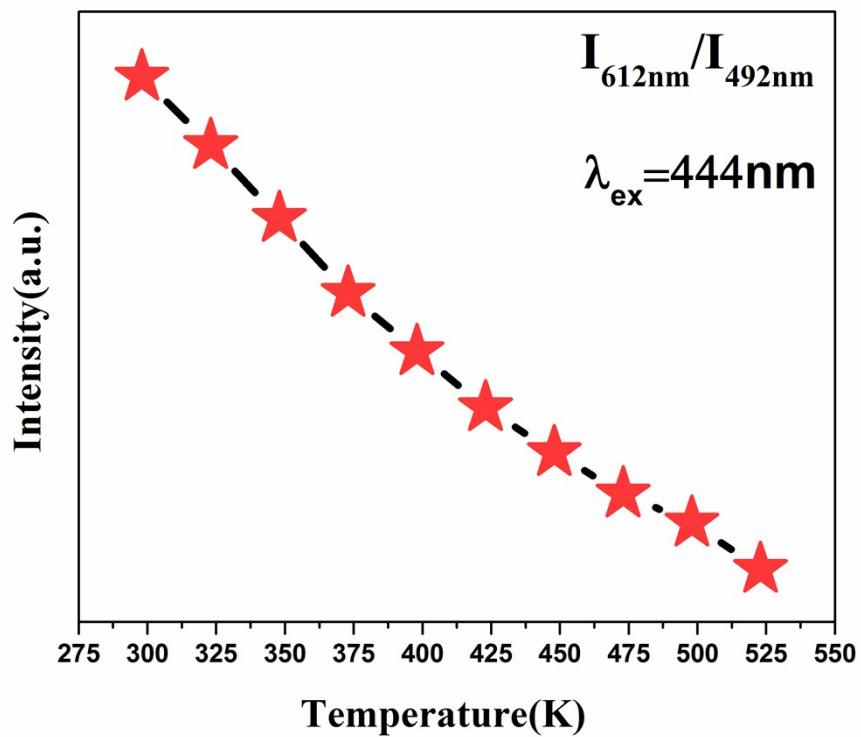


Figure S8, the emission intensity ratio (I_{612}/I_{492} , $\lambda_{\text{ex}} = 444$ nm) of the typical $\text{Na}_2\text{CaGe}_6\text{O}_{14}:0.6\text{mol}\%\text{Pr}^{3+}$ sample as a function of temperature.

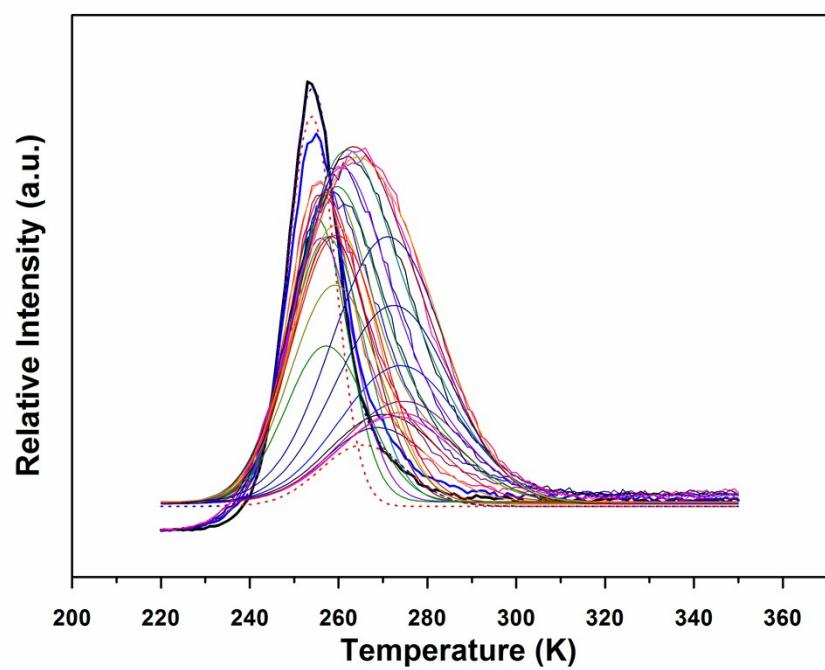


Figure S9, the excitation components at about 254 nm and 266 nm of the typical $\text{Na}_2\text{CaGe}_6\text{O}_{14}\text{:}0.6\text{mol\%Pr}^{3+}$ sample recorded at different temperatures.

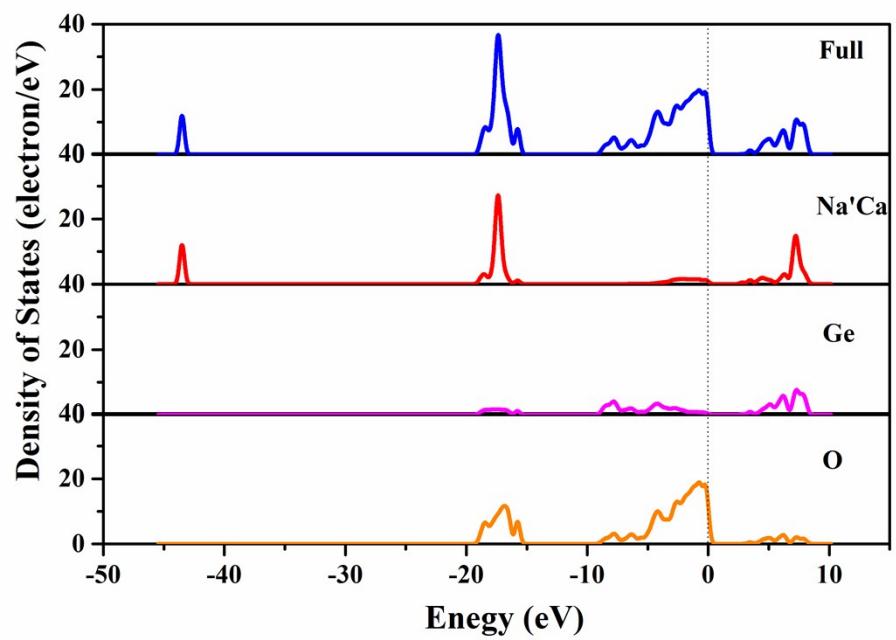


Figure S10, the partial density of the states of the typical $\text{Na}_2\text{Ca}\text{Ge}_6\text{O}_{14}$ sample.

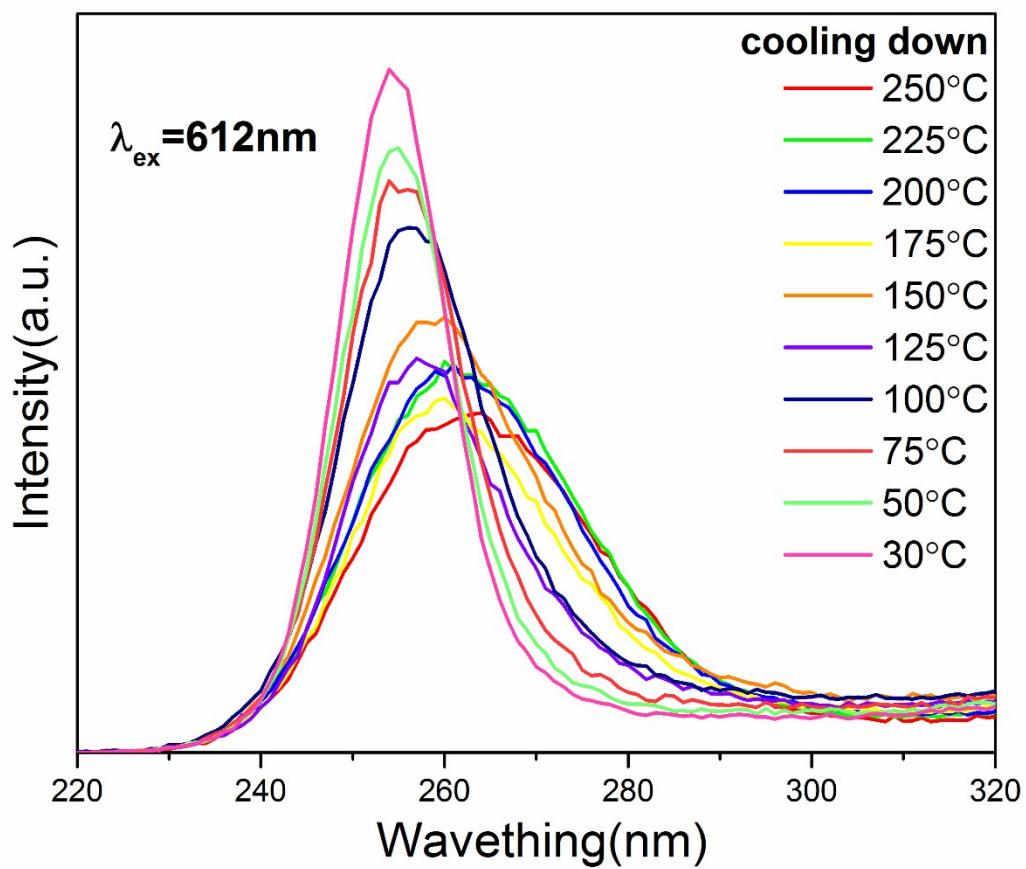


Figure S11, The temperature dependence PL excitation spectra ($\lambda_{\text{em}} = 612 \text{ nm}$) of the $\text{Na}_2\text{Ca}_{0.994}\text{Ge}_6\text{O}_{14}:0.6\%\text{Pr}^{3+}$ sample.

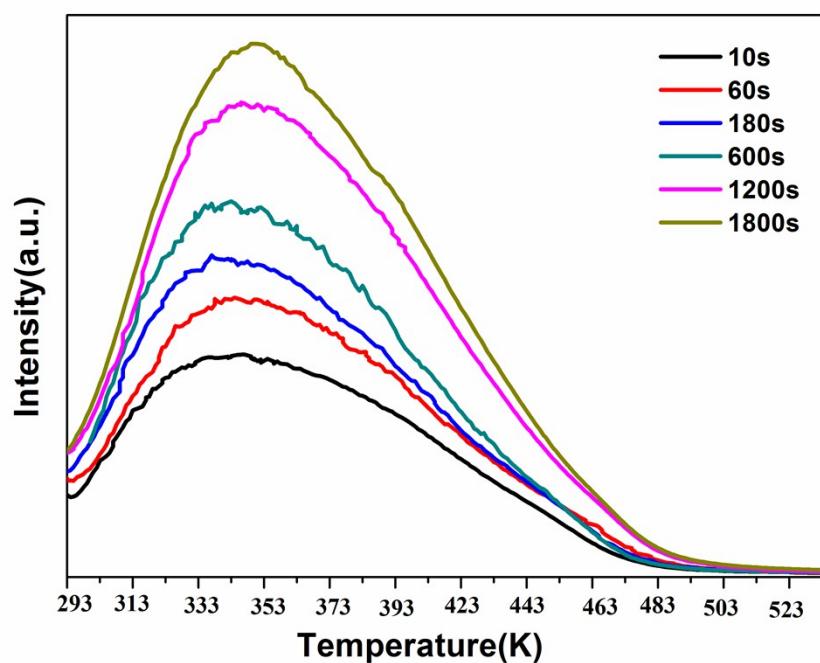


Figure S12, a serial of the TL charging experiments of the typical

$\text{Na}_2\text{CaGe}_6\text{O}_{14}:0.6\text{mol}\%\text{Pr}^{3+}$ sample.

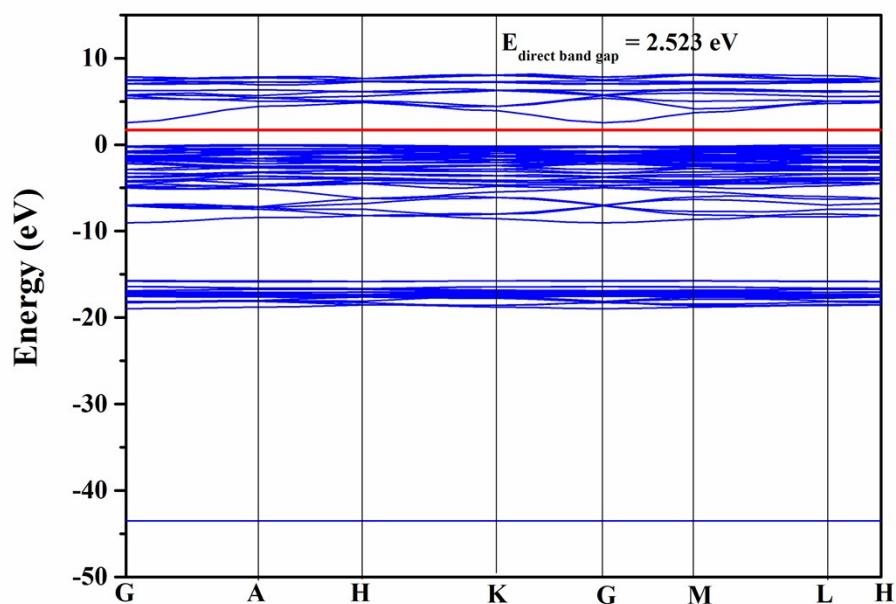


Figure S13, the optimized density functional theory (DFT) calculations on the imperfect crystal of the Na₂CaGe₆O₁₄ with Na⁺ vacancy.

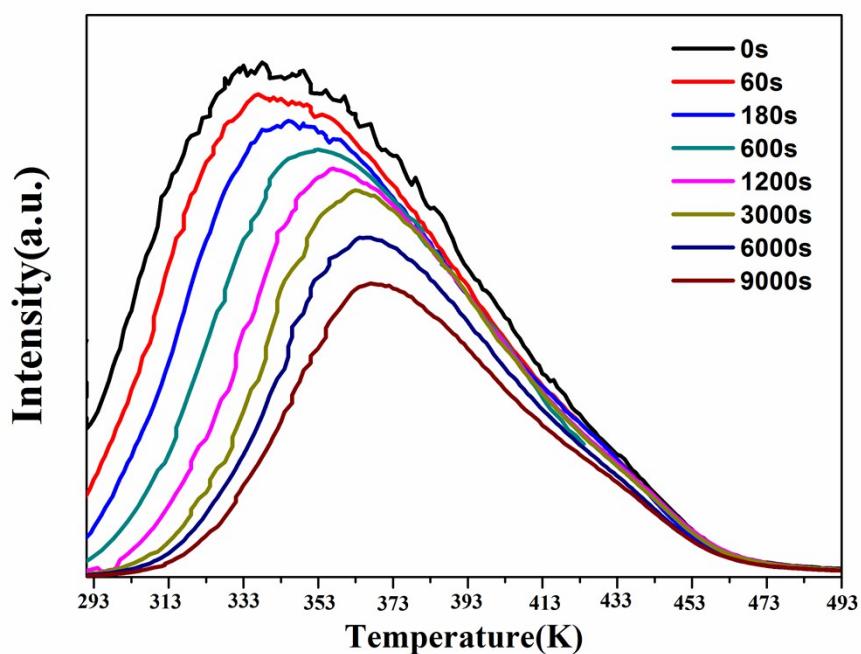


Figure S14, a serial of TL fading experiments of the typical $\text{Na}_2\text{CaGe}_6\text{O}_{14}\text{:}0.6\text{mol\%Pr}^{3+}$ sample at different delay time after stopping the irradiation.

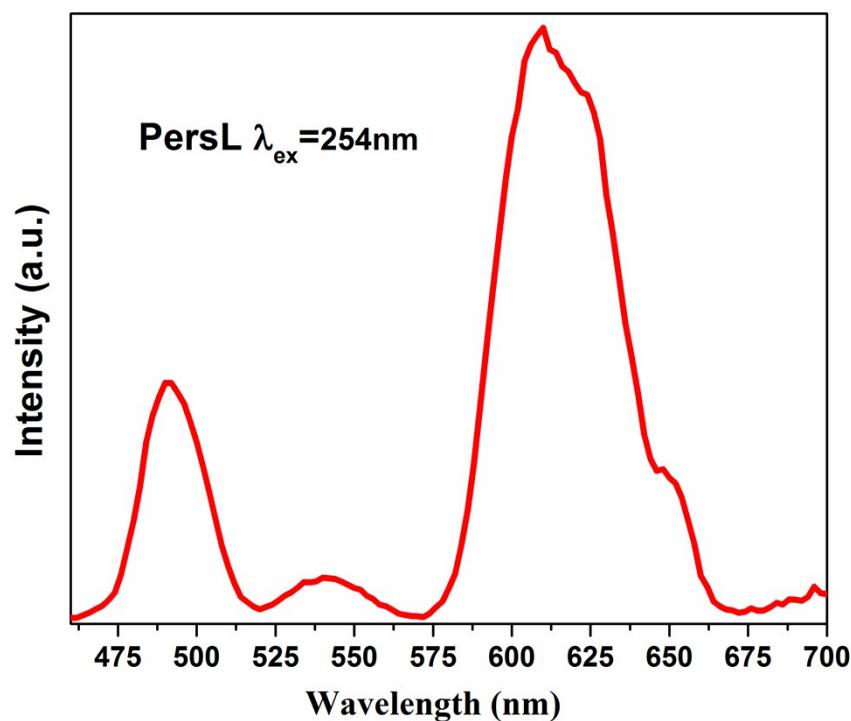


Figure S15a, the persistent luminescence spectrum of the typical $\text{Na}_2\text{CaGe}_6\text{O}_{14}:0.6\text{mol}\%\text{Pr}^{3+}$ sample recorded after 254 nm irradiation for 10 min at room temperature.

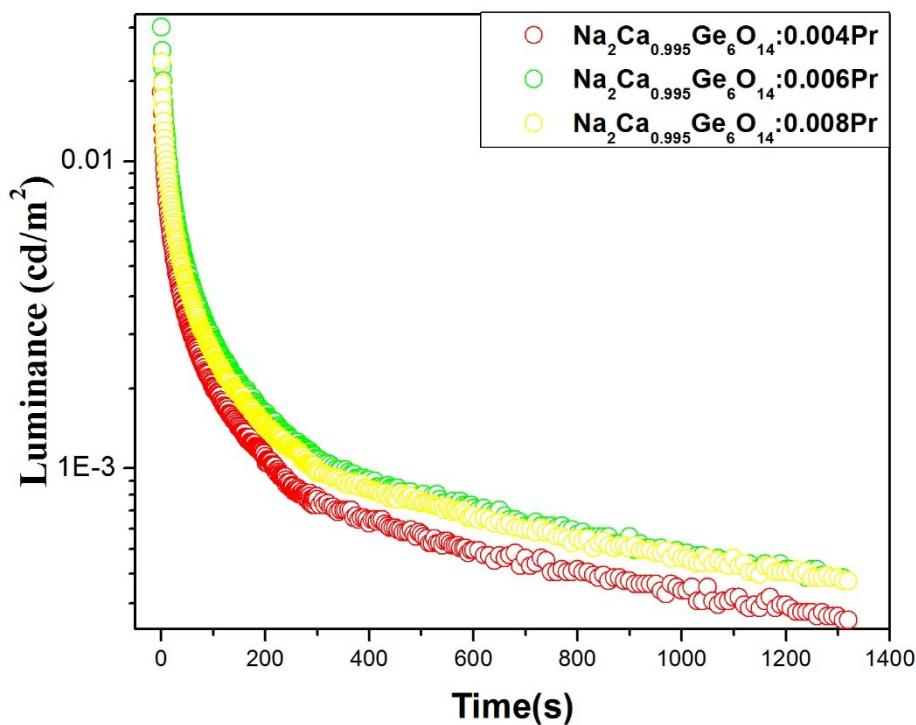


Figure S15b, the persistent luminescence decay curves of the typical $\text{Na}_2\text{Ca}\text{Ge}_6\text{O}_{14}:x\text{mol}\%\text{Pr}^{3+}$ ($x = 0.4, 0.6$ and 0.8) samples recorded after 254 nm irradiation for 10 min at room temperature.

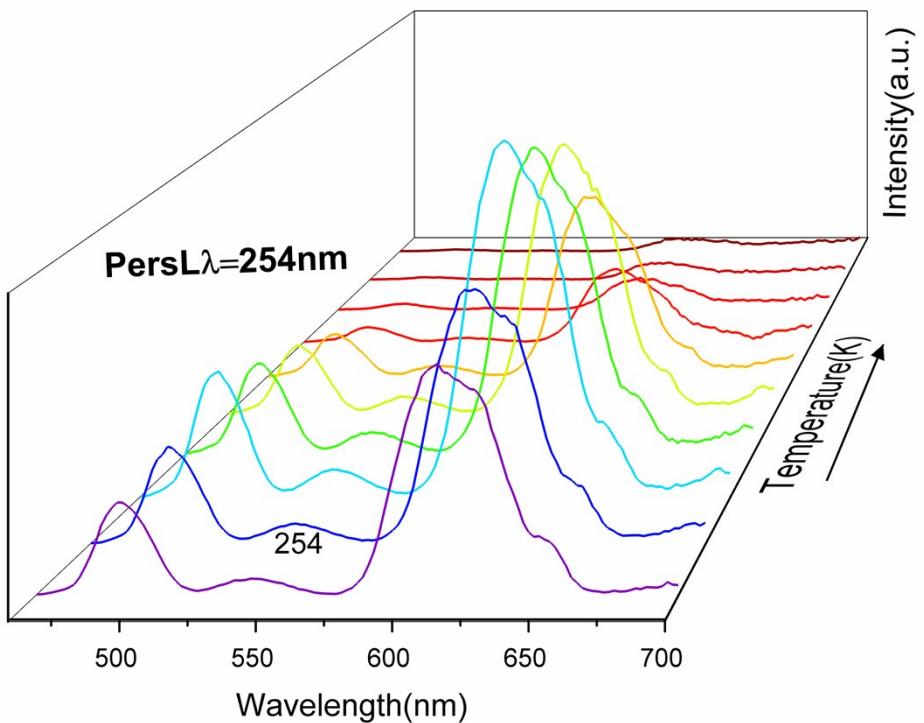


Figure S16, the persistent luminescence spectra of the typical $\text{Na}_2\text{CaGe}_6\text{O}_{14}\text{:}0.6\text{mol}\%\text{Pr}^{3+}$ sample recorded at different temperatures after 254 nm irradiation for 10 min.

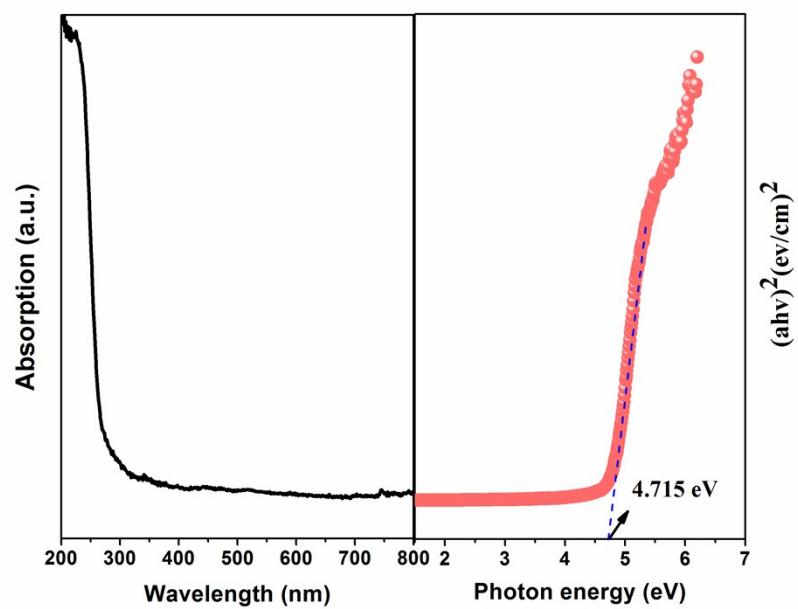


Figure S17, the diffusion reflectance spectrum of the $\text{Na}_2\text{CaGe}_6\text{O}_{14}$ host.

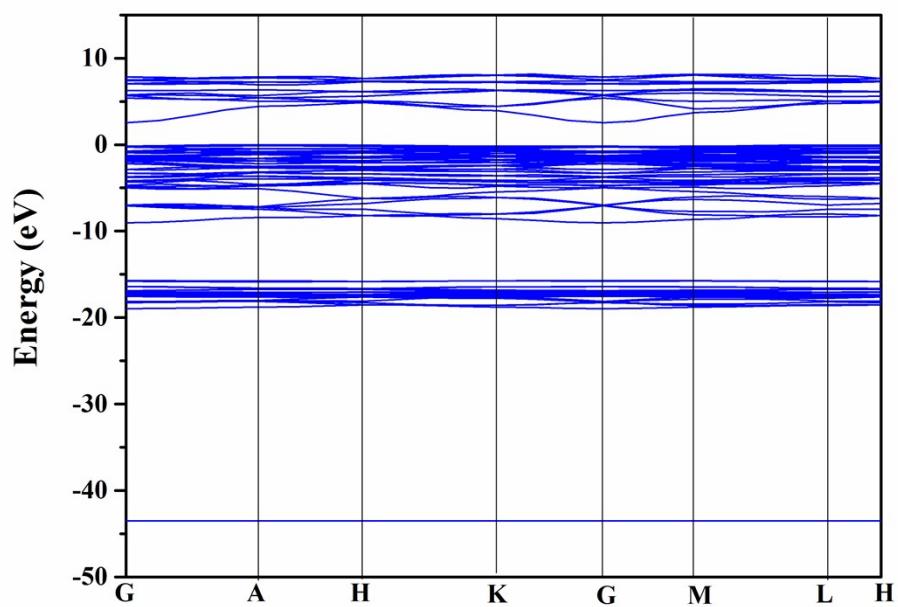


Figure S18, the density functional theory (DFT) calculations on the perfect crystal of
the $\text{Na}_2\text{Ca}\text{Ge}_6\text{O}_{14}$ host.

Table S1, the refined crystallographic data of the Na₂CaGe₆O₁₄.

	Na ₂ CaGe ₆ O ₁₄
Crystal system	Trigonal
Space group	P 321 (150)
Lattice parameters	
a(Å)	8.18493
b(Å)	8.18493
c(Å)	4.84076
$\alpha^\circ = \beta^\circ$	90
γ°	120
Cell volume(Å ³)	280.850
T/K	289
Diffractometer	Rigaku D/Max-2400
Radiation/Å	Cu-Kα ($\lambda = 1.5405$)
Absorption correction	multi-scan
2θ range°/	8-140
Z	1
Calculated Density	2.6552g/cm ³
R-factors	
R _{wp}	0.1694
R _p	0.1222

Table S2, the refined coordinates of the all atoms in the Na₂CaGe₆O₁₄.

Space group		P321 (150) - trigonal			
Cell	a = 8.18493(0) Å; b = 8.18493(0) Å; c = 4.84076(0)				
Ion coordinates	x	y	z	Occupancy	U _{iso}
Na1	0.4238(7)	0.0000(0)	0.0000(0)	1.000(0)	0.002710)
Ca1	0.4237(8)	0.0000(0)	0.0000(0)	1.000(0)	0.009050)
Ge1	0.0000(0)	0.0000(0)	0.0000(0)	1.000(0)	0.041150)
Ge2	0.33330(0)	0.6667(0)	0.3451(16)	1.000(0)	0.503250)
Ge3	0.75299(20)	0.0000(0)	0.5000(0)	1.000(0)	0.052290)
O1	0.33330(0)	0.6667(0)	0.5260(5)	1.000(0)	0.070750)
O2	0.4139(9)	0.2741(9)	0.7412(12)	1.000(0)	0.050510)
O3	0.1851(9)	0.0313(18)	0.4216(27)	1.000(0)	0.413070)

Table S3, the bond lengths of X-O and the unit cell parameters of the $\text{Na}_2\text{CaGe}_6\text{O}_{14}$ as determined by the GSAS program.

The bond lengths of X-O			
Vector	Length (Å)	Vector	Length (Å)
Na1-O2	2.606(8)	Ge1_O3	2.538(15)
Na1-O2	2.483(7)	Ge1_O3	1.722(13)
Na1-O2	2.606(8)	Ge1_O3	2.478(11)
Na1-O3	2.923(12)	Ge2_O1	0.876(8)
Ca1-O2	2.606(8)	Ge2_O2	1.920(7)
Ca1-O2	2.483(8)	Ge3_O2	1.725(6)
Ca1-O2	2.606(8)	Ge3_O3	1.620(15)
Ca1-O3	2.923(12)	Ge3_O3	2.044(10)
Ge1-O3	2.478(11)	Ge3_O3	1.620(15)

Table S4, the ion radius (8 coordinations) and the electronegativity of the Na²⁺, Ca²⁺, Ge⁴⁺, Pr³⁺ ions in the Na₂CaGe₆O₁₄.

Ion	r / Å	r difference / %
Na ⁺	1.18	4.7%
Ca ²⁺	1.12	0.5%
Ge ⁴⁺	0.53	52.9%
Pr ³⁺	1.12	--

$$r \text{ difference} = (r_{\text{solute}} - r_{\text{solvent}}) / r_{\text{solvent}} \times 100\%$$

Table S5, the relative sensitivities of some recently reported optical thermometry

Phosphors	Relative sensitivities (K ⁻¹)	References
Y ₃ Al ₅ O ₁₂ :Eu ³⁺ /Mn ⁴⁺	0.441	[1]
Y ₂ O ₃ :Eu ³⁺ ,Nd ³⁺	0.1	[2]
Zn ₂ SiO ₄ :Mn ²⁺ /Gd ₂ O ₃ :Eu ³⁺	0.07	[3]
Na ₂ La ₂ Ti ₃ O ₁₀ :Pr ³⁺	0.4	[4]
MgLa ₂ TiO ₆ :Pr ³⁺	0.054	[4]
YNbO ₄ :Pr ³⁺	0.105	[4]
CaZnOS:Er ³⁺	0.0033	[5]

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- [3] F. Huang, D. Q. Chen, *J. Mater. Chem. C*, 2017, 5, 5176-5182
- [4] Y. Gao, F. Huang, H. Lin, J. Xu, Y. S. Wang, *Sens. Actuators B*, 2017, 243, 137-143.
- [5] H. L. Zhang, D. F. Peng, W. Wang, L. Dong, C. F. Pan, *J. Phys. Chem. C*, 2015, 119, 28136-28142.

