

Multimodal Dynamic luminescence of self-activated  $\text{Na}_2\text{CaGe}_2\text{O}_6$  phosphors via defects manipulation

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## Experimental section

### Synthesis

A series of  $\text{Bi}^{3+}$  doped  $\text{Na}_2\text{CaGe}_2\text{O}_6$  phosphors were synthesized by a high-temperature solid-state reaction. Reagents of  $\text{Na}_2\text{CO}_3$  (99.99%),  $\text{CaCO}_3$  (99.99%),  $\text{GeO}_2$  (99.99%) and  $\text{Bi}_2\text{O}_3$  (99.99%) were mixed homogeneously in an agate mortar with appropriate amounts of ethanol (A.R.) for 20 min, and all the mixed powder were sintered at 950 °C for 6 h in an ambient atmosphere. Subsequently, the as-obtained samples were naturally cooled to room temperature in furnace and grounded into powder for further analysis.

### Characterizations

The crystal structure of the prepared powder was investigated by X-ray diffraction (XRD) with  $\text{Cu K}\alpha$  Radiation ( $\lambda = 0.154056$  nm) at  $0.02^\circ$  scanning step and 0.2 s time interval. The XRD data were collected in the range of  $10^\circ$  to  $80^\circ$  with a D8ADVANCE/Germany Bruker X-ray diffractometer. The XRD patterns for Rietveld refinement were refined by the Reflex model in Material Studio. The photoluminescence excitation (PLE) and emission spectra (PL) were recorded by a Hitachi F-7000 fluorescence spectrophotometer. Thermoluminescence (TL) curves were recorded using a FJ-427A TL meter (Beijing Nuclear Instrument Factory). The

temperature-dependent PL spectra were measured by using a fluorescence spectrometer (FLS980, Edinburgh Instruments, Edinburgh, UK). The XPS were recorded by using Japan PHI5000 Versaprobe III. The morphology was recorded by a scanning electron microscope (SEM, JIB-4700). Photographs of the as-obtained phosphors were recorded by digital camera of Nikon D7500 (ISO: 12800, AV mode, Focal Length: 16 to 55 mm, shutter: 1/300s.)

### **Computational methodology**

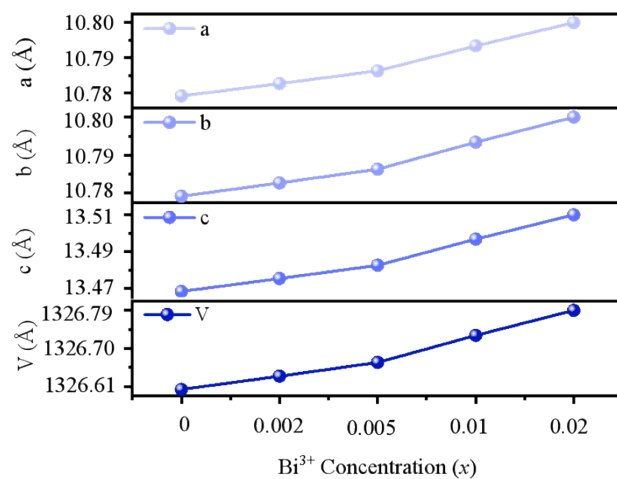
The electronic structure of the phosphor matrix was calculated based on the density functional theory (DFT) using the Cambridge Serial Total Energy Package (CASTEP) package of Materials Studio. All the calculations were based on the Perdew-Burke-Ernzerhof (PBE) generalized function of the generalized gradient approximation (GGA)<sup>1</sup>. The cutoff energy  $E_{\text{cut}}$  and k-point mesh were set to 537 eV and the  $1 \times 1 \times 1$  MonkhorstPack grid, respectively, which are sufficient for energy convergence.

The formation energies ( $E_f$ ) of the two intrinsically defective  $\text{Na}_2\text{CaGe}_2\text{O}_6$  phosphors was calculated by the following equation<sup>2</sup>:

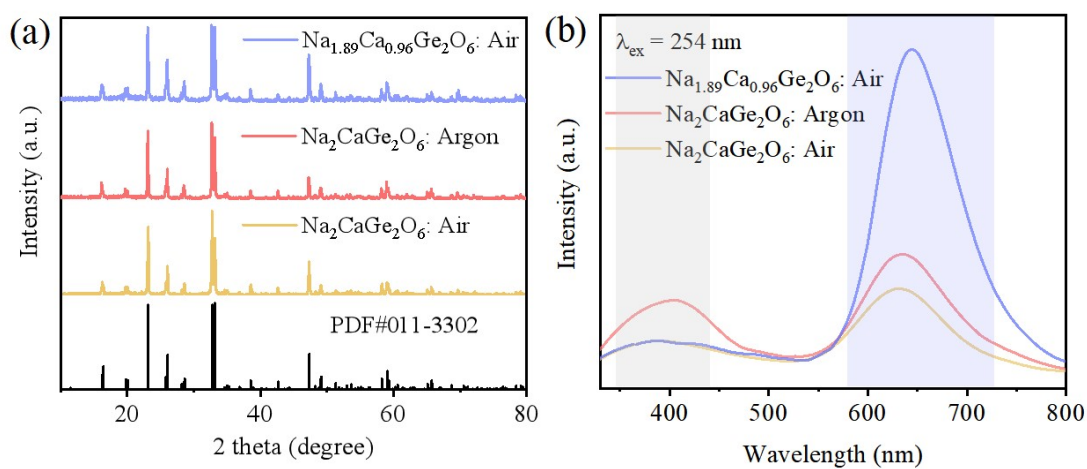
$$E_f = E_{\text{defect}} - E_{\text{Na}_2\text{CaGe}_2\text{O}_6} + \Delta n_x \mu_x$$

where  $E_{\text{defect}}$  is the total energy introduced into the defective systems,  $E_{\text{Na}_2\text{CaGe}_2\text{O}_6}$  is the total energy of  $\text{Na}_2\text{CaGe}_2\text{O}_6$  bulk systems,  $\Delta n_x$  is the number of atoms,  $\mu_x$  is the chemical potential of substituted atoms. In this case,  $x$  represents the atoms Al.

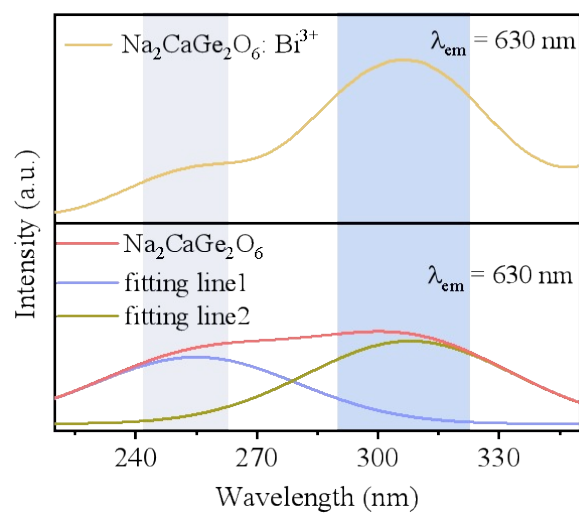
## Supporting figures and tables



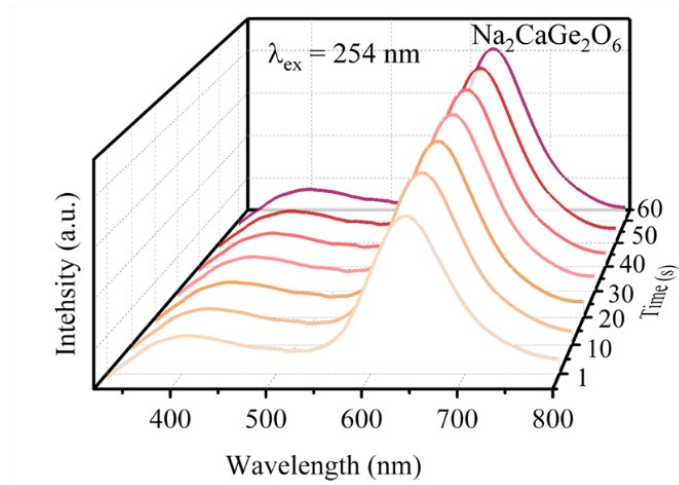
**Fig. S1** Cell parameters dependent on the concentration of  $\text{Bi}^{3+}$  ions.



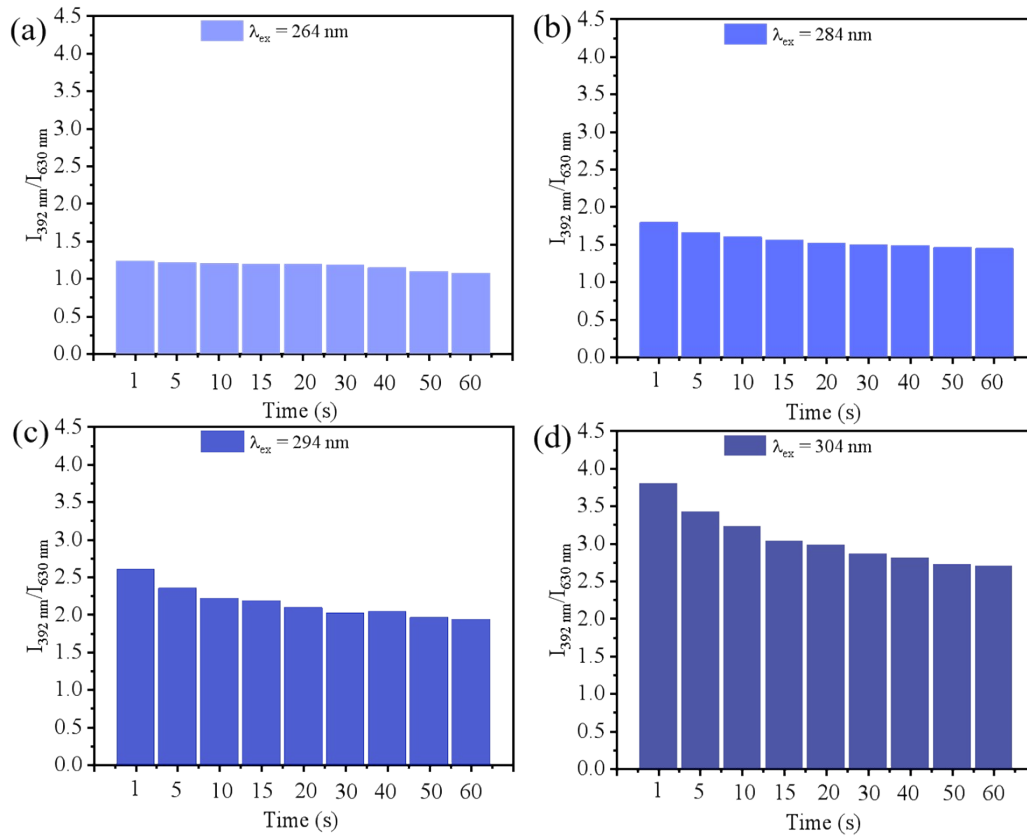
**Fig. S2.** (a) XRD patterns and (b) PL spectra recorded under 254 nm excitation of  $\text{Na}_{1.89}\text{Ca}_{0.96}\text{Ge}_2\text{O}_6$ : Air,  $\text{Na}_2\text{CaGe}_2\text{O}_6$ : Argon, and  $\text{Na}_2\text{CaGe}_2\text{O}_6$ : Air samples, respectively.



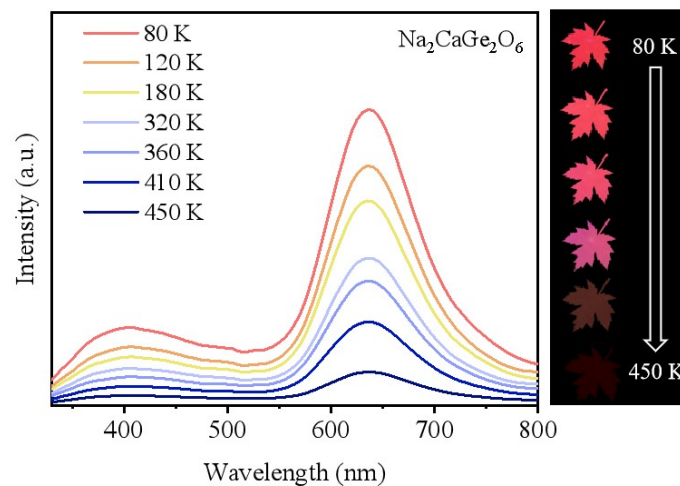
**Fig. S3.** PLE spectra of  $\text{Na}_2\text{CaGe}_2\text{O}_6$  and  $\text{Na}_2\text{CaGe}_2\text{O}_6: \text{Bi}^{3+}$  phosphors, respectively.



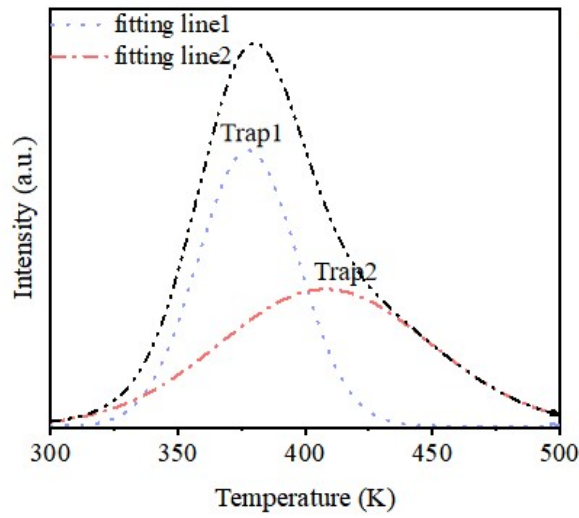
**Fig. S4.** Time-resolved PL spectra of  $\text{Na}_2\text{CaGe}_2\text{O}_6$  sample under 254 nm excitation.



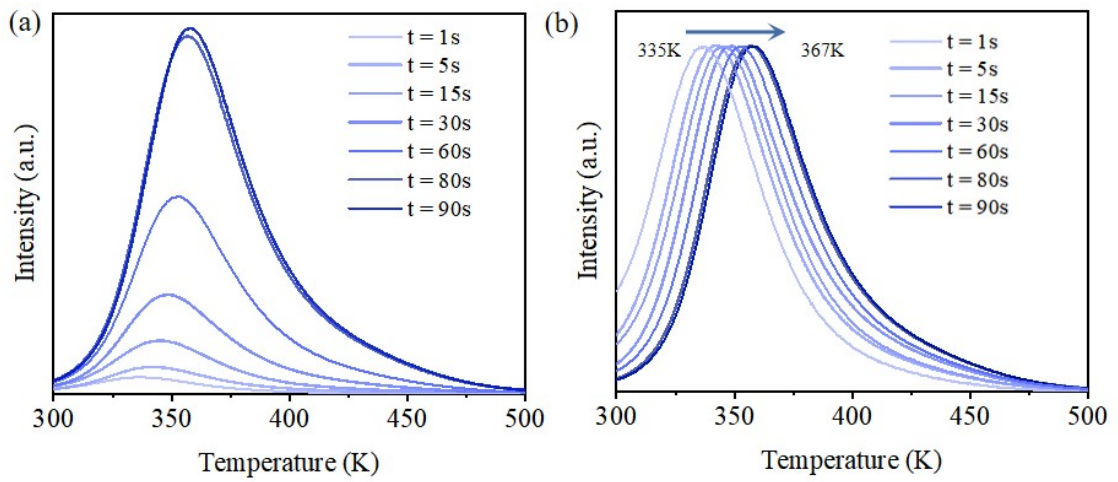
**Fig. S5.** The ration of  $I_{392\text{ nm}}/I_{630\text{ nm}}$  ratio by prolonging the irradiation time from 1 to 60 s under the employed pump sources excitation with (a) 264, (b) 284, (c) 294 and (d) 304 nm, respectively.



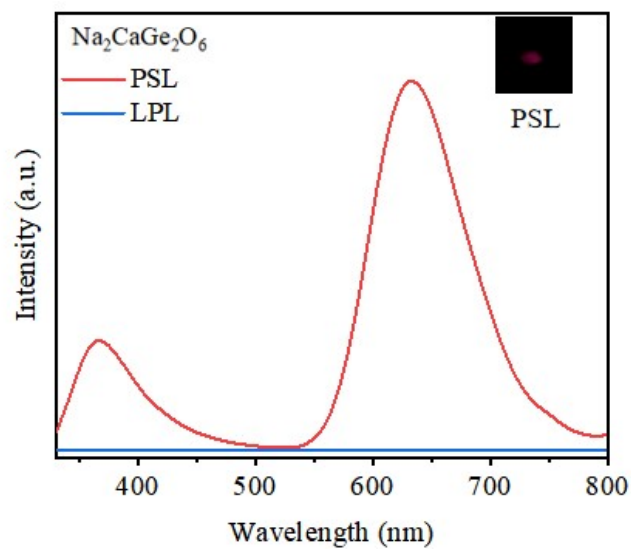
**Fig. S6.** Temperature-dependent PL spectra of  $\text{Na}_2\text{CaGe}_2\text{O}_6$  sample.



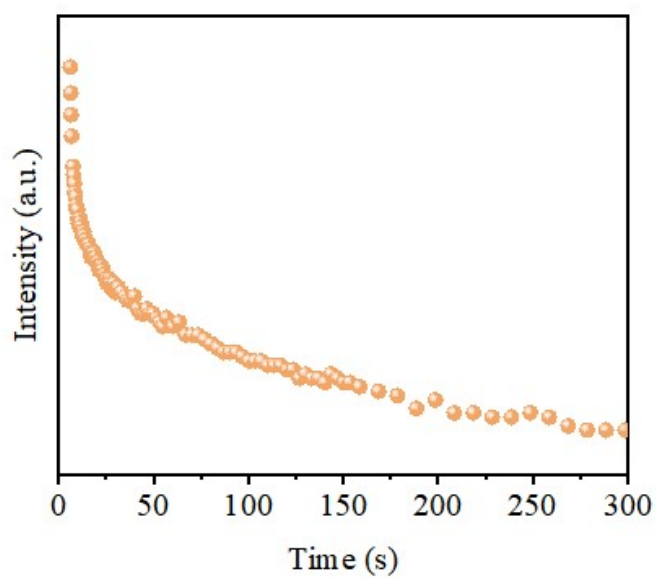
**Fig. S7.** Gaussian fitted TL curves of  $\text{Na}_2\text{CaGe}_2\text{O}_6: 0.002\text{Bi}^{3+}$ .



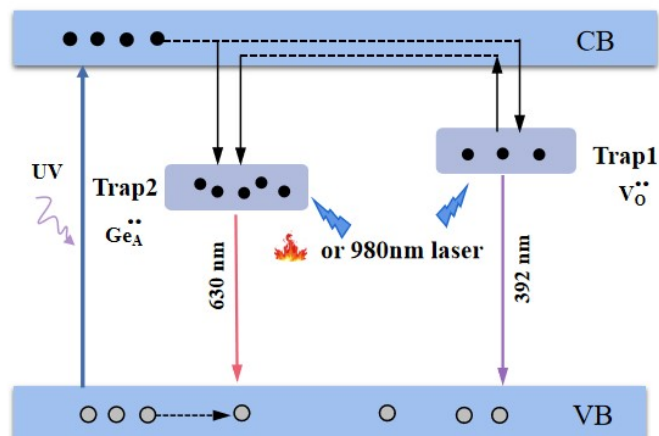
**Fig. S8.** (a) Excitation duration-dependent TL curves, and (b) Normalized TL curves of  $\text{Na}_2\text{CaGe}_2\text{O}_6: 0.002\text{Bi}^{3+}$ , respectively.



**Fig. S9.** LPL and PSL spectra of Na<sub>2</sub>CaGe<sub>2</sub>O<sub>6</sub> sample after being charged by 254 nm UV lamp for 5 min, respectively.



**Fig. S10.** LPL decay curve of Na<sub>2</sub>CaGe<sub>2</sub>O<sub>6</sub>: 0.002Bi<sup>3+</sup> sample after being charged by 254 nm UV lamp for 5 min.



**Fig. S11.** Schematic diagram of the mechanism for PL, LPL, and PSL procedure of  $\text{Na}_2\text{CaGe}_2\text{O}_6: \text{Bi}^{3+}$  sample.

**Table S1.** Gaussian-fitted peaks for O 1s XPS spectra of  $\text{Na}_2\text{CaGe}_2\text{O}_6$ : Argon and  $\text{Na}_2\text{CaGe}_2\text{O}_6$ : Air samples.

Sample	PeakI(eV) /Int.	PeakII(eV) /Int.	PeakIII(eV) /Int.	PeakIV(eV) /Int	I(OI)/ (OII)
$\text{Na}_2\text{CaGe}_2\text{O}_6$ :	528.80/8458.	529.90/112	531.10/757	533.85/689	1.34
Air	98	96.62	8.30	1.98	
$\text{Na}_2\text{CaGe}_2\text{O}_6$ :	529.05/7001.	529.95/119	531.40/618	534.05/605	1.71
Argon	51	45.90	2.15	6.77	



**Table S2.** Typical defects in self-activated materials.

Materials	$\lambda_{em}$ (nm)	Defects	Ref.
AZn <sub>4</sub> (BO <sub>3</sub> ) <sub>3</sub> (A = K, Rb, and Cs)	505, 585	$V_o^{\cdot\cdot}, V_{Zn, O_i}''$	3
YBO <sub>3</sub>	230, 240, 254, 405	$V_o^{\cdot\cdot}$	4
Zn <sub>2</sub> GeO <sub>4</sub>	370-380 , 500-540	$Zn_i^{\cdot\cdot}, V_o^{\cdot\cdot}, V_{Ge}''''', V_{Zn}''$	5
Ca <sub>2</sub> Ge <sub>7</sub> O <sub>16</sub>	310-600	$V_o^{\cdot\cdot}, V_{Ca}''$	6
Na <sub>2</sub> (Zn <sub>0.8</sub> Ga <sub>0.2</sub> )GeO <sub>4</sub>	407	$V_o^{\cdot\cdot}, Zn_i^{\cdot\cdot}, V_{Zn}'' \square$	7
Ca <sub>0.84</sub> Ba <sub>0.16</sub> ZnOS	460, 515, 601	$V_o^{\cdot\cdot}$ and $O_i^{\cdot}$	8
MgGa <sub>2</sub> O <sub>4</sub>	424	$V_o^{\cdot\cdot}, V_{Mg}''', V_{Ga}''''$	9
ZnGa <sub>2</sub> O <sub>4</sub>	1270	$V_o^{\cdot\cdot}, V_{Zn}''', Zn_{Ga}'$	10
SrCaGa <sub>4</sub> O <sub>8</sub>	395, 550	$V_{Ga}''''', V_o^{\cdot\cdot}$	11
SrGa <sub>2</sub> O <sub>4</sub>	373, 401	$V_o^{\cdot\cdot}, V_{Sr}''$	12

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