

Supporting information

Ternary Afterglow and Dynamic Anti-counterfeiting Application of Self-activated Zinc Germanate

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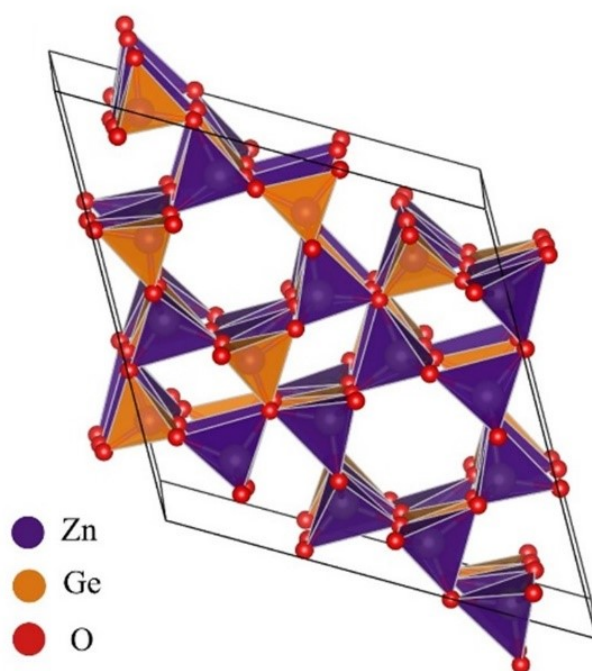


Fig. S1. Crystal structure of ZGO. Purple balls represent Zn atoms, orange balls represent Ge atoms, and red balls represent O atoms.

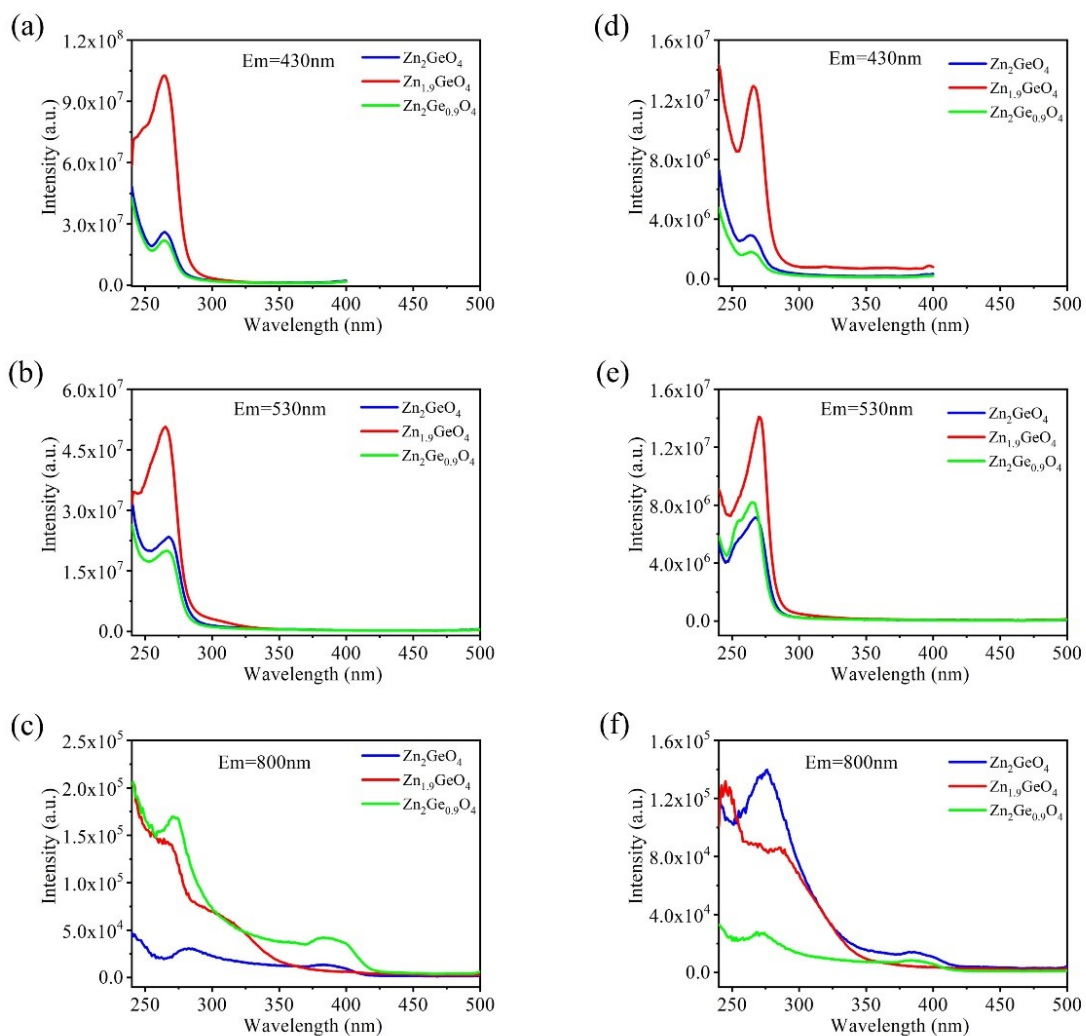


Fig. S2. Excitation spectra of ZGO at emission wavelengths of (a) 430 nm, (b) 530 nm, and (c) 800 nm in air atmosphere and (d) 430 nm, (e) 530 nm, and (f) 800 nm in N₂ atmosphere.

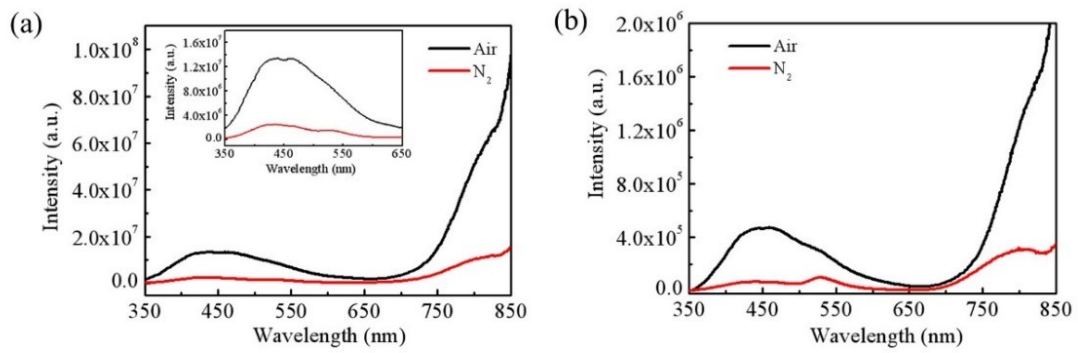


Fig. S3. (a) Steady-state and (b) time-resolved emission spectra of $Zn_{1.9}GeO_4$ in different sintering atmospheres.

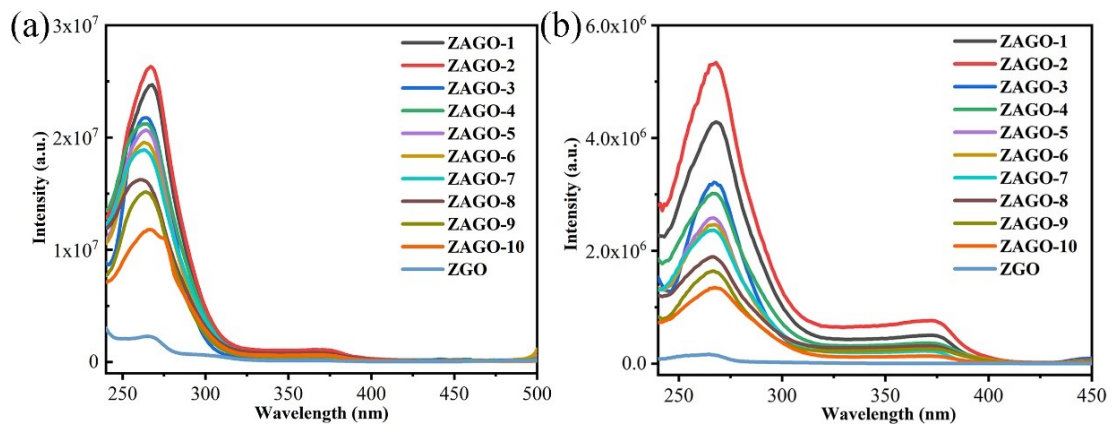


Fig. S4. Excitation spectra of ZAGO at different doping concentrations of Al³⁺ monitored at (a) 530 nm and (b) 632 nm.

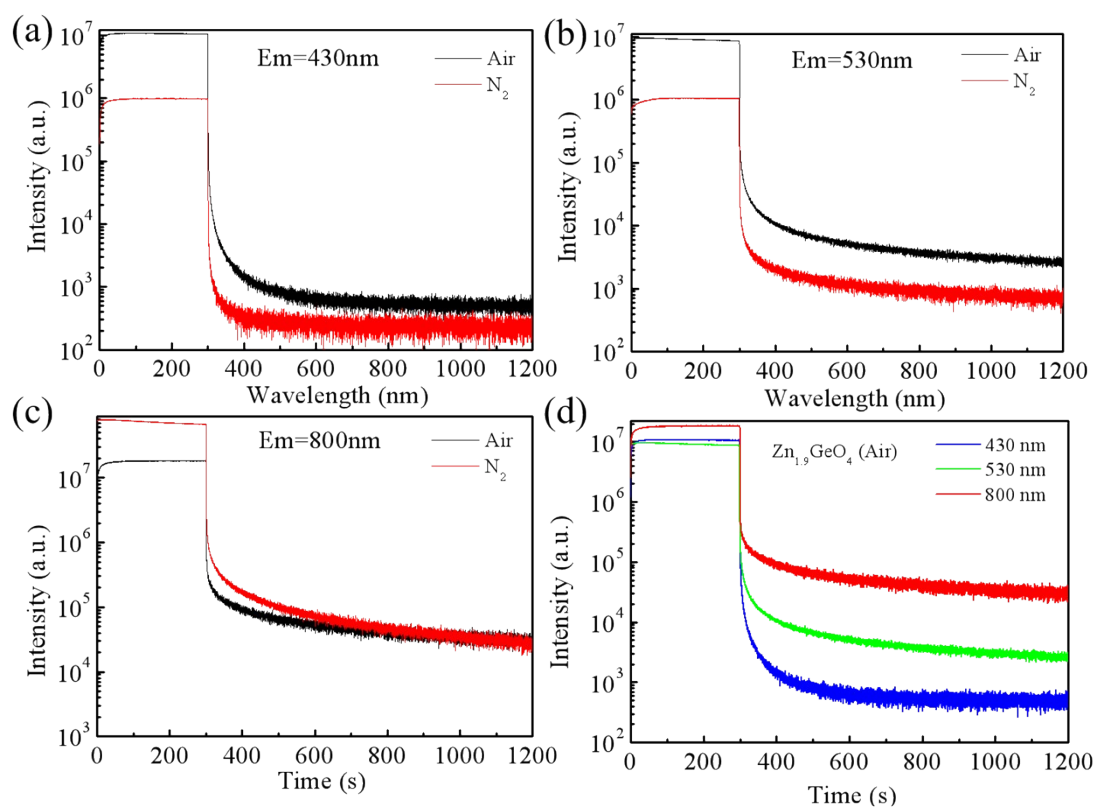


Fig. S5. The decay curves of $Zn_{1.9}GeO_4$ at emission wavelengths of (a) 430 nm, (b) 530 nm, and (c) 800 nm in different sintering atmospheres, together with (d) $Zn_{1.9}GeO_4$ at different emission wavelengths in air atmosphere.

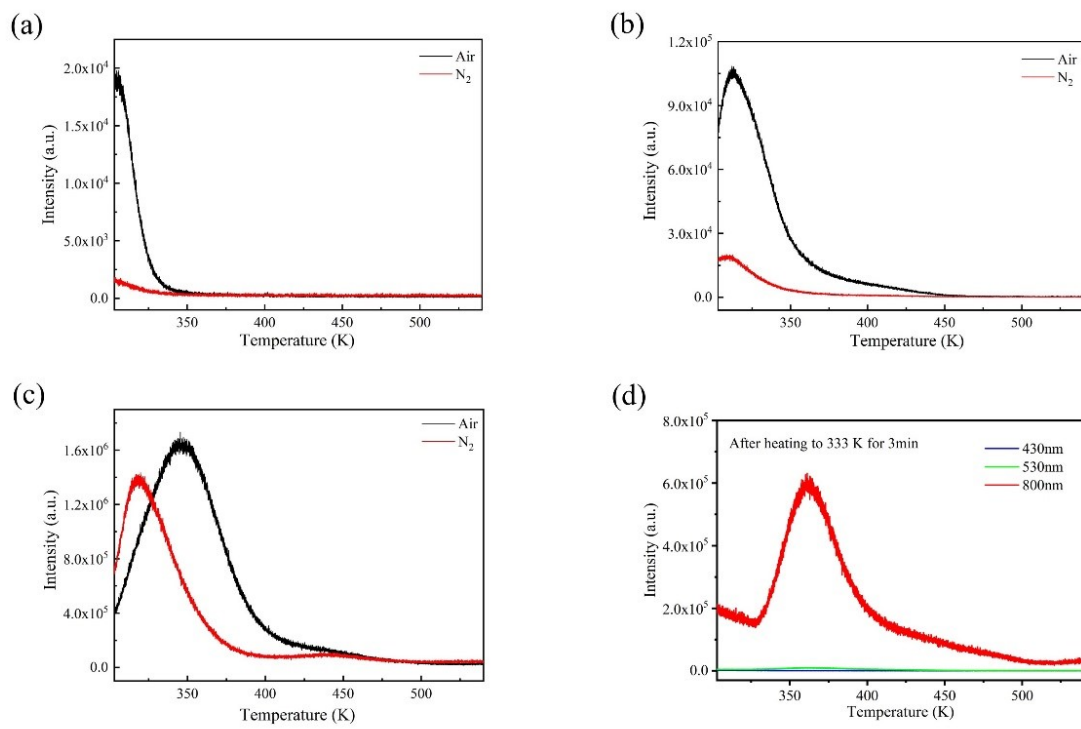


Fig. S6. The thermoluminescence spectra of $Zn_{1.9}GeO_4$ at emission wavelengths of (a) 430 nm, (b) 530 nm, and (c) 800 nm in different sintering atmospheres, together with (d) $Zn_{1.9}GeO_4$ after thermal clearance at 333 K in air atmosphere.

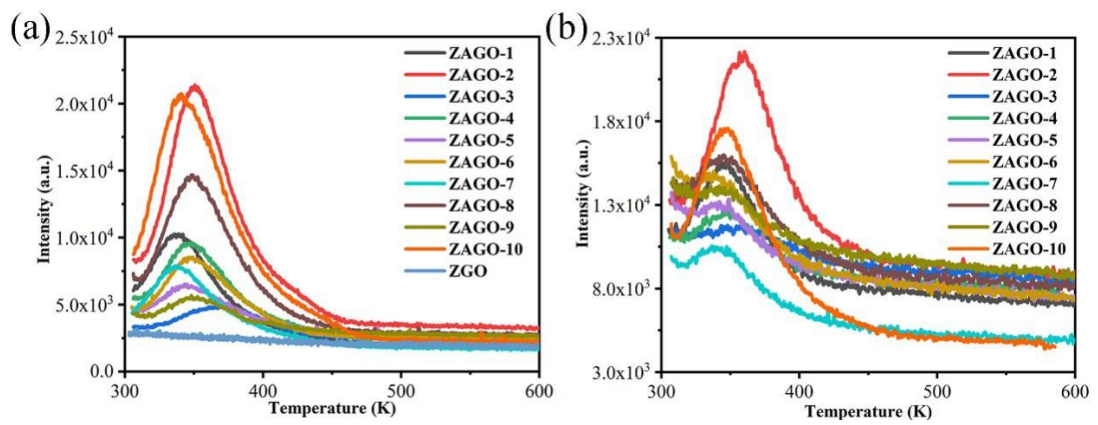


Fig. S7. TL spectra of ZAGO at emission wavelengths of (a) 530 nm, and (b) 632 nm in different atmospheres, together with (c) peak temperature and (d) trap depth of ZAGO at different emissions. ZAGO, Al³⁺-doped zinc germanate; TL, thermoluminescence.

Table S1

The designed stoichiometric ratios and sintering atmospheres for ZGO samples.

Sample	Zn/Ge ratio	Sintering atmosphere
$\text{Zn}_{1.9}\text{GeO}_4$	1.9:1	air, N ₂ , CO
Zn_2GeO_4	2:1	air, N ₂ , CO
$\text{Zn}_2\text{Ge}_{0.9}\text{O}_4$	1:1.9	air, N ₂ , CO

Table S2

The doping content and chemical composition of ZAGO samples.

Sample	Doping content	Chemical composition
ZGO	0	Zn_2GeO_4
ZAGO-1	0.005	$\text{Zn}_2\text{Al}_{0.005}\text{Ge}_{0.995}\text{O}_4$
ZAGO-2	0.01	$\text{Zn}_2\text{Al}_{0.01}\text{Ge}_{0.99}\text{O}_4$
ZAGO-3	0.015	$\text{Zn}_2\text{Al}_{0.015}\text{Ge}_{0.985}\text{O}_4$
ZAGO-4	0.02	$\text{Zn}_2\text{Al}_{0.02}\text{Ge}_{0.98}\text{O}_4$
ZAGO-5	0.025	$\text{Zn}_2\text{Al}_{0.025}\text{Ge}_{0.975}\text{O}_4$
ZAGO-6	0.03	$\text{Zn}_2\text{Al}_{0.03}\text{Ge}_{0.97}\text{O}_4$
ZAGO-7	0.035	$\text{Zn}_2\text{Al}_{0.035}\text{Ge}_{0.965}\text{O}_4$
ZAGO-8	0.04	$\text{Zn}_2\text{Al}_{0.04}\text{Ge}_{0.96}\text{O}_4$
ZAGO-9	0.045	$\text{Zn}_2\text{Al}_{0.045}\text{Ge}_{0.955}\text{O}_4$
ZAGO-10	0.05	$\text{Zn}_2\text{Al}_{0.05}\text{Ge}_{0.95}\text{O}_4$

Table S3

Bandgap widths of ZAGO samples.

Sample	Bandgap width/eV
ZGO	4.40
ZAGO-1	4.37
ZAGO-2	4.36
ZAGO-3	4.35
ZAGO-4	4.30
ZAGO-5	4.33
ZAGO-6	4.32
ZAGO-7	4.07
ZAGO-8	4.23
ZAGO-9	4.31
ZAGO-10	4.31

Table S4

Parameters for double-exponentially fitting afterglow decay of ZGO and a representative ZAGO sample.

Sample	τ_1/s	A_1	τ_2/s	A_2	τ_{avg}/s
ZGO	7.2	2.43	84.63	0.68	66.58
ZAGO-2	8.95	1.81	131.20	1.35	120.95

Table S5

The positions of thermal release peak and the depths of trap in ZGO samples.

Emission Wavelength h		$Zn_2Ge_{0.9}O_4$		Zn_2GeO_4		$Zn_{1.9}GeO_4$	
		air	N ₂	air	N ₂	air	N ₂
430 nm	Temperature (K)	< 303	< 303	303	< 303	303	< 303
	Depth (eV)	< 0.61	< 0.61	0.61	< 0.61	0.61	< 0.61
530 nm	Temperature (K)	< 303	307	307	< 303	313	307
	Depth (eV)	< 0.61	0.61	0.61	< 0.61	0.63	0.61
800 nm	Temperature (K)	311	319	311	319	345	319
		423	408	423	408	453	453
	Depth (eV)	0.62	0.64	0.62	0.64	0.70	0.64
		0.85	0.82	0.85	0.82	0.91	0.91