Electronic Supplementary Information

Lattice-site engineering in ZnGa₂O₄:Cr³⁺ through Li⁺ doping for dynamic luminescence and advanced optical anti-counterfeiting

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Experimental section

Materials and synthesis

The series of ZnGa₂O₄:0.005Cr³⁺,*x*Li⁺ (x = 0-0.1) solid-solution phosphors were synthesized via reacting from 99.99% pure ZnO, Ga₂O₃, Cr₂O₃, and Li₂CO₃, which were purchased from Aladdin Chemical Reagent Co. Ltd (Shanghai, China). According to the chemical formula of Li_{*x*}Zn_{1-*x*}Ga₂O₄:0.005Cr³⁺, stoichiometric amounts of ZnO, Ga₂O₃, Cr₂O₃, and Li₂CO₃ were mixed by grinding with an agate mortar and pestle for 30 minutes. Then the mixed powder was pre-fired in an alumina crucible at 900 °C for 4 h in air. After cooling to room temperature and regrinding for 30 minutes, the powder was heated at 1000 °C for 4 h in air to produce the final phosphors. The heating rate for the two stages of heating is 5 °C min⁻¹.

Characterization techniques

Phase identification was performed by X-ray diffractometry (XRD, Model SmartLab, Rigaku, Tokyo, Japan) operating at 40 kV/40 mA using nickel filtered Cu K α radiation and a scanning speed of 6.0° 20/min. The morphology of the samples was observed by field-emission scanning electron microscopy (FE-SEM, Model S-4800, Hitachi, Tokyo) under an acceleration voltage of 15 kV. The high-resolution transmission electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS) mapping were carried out using JEM2000FX (JEOL) under an accelerating voltage of 200 kV (TEM, Model JEM-2000FX, JEOL). X-ray photoelectron spectroscopy (XPS, Model Axis Supra, Shimadzu-Kratos Analytical Ltd., Manchester, UK) was irradiated by monochromatized Al Ka X-ray (1486.6 eV) excitation. The data of binding energies was corrected by using the C1s peak (284.8 eV) of carbon impurities as the standard. The testing area is $300 \times 700 \ \mu\text{m}^2$. Solidstate ⁷Li DD/MAS NMR spectra were recorded on an Agilent 600 DD2 spectrometer (Agilent, USA, magnetic field strength 14.1 T) at resonance frequency of 199.13 MHz for ⁷Li using the dipole decoupling magic-angle spinning (DD/MAS), and a highpower 1H decoupling. The powder samples were placed in a pencil-type zirconia rotor of 4.0 mm o.d. The spectra were obtained at a spinning speed of 8 kHz (4 µs 90°

pulses), and a recycle delay of 10 s. The EPR spectra of the samples were measured at room temperature using an EPR spectrometer (JESFA200, JEOL, Japan) with an X-band power of 0.998 mW. The Li signal of tetramethylsilane (TMS) at 0 ppm was used as the reference of ⁷Li chemical shift. The scanning number is 5000. The photoluminescence spectra of phosphors were taken by Model JY FL3-21 spectrophotometer (Horiba, Kyoto) using a 450 W xenon lamp for excitation, a scan speed of 500 nm min⁻¹ and a slit-width of 2 nm for both excitation and emission. Diffuse reflectance spectra of the samples were measured using an UV-Vis-NIR spectrophotometer (UV-3600 Plus, Shimadzu, Kyoto) in the spectral range of 200 - 800 nm at room temperature.

Computational details

The calculations were carried out by using density functional theory (DFT), as implemented in the Vienna ab initio Simulation Package (VASP). The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) were used to treat the exchange correlations. The energy cut-off for the plane-wave basis set was kept at a fixed value of 520 eV. Structure optimization was accomplished until the force on each atom is less than 0.01 eV Å⁻¹.

Preparation of anti-counterfeiting logo

Both transparent luminescent inks and glue were used in this study for the design of anti-counterfeiting logo. For screen-printing, the transparent luminescent inks were prepared by mixing the phosphors and transparent ink (commercially polyvinyl chloride), followed by stirring and ultrasonic treatment. The security pattern of "Facial Makeup" and "Auspicious Cloud" were designed through screen printing, which used three different transparent luminescent inks fabricated by $ZnGa_2O_4:0.005Cr^{3+},xLi^+$ (x = 0, 0.02, 0.08) phosphors in different parts of the patterns. While, the translucent glue prepared by phosphors and silicone rubber was used to design the multimodal optical alphanumeric code.

	<i>E</i> (Doped) <i>E</i> (perfect)		μ	$\Delta {E}_{ m f}$
Li-Ga	-307.85	-312.70	0	5.15
Li-Zn	-312.80	-312.70	0	0.10
Li-inters1	-313.96	-312.70	1.91	0.65
Li-inters2	-310.71	-312.70	1.91	3.90
Li-inters3	-313.60	-312.70	1.91	1.01

Table S1. The calculated formation energies (ΔE_f) of Li⁺ doping.



Figure S1. (a, b) TEM image, (c) SAED pattern, (d) HR-TEM image, (e-h) elemental mapping, and (i) XPS survey spectrum of ZGLC sample (x = 0.06). (e-h) are the element distribution of (e) Zn, (f) Ga, (g) O, (h) Cr, respectively.

Table S2. The binding energies of the Li 1s core-levels of ZGCL.

x	Binding energy (eV)	Area percent (%)	FWHM
0.02	54.88	100	2.28
0.04	54.96	100	1.78
0.06	54.95	100	1.47
0.08	55.03	80.3	1.21
	53.93	19.7	1.38

Table S3. The binding energies of the O 1s core-levels of ZGCL

x	Binding energy (eV)	Area percent (%)	FWHM
0	530.62	68.82	1.32
	531.85	31.18	2.34
0.02	530.63	65.52	1.32
	531.80	34.48	2.35
0.04	530.63	61.42	1.29
	531.72	38.58	2.52
0.06	530.58	50.62	1.39
	531.62	49.38	2.39
0.08	530.59	54.69	1.28
	531.65	45.31	2.56



Figure S2. CIE chromaticity diagram and fluorescent lighting images for the ZGCL phosphors.

Table S4. CIE chromaticity coordinate of ZGCL ($\lambda_{ex} = 254 \text{ nm}$)

x	CIE x	CIE y
0	0.389	0.196
0.02	0.293	0.271
0.04	0.300	0.305
0.06	0.318	0.333
0.08	0.337	0.352

Table S5. CIE chromaticity coordinate of ZGCL ($\lambda_{ex} = 302 \text{ nm}$).

x	CIE x	CIE y
0	0.436	0.294
0.02	0.401	0.448
0.04	0.373	0.436
0.06	0.359	0.431
0.08	0.354	0.427



Figure S3. NIR-persistent luminescence decay curves of ZGCL obtained after 5-min illumination with 254 nm (a, c) and 302 nm UV light (b, d). The insets in (a-d) are the decay curves in semi-log scale. (e) is NIR afterglow images after 5-min illumination with 254 nm and a-e are x = 0-0.08, respectively.

Figure S4. TL glow curves of ZGCL samples.

Table S6. The parameters of the TL curves of ZGCL.

Samples	<i>x</i> =0	<i>x</i> =0.02	<i>x</i> =0.04	<i>x</i> =0.06	<i>x</i> =0.08
$T_{\rm m}({\rm K})$	408	412	414	415	419
<i>E</i> (eV)	0.819	0.824	0.828	0.830	0.838

Figure S5. FIR of I_{470}/I_{695} and I_{520}/I_{695} at different temperatures for x = 0.06 sample at excitation of (a) 254 nm and (b) 302 nm.

Figure S6. CIE chromaticity diagram of x = 0.06 sample at different temperature under different 254 nm (a) and 302 nm (b) UV light.

Figure S7. The image of ZGCL powders under natural light.

Figure S8. Emission images of the pattern of "Auspicious Cloud" printed with transparent luminescent inks.