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Supporting Information

Dual center luminescence characteristics and multifunctional applications of Li₂Ge₇O₁₅:Cr³⁺ near-infrared phosphors

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Supplementary Experimental Part

1 Material synthesis and preparation

A series of $\text{Li}_2\text{Ge}_7\text{O}_{15}$:xCr³⁺ (x = 0-0.1) (LG:xCr³⁺) NIR phosphors were prepared by hightemperature solid-phase method. The high purity Li₂CO₃(99%), GeO₂(99.99%) and Cr₂O₃(99%) were weighed strictly according to the stoichiometric ratio and transferred to an agate mortar. They were ground thoroughly for 30 min and then placed in an alumina crucible and sintered at 1500 °C for 8 h. The heating rate is 3°C/min. After natural cooling, the final products were collected samples for further characterization.

2 Characterization

The phase structure was studied by a Cu K α ($\lambda = 1.5406$ Å) radiation (Bruker D8 Advance) Xray diffractometer. The morphology and elemental distribution of the phosphors were observed by a scanning electron microscope (SEM) equipped with an X-ray energy spectrometer (EDS). X-ray photoelectron spectroscopy (XPS) spectra were acquired using an AXIS SUPRA+ model from Shimadzu to analyze the surface elements and chemical states of the materials. The diffuse reflectance spectra of the prepared samples were recorded with a Cary 5000 UV-Vis spectrophotometer. Structural optimization was performed by Vienna Ab-initio Simulation Package (VASP)¹ with the projector augmented wave (PAW) method². The exchange-functional was treated using the Perdew-Burke-Ernzerhof (PBE)³ functional to describe the weak interactions between atoms. The cut-off energy of the plane-wave basis was set at 400 eV in structural optimization. Emission spectra, excitation spectra and fluorescence decay of the synthesized samples were tested by an Edinburgh Instruments FLS-1000 spectrometer in conjunction with an Edinburgh Instruments integrating sphere. The temperature-dependent emission spectra were tested with exciting spectra and thermal quenching analyzer for phosphor. An integrating sphere spectroradiometer system (HASS-2000, 350-1650 nm, Everfine) were tested with pc-LEDs performance.

3 NIR-LEDs

The NIR pc-LEDs were prepared with 410 nm blue chips and LG: $0.02Cr^{3+}$ phosphors. The epoxy resins A and B gels were mixed with LG: $0.02Cr^{3+}$ phosphors, and then coated on the 410 nm chip, followed by curing at 120°C for 2 h.

Supplementary Notes

1.Calculation of the crystal field

It is well known that its optical band gap (i.e., Eg) can be estimated using the Kubelka-Munk expression as follows.

$$[F(R)hv] = A(hv - E_g)^n \tag{1}$$

$$F(R) = \frac{(1-R)^2}{2R}$$
(2)

In these equations, the parameters R, h, and v are the reflection constant, Planck's coefficient, and frequency, respectively, while the value of n is dictated by the nature of the optical transition in the material, with n being equal to 1/2 in the case of an indirect transition. The optical band gap of LAGS is 3.27 eV as shown in Figure 1h.

2.Calculation of the crystal field

According to the crystal field theory, the spectroscopic parameters can be calculated by the following equation:

$$10Dq = E({}^{4}T_{2} - {}^{4}A_{2})$$
(3)
$$Dq = 15(y - 8)$$

$$\frac{Dq}{B} = \frac{15(y-8)}{y^2 - 10y} \tag{4}$$

$$y = \frac{E({}^{4}T_{1} - {}^{4}A_{2}) - E({}^{4}T_{2} - {}^{4}A_{2})}{Dq}$$
(5)

$$\frac{E(^{2}E_{g} - {}^{4}A_{2})}{B} = \frac{3.05C}{B} - \frac{1.8B}{Dq} + 7.9$$
(6)

Here, the peak position of the ${}^{2}E_{g}$ - ${}^{4}A_{2}$ transition is 695 nm.

Supporting Figures and tables



Figure S1. Rietveld refinement data of LG:0.02Cr³⁺(a) and LG:0.10Cr³⁺(b).



Figure S2. Emission (a), normalized excitation (b-c) spectra of LG:xCr³⁺.



Figure S3. PL decay time spectra.



Figure S4. (a) Formation energy of LG with case 1: $Cr \rightarrow Li$, case 2: $Cr \rightarrow Ge$, case 3: $3Cr \rightarrow Li\&2Ga$, (b) Two-dimensional display of the slice.



Figure S5. FIR values of LG: $0.02Cr^{3+}$ (a)-(b) and LG: $0.10Cr^{3+}$ phosphors (c)-(d).

Termement.			
Formula	x = 0.00	x = 0.02	x = 0.10
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pbcn	Pbcn	Pbcn
a [Å]	7.37374	7.37241	7.37134
b [Å]	16.74240	16.74640	16.7465
c [Å]	9.71887	9.72142	9.72030
$\alpha = \beta = \gamma [\circ]$	90.0000	90.0000	90.0000
Cell volume [Å ³]	1199.83	1200.22	1199.91
$R_{\rm p}$ (%)	4.65	5.52	3.86
$R_{ m wp}$ (%)	6.14	6.95	4.78
χ^2	1.525	1.428	1.284

Table S1. Lattice parameters of the LG:xCr³⁺ phosphors obtained from the Rietveld XRD refinement.

		x = 0.00		
Site	X	V	Z	Occ
Gel	0.00000	0.41300	0.25000	1.00000
Ge2	0.21350	0.21350 0.05830 0.24900		1.00000
Ge3	0.28370	0.34040	0.03310	1.00000
Ge4	0.28630	0 34470	0 47140	1 00000
01	0.00000	0.01590	0.25000	1.00000
02	0.28860	0.08890	0.23000	1.00000
03	0.18940	0.14790	0.15240	1.00000
04	0.10040	0.24910	0.13240	1.00000
05	0.13880	0.33060	0.43000	1.00000
06	0.19000	0.35910	0.17040	1.00000
00	0.1//00	0.33710	0.00470	1.00000
08	0.14490	0.41720	0.40340	1.00000
1.1	0.14180	0.49320	0.10780	1.00000
	0.00000	0.30000	0.00000	1.00000
L12	0.00000	0.24140	0.23000	1.00000
		x = 0.02		
Site	Х	У	Z	Occ
Gel	0.00000	0.41300	0.25000	0.98660
Cr1	0.00000	0.41300	0.25000	0.01340
Ge2	0.21350	0.21350 0.05830 0.24900		1.00000
Ge3	0.28370	0.34040	0.03310	1.00000
Ge4	0.28630	0.34470	0.47140	1.00000
O1	0.00000	0.01590	0.25000	1.00000
O2	0.28860	0.08890	0.41170	1.00000
O3	0.18940	0.14790	0.15240	1.00000
O4	0.20170	0.24910	0.43860	1.00000
05	0.13880	0.33060	0.17040	1.00000
O6	0.49940	0.35910	0.09470	1.00000
07	0.14490	0.41720	0.40840	1.00000
O8	0.14180	0.49320	0.16780	1.00000
Li1	0.00000	0.50000	0.00000	0.99690
Cr2	0.00000	0.50000	0.00000	0.00310
Li2	0.00000	0.24140	0.25000	0.99650
Cr3	0.00000	0.24140	0.25000	0.00350
		r = 0.10		
Site	v	л 0.10 V	7	Occ
Gel	0 00000	y 0.41300	0 25000	0 93300
	0.00000	0.41300	0.25000	0.06700
Ge?	0.00000	0.41300	0.23000	1,00000
Ge2	0.21330	0.03030	0.2-1900	1 00000
Gel	0.20570	0.34040	0.05510	1 00000
004	0.20030	0.04470	0.7/140	1.00000
01	0.00000	0.01390	0.23000	1.00000
02	0.2000	0.08890	0.411/0	1.00000
03	0.18940	0.14/90	0.13240	1.00000
04	0.20170	0.24910	0.43860	1.00000
05	0.13880	0.33060	0.1/040	1.00000
06	0.49940	0.35910	0.09470	1.00000
07	0.14490	0.41720	0.40840	1.00000

Table S2. Atomic positions, occupancies, and atomic displacement parameters of LGAO: xCr^{3+} with x = 0, 0.02 and 0.10.

Li1 0.00000 0.50000 0.00000 0.98500	08	0.14180	0.49320	0.16780	1.00000
	Li1	0.00000	0.50000	0.00000	0.98500
Cr2 0.00000 0.50000 0.00000 0.01500	Cr2	0.00000	0.50000	0.00000	0.01500
Li2 0.00000 0.24140 0.25000 0.98200	Li2	0.00000	0.24140	0.25000	0.98200
Cr3 0.00000 0.24140 0.25000 0.01800	Cr3	0.00000	0.24140	0.25000	0.01800

Table S3. Bond lengths (R) of LG:Cr³⁺.

D	$\frac{c}{Cr}$ 01	$Cr \Omega^2$	Cr O3	Cr O4	Cr 05	Cr 06
K	01-01	01-02	05	CI-04	05	01-00
Cr_{Li}	2.38967	1.99065	2.01623	2.09435	2.29277	2.13473
Cr _{Ge}	1.95140	2.26448	1.84954	1.90714	1.94187	2.77616

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