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Influence of framework disordering on luminescence performance in Cr^{3+}-doped near-infrared phosphor: a case study of $A_3B_6O_{14}$-type hosts

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Synthesis, characterization and calculation

The $Ca_{3-x}Na_xGa_{2-x}Ge_{4+x}O_{14}:Cr^{3+}$ phosphors were synthesized by solid-state method. Stoichiometric raw materials of Na_2CO_3, $CaCO_3$, Ga_2O_3, GeO_2 and Cr_2O_3 were mixed and ground in a mortar for 30 min. The mixtures were transferred to a furnace and heated for 4 h at 1100-1400 °C under an air atmosphere. The sintered materials were ground into powder for further characterization.

The detailed stoichiometries of $Ca_{3-x}Na_xGa_{2-x}Ge_{4+x}O_{14}$ and $Ca_{3-x}Na_xGa_{2-x}Ge_{4+x}O_{14}:Cr^{3+}$ are below.

For $Ca_{3-x}Na_xGa_{2-x}Ge_{4+x}O_{14}$:

$Ca_3Ga_2Ge_4O_{14}$ ($x = 0$)

$NaCa_2GaGe_5O_{14}$ ($x = 1$)

$Na_2CaGe_6O_{14}$ ($x = 2$)

For $Ca_{3-x}Na_xGa_{2-x}Ge_{4+x}O_{14}:Cr^{3+}$:

$Ca_3Ga_{1.94}Cr_{0.06}Ge_4O_{14}$ ($x = 0$)

$NaCa_2Ga_{0.94}Cr_{0.06}Ge_5O_{14}$ ($x = 1$)

$Na_{1.94}Ca_{1.06}Cr_{0.06}Ge_{5.94}O_{14}$ ($x = 2$)

XRD were measured using a X'Pert powder diffractometer with Cu-*K*α radiation. The Rietveld refinement was performed by the Z-Code software V1.1.3.[S1, 2] The PL, PL excitation (PLE) and temperature-dependent PL spectra were taken on an Edinburgh FLS980 fluorescence spectrophotometer with a 450W xenon lamp. QY of the phosphors were measured on a Hamamatsu UV-VIS absolute PL quantum yield spectrometer C13534 using 450 nm excitation. The diffuse reflectance spectra were taken on a Shimadzu UV-3600 plus UV-Visible-NIR spectrophotometer with white BaSO4 powder as the standard reference.

DFT calculations were performed using the Vienna ab-initio Simulation Package (VASP) V6.2 and WIEN2K V21.1.[S3, 4] In total energies and structural optimization calculations, the exchange-correlation was described by revised Perdew-Burke-Ernzerhof functional for solid (PBEsol).[S5] The cut-off energy and convergence criterion were set to 500 eV and 10^{-8} eV, respectively. The band structures and density of states were calculated using the modified Becke-Johnson (MBJ) potential method based on the optimized models by WIEN2K.[S6, 7] The Debye temperature Θ_D was calculated based on the harmonic Debye model, relying on the bulk modulus and shears modulus:[8]

$$\Theta_D = \frac{h}{k_B}\left[\frac{3n}{4\pi} \times \frac{N_A \rho}{M}\right]^{1/3} \nu_m \quad \text{(Eq. S1)}$$

Where h is the Planck constant, k_B is the Boltzmann constant, n is the number of atoms in the formula, N_A is the Avogadro constant, ρ is density of the material,

M is the molecular mass corresponding to n and v_m is calculated by the equations below:

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_s^3} + \frac{1}{v_l^3}\right)\right]^{-1/3} \quad \text{(Eq. S2)}$$

$$v_s = \left(\frac{G_H}{\rho}\right)^{1/2} \quad \text{(Eq. S3)}$$

$$v_l = \left(\frac{B_H + \frac{4}{3}G_H}{\rho}\right)^{1/2} \quad \text{(Eq. S4)}$$

Where B_H and G_H are bulk and shears modulus, respectively.

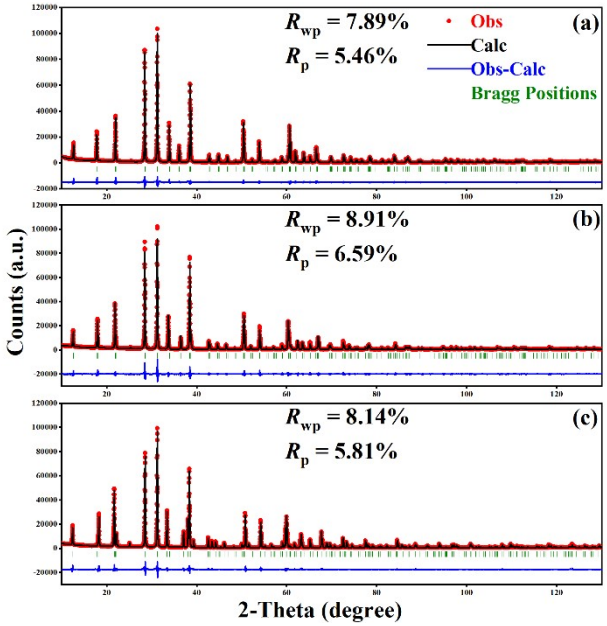

Figure S1. Rietveld refinement results of (a) $Ca_3Ga_{1.94}Cr_{0.06}Ge_4O_{14}$, (b) $NaCa_2Ga_{0.94}Cr_{0.06}Ge_5O_{14}$ and $Na_2CaGe_{5.94}Cr_{0.06}O_{14}$.

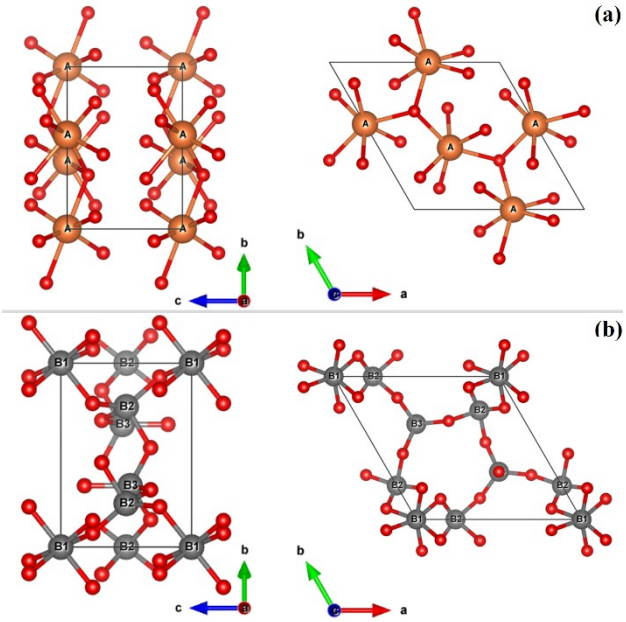

Figure S2. Crystal structure of $A_3B_6O_{14}$-type material showing (a) A cations and (b) B cations coordinated by O^{2-}.

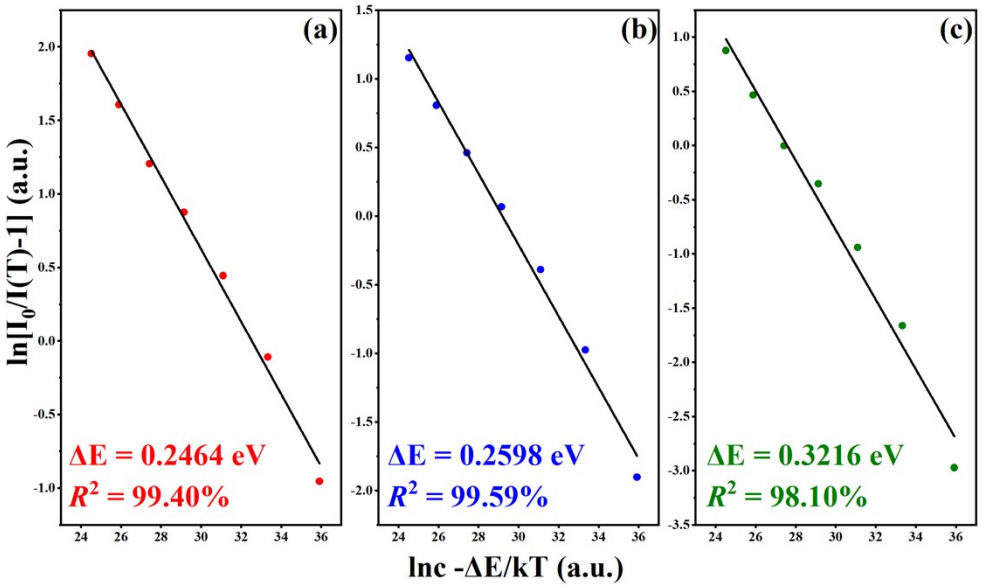

Figure S3. Arrhenius fitting of (a) $Ca_3Ga_2Ge_4O_{14}:Cr^{3+}$, (b) $NaCa_2GaGe_5O_{14}:Cr^{3+}$ and (c) $Na_2CaGe_5O_{14}:Cr^{3+}$.

The activation energy ΔE can be obtained by fitting the Arrhenius formula:[9]

$$I(T) = \frac{I_0}{1 + c \times e^{\left(-\frac{\Delta E}{kT}\right)}} \quad \text{(Eq. S5)}$$

Where I_0 and $I(T)$ are the integral emission intensity at room temperature and testing temperature (25~200 °C), respectively. k is the Boltzmann constant (8.617×10^{-5} eV/K) and c is the fitting constant.

The Eq. S1 was revised as:

$$ln\left[\frac{I_0}{I(T)} - 1\right] = lnc - \frac{\Delta E}{kT} \quad \text{(Eq. S6)}$$

By linear fitting of $lnc - \frac{\Delta E}{kT}$ and $ln\left[\frac{I_0}{I(T)} - 1\right]$, the slope ($-\Delta E$) can be obtained.

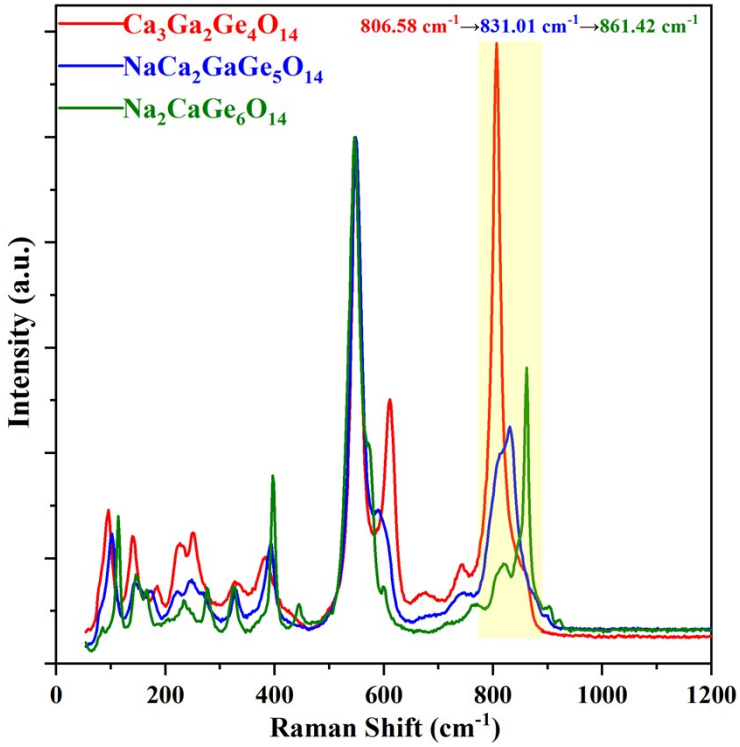

Figure S4. Raman spectra of $Ca_3Ga_2Ge_4O_{14}$, $NaCa_2GaGe_5O_{14}$ and $Na_2CaGe_5O_{14}$ hosts.

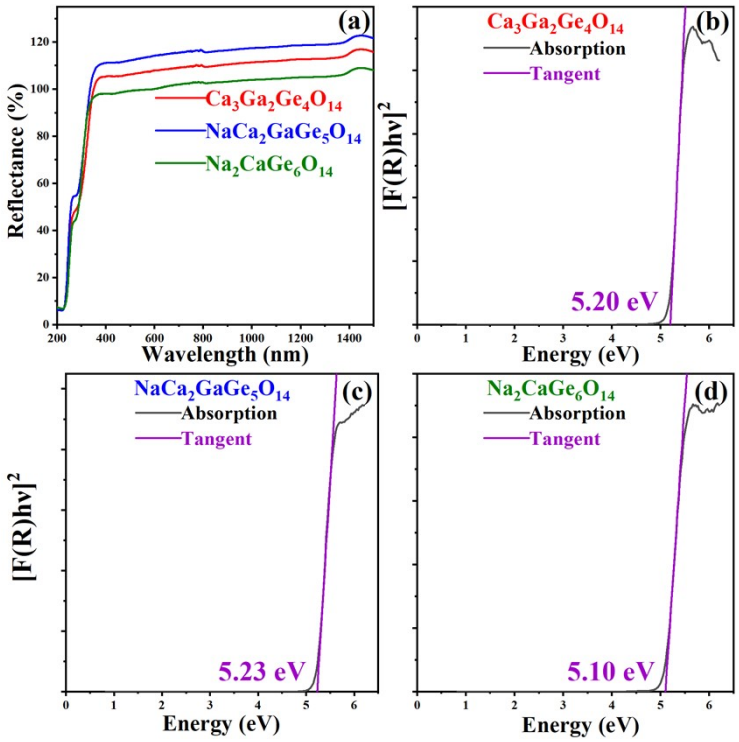

Figure S5. (a) Reflectance spectra of $Ca_3Ga_2Ge_4O_{14}$, $NaCa_2GaGe_5O_{14}$ and $Na_2CaGe_6O_{14}$, absorption spectra of (b) $Ca_3Ga_2Ge_4O_{14}$, (c) $NaCa_2GaGe_5O_{14}$, (d) $Na_2CaGe_6O_{14}$.

The absorption spectrum was calculated using the reflectance spectrum by the Kubelka–Munk function:

$$F(R) = \frac{(1-R)^2}{2R} \quad \text{(Eq. S7)}$$

$$[F(R)h\nu]^{\frac{1}{n}} = C_2(h\nu - E_g) \quad \text{(Eq. S8)}$$

where R is the reflectance (%), $h\nu$ is the photonic energy, n is 1/2 for direct bandgap and 2 for indirect bandgap materials, C_2 is the absorption constant and E_g is the bandgap value.[S10-12] In our case, n is 1/2 based on the band structure calculation (Figure S4). The tangent fitting of the linear part was performed to obtain the E_g (intercept).

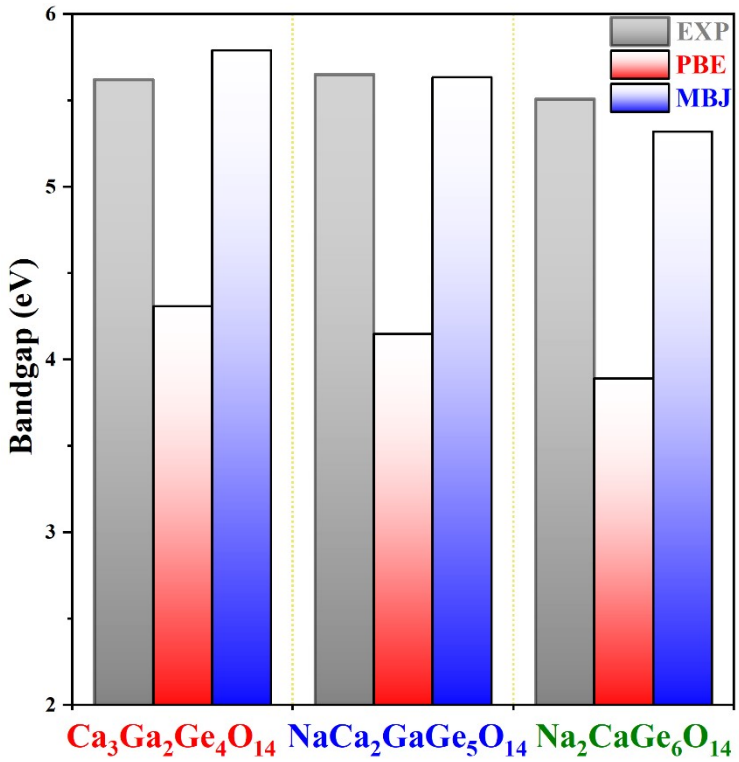

Figure S6. Bandgap values of $Ca_3Ga_2Ge_4O_{14}$, $NaCa_2GaGe_5O_{14}$ and $Na_2CaGe_6O_{14}$, by experimental method, PBE and MBJ calculation.

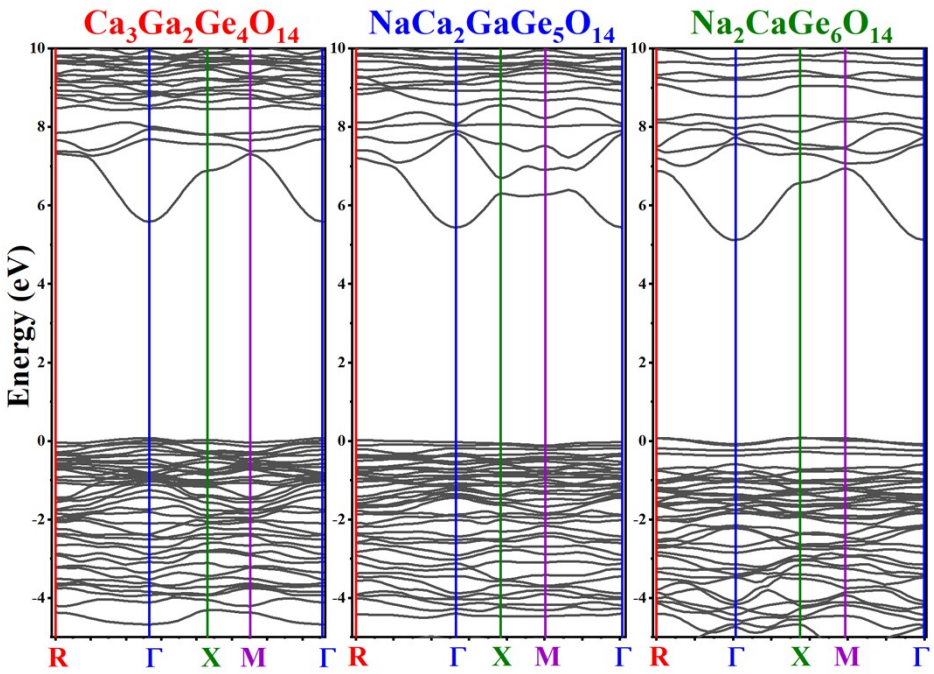

Figure S7. Band structures of $Ca_3Ga_2Ge_4O_{14}$, $NaCa_2GaGe_5O_{14}$ and $Na_2CaGe_6O_{14}$.

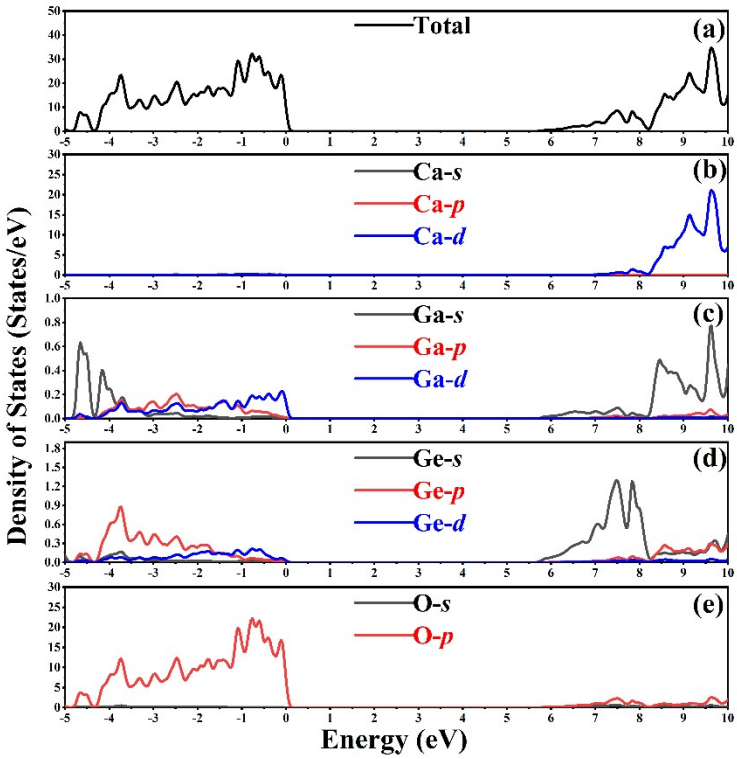

Figure S8. Density of state of (a) $Ca_3Ga_2Ge_4O_{14}$ and the corresponding elements of (b) Ca, (c) Ga, (d) Ge, (e) O.

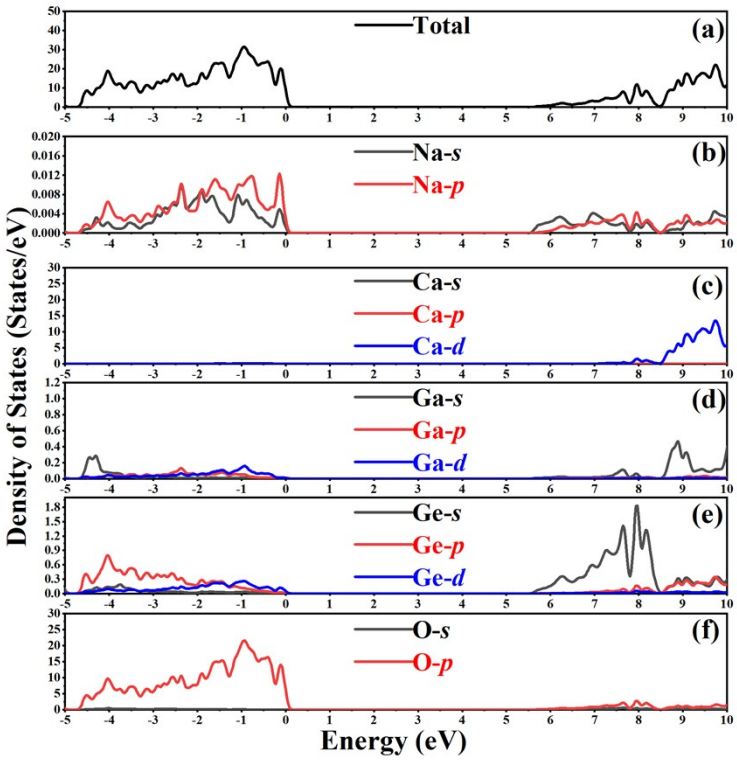

Figure S9. Density of state of (a) $NaCa_2GaGe_5O_{14}$ and the corresponding elements of (b) Na, (c) Ca, (d) Ga, (e) Ge, (f) O.

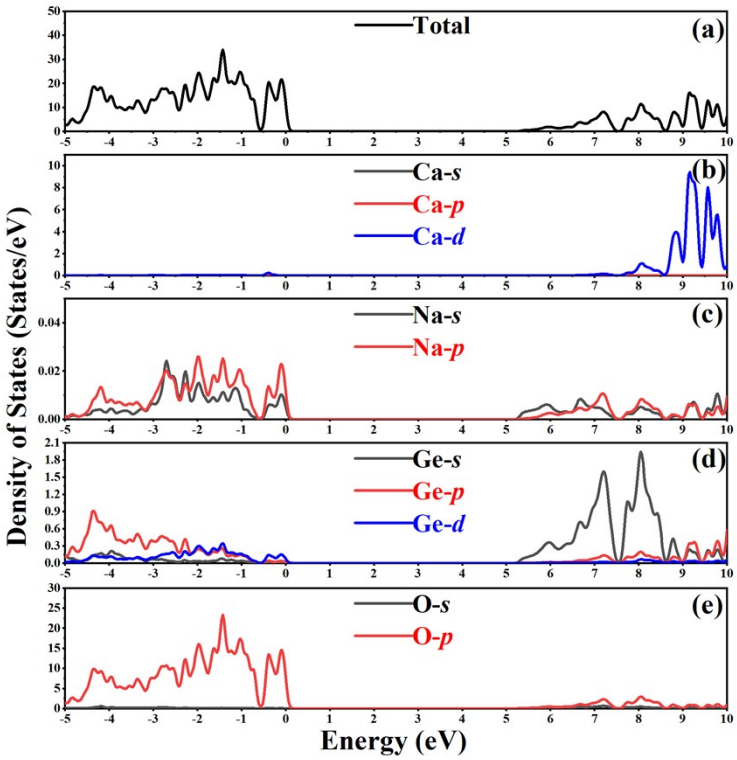

Figure S10. Density of state of (a) $Na_2CaGe_6O_{14}$ and the corresponding elements of (b) Na, (c) Ca, (d) Ge, (e) O.

Table S1. Structural parameters of $Ca_3Ga_{1.94}Cr_{0.06}Ge_4O_{14}$.

Space Group:							
*P*321 (NO. 150)		*a* = *b* = 8.068249(9) Å		*c* = 4.966600(10) Å		*V* = 279.99 Å^3	
Site	Atom	Wyckoff Position	Occupancy	*x*	*y*	*z*	*B* (Å^2)
A	Ca	3*e*	1	0.57986(15)	0	0	0.81(2)
B1	Ga/Ge	1*a*	0.3333/0.6667	0	0	0	0.606(19)
B2	Ga/Ge	3*f*	0.5/0.5	0.23714(6)	0	0.5	0.692(15)
B3	Ga/Ge	2*d*	0.0833/0.9167	0.333333	0.666667	0.5298(2)	0.489(15)
O1	O	2*d*	1	0.333333	0.666667	0.1811(8)	0.64(6)
O2	O	6*g*	1	0.4596(6)	0.1485(6)	0.3134(6)	1.52(6)
O3	O	6*g*	1	0.1438(5)	0.2190(5)	0.2433(7)	1.24(6)

Due to the low concentration of Cr^{3+}, the related parameters were not refined.

Table S2. Structural parameters of $NaCa_2Ga_{0.94}Cr_{0.06}Ge_5O_{14}$.

Space Group: *P*321 (NO. 150)		*a* = *b* = 8.109819(11) Å		*c* = 4.919419(11) Å		*V* = 280.20 Å^3	
Site	Atom	Wyckoff Position	Occupancy	*x*	*y*	*z*	*B* (Å^2)
A	Na/Ca	3*e*	0.3333/0.6667	0.58107(15)	0	0	0.95(3)
B1	Ge	1*a*	1	0	0	0	1.01(2)
B2	Ga/Ge	3*f*	0.3333/0.6667	0.24143(6)	0	0.5	0.687(17)
B3	Ge	2*d*	1	0.333333	0.666667	0.52553(18)	0.482(16)
O1	O	2*d*	1	0.333333	0.666667	0.1826(6)	0.36(6)
O2	O	6*g*	1	0.4609(4)	0.1452(4)	0.3215(4)	0.48(5)
O3	O	6*g*	1	0.1467(4)	0.2200(4)	0.2278(6)	1.17(6)

Due to the low concentration of Cr^{3+}, the related parameters were not refined.

Table S3. Structural parameters of $Na_2CaGe_{5.94}Cr_{0.06}O_{14}$.

Space Group:							
*P*321 (NO. 150)		*a* = *b* = 8.17478(3) Å		*c* = 4.83834(2) Å		*V* = 280.01 Å^3	
Site	Atom	Wyckoff Position	Occupancy	*x*	*y*	*z*	*B* (Å^2)
A	Na/Ca	3*e*	0.6667/0.3333	0.58399(14)	0	0	1.06(2)
B1	Ge	1*a*	1	0	0	0	0.572(12)
B2	Ge	3*f*	1	0.24739(4)	0	0.5	0.459(9)
B3	Ge	2*d*	1	0.333333	0.666667	0.52035(18)	0.502(10)
O1	O	2*d*	1	0.333333	0.666667	0.1812(7)	0.87(3)
O2	O	6*g*	1	0.4556(4)	0.1530(3)	0.3126(4)	0.80(3)
O3	O	6*g*	1	0.1207(4)	0.2098(3)	0.2293(4)	0.87(3)

Due to the low concentration of Cr^{3+}, the related parameters were not refined.

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