

Design and control the luminescence of Cr³⁺ doped phosphors in NIR I region by fitting the crystal field

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Supplementary Characterization

Diffuse reflection spectra. The diffuse reflection spectra were measured with a Hitachi U4100 UV-VIS-NIR Spectroscopy, with a scanning wavelength from 200 to 700 nm, scanning at 240 nm/min.

Density functional theory calculations. The density functional theory calculations were performed using Materials Studio 7.0, in which the first-principles wave-basis pseudo-potential method is used within the density functional theory (DFT). The CASTEP program was employed to perform geometry optimization using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm. Generalized gradient approximation (GGA) under the scheme of the Perdew-Burke-Ernzerhof (PBE) functional is used for the electron exchange-correlation interactions. A plane-wave basis set with an energy cut-off of 340 eV is employed. The Monkhorst-Pack k-point grid

employed $1\times 1\times 1$ for the interface calculation. The self-consistent field tolerance threshold is 1.0×10^{-6} eV/atom.

Supplementary Figures

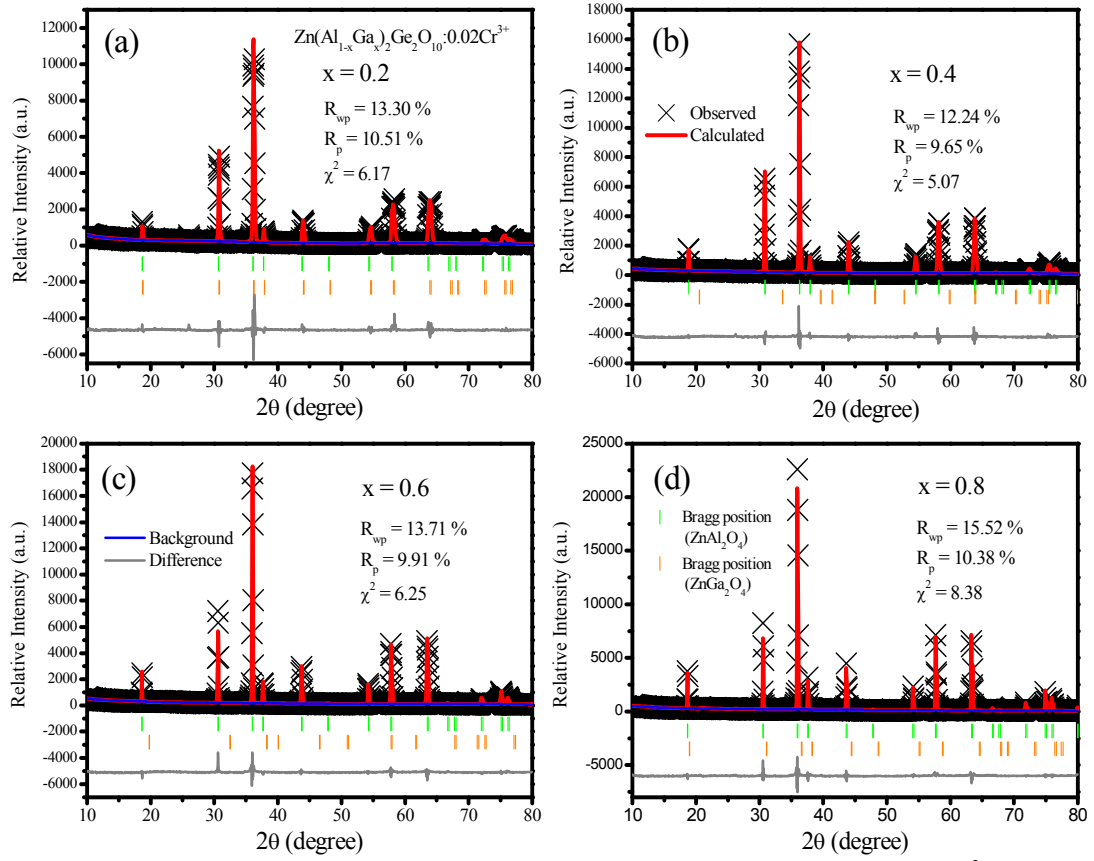


Figure S1. Rietveld analysis patterns of XRD of $\text{Zn}_3(\text{Al}_{1-x}\text{Ga}_x)_2\text{Ge}_2\text{O}_{10}:0.02\text{Cr}^{3+}$ ($x = 0.2, 0.4, 0.6, 0.8$).

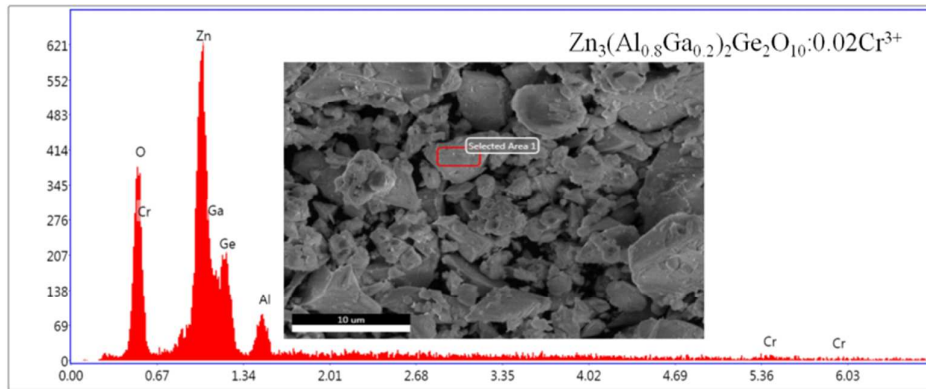


Figure S2. SEM image and EDX data of $\text{Zn}_3(\text{Al}_{0.8}\text{Ga}_{0.2})_2\text{Ge}_2\text{O}_{10}:0.02\text{Cr}^{3+}$.

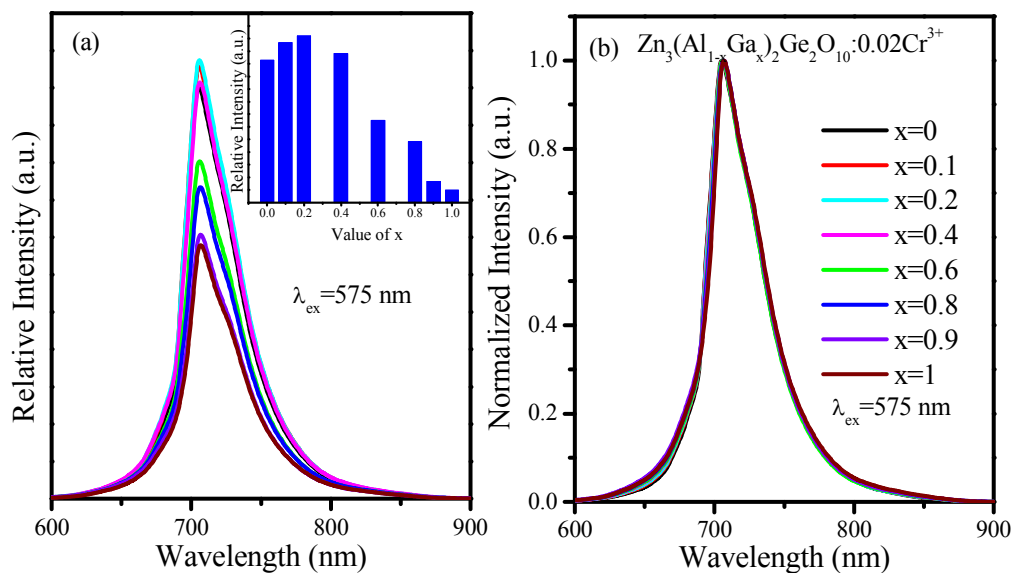


Figure S3. Emission spectra (a) and normalized emission (b) of $\text{Zn}_3(\text{Al}_{1-x}\text{Ga}_x)_2\text{Ge}_2\text{O}_{10}:0.02\text{Cr}^{3+}$ excited by 575 nm. The emission intensity in dependence of the Ga^{3+} concentration (inset).

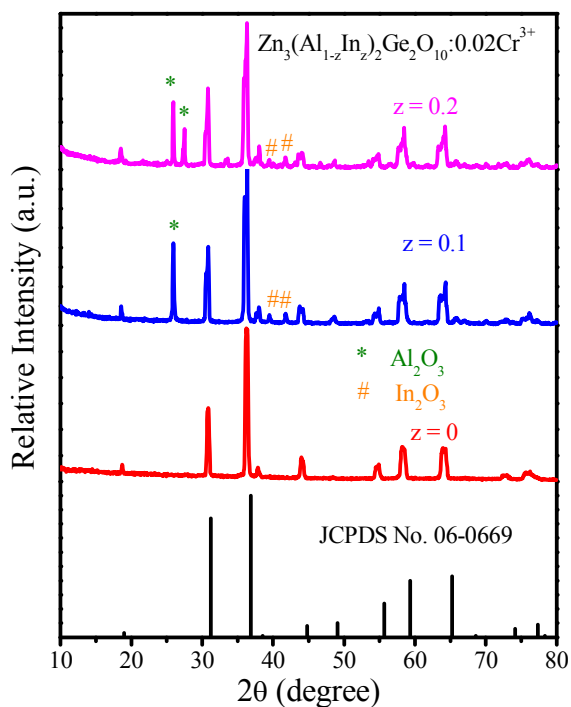


Figure S4. XRD patterns of $\text{Zn}_3(\text{Al}_{1-z}\text{In}_z)_2\text{Ge}_2\text{O}_{10}:0.02\text{Cr}^{3+}$.

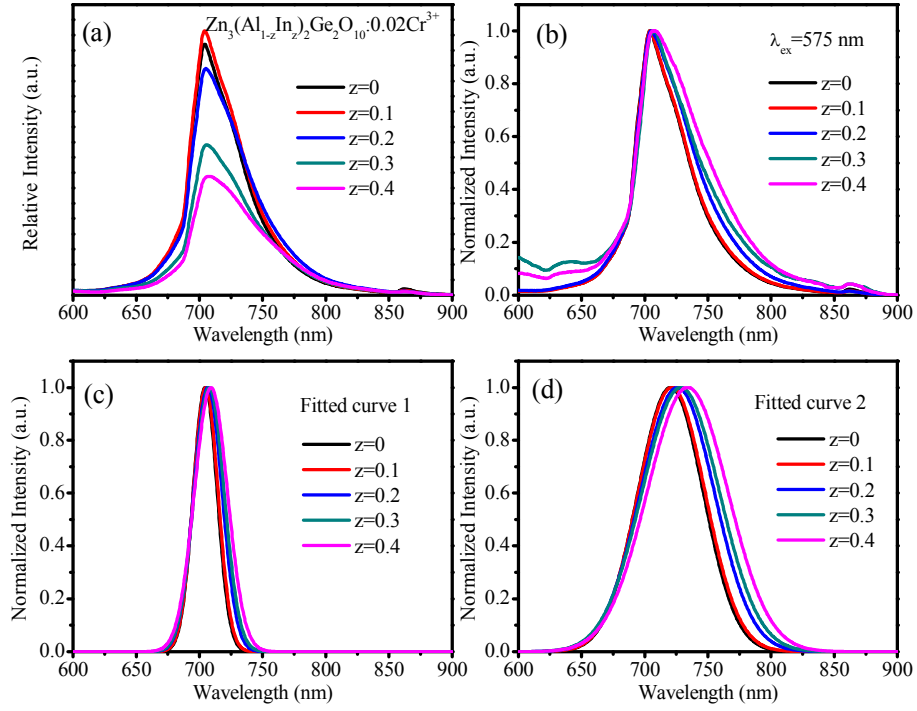


Figure S5. Emission (a) and normalized emission (b) spectra of $\text{Zn}_3(\text{Al}_{1-z}\text{In}_z)_2\text{Ge}_2\text{O}_{10}:0.02\text{Cr}^{3+}$ excited by 575 nm. (c-d) The corresponding Gaussian fitting results (705 and 721 nm) of $\text{Zn}_3(\text{Al}_{1-z}\text{In}_z)_2\text{Ge}_2\text{O}_{10}:0.02\text{Cr}^{3+}$.

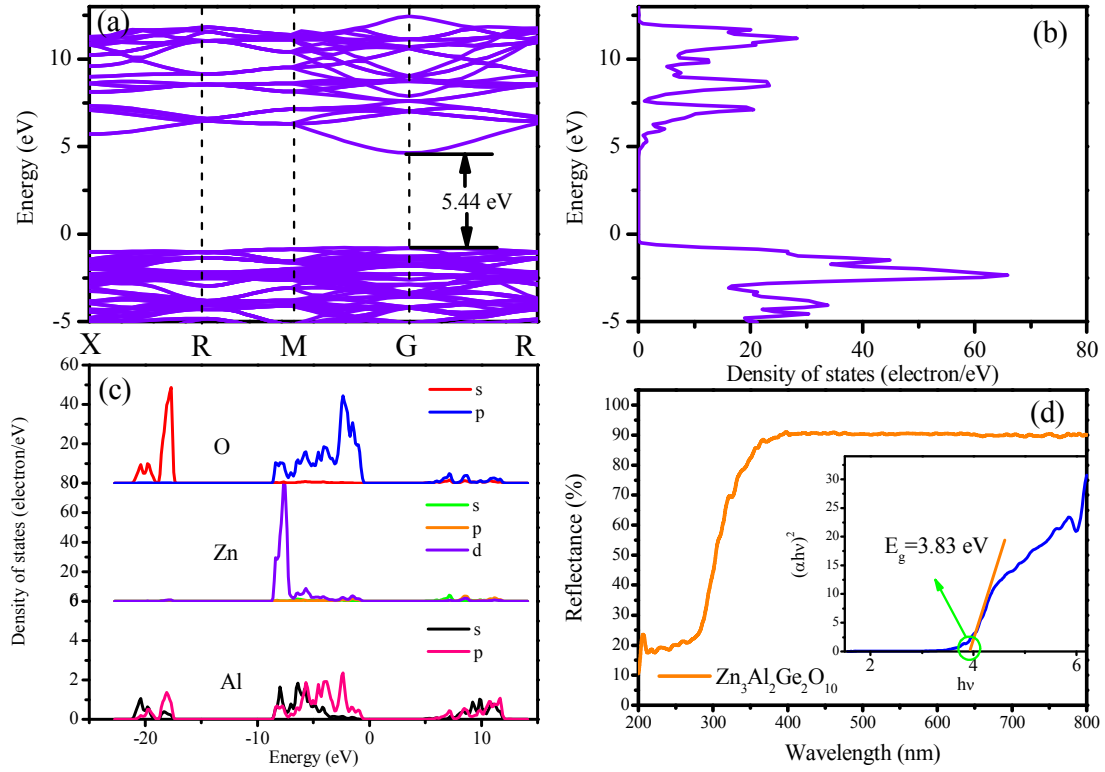


Figure S6. (a) The calculated energy band structure of ZnAl_2O_4 . (b) The total DOS of ZnAl_2O_4 . (c) Partial DOSs of ZnAl_2O_4 . (d) Diffuse reflectance spectrum of $\text{Zn}_3\text{Al}_2\text{Ge}_2\text{O}_{10}$. The insert shows the corresponding Tauc plot curve and determination of the energy band gap.

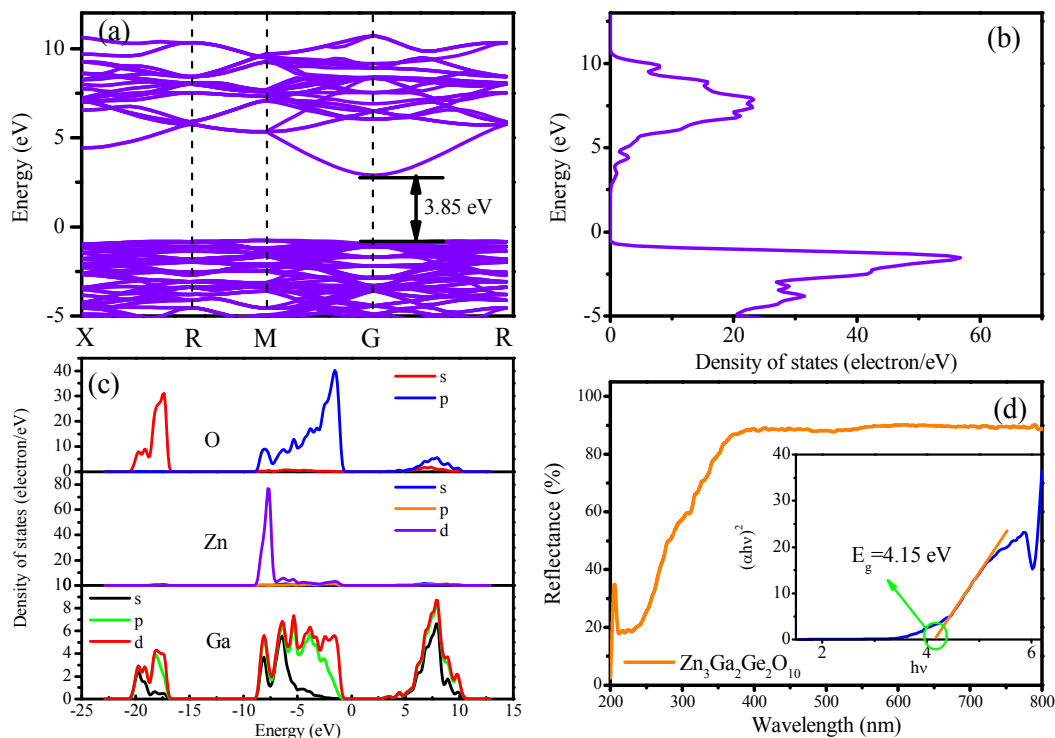


Figure S7. (a) The calculated energy band structure of ZnGa_2O_4 . (b) The total DOS of ZnGa_2O_4 . (c) Partial DOSs of ZnGa_2O_4 . (d) Diffuse reflectance spectrum of $\text{Zn}_3\text{Ga}_2\text{Ge}_2\text{O}_{10}$. The insert shows the corresponding Tauc plot curve and determination of the energy band gap.

To further prove the crystal structures of $\text{Zn}_3\text{Al}_2\text{Ge}_2\text{O}_{10}$ is isostructural with $\text{Zn}_3\text{Ga}_2\text{Ge}_2\text{O}_{10}$, the crystal structure optimization and electronic structure are investigated by first principle calculation, and the calculated band structures are shown in Figure S6a and S7a, respectively. It revealed that both of the hosts have direct band gap of 5.44 and 3.85 eV due to that the valence band maximum and the conduction band minimum are located at the same point (G point to G point). Although the calculated value and the experimental value are different, they are within the error range, due to that the calculated band gaps are always underestimated when using the density functional theory approximation (GGA). To investigate the composition of the energy bands, the total and partial density of states (DOS) of ZnAl_2O_4 are calculated, as shown in Figure S6b and c respectively. It can be seen that the valence band consists of dominant O-2p and small contribution of Al-3p states ranging from -5 eV to the Fermi level. O-2s, Zn-3d, Al-3s3p are the dominated states varying from -25 eV to -5 eV. The

bottom of the conduction band in ZnAl_2O_4 ranging from 5 eV to 12 eV is mainly formed by Al-3s3p and a slight contribution of the O-2p. These results suggest that host absorptions can be mainly ascribed to the charge transition from Al-3p to O-2p state. Figure S7b and c show the total and partial density of states of ZnGa_2O_4 , respectively, it can be found that the main contributor into the bottom of the conduction band is Ga-4s4p3d, and that the O-2p state is the main contributor into the top of the valence band. This indicates that the host absorption of ZnGa_2O_4 originates mainly from the charge transfer from Ga-3d to O-2p state.

The diffuse reflectance spectra of $\text{Zn}_3\text{Al}_2\text{Ge}_2\text{O}_{10}$ and $\text{Zn}_3\text{Ga}_2\text{Ge}_2\text{O}_{10}$ are depicted in Figure S6d and S7d, and the insets show the optical band gap calculated by the Kubelka-Munk function, respectively. The strong absorption edge of $\text{Zn}_3\text{Al}_2\text{Ge}_2\text{O}_{10}$ and $\text{Zn}_3\text{Ga}_2\text{Ge}_2\text{O}_{10}$ are near 300 and 350 nm, respectively. The optical band gap energy E_g can be calculated using the following equation:

$$\alpha h\nu \propto (h\nu - E_g) \quad (1)$$

where α is the absorbance, h is the Planck constant, n is the photon energy. n is determined by the transition type ($n = 1/2, 2, 3/2$ or 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect electronic transitions, respectively). According to the calculation results of band structures from density function theory, $\text{Zn}_3\text{Al}_2\text{Ge}_2\text{O}_{10}$ and $\text{Zn}_3\text{Ga}_2\text{Ge}_2\text{O}_{10}$ are confirmed to be allowed direct band gap materials, therefore, $n = 1/2$:

$$(\alpha h\nu)^2 \propto h\nu - E_g \quad (2)$$

From the plot of $(\alpha h\nu)^2$ versus $h\nu$, the band gaps E_g of $\text{Zn}_3\text{Al}_2\text{Ge}_2\text{O}_{10}$ and $\text{Zn}_3\text{Ga}_2\text{Ge}_2\text{O}_{10}$ are calculated to be 3.83 and 4.15 eV, which illustrates that $\text{Zn}_3\text{Al}_2\text{Ge}_2\text{O}_{10}$ and $\text{Zn}_3\text{Ga}_2\text{Ge}_2\text{O}_{10}$ have similar band gaps.