

Reversible Luminescence of Bi³⁺ Ions by X-Ray Induced Crystal Field Regulation

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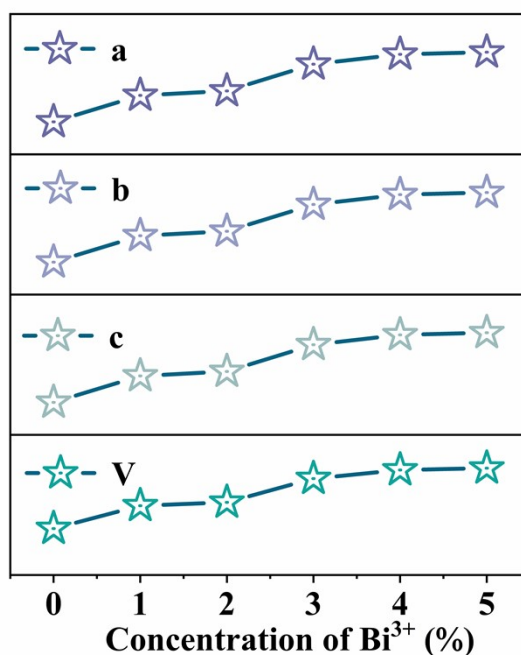


Figure S1. Variation of lattice parameters of Cs₂KGdF₆: x%B³⁺ (where x = 0, 1, 2, 3, 4, 5).

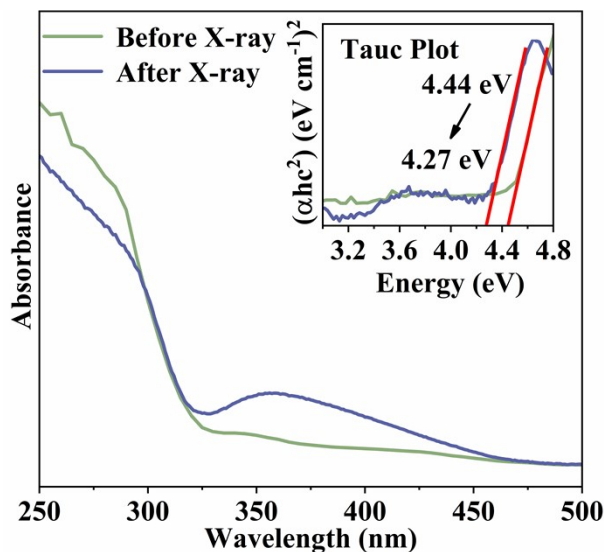


Figure S2. The UV absorption spectra of $\text{Cs}_2\text{KGdF}_6: \text{Bi}^{3+}$ before and after X-ray irradiation, and the illustration is the band gap changes before and after X-ray irradiation.

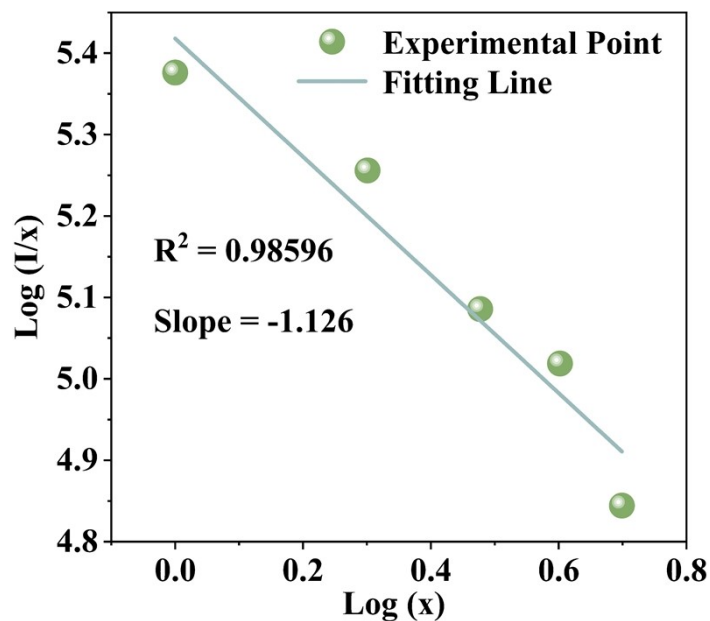


Figure S3. Diagram of $\log(I/x)$ versus $\log(x)$.

The critical distance (R_c) of adjacent doped ions is an important criterion for comprehending the non-radiative energy transfer mechanism. In general, non-radiative energy transfer among neighboring dopants can be attributed to either exchange interaction or multipole-multipole interaction. When R_c is less than 5 Å, exchange interaction will occur. Otherwise, multipole-multipole interaction will occur. Based on Blasse theory, the R_c parameters can be calculated by Equation:

$$R_c = 2 \left[\frac{3V}{4\pi X_c Z} \right]^{\frac{1}{3}}$$

where V is the volume per unit cell, X_c is the critical concentration, and Z is the number of positions that the doped ions can be occupy. The calculated value R_c is 23.97 Å. Since the critical distance between the two samples is greater than 5 Å, the influence of interaction can be excluded. The type of electrical multipolar interaction can be determined according to the following Dexter formula:

$$\frac{I}{x} = K \left[1 + \beta(x) \frac{\theta}{3} \right]^{-1}$$

where I and x represent emission intensity and the content of doped ions, respectively.

k and β are constants. When the value of θ is 6, 8, 10, it represents the dipole - dipole, dipole - quadrupole, and quadrupole -quadrupole interactions, respectively. **Fig. S2** depicts the pattern of $\log(I/x)$ with $\log(x)$ of these samples. The curve can be well fitted to a linear correlation with a slope equal to -1.126. The calculated q value approaches 6 indicating that the quenching mechanism is dipole-dipole interaction in the Cs_2KGdF_6 host.

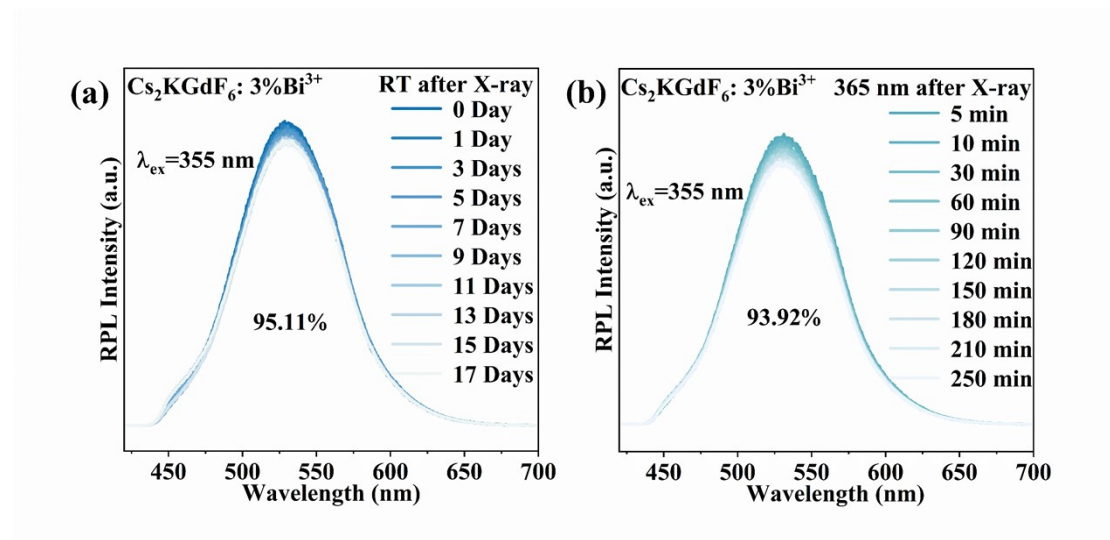


Figure S4. (a)RPL (Radio photoluminescence) of $\text{Cs}_2\text{KGdF}_6: 3\%\text{Bi}^{3+}$ under RT and (b) 365 nm UV irradiation.

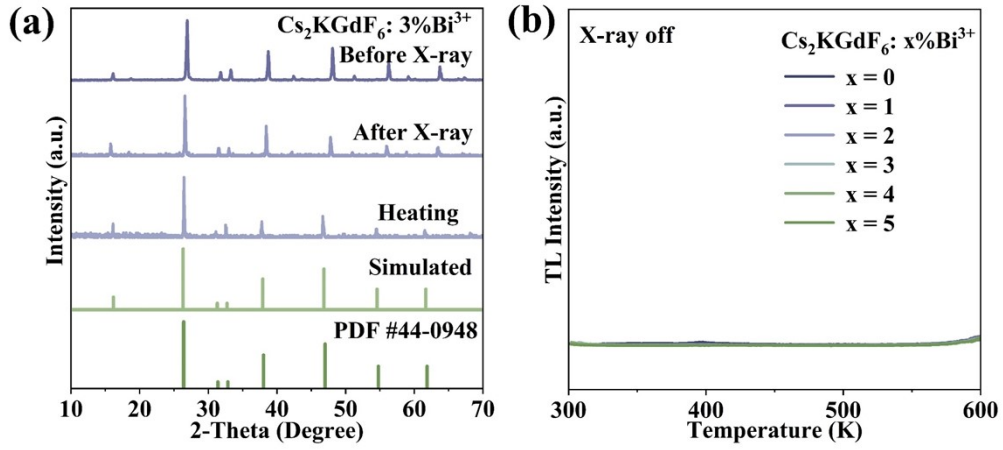


Figure S5. (a) XRD of $\text{Cs}_2\text{KGdF}_6: 3\%\text{Bi}^{3+}$ before and after X-ray irradiation and after heating. (b) TL of $\text{Cs}_2\text{KGdF}_6: x\%\text{Bi}^{3+}$ ($x = 0, 1, 2, 3, 4, 5$).

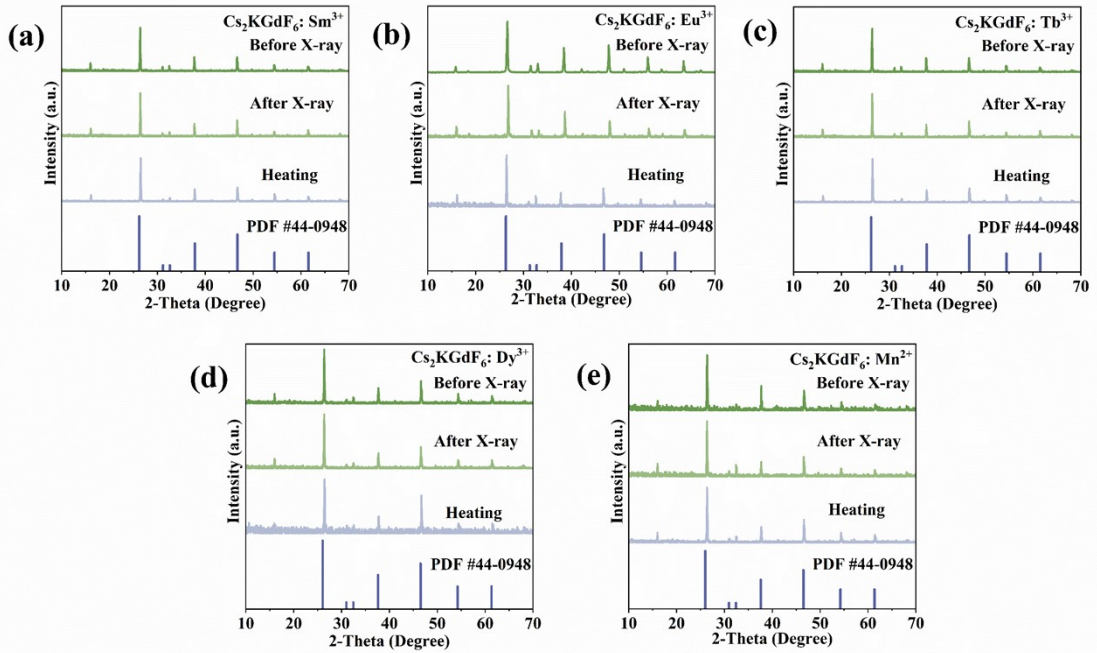


Figure S6. XRD before and after X-ray irradiation and after heating of (a) $\text{Cs}_2\text{KGdF}_6: \text{Sm}^{3+}$, (b) $\text{Cs}_2\text{KGdF}_6: \text{Eu}^{3+}$, (c) $\text{Cs}_2\text{KGdF}_6: \text{Tb}^{3+}$, (d) $\text{Cs}_2\text{KGdF}_6: \text{Dy}^{3+}$, (e) $\text{Cs}_2\text{KGdF}_6: \text{Mn}^{2+}$.

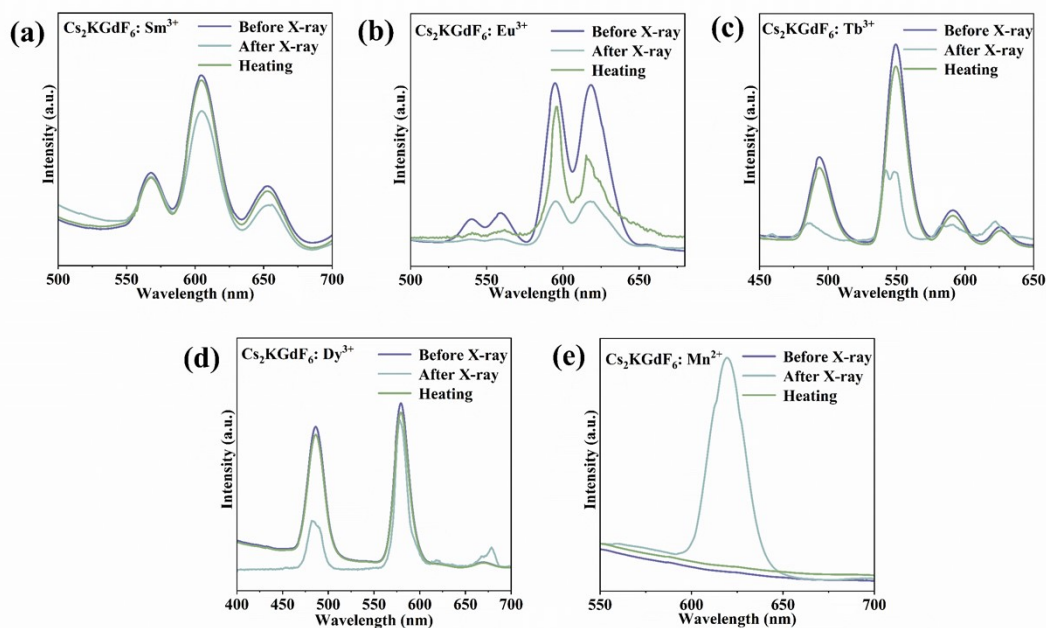


Figure S7. PL before and after X-ray irradiation and after heating of (a) Cs_2KGdF_6 : Sm^{3+} , (b) Cs_2KGdF_6 : Eu^{3+} , (c) Cs_2KGdF_6 : Tb^{3+} , (d) Cs_2KGdF_6 : Dy^{3+} , (e) Cs_2KGdF_6 : Mn^{2+} .

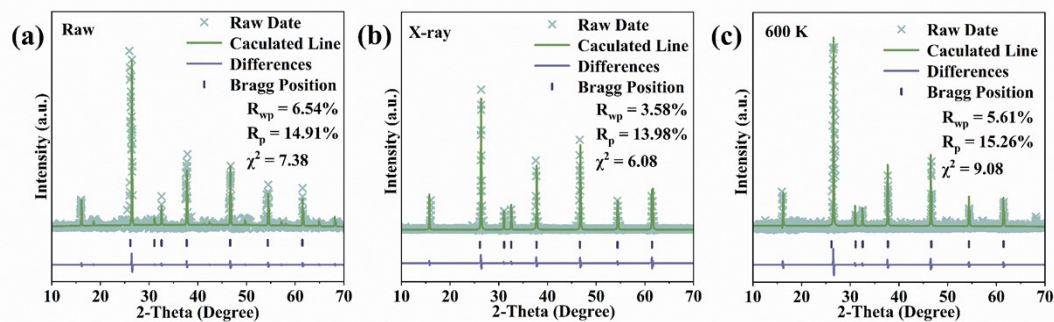


Figure S8. XRD of Cs_2KGdF_6 : 3% Bi^{3+} (a) before and (b) after X-ray irradiation and (c) after heating.

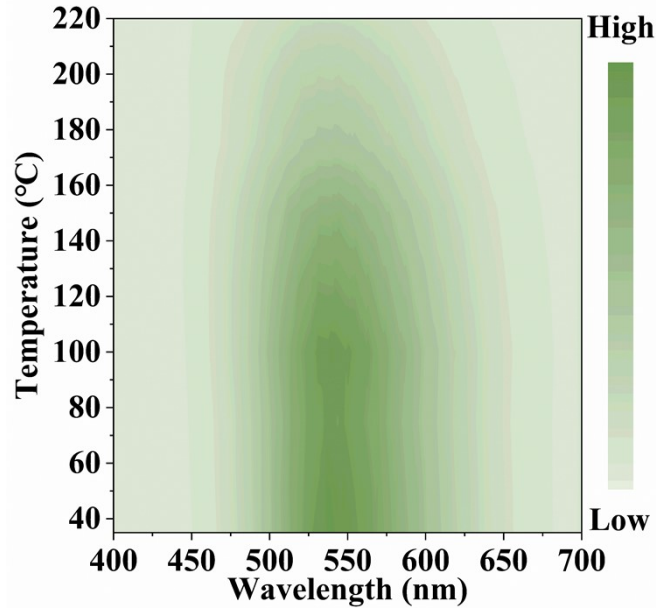


Figure S9. Temperature dependent spectrum of $\text{Cs}_2\text{KGdF}_6: 3\%\text{Bi}^{3+}$.

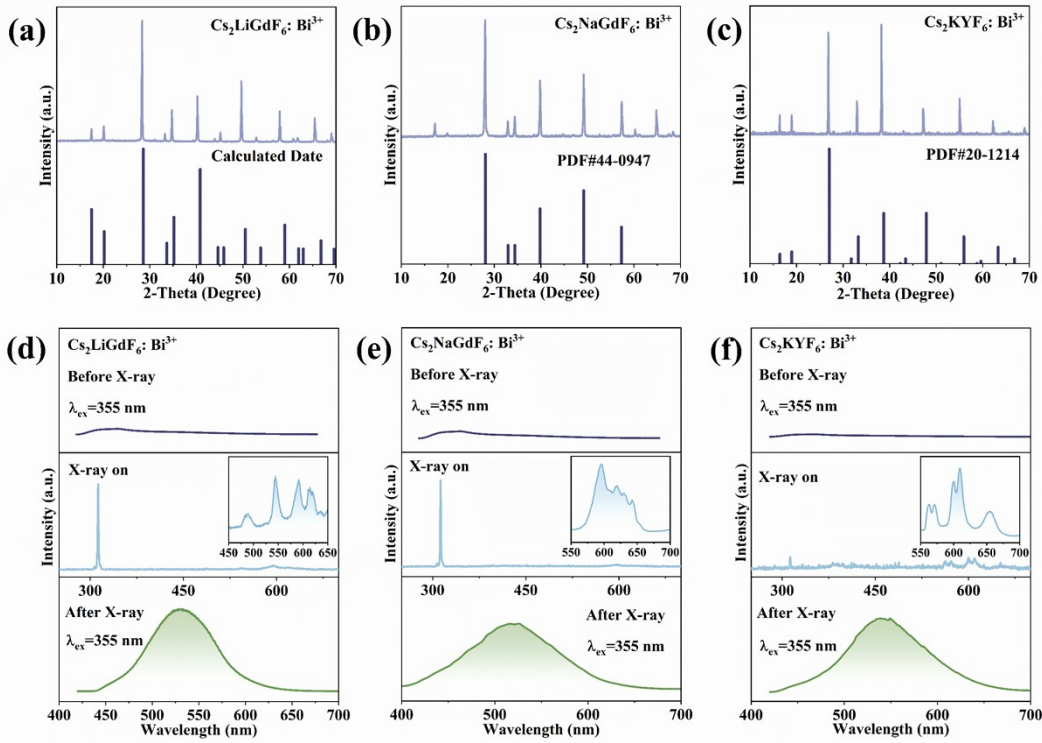


Figure S10. XRD of (a) $\text{Cs}_2\text{LiGdF}_6: \text{Bi}^{3+}$ (b) $\text{Cs}_2\text{NaGdF}_6: \text{Bi}^{3+}$ (c) $\text{Cs}_2\text{NaGdF}_6: \text{Bi}^{3+}$.
PL, RL, and RPL of (d) $\text{Cs}_2\text{LiGdF}_6: \text{Bi}^{3+}$ (e) $\text{Cs}_2\text{NaGdF}_6: \text{Bi}^{3+}$ (f) $\text{Cs}_2\text{NaGdF}_6: \text{Bi}^{3+}$.

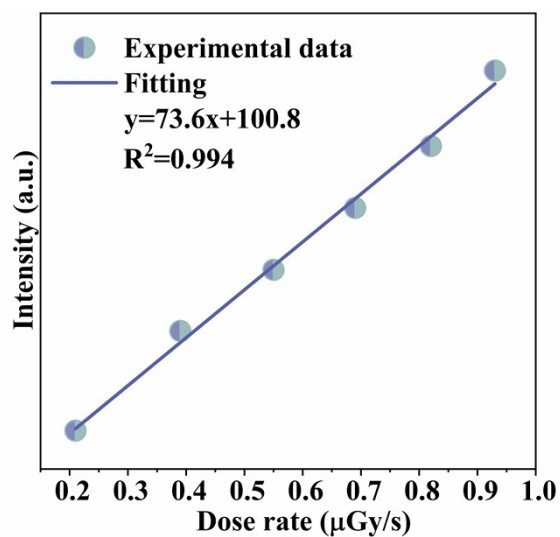


Figure S11. The RPL intensity of the $\text{Cs}_2\text{KGdF}_6: \text{Bi}^{3+}$ as a function of the X-ray dose.

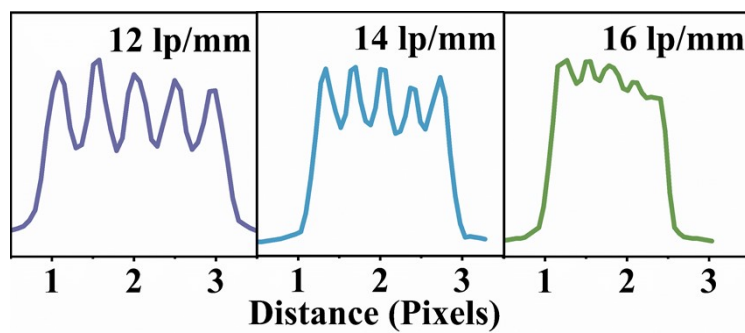


Figure S12. The gray value map corresponding to Figure 5h.