

SUPPORTING INFORMATION

Luminescence and Cationic-Size Driven Site Selection of Eu³⁺, Ce³⁺ Ions in Ca₈Mg(SiO₄)₄Cl₂

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I. The calculation of chemical bond parameters of CMSOC host

Based on the decomposed result of complex crystal, the macroscopic linear susceptibility χ of CMSOC compound can be expressed as the collective contributions of the obtained $A_{m_i}^i B_{n_j}^j$ compounds with μ type bonds:

$$\chi = (\varepsilon - 1)/4\pi = \sum_{\mu} F^{\mu} \chi^{\mu} \quad (1)$$

where ε is the dielectric constant of CMSOC compound that is related to the refraction index n by the equation $\varepsilon = n^2$. F^{μ} is the fraction of μ bonds composing the CMSOC compound. χ^{μ} is the macroscopic susceptibility of $A_{m_i}^i B_{n_j}^j$ compound that is composed of μ bonds and can be expressed as:

$$\chi^{\mu} = (4\pi)^{-1} \left[(\hbar \Omega_p^{\mu})^2 / (E_g^{\mu})^2 \right] \quad (2)$$

where Ω_p^{μ} is the plasma frequency which is calculated from the effective valence electron density of μ type bond $(N_e^{\mu})^*$ using the following equation:

$$(\Omega_p^{\mu})^2 = [4\pi(N_e^{\mu})^* e^2/m] D^{\mu} A^{\mu} \quad (3)$$

where e and m are the electronic charge and mass, respectively. D^{μ} and A^{μ} are the correction factors that are defined in Ref S1. In addition, the average energy gap E_g^{μ} of μ bond, viz., the average energy difference between the bonding and antibonding orbitals, can be separated into covalent or homopolar E_h^{μ} and ionic or heteropolar C^{μ} parts as Eq. (4):

$$(E_g^{\mu})^2 = (E_h^{\mu})^2 + (C^{\mu})^2 \quad (4)$$

The homopolar part E_h^{μ} , representing the interaction of dipole moment and other multiple moments between bonding ions, is determined by the bond length d^{μ} (in Å) of μ bond:

$$E_h^{\mu} = 39.74/(d^{\mu})^{2.48} \text{ (eV)} \quad (5)$$

While the heteropolar part C^{μ} , i.e. the contribution of the interaction of point charge, is given as:

$$C^{\mu} = 14.4 b^{\mu} \exp(-k_s^{\mu} r_0^{\mu}) \left| \left((Z_{A^i}^{\mu})^* / r_0^{\mu} \right) - \left(n_j / m_i \right) \left((Z_{B^j}^{\mu})^* / r_0^{\mu} \right) \right| \text{ (eV)}$$

$$(\text{if } n_j \geq m_i) \quad (6a)$$

$$C^\mu = 14.4 b^\mu \exp(-k_s^\mu r_0^\mu) \left| \left(m_i/n_j \right) \left((Z_{A^i}^\mu)^*/r_0^\mu \right) - \left((Z_{B^j}^\mu)^*/r_0^\mu \right) \right| \text{ (eV)} \\ (\text{if } m_i \geq n_j) \quad \quad \quad (6b)$$

where

$$\begin{aligned} b^\mu &= \beta \langle N_c^\mu \rangle^p \\ \langle N_c^\mu \rangle &= \frac{m_i}{m_i + n_j} N_{CA^i}^\mu + \frac{n_j}{m_i + n_j} N_{CB^j}^\mu \\ k_s^\mu &= (4k_F^\mu / \pi a_B)^{1/2} \text{ (Å}^{-1}) \\ k_F^\mu &= [3\pi^2 (N_e^\mu)^*]^{1/3} \text{ (Å}^{-1}) \\ r_0^\mu &= d^\mu / 2 \text{ (Å)} \end{aligned} \quad (7)$$

The parameter b^μ is a correction factor and is related to the average coordination number $\langle N_c^\mu \rangle$ of μ bond. The exponential factor p has a range of 1.48 – 2, which is determined by $\langle N_c^\mu \rangle$. Factor β depends on the actual crystal structure and can be obtained by using the refraction index n and eq. (1)-(8)^{S2}. $N_{CA^i}^\mu$ and $N_{CB^j}^\mu$ are the coordination numbers of ions A^i and B^j , respectively. $\exp(-k_s^\mu r_0^\mu)$ is the Thomas-Fermi screening factor. k_F^μ is the Fermi wave vector. a_B is the Bohr radius (0.529 Å). The effective valence electron density of μ bond $(N_e^\mu)^*$ can be expressed as follows:

$$\begin{aligned} (N_e^\mu)^* &= (n_e^\mu)^* / v_b^\mu \text{ (Å}^{-3}) \\ (n_e^\mu)^* &= (Z_{A^i}^\mu)^* / N_{CA^i}^\mu + (Z_{B^j}^\mu)^* / N_{CB^j}^\mu \\ v_b^\mu &= (d^\mu)^3 / \sum_\mu (d^\mu)^3 N_b^\mu \text{ (Å}^3) \end{aligned} \quad (8)$$

$(n_e^\mu)^*$ is the number of effective valence electrons in μ bond. $(Z_{A^i}^\mu)^*$ and $(Z_{B^j}^\mu)^*$ are respectively the numbers of effective valence electrons of A^i and B^j ions in μ bond and can be calculated by the methods in Refs S3-S4. The bond volume v_b^μ is expected to be proportional to $(d^\mu)^3$. N_b^μ is the density of μ bond and the sum over the any types of μ bonds in the unit cell in the denominator is to normalize the bond volume.

The refraction index of CMSOC crystal is reported to be 1.691^{S5}, so the factor β in

eq. (7) is fitted to be 0.092 in this case. Furthermore, by using the Eq. (4)-(9) and the crystal structural information of CMSOC compound in Table 2, the bond covalency f_c^μ and ionicity f_i^μ of any type of μ bond can be finally calculated:

$$f_c^\mu = (E_h^\mu)^2 / (E_g^\mu)^2$$

$$f_i^\mu = (C^\mu)^2 / (E_g^\mu)^2 \quad (9)$$

Some obtained parameters during the calculation process are tabulated in Table S1.

According to the Lorentz-Lorenz equation, the bond volume polarizability (α_b^μ) of μ chemical bond can be given by:

$$\varepsilon^\mu = 1 + 4\pi\chi^\mu$$

$$\alpha_0^\mu = \frac{3(\varepsilon^\mu - 1)}{4\pi(\varepsilon^\mu + 2)}$$

$$\alpha_b^\mu = \alpha_0^\mu v_b^\mu \text{ (\AA}^3\text{)} \quad (10)$$

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II. Figures and tables

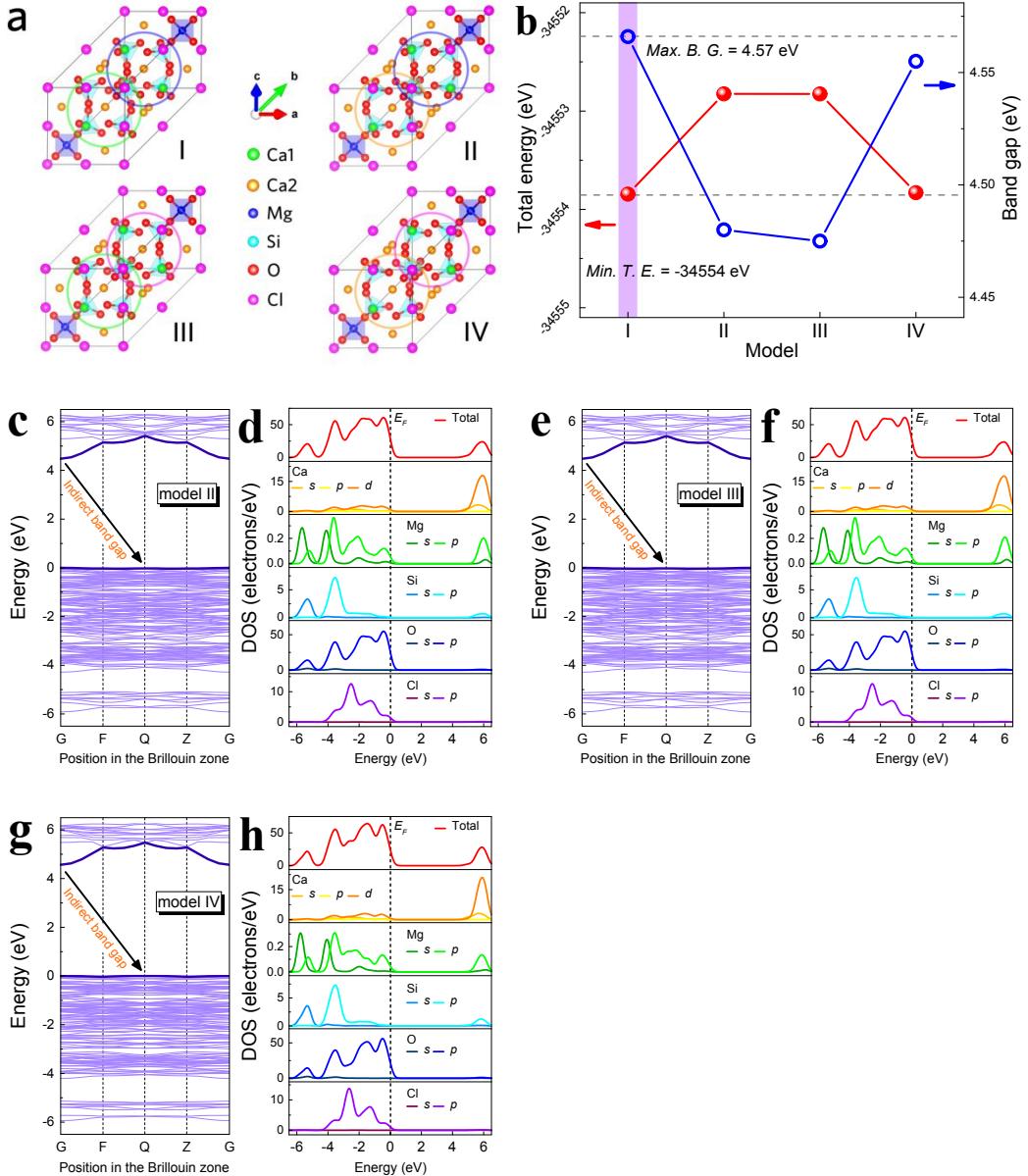


Figure S1. (a) Structural diagrams of four models for DFT calculations. (b) Calculated total energies and band gap values of four models. (c-h) Calculated band structures and total and partial densities of states of the models (II, III, IV).

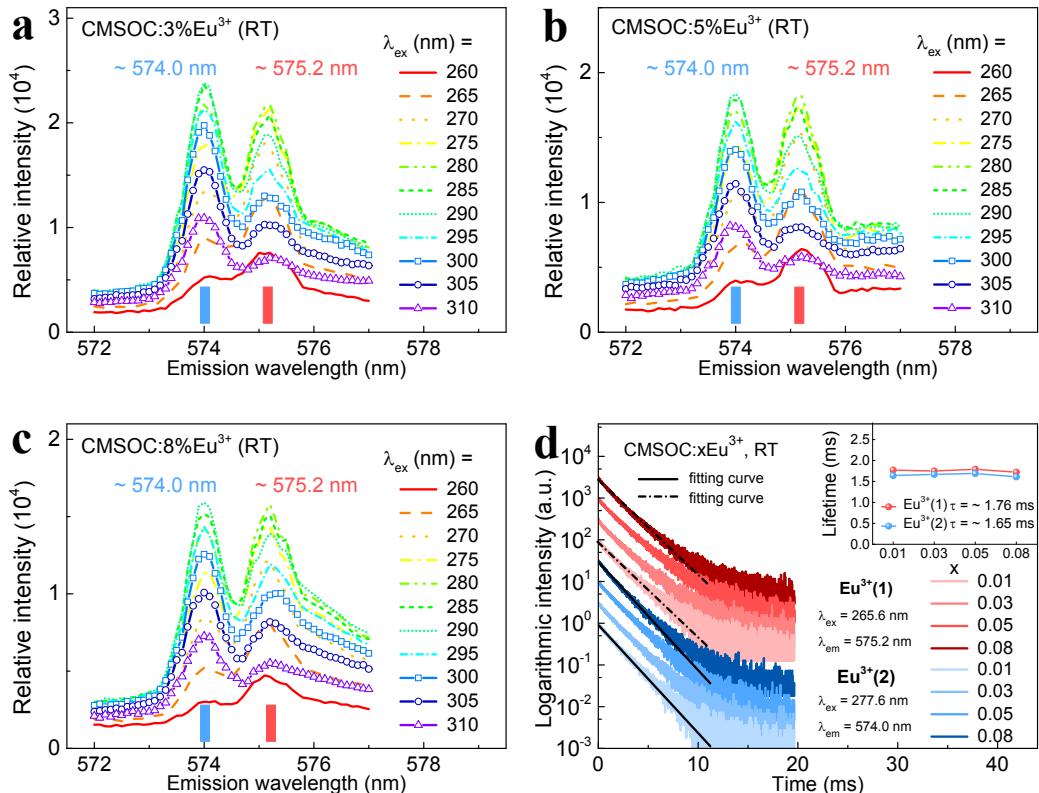


Figure S2. (a,b,c) High-resolution emission spectra of samples CMSOC: xEu³⁺ (x = 0.03–0.08) under different excitation wavelengths in a range of 260–310 nm at RT. (d) Luminescence decay curves of Eu³⁺(1) ($\lambda_{ex} = 265.6$ nm, $\lambda_{em} = 575.2$ nm) and Eu³⁺(2) ($\lambda_{ex} = 277.6$ nm, $\lambda_{em} = 574.0$ nm) in samples CMSOC: xEu³⁺ (x = 0.01–0.08) at RT. The inset shows the lifetime values of Eu³⁺ emissions at different concentrations.

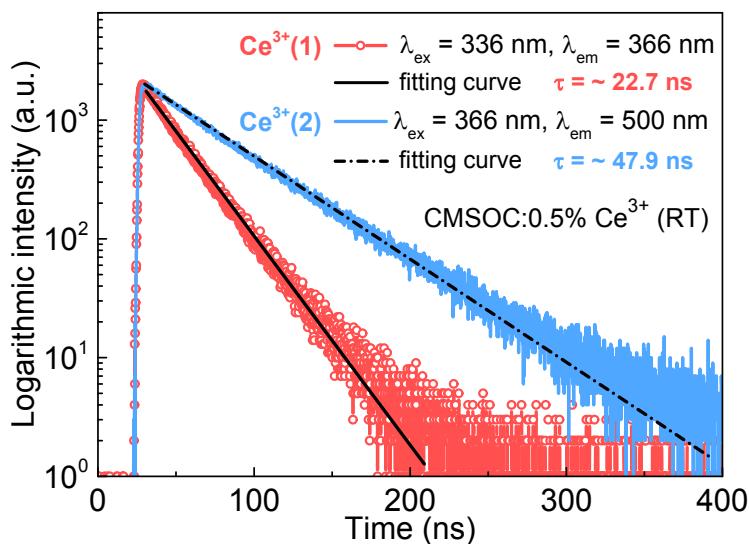


Figure S3. Luminescence decay curves of two different Ce³⁺ centers at RT.

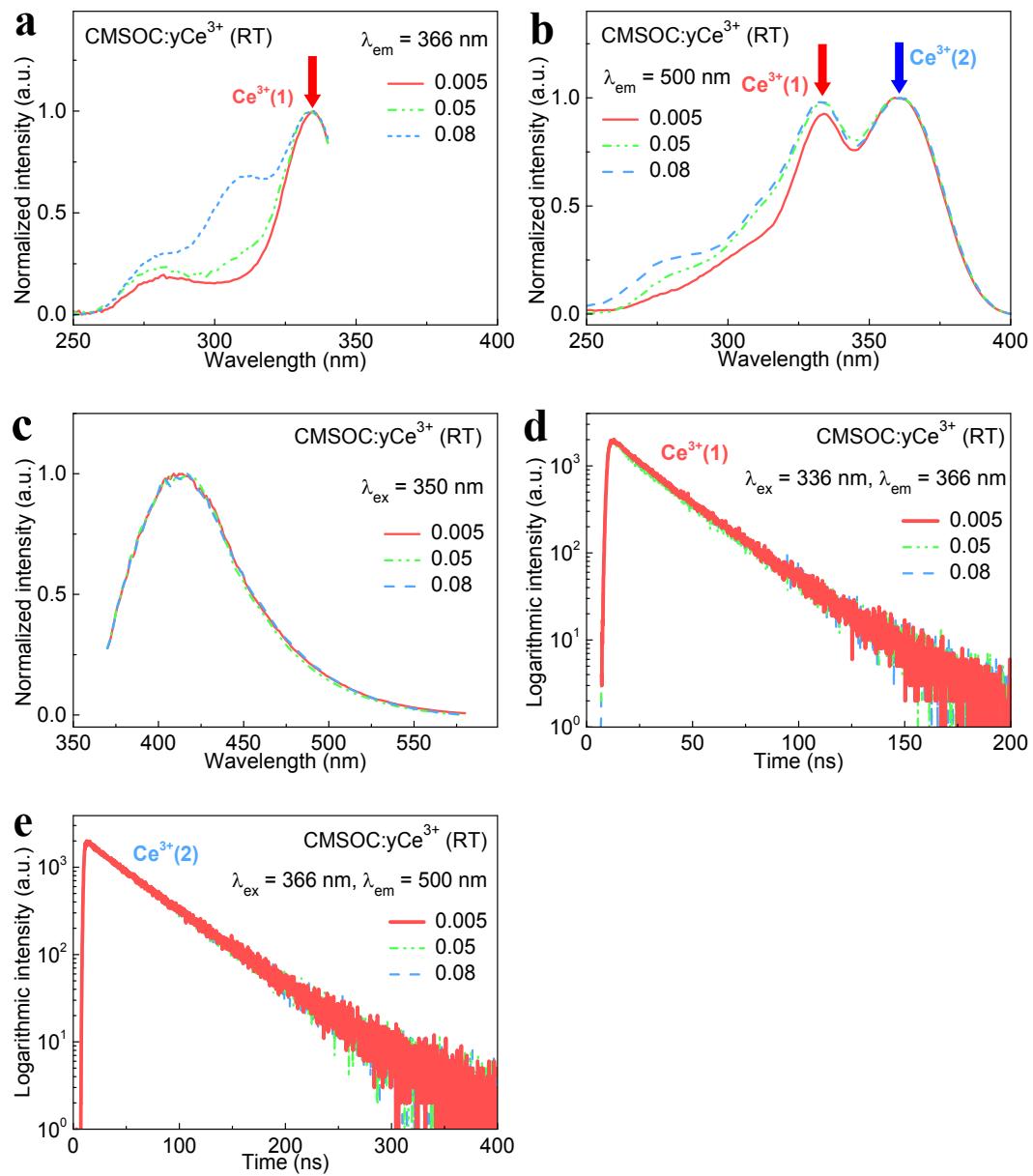


Figure S4. Luminance properties of samples CMSOC: yCe³⁺ ($y = 0.005\text{--}0.08$) at RT. **(a)** Highest-height-normalized excitation spectra ($\lambda_{\text{em}} = 366 \text{ nm}$). **(b)** Highest-height-normalized excitation spectra ($\lambda_{\text{em}} = 500 \text{ nm}$). **(c)** Highest-height-normalized emission spectra ($\lambda_{\text{ex}} = 350 \text{ nm}$). **(d)** Luminescence decay curves ($\lambda_{\text{ex}} = 336 \text{ nm}, \lambda_{\text{em}} = 366 \text{ nm}$). **(e)** Luminescence decay curves ($\lambda_{\text{ex}} = 366 \text{ nm}, \lambda_{\text{em}} = 500 \text{ nm}$).

Table S1. The bond type, structural information and calculated bond parameters of CMSOC compound via the dielectric chemical bond theory.

| Bond type | d^μ (Å) | $\langle N_c^\mu \rangle$ | $(n_e^\mu)^*$ | v_b^μ (Å ³) | $(N_e^\mu)^*$ (Å ⁻³) | r_0^μ (Å) | E_h^μ (eV) | C^μ (eV) | E_g^μ (eV) |
|------------|-------------|---------------------------|---------------|-----------------------------|----------------------------------|---------------|----------------|--------------|----------------|
| Ca(1)-O(2) | 2.432 | 4.800 | 1.138 | 4.464 | 0.255 | 1.216 | 4.386 | 8.352 | 9.433 |
| Ca(2)-O(1) | 2.748 | 6.154 | 1.209 | 6.440 | 0.188 | 1.374 | 3.239 | 10.35 | 10.84 |
| Ca(2)-O(2) | 2.243 | 5.333 | 1.209 | 3.502 | 0.345 | 1.122 | 5.360 | 14.80 | 15.75 |
| Ca(2)-Cl | 3.099 | 6.857 | 2.418 | 9.237 | 0.262 | 1.550 | 2.404 | 7.284 | 7.671 |
| Mg-O(1) | 1.941 | 4.444 | 2.046 | 2.270 | 0.902 | 0.971 | 7.672 | 10.22 | 12.78 |
| Si-O(1) | 1.631 | 4.444 | 3.847 | 1.347 | 2.857 | 0.816 | 11.81 | 15.01 | 19.10 |
| Si-O(2) | 1.641 | 4.000 | 3.847 | 1.371 | 2.805 | 0.821 | 11.64 | 13.92 | 18.14 |

Table S2. The bond parameters, calculated environmental factors and simulated transition energies of Eu³⁺ and Ce³⁺ at two Ca²⁺ sites.

| Site | Bond number | N | Q_B^μ | α_b^μ (Å ³) | E_h^μ (eV) | f_c^μ | f_i^μ | h_e | F_c | E_{CT} (eV) | E_{cs} (K cm ⁻¹) | E_{cfs} (K cm ⁻¹) |
|-------|----------------|-----|-----------|----------------------------------|----------------|-----------|-----------|-------|-------|---------------|--------------------------------|---------------------------------|
| Ca(1) | Ca(1)-O(2) × 6 | 6 | 1.138 | 0.637 | 4.386 | 0.216 | 0.784 | 1.034 | 0.652 | 4.69 | 19.61 | 12.62 |
| | Ca(2)-O(1) × 2 | | 1.511 | 0.667 | 3.239 | 0.089 | 0.911 | | | | | |
| Ca(2) | Ca(2)-O(2) × 4 | 8 | 1.209 | 0.339 | 5.360 | 0.116 | 0.884 | 1.120 | 0.607 | 4.49 | 20.67 | 11.97 |
| | Ca(2)-Cl × 2 | | 1.814 | 1.165 | 2.404 | 0.098 | 0.902 | | | | | |