Supporting material – Defect properties in Yb³⁺-doped CaF₂ from first-principles calculation: A lead to defect engineering for up- and down-conversion photoluminescence

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Defect formation energy calculation

We calculated the formation energy (enthalpy) of point and pair defects as a function of Fermi energy (E_F) using the well-estabilished equation as follows [1].

$$H_f[D^q] \cong E[D^q] - E_{\text{perf}} - \sum_i n_i \mu_i(T, P) + qE_F + E_{\text{corr}}[D^q]$$
(1)

Here, E_{perf} is the total energy of the perfect supercell and n_i is the number of added $(n_i > 0)$ or removed $(n_i < 0)$ *i*-type species with chemical potential of μ_i , while $E[D^q]$ is the DFT (density functional theory) total energy of the supercell containing the defect with charge state D^q and $E_{\text{corr}}[D^q]$ is the correction term for the finite size effect of supercell.

 $E_{\text{corr}}[D^q]$ mainly accounts for the electrostatic interactions between peoriodically charged supercells with neutralizing background for a computational convergence.

We used the Makov-Payne correction method [2] implemented in Quantum ESPRESSO code without considering quadrupole moment.

$$E_{\rm corr}^{\rm MP}[D^q] = \alpha q^2 / \varepsilon L \tag{2}$$

Here α , ε and L are the Madelung constant, static dielectric constant and supercell lattice constant respectively. $E_{\text{corr}}[D^q]$ also should include the band-dispersion correction for shallow defects according to the following equation [1].

$$E_{\rm corr}^{\rm band}[D^q] = \begin{cases} -\sum_k w_k f_k [\epsilon_{\rm CB}(k) - \epsilon_{\rm CBM}] & ; \text{ shallow donor} \\ \\ \sum_k w_k (1 - f_k) [\epsilon_{\rm VB}(k) - \epsilon_{\rm VBM}] & ; \text{ shallow acceptor} \end{cases}$$
(3)

Defect band occupations f_k were taken from the output file of PDOS (projected density of states) calculation and multiplied by their weights w_k . $\epsilon_{VB}(k)$ ($\epsilon_{CB}(k)$) is the eigen-energy of each k state on fully occupied upper valence band (unoccupied lower conduction band).

 $E_{\rm F}$ means the chemical potential of electron-reservoir with which the defects exchange electrons to be charged differently. It can possess the value between the VBM (valence band maximum) and the CBM (conduction band minimum) of the perfect bulk material. When a defect is formed, $E_{\rm F}$ should represent the potential shift of the reservoir. The potential alignment term ΔV was estimated by comparing deep-lying 3s state of Ca atom farthest away from a defect in defective supercell with the one in perfect supercell.

Next, chemical potential $\mu_i(T, P)$ represents the environmental thermodynamic condition of *i*-type species. Under thermodynamic equilibrium condition of CaF₂ host, following equation is estabilished.

$$\mu_{\rm Ca} + 2\mu_{\rm F} = \mu_{\rm CaF_2} \cong E_{\rm CaF_2}^{\rm DFT} \tag{4}$$

To determine the upper and lower limits of $\mu_i(T, P)$, conventionally, DFT total energies of Ca-bulk and F₂-gas were calculated to set their maximum values. The lower limits were determined by Eq. S4.

$$E_{\text{CaF}_2}^{\text{DFT}} - E_{\text{F}_2}^{\text{DFT}}(\text{gas}) \le \mu_{\text{Ca}}(T, P) \le E_{\text{Ca}}^{\text{DFT}}(\text{bulk})$$
(5)

$$\frac{1}{2}[E_{\text{CaF}_2}^{\text{DFT}} - E_{\text{Ca}}^{\text{DFT}}(\text{bulk})] \le \mu_{\text{F}}(T, P) \le \frac{1}{2}E_{\text{F}_2}^{\text{DFT}}(\text{gas})$$
(6)

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With the adoption of formation enthalpy of CaF₂

$$\Delta H_{\text{CaF}_2}^f(0, 0) \cong E_{\text{CaF}_2}^{\text{DFT}} - E_{\text{Ca}}^{\text{DFT}}(\text{bulk}) - E_{\text{F}_2}^{\text{DFT}}(\text{gas})$$
(7)

Eq. S5 and Eq. S6 change into

$$\Delta H_{\text{CaF}_a}^f(0, 0) \le \mu_{\text{Ca}}(T, P) - E_{\text{Ca}}^{\text{DFT}}(\text{bulk}) = \Delta \mu_{\text{Ca}}(T, P) \le 0$$
(8)

$$\frac{1}{2}\Delta H_{\text{CaF}_2}^f(0, 0) \le \mu_{\text{F}}(T, P) - \frac{1}{2}E_{\text{F}_2}^{\text{DFT}}(\text{gas}) = \Delta \mu_{\text{F}}(T, P) \le 0$$
(9)

 $\Delta H_{CaF_2}^f(0, 0)$ is calculated to be -11.91 eV and -13.10 eV for PBEsol and HSE06, respectively, while the experimental value is -12.67 eV [3].

For the Yb-dopant, upper limit is determined by another thermodynamical constraint of $\mu_{Yb} + 3\mu_F \leq \mu_{YbF_3}$ as well as by the DFT bulk energy.

$$\mu_{Yb}(T, P) \leq \begin{cases} E_{YbF_3}^{DFT}(bulk) - 3\mu_F(T, P) \\ E_{Yb}^{DFT}(bulk) \end{cases}$$
(10)

In Table S1 we show the optimized lattice constants and DFT total energies of bulk and gas materials necessary for the treatment of $\mu_i(T, P)$ as explained above.

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Table S1. Lattice constants of crystals and bond length of fluorine molecule optimized with PBEsol functional and their DFT total energies per formula unit (f.u.) calculated by using PBEsol and HSE06 functionals.

Compound	Phase	Lattice constants / Bond lengths (Å)		$E_{\rm DFT}$ (Ry/f.u.)		
		Cal.	Exp.	PBEsol	HSE06	
CaF ₂	$Fm\overline{3}m$	a = 5.40	$a = 5.45^{a}$	-249.871	-211.480	
Ca	Pnma	a = 5.40	$a = 5.58^{b}$	-131.782	-103.532	
Yb	$Fm\overline{3}m$	a = 5.33	$a = 5.48^{b}$	-1720.744	-1402.350	
YbF3	Pnma	a = 6.24, b = 6.78, c = 4.13	$a = 6.22, b = 6.78, c = 4.43^{c}$	-1897.467	-1563.861	
F ₂	gas	$d_{\rm F-F} = 1.404$	$d_{\rm F-F} = 1.412^{b}$	-117.213	-106.986	
^a Ref. [4], ^b Ref. [3], ^c Ref. [5]						

Table S2. Determination of optical ${}^{2}F_{7/2}$ level of 4f electrons in Yb³⁺ ion by the Fermi energy of Ybcontaining defects in which Yb ions are nominally charged with 3+. Defect-induced potential shifts were corrected.

Func.	Defect	$E_{\rm F}~({\rm eV})$	$E_{\rm F} - E_{\rm VBM} \ ({\rm eV})$
	$[Yb_i - F_i]^{2+}$	4.64	1.03
PBEsol	Yb_{Ca}^{1+}	4.64	1.03
	$[Yb_{Ca}-F_i]^0$	4.69	1.08
	$[Yb_i - F_i]^{2+}$	4.34	2.76
HSE06	Yb_{Ca}^{1+}	4.30	2.72
	$[Yb_{Ca}-F_i]^0$	4.34	2.76



Figure S1. Optimized structures of CaF_2 (2×2×2) supercells containing dominantly charged point defects. After building a supercell from the optimized unit-cell, point defects are formed and all the atoms are relaxed fully within the fixed cubic lattice. Charges are given by changing the parameters of "tot_charge" and "starting_charge" in the input file of Quantum ESPRESSO code. Interstital and vacant defects of F atoms are highlighted in red and blue, respectively, and those of Ca atoms are green and purple, respectively. Interstitial and substituted Yb atoms are dark grey.



Figure S2. Optimized structures of CaF_2 (2×2×2) supercells containing differently charged pair defects. After building a supercell from the optimized unit-cell, point defects are formed and all the atoms are relaxed fully within the fixed cubic lattice. Charges are given by changing the parameters of "tot_charge" and "starting_charge" in the input file of Quantum ESPRESSO code. Yb_{Ca} -F_i and $2(Yb_{Ca}$ -F_i) represent the Yb-monomer and -dimer, respectively, while Yb_{Ca} -2F_i is set as their intermediate state. Interstital F atoms are highlighted in red and Yb atoms are dark grey.



Figure S3. Total and atom-projected density of states (DOS) in perfect and defect-containing CaF_2 calculated by using PBEsol functional. The calculated band gap of perfect CaF_2 is 7.33 eV. The upper valence band is from F-2*p* states and the lower conduction band is from mostly Ca-4*p*, while anti-bonding state betweem F-2*p* and Ca-3*p* represents the CBM. Defects are not charged and 4*f*-levels are clearly positioned in the band bap for Yb_i, Yb_{Ca}, Yb_i-F_i, and Yb_{Ca}-F_i.



Figure S4. Defect formation energy diagrams under (a) F-rich (Ca-poor) and (b) F-poor (Ca-rich) conditions as a function of Fermi energy calculated by using PBEsol functional. The VBM was set as zero. In F-rich condition, point defects of F_i^{1-} and V_{Ca}^{2-} have the lowest formation energies in the most range of E_F , while, in F-poor condition, Ca_i^{2+} and V_F^{1+} are the dominant defects with the lowest values. In the lower part of E_F , Yb_{Ca} charged with 1+ becomes stable with smaller formation energy than the neutral one. The formation energy of Yb_i is always much bigger than that of Yb_{Ca} in F-rich condition. In F-poor condition, two formation energy lines are intersecting at E_F =4.40 eV (for HSE06, at E_F =6.64 eV) below which Yb_i gets more stable than Yb_{Ca}.



Figure S5. Binding energies of pair defects from their component point defects as a function of Fermi energy calculated by using PBEsol functional. All the complex defects tend to minimize their binding energies near the VBM and the CBM. Yb_{Ca} - F_i follows the binding mechanism of Yb_{Ca}^{1+} + $F_i^0 \rightarrow [Yb_{Ca}$ - $F_i]^{1+}$ near the VBM resulting in the negative binding energy of -0.09 eV and the mechanism of Yb_{Ca}^0 + $F_i^1 \rightarrow [Yb_{Ca}$ - $F_i]^{1-}$ with very small value of 0.04 eV around the CBM.