

Suppression of Defect-Induced Quenching via Chemical Potential Tuning: A Theoretical Solution for Enhancing Lanthanide Luminescence

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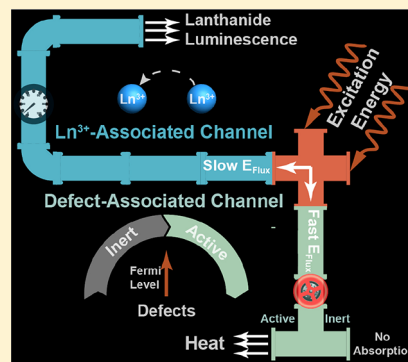
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Supporting Information

ABSTRACT: Nonradiative decay occurring at lattice defect sites may constitute an essential pathway for luminescence quenching in lanthanide-doped upconversion nanomaterials. Considerable efforts have been dedicated to alleviating such quenching effects through controlled single-crystal growth and stringent chemical processing. However, it is not feasible to remove all lattice defects in the crystals. The fabrication of highly luminescent upconversion materials is thus impeded by an incomplete understanding of defect-induced quenching behavior. Here, we propose a theoretical solution for enhancing the luminescence efficiency through the deactivation of deleterious defect centers. To address the exact nature of defect-induced energy dissipation, we systematically study the electronic structure and the stability of five different types of intrinsic defects in cubic NaYF₄ crystal through *ab initio* calculations. Based on the calculated single-particle energy levels and absorption coefficients, we identify optically responsive defect centers which can effectively harvest 980 nm excitation energy due to their larger absorption coefficients. Such active defect centers are more capable of trapping excitation energy than the lanthanides, thus significantly mitigating the process of photon upconversion. By tuning the position of the Fermi level within the range of 1.75–6.94 eV, the initially active defect centers can be deactivated, resulting in the formation of inert defects and the suppression of energy dissipation. These findings not only provide new insight into the underlying mechanism of defect-induced luminescence quenching in lanthanide-doped crystals but also offer a theoretical toolbox that enables rapid identification of defect-tolerable hosts in search of high-efficiency upconversion phosphors.



INTRODUCTION

When doping inorganic crystalline solids with a lanthanide ion, the odd parity component of the crystal field partially breaks the Laporte rule, thus enabling optical transitions within the lanthanide's 4f manifolds. Given the existence of intermediate long-lived 4f energy states, lanthanide-activated upconversion luminescence can be achieved by the successive absorption of energy, followed by the emission of a photon with energy higher than the excitation flux.^{1,2} To date, such anti-Stokes optical behaviors in combination with high photostability, low background noise, and emission color tunability have aroused tremendous research interests because of the high potential for applications ranging from 3D volumetric display and anticounterfeiting to biological imaging and optogenetics.^{3–7}

Despite rapid development over the past decade, low upconversion efficiency of lanthanide-doped crystals remains the major hurdle that limits their widespread technological applications.⁸ It is a consensus that the preservation of excitation energy in an efficient light-harvesting system can power the access to high upconversion efficiency.

To enhance the light harvesting of a typical upconverter comprising lanthanide sensitizer–activator pairs, the most straightforward strategy is to elevate the concentration of the sensitizer. However, a high doping level always causes significant depletion of excitation energy owing to cross relaxation between sensitizer ions and fast energy migration from the sensitizers to lattice defects where the conversion of the excitation energy to heat occurs via nonradiative recombination. Such defect-induced depletion could be more severe when it comes to nanomaterials due to the existence of high-density surface defects. As such, surface passivation through core–shell engineering has proven effective to preserve the excitation energy by minimizing the surface quenching effect. Nonetheless, it has been challenging to mitigate the effect of defect quenching dominated by the core lattice. Moreover, given the lattice mismatch between the core

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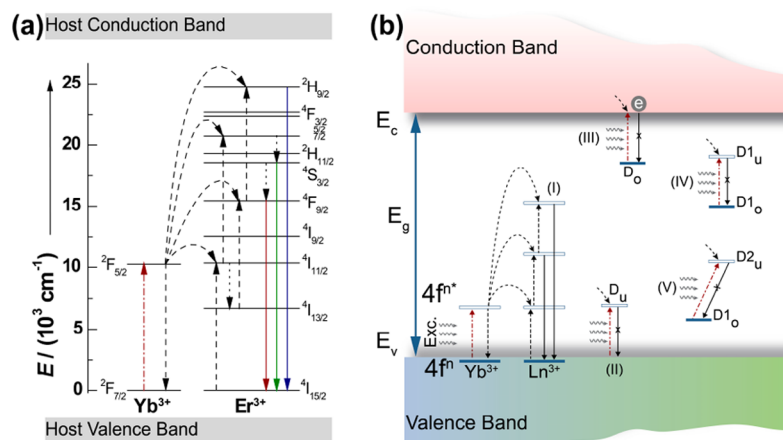


Figure 1. (a) Schematic energy transfer processes showing the upconversion in Yb³⁺- and Er³⁺-codoped crystals upon 980 nm diode laser excitation. (b) Schematic diagram showing a lanthanide-induced pathway for upconversion luminescence and defect-induced pathways for dissipation of excitation energy. Route I: Ln³⁺-based activator accepting energy from Yb³⁺ sensitizers. Route II: electrons located in the valence band maximum are excited to defect states. Route III: electrons located in defect levels are excited to the conduction band. Route IV: electrons are excited from defect-induced occupied states to unoccupied states (both occupied and unoccupied states originate from the same defect). Route V: electrons are excited from defect-induced occupied states to unoccupied states (occupied and unoccupied states originate from defects 1 and 2, respectively). The red dashed-dotted, dashed, dotted, and full arrows represent photon excitation, energy transfer, multiphonon relaxation, and emission processes, respectively. D₀: defect-induced occupied states. D₁: defect-induced unoccupied states. The superscripts “1” and “2” are used to differentiate two different defects. E_c: Conduction band minimum. E_v: Valence band maximum. E_g: Band gap. Ln³⁺: Lanthanide in the +3 oxidation state.

and shell layer, the interface is generally considered as a distorted area, where defects form with relative ease compared to the area with high crystallinity.

Another commonly employed method for defect removal is high-temperature annealing, which can initiate unwanted phase transition or dopant diffusion. More importantly, it remains questionable whether lattice defects in a given host are optically responsive. Therefore, to effectively avoid defect-induced quenching, questions concerning how defects participate in the photon conversion processes and what types of defects can quench excitation energy need to be answered at the outset. However, such a research field remains uncharted territory largely due to the lack of experimental techniques on the atomic scale. To the best of our knowledge, only the site symmetry of lanthanide ions has been probed experimentally by high-resolution photoluminescence spectroscopy,⁹ while theoretical research is limited to the studies of the electronic structures of an intact host and the energy-level splitting of lanthanides with particular 4fⁿ configurations.^{10–13} A systematic study of defect-induced quenching in lanthanide-doped phosphors has yet to be reported.

Here we perform a theoretical investigation on the lattice defect-induced dissipation of excitation energy in lanthanide-doped crystals via *ab initio* calculation based on the density functional theory (DFT). We show that the control over the formation and the deactivation of the lattice defects through chemical potential tuning is likely to achieve an enhanced upconversion emission. In this work, Yb³⁺-sensitized cubic NaYF₄ was employed. As illustrated in Figure 1a, Yb³⁺ ions serve as sensitizers harvesting 980 nm excitation energy, while Er³⁺ ions act as representative activators to receive the excitation energy from Yb³⁺ ions upon irradiation. Theoretically, the existence of defects may alter the electronic structures of the doped system. The disturbance of electronic structures may provide another channel to compete for 980 nm absorption with sensitizers and enable the generation of new energy reservoirs for energy trapping (Figure 1b). The

formation of defects is also likely to alter the energy-level alignment of the lanthanides.¹⁴ All the energy trapped at the defect sites will release in the form of heat via nonradiative decay as the phonon energy of the defective lattice could be higher than that of its intact counterpart. Consequently, this event significantly consumes the excitation energy required for the upconversion processes.

COMPUTATIONAL METHODS

To validate this hypothesis, we investigated the electronic structure and the stability of lattice defects in α-NaYF₄. The formation energies of intrinsic defects were calculated according to the following expression

$$E_f = E(D : q) - E(P) - \sum_i n_i \mu_i + q(\epsilon_F + E_v + \Delta V) \quad (1)$$

where $E(D : q)$ and $E(P)$ are the total energies of the supercell containing a defect at charge state of q and of the perfect supercell, respectively. When it comes to neutral defect, q turns to zero, making a simple formula for the calculation of formation energy. n_i is the number of removed ($n_i < 0$) or added ($n_i > 0$) atoms of species i during the defect formation, and μ_i is the corresponding chemical potential of element i . E_v is the valence band maximum (VBM) of the intact host, and a correction term of ΔV that depicts the difference in electrostatic potential between the defective and perfect system was also included. Note that ϵ_F represents Fermi level that varies within the band gap of the fluoride crystal. More details on the currently used methodology are illustrated elsewhere.¹⁵

The thermodynamic transition level $\epsilon(q/q')$ related to a given defect is defined as the Fermi level at which the formation energies of the defect with the charge state of q and q' are equal to each other. $\epsilon(q/q')$ can be obtained by solving

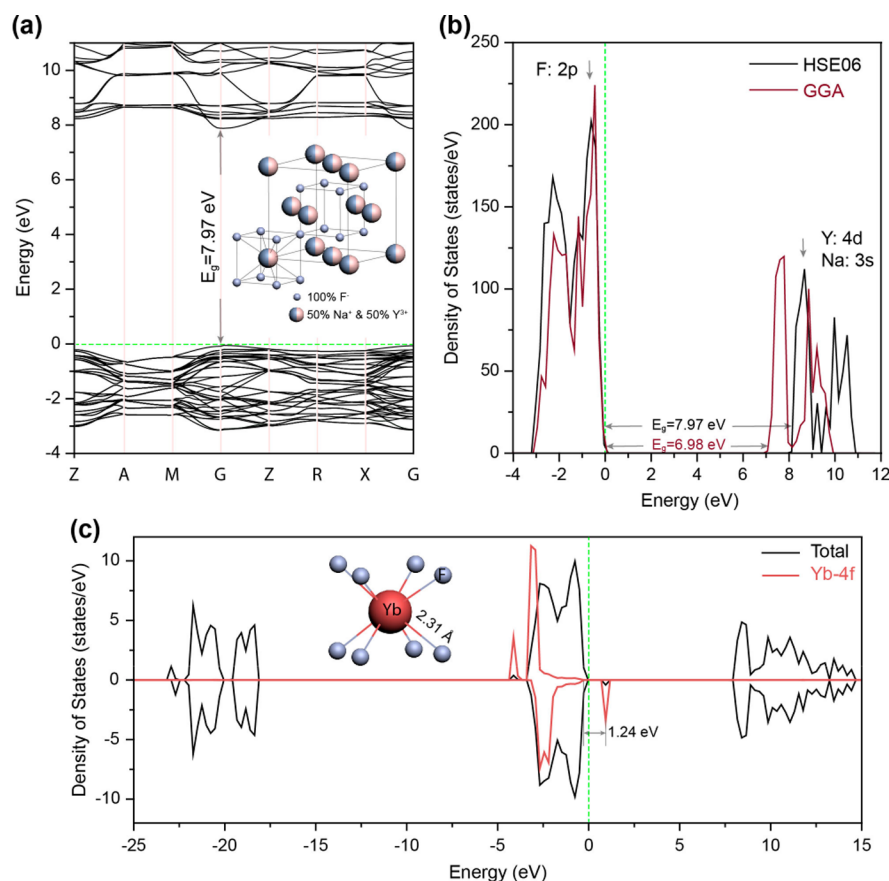


Figure 2. (a) Band structure of bulk α -NaYF₄ using HSE06 functionals. Inset is the atomic scheme of a disordered α -NaYF₄ crystal. (b) Total DOS of bulk α -NaYF₄ using both GGA and HSE06 functionals. (c) Total DOS and projected DOS of the α -NaYF₄:Yb system. Inset is the optimized coordination shell of Yb residing at the host Y site. The green dotted line represents the Fermi level which is set to zero. Note that the values of the total DOS in (c) are scaled down to one-tenth of their original values for comparison purposes.

$$\varepsilon(q/q') = \frac{E_{D,q'} - E_{D,q}}{q - q'} \quad (2)$$

where $E_{D,q}$ and $E_{D,q'}$ are the formation energies of the given defect with charge states of q and q' , respectively.

All the energetic and electronic calculations were performed within the framework of DFT implemented in the Vienna *ab initio* simulation package (VASP)¹⁶ with the projector augmented wave (PAW) method.¹⁷ The exchange-correlation interaction was evaluated by the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA-PBE).¹⁸ To obtain more precise electronic structures, the screened-exchange hybrid density functional HSE06 was used, where 12% of the GGA-PBE functional is replaced by the Hartree–Fock (HF) exchange interaction.^{19,20} An energy cutoff of the plane-wave basis expansion was set at 500 eV. For the k-point sampling, we employed $4 \times 4 \times 2$ and $2 \times 2 \times 2$ Monkhorst–Pack (MP) meshes for unit cell and supercell, respectively. For all calculations, the energy convergence criterion was set at 1×10^{-4} eV, and the maximum residual force on each atom was less than 0.02 eV/Å. To evaluate the absorption coefficients of the defective systems, the dielectric functions were calculated using the CASTEP code implemented in Materials Studio.²¹

To approximately simulate a solely existing defect, a supercell of $2 \times 2 \times 1$ containing 96 atoms was adopted. We tested even larger supercells containing 144 atoms and found tiny changes in the formation energies of defects. Considering that the impurity levels introduced by defects are

much localized, a 96-atom supercell would be large enough to eliminate the spurious interaction between defects and their images caused by the periodic boundary conditions. Note that the supercell lattices are fixed after optimizing the lattice constants of the unit cell, while all the atoms in the supercell are allowed to relax until all the convergence criteria are met.²²

To calculate the disordered structure, a transformation from disorder to order was imposed on the lattice using the supercell approach. Hence, the ordered lattice turns into a tetragonal structure with a lowered symmetry (D_{4h}), where both the Na and Y cations are 8-fold coordinated. The optimized lattice constants ($a = b = 5.498$ Å and $c = 10.823$ Å) slightly deviate from the experimental one ($a = b = c = 5.47$ Å and $2c = 10.96$ Å). As shown in Figure 2a, α -NaYF₄ shows a direct band gap of 7.97 eV at the Γ point. Compared to 6.98 eV calculated using the pure GGA functional, the use of a hybrid functional makes the bandgap comparable with the calculated value of 8.007 eV using the DFT+*U* method¹³ and the experimental value of ~ 8 eV.²³ Similar to other ionic crystals, the upper valence bands are mainly composed of F 2p orbitals, while the bottom conduction bands originate from Y 4d orbitals, along with a tiny contribution from the s orbitals of Na (Figure 2b).

Upon replacing host Y ions with Yb dopants, the spin-up 4f states of Yb are fully occupied, and the spin-down states split into occupied and unoccupied sublevels, with splitting energy of 1.24 eV (Figure 2c). This energy gap is very close to the energy gap (~ 1.27 eV) between Yb³⁺s $^2F_{7/2}$ and $^2F_{5/2}$ states,²⁴ demonstrating that hybrid functional-based DFT can properly

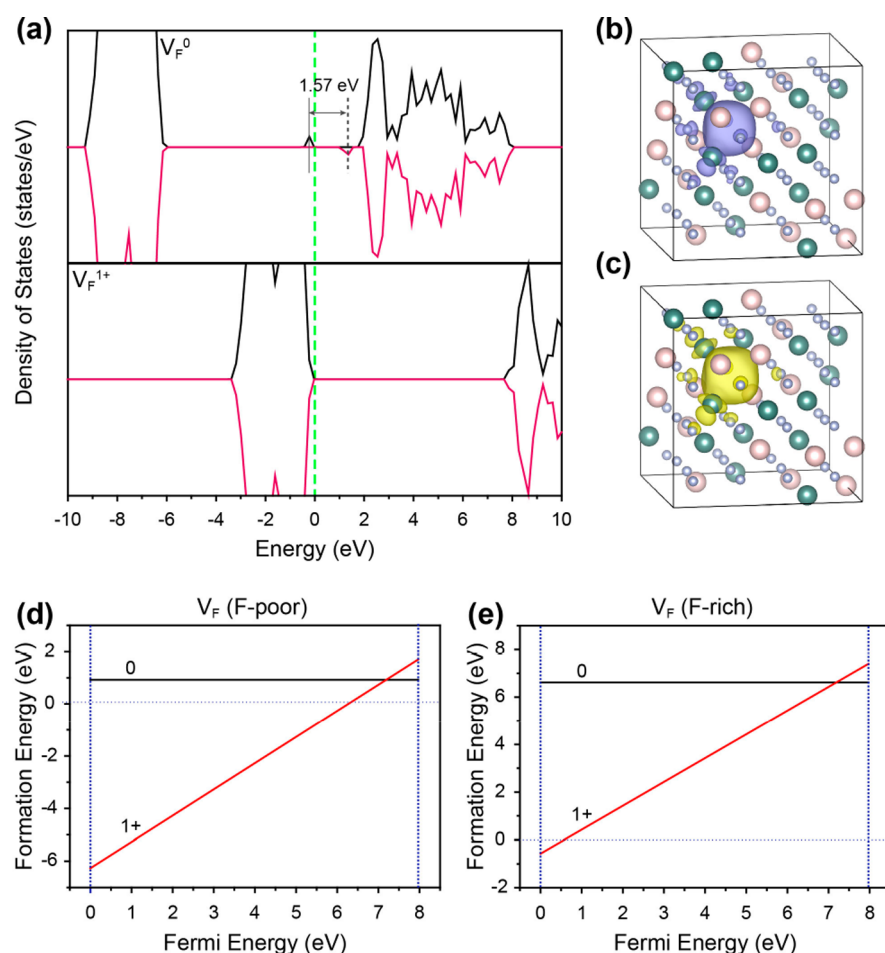


Figure 3. (a) Total DOS of α -NaYF₄ containing one neutral (0) or single positive (1+) fluorine vacancy. The green dashed line located at zero indicates the position of the Fermi level. (b) and (c) The spatial distribution of partial charge densities of V_F^0 -induced localized levels within the band gap. Purple and yellow iso-surfaces are used for occupied and unoccupied localized states, respectively. Pink, cyan, and gray balls stand for sodium, yttrium, and fluorine atoms, respectively. (d) and (e) The formation energies of V_F with different charge states under F-poor and F-rich chemical potential limits.

position the 4f levels of Yb. It is worth noting that upon 980 nm irradiation Yb³⁺ ions would experience a collective-state transition from $^2F_{7/2}$ to $^2F_{5/2}$ owing to the energy match between pumping source and the $^2F_{7/2}$ – $^2F_{5/2}$ gap. Given the validity of estimating multiconfiguration energy differences through the subtraction of single-particle energy levels,¹¹ it is rational to infer that the Yb³⁺ f electrons located at the occupied spin-down orbitals are excited to the unoccupied orbitals with the same spin alignment upon 980 nm laser excitation.

RESULTS AND DISCUSSION

When it comes to inherent lattice defects, it usually means that the creation of defects does not introduce additional chemical elements other than the elements composing the host crystal. Here, the electronic structures and the formation energies were studied for five groups of native defects, including vacancies, interstitials, antisite defects, and Frenkel defects, as well as Schottky defects. By removing one Na, Y, or F atom from the supercell lattice, the corresponding V_{Na} , V_Y , or V_F vacancies can be created at a low concentration. Let us consider the cases of V_F and V_Y to understand how the defects alter the electronic structure of the system. Compared with the intact crystal featuring clean band gap, the defective crystal containing one

neutral V_F possesses two impurity states which are not degenerate in energy, as shown in Figure 3a. One of the states is a spin-up occupied state, while the other is a spin-down unoccupied state. Both the unoccupied and the occupied states are localized around the V_F site, with the contribution from the hybridized Y-d and Na-s orbitals, as corroborated by the partial density distribution with s–d mixed orbital shape (Figures 3b and 3c).

According to the Bader analysis, the neighboring Y and Na atoms share one electron upon the removal of one F atom. It means that this electron may cause partial occupation of the impurity levels, leading to the splitting of levels with an energy interval of 1.57 eV. The filled and empty levels serve as hole and electron trapping states when free charge carriers are created upon illumination. For example, the electrons drifting within the conduction band can be spontaneously trapped by the empty states below the host conduction band minimum (CBM). Unlike the neutral V_F , V_F^{1+} does not introduce any localized states within the band gap, and all the empty states are pushed up to higher energy, resonating with the host conduction band (Figure 3a). Hence, the band gap of the NaYF₄ crystal comprising V_F^{1+} is ~ 0.31 eV smaller than that of the intact crystal.

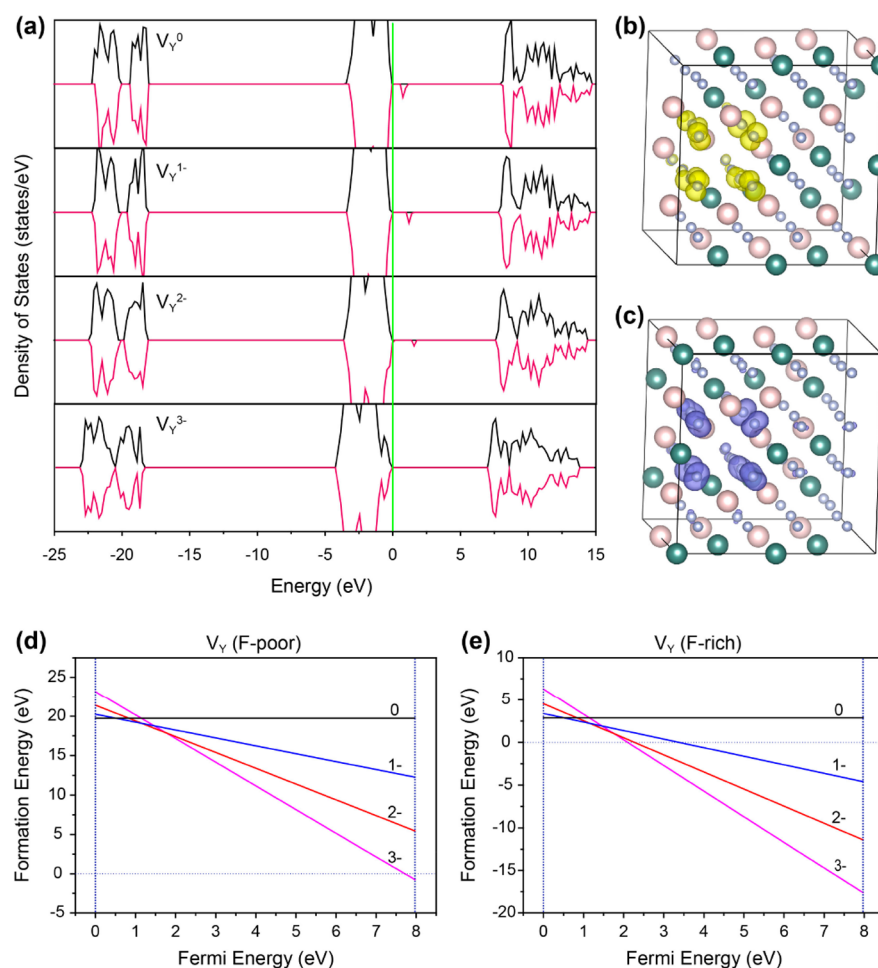


Figure 4. (a) Total DOS of α -NaYF₄ containing one neutral (0) or single negative (1[−]) or double negative (2[−]) or triple negative (3[−]) yttrium vacancy. The green dashed line located at zero indicates the position of the Fermi level. (b) and (c) The spatial distribution of partial charge densities of V_Y^{0-} and V_Y^{3-} -induced localized levels within the bandgap. Purple and yellow iso-surfaces are used for occupied and unoccupied localized states, respectively. Pink, cyan, and gray balls stand for sodium, yttrium, and fluorine atoms, respectively. (d) and (e) The formation energies of V_Y with different charge states under F-poor and F-rich chemical potential limits.

To better account for the stability of defects, we calculated the formation energies of V_F with different charge states according to eq 1. Figures 3d and 3e show the correlation between the formation energy and the position of Fermi level ϵ_F under F-poor and F-rich chemical potential limits, respectively. In agreement with the general trend, V_F is found to be formed more easily under F-poor conditions than under F-rich conditions. Specifically, neutral V_F can be formed by overcoming an energy barrier of 0.92 eV under F-poor limit. In general, such moderate energy can be gained even under infrared light stimulation. It is noteworthy that the neutral V_F is less stable than its single positive state when ϵ_F is in the range of 0–7.18 eV. Moreover, the V_F^{1+} forms spontaneously when ϵ_F is smaller than 6.26 eV. Under the F-rich conditions, the neutral V_F are rarely formed due to a formidable formation energy of 6.6 eV, and the V_F^{1+} can form only when ϵ_F lies very close to the host VBM.

In contrast to the anion vacancy, holes can be left by removing cations from the lattice. Here, we take V_Y as an example for detailed illustration. As shown in Figure 4a, the existence of V_Y^0 , V_Y^{1-} , and V_Y^{2-} can introduce one unoccupied spin-down level within the band gap. All these unoccupied states originate from the p orbital of neighboring F atoms (Figure 4b). Note that V_Y^{3-} does not introduce any gap states

because the added electron occupies the empty level, subsequently lowering the energy and leading to a mixing of gap states with the host valence band. The calculated partial charge distribution also indicates that the extra electron stays in the p orbital of the neighboring F atoms (Figure 4c). Despite the clean gap, we observed a decrease of 0.97 eV in the band gap of the V_Y^{3-} -containing NaYF₄ crystal because the newly formed occupied states push the valence band to higher energy. In light of the calculated formation energies shown in Figure 4d and 4e, it is found that the V_Y hardly forms under F-poor conditions, and only the V_Y^{3-} could exist when ϵ_F lies close to the host CBM. Under the F-rich conditions, neutral V_Y shows mild formation energy of 2.87 eV, and V_Y^{3-} forms spontaneously when ϵ_F is 2.1 eV higher than the host VBM.

By analyzing the electronic structures of V_{Na} -containing NaYF₄, it is surprising that both V_{Na}^0 and V_{Na}^{1-} do not cause gap states, mainly keeping the electronic structure intact (Figure S1). This is due to the mixing of V_{Na}^0 -induced unoccupied states with the host valence band. In the cases of interstitial defects, we found that only I_{Na}^{1+} -containing crystal shows a clean gap, and the remaining defects, including $I_F^{0/1-}$, I_{Na}^0 , and $I_Y^{0/1+/2+/3+}$, introduce occupied or unoccupied impurity levels within the band gap (Figures S2–S4). The formation energies of these defects are summarized in Table

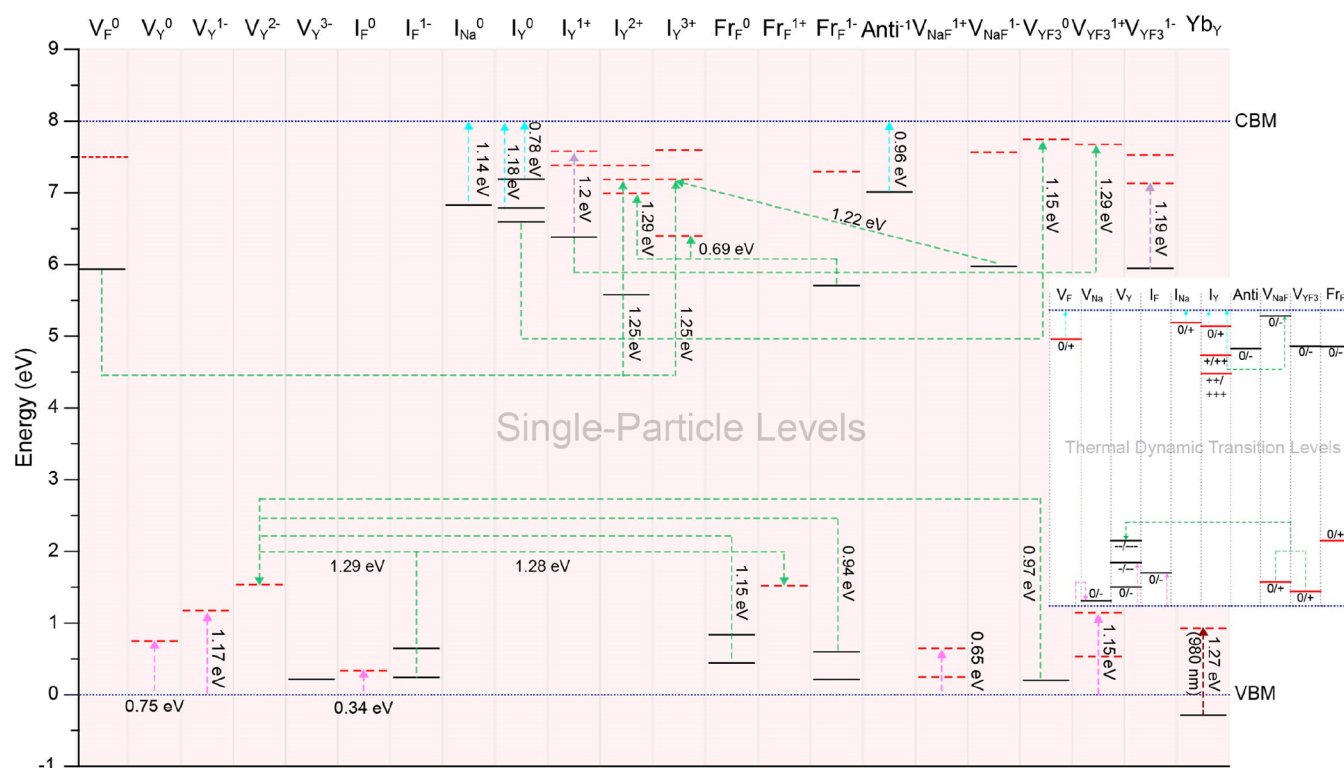


Figure 5. Single-particle levels of Yb dopant and native defects with different charge states. Note that the defect-induced levels which are resonant with host band edges or deeply embedded into host bands are not summarized here. The black solid and red dashed lines represent occupied and unoccupied levels, respectively; the deep-pink dashed arrows are the channels where electrons can be excited from valence band to defect-induced unoccupied states upon 980 nm light stimulation; the blue dashed arrows are the channels where electrons can be excited from defect-induced occupied states to the conduction band; the light-purple dashed arrows are the channels where optical transitions can occur between unoccupied and occupied states induced by the same defects; and the green dashed arrows are the channels where optical transitions take place between unoccupied and occupied states originated from different defects. The inset shows the thermodynamic transition levels of different charge states of the intrinsic defects under study.

S1. Taken together, these data suggest that V_F , I_{Na} , and I_Y are prone to appear under F-poor limits, while V_{Na} , V_Y , and I_F can exist when experimental conditions match F-rich chemical potential limit.

Aside from vacancies and interstitials, our study also examines the native defect complexes having self-compensated charges, such as antisite pair and Frenkel and Schottky defects. An antisite defect is usually defined as a host atom at site A that is replaced by another host atom originally located at site B. This type of defect has been widely recognized as dominant defects in less ionic compounds such as GaAs.²⁵ Given the disordered nature of the NaYF₄ crystal, Na and Y atoms may switch their positions during synthesis at an elevated temperature, named antisite defects. Here, the antisite pair (Na_Y-Y_{Na}) was considered with single negative, neutral, and single positive charge states. Indeed, the result shows low formation energy of 1.25 eV for a neutral antisite pair, indicating that even the 980 nm diode laser commonly used to excite the NaYF₄:Ln³⁺ sample can cause the formation of such defects. Compared to the neutral state, the single negative state can only exist when ϵ_F is close to the host CBM, and the single positive state is not stable for all values of ϵ_F . The existence of a neutral antisite defect causes no gap states but leads to a reduction of 0.9 eV in the band gap, whereas its single negative state not only introduces one occupied state located 0.96 eV lower than the host CBM but also causes a reduction in the band gap (Figure S5).

Frenkel defects can be considered as a combination of a vacancy and an interstitial defect of the same chemical species. As the formation of I_{Na} and I_Y requires high energy, we only studied anion Frenkel defects (V_F-I_F). Such a neutral defect can also be formed by overcoming an energy barrier of 1.59 eV, and single positive and single negative charge states can be reached when ϵ_F lies close to the host VBM and CBM, respectively. The total DOS shows that the anion Frenkel defect at 1−, 0, and 1+ states can cause a decrease in the band gap, and only a 1− charge state introduces one occupied level close to the host CBM (Figure S6).

In the case of Schottky defects, two types of defects were taken into consideration: one is caused by the removal of a Na–F pair (V_{NaF}), and the other involves removing a YF₃ unit (V_{YF3}). It should be noted that the formation energies of these two defects are in the range of 0.51 to 2.02 eV under F-poor and F-rich conditions, indicating a high probability of occurrence. Compared to V_{YF3} , V_{NaF} presents lower formation energies for all charge states. This is likely due to the smaller structural size of the NaF pair than that of the YF₃ unit. Among these defects, only neutral V_{NaF} has a clean gap (Figures S7 and S8).

To address how these native defects affect energy transfer within the lattice, we position these defect-induced single-particle levels with respect to the host VBM and CBM for further analysis (Figure 5). As aforementioned, only one unoccupied 4f state exists within the band gap when Yb is solely doped into the NaYF₄ lattice. The highest occupied 4f

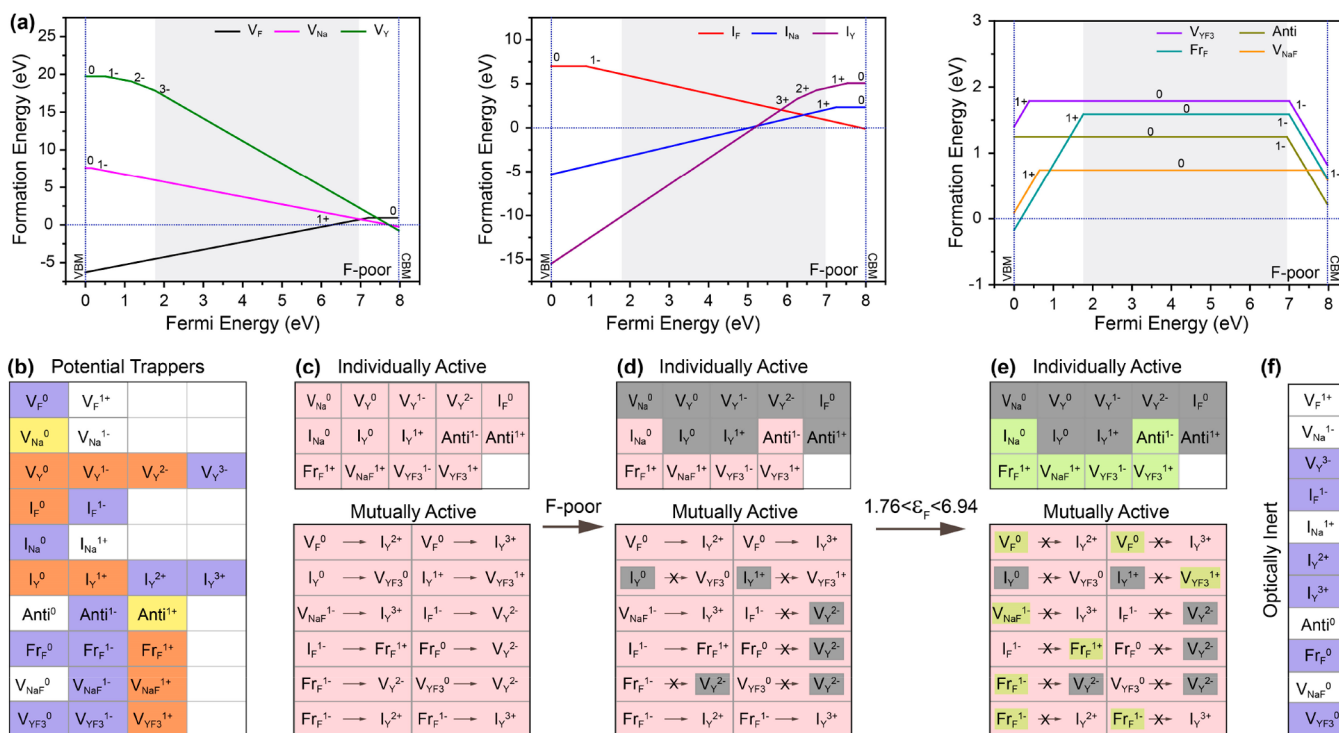


Figure 6. (a) Summarized formation energies of native defects with different charge states under F-poor chemical potential limit. The valence band maximum and conduction band minimum are set to zero and 7.97 eV, respectively. Note that the formation energies of antisite and anion-Frenkel keep constant irrespective of chemical potential limits. (b) Compiled five different types of native defects. Purple grid: defects that induce gap states. Yellow grid: defects that show nonzero absorption coefficient. Orange grid: defects that introduce gap states and show nonzero absorption coefficient simultaneously. White grid: inert defects showing no gap states and zero absorption coefficient. (c) Identified individually and mutually active defect centers (marked in pink grids) that trap 980 nm excitation energy. (d) Identified active defect centers (marked in pink grids) under F-poor chemical potential limit. The dark-gray grid indicates the corresponding defect centers can hardly form under F-poor chemical potential limit due to formidable formation energies. (e) Deactivated defects (marked in green grids) through chemical potential manipulation. (f) Inert defects which may exist in the as-synthesized cubic NaYF₄ crystal when chemical potential is within the range of 1.76 to 6.94 eV as indicated by the gray area in a.

orbital lies slightly lower than the host VBM. Upon 980 nm laser excitation, the electrons located at the highest occupied 4f orbitals directly jump to the unoccupied 4f orbitals owing to the energy match principle, as illustrated by the red dashed arrow in Figure 5. Since the 5d orbitals are positioned well above the host CBM, it is thus believed that there are no other causes that disturb the optical transitions within the Yb's 4f manifolds. However, the situation becomes quite different in the presence of defects. Figure 5 provides a picture of compiled single-particle energy levels of defective systems, with dashed arrows showing possible pathways for optical transitions upon 980 nm excitation.

In addition to the direct absorption by Yb³⁺ ions, we found that under 980 nm stimulation electronic transitions in defective systems can occur via four different pathways, referred to as VBM → D, D → CBM, D₁ → D₁, and D₁ → D₂. The subscripts represent the types of defects. The first pathway (VBM → D) is that electrons can be excited from the host VBM to the defect-induced unoccupied levels, as illustrated by the deep-pink dashed lines in Figure 5. These unoccupied levels, such as V_Y¹⁻ and V_{YF3}¹⁺-induced levels, locate at ~1.2 eV relative to the host VBM. The second pathway (D → CBM) is related to the transition from the defect-induced occupied level to the host conduction band (blue dashed arrows). Given that the energy gap between the localized levels and the host CBM is smaller than 1.27 eV, electrons in the filled levels can be excited to the conduction

band upon irradiation of 980 nm light. These excited electrons may nonradiatively relax to their original position by dissipating energy through lattice vibration or become trapped at other empty levels below the host CBM. Such pathways are mainly responsible for 980 nm absorption in the presence of I_{Na}⁰, I_Y⁰, and Anti¹⁻.

The third pathway (D₁ → D₁) can be explained by considering the fact that one defect can introduce both filled and empty levels, along with a gap of ~1.27 eV between them. It means that electrons can be excited from the filled orbital to the empty orbital, thus creating a 980 nm responsive center just like the Yb³⁺ sensitizer. As shown in Figure 5, such pathways marked by light-purple arrows form when the host embraces I_Y¹⁺ and V_{YF3}¹⁻ defects. The fourth pathway (D₁ → D₂) is the most complicated one that can be ascribed to optical transitions among different defects. The promotion of the electrons in the filled levels caused by one defect to the empty levels induced by another defect can be guided by the green dashed arrows. Note that such pathways are possible only in the presence of both types of defects. Here, the defect combinations that create such interdefect pathways include V_F⁰-I_Y²⁺/I_Y³⁺, I_Y⁰-V_{YF3}⁰, I_Y¹⁺-V_{YF3}¹⁺, V_{NaF}¹⁻-I_Y³⁺, I_F¹⁻-V_Y²⁻/Fr_F¹⁺, Fr_F⁰-V_Y²⁻, Fr_F¹⁻-V_Y²⁻/I_Y²⁺/I_Y³⁺, and V_{YF3}⁰-V_Y²⁻. Additionally, the thermodynamic transition levels show potential transportation pathways for charge carriers, which is in reasonable agreement with the speculation involving single-particle energy levels (inset in Figure 5).

In addition to the absorption channels predicted through single-particle energy levels, direct calculation on optical absorption of the system could also provide additional evidence on the existence of defect-induced absorption channels. Given the forbidden nature of the f – f transitions, the absorption cross-section of lanthanide ions is very small. Yb^{3+} ion has the largest cross-section to 980 nm light among the lanthanide series, thus making it an ideal sensitizer for near-infrared light harvesting. However, the transitions between host bands and defect-induced levels are electric dipole allowed, resulting in a large cross-section. Hence, the transitions occurring via the four pathways described above have a higher probability than that through f – f transitions. In this respect, these defect-induced active centers are more capable of absorbing 980 nm light than Yb ions at comparable concentrations. To quantify the absorption capability of each system, one can correlate the bulk absorption coefficient α , on the basis of the exponential attenuation law, with the real part of the refractive index as well as the imaginary part of the dielectric constant through

$$\alpha = \frac{\omega \varepsilon_2}{nc} \quad (3)$$

where ω is the angular frequency; c is the speed of light in vacuum; n is the real part of the refractive index; and ε_2 is the imaginary part of the dielectric constant. The estimated absorption coefficients of NaYF_4 crystal containing lattice defects or lanthanide ions are listed in Table S2. Among these defects of interest, we found that 11 defects, including V_{Na}^0 , $\text{V}_{\text{Y}}^{0/1-2-}$, I_{F}^0 , $\text{I}_{\text{Y}}^{0/1+}$, $\text{Fr}_{\text{F}}^{1+}$, Anti^{1+} , $\text{V}_{\text{NaF}}^{1+}$, and $\text{V}_{\text{YF3}}^{1+}$, can affect the absorption capacity of the corresponding systems. Their absorption coefficients are 1 order of magnitude larger than that of Yb-doped NaYF_4 . When considered together, the proposed channels for optical transitions can be recognized as competing channels to Yb ions during the energy-harvesting process.

Despite the possibility of many defect-induced transition pathways, some of them may not exist due to the high formation energy or low stability of the defects. Under the standard synthesis conditions, lanthanide-doped NaYF_4 crystals tend to form in the cubic phase when the ratio of F^- to Y^{3+} is less than 4.²⁶ The formation energies of the native defects under F-poor conditions are compiled in Figure 6a. Without the restriction on the chemical potential limit of fluorine, 23 defects highlighted in Figure 6b are identified to be responsible for the existence of gap states and nonzero absorption coefficients. Note that the optically unresponsive defects are marked with white grids. These defects can be broken down into two categories, namely, individually and mutually active defect centers (Figure 6c). By applying the F-poor chemical potential limit, 7 individually active defects can be ruled out because they hardly exist under F-poor conditions, as marked in the dark-gray grid (Figure 6d). Note that the Anti^{1+} defect can also be excluded as it is not stable when compared with its neutral and single negative counterparts. As a consequence, the mutually active centers containing any of the 8 defects shown in dark gray in the individually active defects are thus not available. At the current stage, the quantity of the defect-induced pathways for optical transitions can be largely reduced. Specifically, the existence of $\text{V}_{\text{NaF}}^{1+}$, $\text{V}_{\text{YF3}}^{1+}$, and $\text{Fr}_{\text{F}}^{1+}$ can activate the VBM–D pathway; I_{Na}^0 and Anti^{1-} are responsible for the realization of the D–CBM channel; and only $\text{V}_{\text{YF3}}^{1-}$ is capable of initiating D_1 – D_1 transition; and six

interdefect combinations including V_{F}^0 – $\text{I}_{\text{Y}}^{2+/3+}$, $\text{V}_{\text{NaF}}^{1-}$ – I_{Y}^{3+} , I_{F}^{1-} – $\text{Fr}_{\text{F}}^{1+}$, and $\text{Fr}_{\text{F}}^{1-}$ – $\text{I}_{\text{Y}}^{2+/3+}$ are possible for D_1 – D_2 transitions. As demonstrated, it is apparent that the formation of a given defect could be controlled by tuning the chemical potentials of the species involved in the synthesis processes. Given the dependence of element chemical potential on temperature and pressure, the defect formation energy could be generally manipulated by varying the experimental temperature or pressure.

Following the determination of active defect centers, we argue that these defects mainly participate in two optical processes: excitation energy absorption and energy transfer. Let us revisit the compiled single-particle energy levels (Figure 5) and the calculated 980 nm absorption coefficients (Table S2). Given the larger absorption coefficients of defect-related transition channels, the aforementioned 12 active defect centers would be more capable of harvesting 980 nm excitation energy than the Yb^{3+} sensitizer. Unlike the previously reported defect-mediated persistent emission,^{27,28} the absorbed excitation energy is more likely to dissipate through lattice vibrations. This arises due to the highly ionic nature of the fluoride crystal and its large band gap, thus leading to a soft lattice featuring a low Debye temperature.

On the basis of the correlation between the Debye temperature and the quantum yield, a low Debye temperature often implies low quantum efficiency.^{29,30} On a separated note, inspired by the predictive theory of nonradiative decay in molecular systems,^{31,32} the identification of defect-induced conical intersections has also been employed to convey nonradiative combination in inorganic crystals.³³ This study suggests that the system is likely to suffer efficient nonradiative recombination when a defect-induced conical intersection exists and can be kinetically or dynamically accessed. Specifically, it is believed that if a given defect can introduce midgap states it also introduces the conical intersection. Moreover, the more significant the distortion is around the defect, the more accessible such intersection points are.^{34,35} Considering that most lattice defects under investigation introduce midgap states and lattice distortions, it is rational to infer that these active defect centers are more prone to promote nonradiative recombination via heat release other than serving as energy suppliers for a subsequent upconversion process. Collectively, we believe that the defect-harvested excitation energy dissipates nonradiatively, leading to a significant reduction in excitation energy for the subsequent emission process. Apart from the formation of competing channels, defects can also alter the valence states of Yb^{3+} sensitizer.³⁶ For instance, in light of the Bader analysis and single-particle energy levels, a reduction of Yb^{3+} to Yb^{2+} occurs when a Yb dopant and I_{Na}^0 defect coexist in the same system, further lowering the overall energy absorption by Yb^{3+} ions (Figure S9).

In addition to the interference of the energy-harvesting process, the defects can also serve as energy trapping centers that compete with lanthanide activators. It is well accepted that the energy transfer between the lanthanide sensitizer and activator is via a nonradiative electrical coupling, where the transfer efficiency significantly depends on donor–acceptor distance and spectral overlap of the donor’s emission with the acceptor’s absorption. To qualitatively estimate the distribution of dopants and defects, we compare the total energy of the systems containing Yb–Yb, Yb–Er, and Yb–defect pairs. From the energetic point of view, it is found that lanthanide ions

tend to occupy Y sites randomly without preference of segregation, while the defects are prone to stay just near the Yb dopant except for the fluorine interstitial defect. Hence, the distance between Yb and Er is supposed to be larger than that of the Yb defect at comparable defect and dopant concentration. As a consequence, the energy transfer between Yb dopant and defect centers is more efficient when comparing with the lanthanide-based donor–acceptor pair. In addition to the distance, the spectral overlap between Yb emission and defect absorption should also be larger than that of the Yb–Er pair. This arises because the absorption coefficients of defect centers are 3 orders of magnitude larger than that of Er^{3+} ions (Table S2). Moreover, the dipole-allowed optical transitions at defect centers should have much faster decay rate than that of f–f transition, thus indicating that energy consumption at defect centers should be larger than that of at lanthanide sites. Such speculation can be supported by a pioneering work which pointed out that the OH^- defect can shorten the nonradiative decay rate of the F center to ~ 10 ns.³⁷ When considered all together, these active defect centers are capable of trapping excitation energy at first and then dissipating the energy through nonradiative recombination.

In principle, a host material can tolerate an appreciable level of defects, as evidenced by the identified inert defects, such as Anti^0 and V_{NaF}^0 . To this regard, it is feasible to suppress the dissipation of the excitation energy by deactivating the identified active defect centers rather than removing all the lattice defects. Since the stability of a given defect depends on the electron chemical potential, one could achieve such a mode of deactivation by tuning such chemical potentials through experimental design. Note that the electron chemical potential, named Fermi energy, is defined as the change in free energy when electrons are added or removed from the computational model of $\alpha\text{-NaYF}_4$.

To deactivate these defect centers, the electron chemical potentials need to fall into a particular energy range where the defects are unstable. As indicated in Figure 6a, all individually and mutually active defect centers can be deactivated by controlling the electron chemical potential ε_{F} within the range of 1.76 to 6.94 eV. To illustrate the deactivation process, let us take two individually active defects (Anti^{1-} and $\text{Fr}_{\text{F}}^{1+}$) for examples as the stability of these two defects determines the upper and lower bounds of the electron chemical potentials (Figure 6e). When ε_{F} is smaller than 6.94 eV, the Anti^{1-} is no longer stable as its neutral state shows lower formation energy, while the $\text{Fr}_{\text{F}}^{1+}$ is converted to Fr_{F}^0 when ε_{F} is larger than 1.76 eV. Accordingly, the remaining four individually active defects (I_{Na}^0 , $\text{V}_{\text{NaF}}^{1+}$, and $\text{V}_{\text{YF}_3}^{1-/1+}$) transform into their inert counterparts ($\text{I}_{\text{Na}}^{1+}$, V_{NaF}^0 , and $\text{V}_{\text{YF}_3}^0$) when ε_{F} varies in the range of 1.76 to 6.94 eV. For mutually active defect centers, with the deactivation of the above defect $\text{Fr}_{\text{F}}^{1+}$, the optical transition through the $\text{I}_{\text{F}}^{1-} \rightarrow \text{Fr}_{\text{F}}^{1+}$ channel is unlikely to occur as the I_{F}^{1-} is not optically responsive to 980 nm light. Similarly, the defect components V_{F}^0 , $\text{V}_{\text{NaF}}^{1-}$, and $\text{Fr}_{\text{F}}^{1-}$ can also transform into V_{F}^{1+} , V_{NaF}^0 , and Fr_{F}^0 , respectively, thus deactivating the transition pathways of $\text{V}_{\text{F}}^0 \rightarrow \text{I}_{\text{Y}}^{2+/3+}$ and $\text{Fr}_{\text{F}}^{1-} \rightarrow \text{I}_{\text{Y}}^{2+/3+}$. Consequently, defects listed in Figure 6f may exist in the as-synthesized cubic NaYF_4 crystals. It should be noted that none of them can harvest or dissipate the 980 nm excitation energy individually or mutually. Such inert defects could render lanthanide-doped upconversion materials highly emissive. Given the proposed wide energy range (1.76–6.94 eV), approaches on the tuning of the electron chemical

potential would be quite accessible by changing experimental conditions.

To tune the electron chemical potential of a given system, the commonly used strategies include extrinsic doping, external strain modulation, and external field manipulation, which have been widely applied to various semiconductors and insulators.^{38–40} Indeed, these methods have been demonstrated to be useful for enhancing the photon conversion efficiency of lanthanide-doped upconversion phosphors. However, without knowing their exact effect on the manipulation of electron chemical potential and the subsequent stability of the defects, the enhanced luminescence is, in many cases, simply ascribed to the elimination of surface defect or the reduction in the coordination symmetry of lanthanides. Given that Li-doping, core–shell-induced strain, and electric field can tune the position of the Fermi level of the corresponding systems, it is rational to infer that the deactivation of optically responsive defect centers can also be realized through these methods. Recently, spectroelectrochemical experiments on CsPbBr_3 nanocrystals have demonstrated the effectiveness of control over the emission intensity by altering the position of the Fermi level through the application of external potentials.⁴¹ Therefore, in addition to the decreased crystal field symmetry, the suppression of active defect centers is also likely to be one of the causes of luminescence enhancement.

CONCLUSIONS

Enhancing the emission efficiency of lanthanide-doped upconversion materials is of paramount importance for versatile, practical applications. In previous studies, the Laporte selection rule was generally employed to explain the low intensity and quantum yield of upconversion luminescence originated from 4f–4f optical transitions. As native lattice defects exist in all forms of crystals, questions concerning how these defects affect the luminescence processes of lanthanide-doped compounds remain unclear. In this regard, we have demonstrated theoretically that four types of defect-induced pathways can exist, competing with the Yb^{3+} -based channel for 980 nm incident light harvesting. Moreover, these optically active defects can also serve as energy trapping centers, competing with lanthanide-associated activators. The trapped excitation energy can be dissipated via nonradiative combination by converting photon energy to heat. On the basis of our calculations, lattice defects, including $\text{V}_{\text{NaF}}^{1+}$, $\text{V}_{\text{YF}_3}^{1+}$, $\text{Fr}_{\text{F}}^{1+}$, I_{Na}^0 , Anti^{1-} , $\text{V}_{\text{YF}_3}^{1-}$, V_{F}^0 – $\text{I}_{\text{Y}}^{2+/3+}$, $\text{V}_{\text{NaF}}^{1-}$ – I_{Y}^{3+} , I_{F}^{1-} – $\text{Fr}_{\text{F}}^{1+}$, and $\text{Fr}_{\text{F}}^{1-}$ – $\text{I}_{\text{Y}}^{2+/3+}$, are demonstrated to be active defect centers that grab 980 nm energies during the absorption and energy transfer processes in lanthanide-doped $\alpha\text{-NaYF}_4$. To deactivate these competing pathways, the best strategy proposed here is to tune the electron chemical potential in the range from 1.76 to 6.94 eV through external stimulations. These findings should provide new insights into the fundamental understanding of lanthanide-activated upconversion luminescence processes. Moreover, our results provide a potential route toward the synthesis of crystals without optically active defect centers, potentially enabling the development of high-efficiency luminescent materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b02596.

Calculated formation energies, 980 nm-associated dielectric constant, refractive index, absorption coefficient, DOS, and partial charge density of defective systems (PDF)

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Notes

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