

First-principles study of intrinsic and Fe^{3+} -related luminescence mechanisms in feldspar

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Feldspar is the most abundant mineral group in the Earth's continental crust and almost invariably contains Fe^{3+} impurities in natural samples. These impurities dominate the characteristic deep-red luminescence of feldspar, while the host lattice itself also exhibits intrinsic luminescence associated with self-trapped excitons (STEs). Despite the central role of feldspar in luminescence dosimetry and geochronology, the microscopic mechanisms underlying both intrinsic and Fe^{3+} -related luminescence remain incompletely understood. Here, we present a comprehensive first-principles investigation of disorder, intrinsic defects, and impurity-related charge trapping in K-feldspar. Using a cluster expansion trained on density functional theory calculations, we determine the ground-state Al–Si ordering and quantify the formation of Al–O–Al linkages at high temperatures. Based on this structure, we identify energetically favorable intrinsic defects and demonstrate that hole polarons localize preferentially on oxygen atoms bridging AlO_4 and SiO_4 tetrahedra, while Si–O–Si bridges do not stabilize holes. Rare Al–O–Al bridges formed at melting temperatures are shown to be particularly efficient hole traps. We compute STE configurations and vertical emission energies using a hybrid functional approach, obtaining emission energies in excellent agreement with experimental measurements. Furthermore, we show that Fe^{3+} impurities strongly modify local charge trapping: Fe^{3+} preferentially captures electrons to form Fe^{2+} , while also stabilizing hole polarons on neighboring oxygen sites, forming metal-oxyl complexes. Based on these results, we propose a microscopic mechanism for Fe^{3+} -related luminescence in which electron capture by Fe^{3+} is followed by spin-selective recombination that populates the Fe^{3+} excited state 4T_1 . Our results provide a unified atomistic picture of intrinsic and impurity-driven luminescence in feldspar and establish a quantitative foundation for modeling charge trapping and recombination processes relevant to luminescence dating.

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I. INTRODUCTION

Feldspar constitutes the most abundant mineral group in the Earth's continental crust [1] and plays a central role in a wide range of geological processes. Owing to its ability to store and release radiation-induced charge carriers, feldspar also serves as a natural archive in geochronology and thermochronology [2] through the application of luminescence dating techniques [3,4]. Luminescence dating is widely used to understand past climate change [5,6], reconstruct rates of Earth surface processes [7], and unravel human evolution and dispersal over timescales extending to several hundred thousand years [8,9]. Luminescence dating relies on defects in crystal lattices, which form long-lived metastable states through the capture of free electrons and holes induced by environmental ionizing radiation. Given the large band gap of

natural minerals such as quartz and feldspar, deep metastable states can persist for millions of years at ≈ 300 K. Excitation by heat or light causes detrapping and subsequent electron-hole recombination, a process that results in luminescence emission.

The intensity of luminescence emission is proportional to the population of metastable states, which in turn is a function of the ionizing radiation dose (Gy) absorbed by the sample in nature. During geological transport, for example, these metastable states are erased by sunlight exposure. Subsequent burial of sediment kick-starts the charge trapping process, the rate of which is proportional to the environmental dose rate. The burial time, or sedimentation age of the sample, is estimated as the ratio of the absorbed dose (measured using luminescence) to the dose rate [3,4]. See a recent review by McKeever [10], which discusses various recombination pathways and kinetics, including tunneling of trapped electrons to neighboring recombination centers [11]. Trapping energies associated with different luminescence centers are commonly extracted by fitting luminescence decay curves using selected kinetic models. However, the resulting energetics are inherently model dependent, which limits their reliability and can lead to errors in the interpretation of absorbed dose, particularly for samples that have experienced a dynamic thermal history [9]. It is therefore desirable to determine trap parameters independently and use them as fixed

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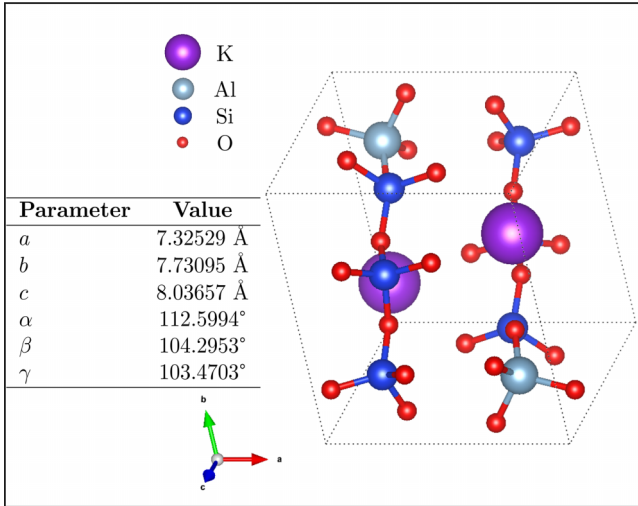


FIG. 1. The optimized ground-state structure of a K-feldspar unit cell with the Perdew-Burke-Ernzerhof functional. The lattice parameters are listed beside the structure.

inputs to kinetic models, thereby avoiding interdependencies between parameters and the assumed kinetic framework. This calls for a comprehensive atomistic study of the intrinsic defects in feldspar and their role in storing charge carriers. In this study, we focus on a ubiquitous aluminosilicate feldspar that is widely used in luminescence geochronology, with the aim of ultimately establishing a link between defect-scale processes and the bulk luminescence response.

Feldspar occurs in a range of compositions across KAlSi_3O_8 , $\text{NaAlSi}_3\text{O}_8$, and $\text{CaAl}_2\text{Si}_2\text{O}_8$ end members [10]. In this work, we focus on K-feldspar (KAlSi_3O_8), which is well studied experimentally, and provide commentary on Na-feldspar where relevant. K-feldspar crystallizes in a low-symmetry triclinic structure with a space group of $P\bar{1}$. Its lattice structure consists of three SiO_4 tetrahedra linked to one AlO_4 tetrahedron. The tetrahedra form four-membered rings that are further linked to create “crankshaft” chains. SiO_4 tetrahedra are connected to both other SiO_4 tetrahedra (Si–O–Si bonds) and AlO_4 tetrahedra (Al–O–Si bonds). By contrast, generally, AlO_4 tetrahedra are not directly linked to each other (Al–O–Al bonds are rare or absent). Instead, AlO_4 tetrahedra are typically fully connected to SiO_4 tetrahedra (Al–O–Si). In addition, K^+/Na^+ ions occupy the interstitial sites to maintain charge neutrality (see the example structure in Fig. 1).

Luminescence in feldspar arises from intrinsic self-trapped excitons or extrinsic defects and impurities. The most typical luminescence observed in feldspar comes from Iron (Fe) impurities that enter the lattice replacing Al^{3+} ions. Iron impurities are commonly found in natural feldspar samples and are responsible for the broad deep-red emission arising from spin-forbidden $d-d$ transitions $^4T_1 \rightarrow ^6A_1$ [12,13]. This characteristic emission serves as an indicator in luminescence dosimetry, which is used to quantify the radiation dose absorbed by feldspar [14]. However, the mechanisms underlying Fe-centered luminescence in feldspar remain under debate. Some studies suggest that Fe^{3+} ions capture electrons first to form Fe^{2+} [13], which subsequently

recombines with a hole and forms Fe^{3+} in its excited state 4T_1 , whereas others propose that Fe^{3+} instead captures a hole first, forming Fe^{4+} [14], which then recombines with an electron forming a 4T_1 state. These differing experimental interpretations are based on the underlying assumptions about which luminescence pathway (i.e., thermoluminescence or infrared-stimulated luminescence) dominates during the recombination process. Nevertheless, comprehensive insights into the relative stabilities of Fe^{2+} and Fe^{4+} in feldspar, together with their interactions with native defects such as polarons, is yet to be established. This work seeks to bridge this knowledge gap by employing high-accuracy first-principles simulations.

In order to understand Fe-related luminescence, it is useful to first understand the intrinsic luminescence in feldspar. Intrinsic luminescence in this case is attributed to self-trapped excitons, which form when a hole localizes on a bridging oxygen atom and is surrounded by a semilocalized electron, which recombine to give rise to the emission [12]. Importantly, the intrinsic luminescence energy varies with the local atomic environment of the hole. Different oxygen coordination environments, such as those bridging Si–O–Al, Al–O–Al, or Si–O–Si tetrahedra, give rise to distinct trapping energetics and recombination energies. Therefore, it is important to understand Al–Si distribution in feldspar, and of the likelihood of forming Al–O–Al bonds.

This paper is structured as follows. Section II describes all the computational methods used in this work. We begin by outlining our methodology for studying Al–Si disorder in feldspar, which is based on a Cluster Expansion (CE) approach trained on Density Functional Theory (DFT) calculations. We then describe the computational approach used to investigate the formation energies of different intrinsic defects and the localization of electrons and holes in their vicinity. Finally, we provide details of the Nudged Elastic Band (NEB) and ΔSCF methods employed to determine hole diffusion barriers and emission energies. Section III presents the results, including defect formation energies, favorable polaron localization sites and their associated trapping energies based on the identified ground-state structure, followed by self-trapped exciton (STE) configurations and their vertical emission energies, which provides validations of chosen computational methods. This section also discusses mechanisms of electrons and holes trapped by Fe^{3+} and the resulting possible pathways leading to the Fe^{3+} in excited state 4T_1 . Finally, Sec. IV summarizes the key conclusions and outlines their implications for understanding feldspar luminescence.

II. COMPUTATIONAL DETAILS

A. Al–Si disorder

It is experimentally recognized that the Al and Si atoms in feldspar exhibit significant disorders across the tetrahedral sites [15]. Since the emission energies are strongly controlled by the local atomic environment of trapped holes, Al–Si disorder is expected to have a direct impact on the luminescence properties. In this context, rare Al–O–Al bonds have been proposed as candidate luminescence centers responsible for the blue emission observed in K-feldspar [15].

Quantifying the concentration of Al–O–Al bonds at temperatures close to the melting point, where the feldspar structure is established, is therefore essential for understanding the microscopic origin of the luminescence. A direct enumeration of all possible Al–Si configurations and their energies is, however, computationally intractable: the number of configurations grows combinatorially with system size, while the cost of DFT scales as N^3 with the number of electrons N . We therefore employ the cluster expansion approach [16], which parametrizes the configuration-dependent energetics using a limited set of DFT calculations [17]. This enables efficient sampling of large configurational spaces and reliable predictions of Al–O–Al bond concentrations in thermodynamically relevant regimes.

The CE model was trained on 110 structures generated by randomly swapping Al and Si while maintaining an Al:Si ratio of 1:3. Structures were generated using supercells of various sizes so that the model could capture size-dependent effects and yield reliable energy predictions for larger supercells. In this work, supercells containing up to 312 atoms were used. These unique structures were generated using the cleave code [18], and their total energies were calculated within DFT using the Perdew-Burke-Ernzerhof (PBE) [19] exchange-correlation functional. All DFT calculations were performed with the Vienna *ab initio* Simulation Package (vasp) [20]. Core-valence interactions were described by the projector augmented-wave (PAW) method [21], while the valence states were expanded in a plane-wave basis with a kinetic-energy cutoff of 520 eV. The valence electron configurations for the elements in two feldspar compositions are as follows: - Potassium (K): $3p^6 4s^1$ - Aluminum (Al): $3s^2 3p^1$ - Silicon (Si): $3s^2 3p^2$ - Oxygen (O): $2s^2 2p^4$ - Sodium (Na): $3s^1$. Gaussian smearing with a width of 0.05 eV was applied to assign occupations to electronic states around the Fermi level. The Brillouin zone was sampled using a $2 \times 2 \times 2$ Monkhorst-Pack grid for supercells containing fewer than 200 atoms, and using only Γ -point for larger supercells. The convergence criteria for the electronic self-consistent loop was set to 10^{-5} eV and atomic positions were relaxed until the residual forces were less than 0.05 eV/Å.

A λ parameter together with ℓ_1 norm regularization was used to control the sparsity of the CE model and avoid overfitting. The optimal λ value was determined through a leave-one-out cross-validation scheme. The CE model was further validated by requesting the ground-state structure within a $2 \times 2 \times 2$ supercell. This was achieved by performing a simulated-annealing Monte Carlo search over the full configurational space of Al–Si disorder, with energies evaluated in seconds using the trained CE model across a sequence of decreasing temperatures to 1 K. At high temperature, the algorithm samples a wide variety of atomic arrangements of Al–Si, whereas at low temperature it progressively converges toward low-energy configurations. If the predicted ground-state structure from CE is not included in the training set, we calculated its total energy using DFT and added it to the training set to retrain the CE model. This iterative procedure continued until the predicted ground-state structure was included in the training set and consistently identified as the lowest-energy configuration.

B. Intrinsic defects

Once the ground-state structure was determined from the CE model, it was used as the starting point for all subsequent defect calculations. Defects were modeled in a $2 \times 2 \times 2$ supercell (208 atoms in total). To keep the computational cost manageable, all candidate defects including vacancies of K, O, Al, and Si, as well as antisites and interstitials in various charge states were first screened with the PBE functional. The electronic self-consistent field convergence criterion was set to 10^{-6} eV and the force convergence threshold was set to 0.01 eV/Å. Semilocal PBE calculations are computationally cheap and well suited for describing the thermodynamics of Al–Si disorder. However, defect properties are highly sensitive to the underlying electronic structure, particularly to the positions of the band edges. Because the PBE functional systematically underestimates the band gap, we employed the more computationally demanding hybrid functional for defect calculations. The hybrid functional yields a more reliable band gap and improves the description of localized defect states. The lowest-energy defects were fully relaxed and their formation energies reevaluated using the range-separated Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional [22]. The fraction of exact Hartree-Fock exchange was determined to be 0.385 by fitting to the experimental band gap that was taken from Ref. [23]. Γ -only sampling was used in all HSE06 calculations.

C. Hole and electron trapping

In the previous section, the localization of electron and hole polarons as intrinsic defects in the ground-state structure of K-feldspar was included. In addition, we have also studied such a localization in structures with enforced Al–O–Al bonds and also in the surroundings of an Fe impurity. For Fe-containing calculations, the PAW pseudopotential within the PBE exchange-correlation functional was employed and the pseudopotential treats eight valence electrons: $3d^7 4s^1$. A Climbing image nudged elastic band method [24] was employed to evaluate the migration barrier for polaron hopping between two neighboring oxygen sites. We used six intermediate images between the initial and final states and relaxed the images until the net forces were less than 0.05 eV/Å. For the hole and electron polaron calculations, one electron was removed from or added to the supercell, and the difference between the number of spin-up and spin-down electrons was constrained to 1, and then optimized with the HSE06 functional. For self-trapped exciton calculations, we enforce a triplet state by fixing the difference between the number of spin-up and spin-down electrons to 2. The Δ SCF method [25] was employed to evaluate the vertical emission energies associated with the self-trapped exciton.

III. RESULTS

A. Ground-state structure

The root-mean-square error of the total energies predicted by our CE model is 4.616 meV/atom as shown in Supplemental Material Fig. S1 [26]. The CE-predicted energies align well with the DFT reference values, particularly for struc-

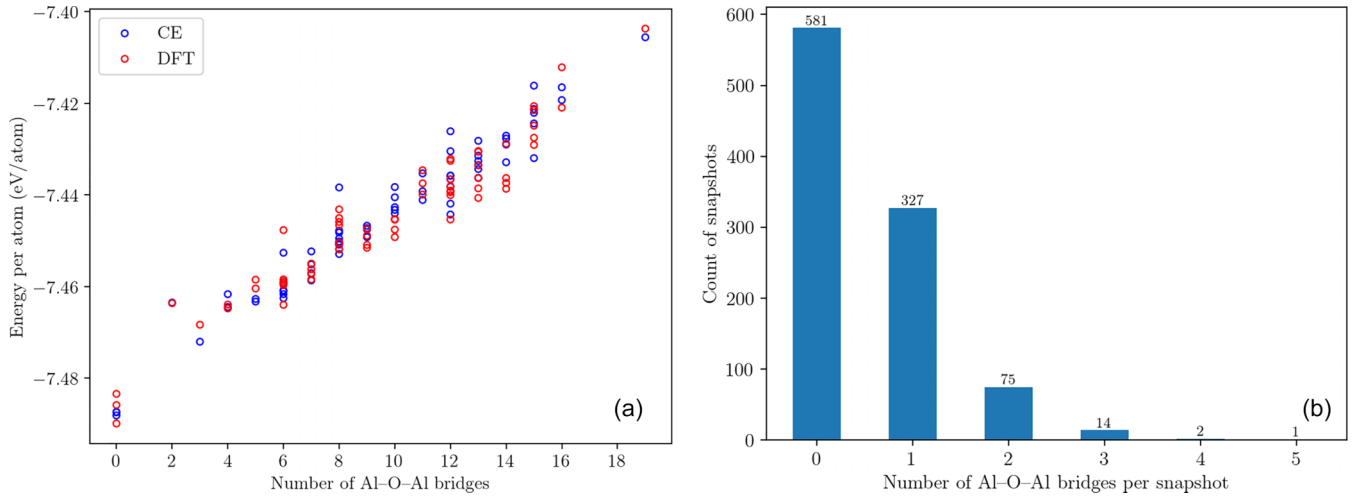


FIG. 2. Correlation between the number of Al–O–Al bonds and the total energy of K-feldspar structures evaluated by DFT using the PBE functional and trained CE model. (a) Total energies of 208-atom structures computed with DFT and CE model plotted against the number of Al–O–Al bonds in each configuration. (b) Distribution of the number of Al–O–Al bonds across 1000 configurations in K-feldspar at 1500 K obtained from Monte Carlo simulations.

tures in the low-energy region. The ground-state structure predicted by the CE model (see Fig. 1) matches the structure reported in the Materials Project [27]. Figure 2(a) shows the energy per atom of various disordered configurations (each containing 208 atoms) calculated using both DFT and the CE model as a function of the number of Al–O–Al bonds in each structure. The predicted CE energy closely follows the DFT results, confirming the accuracy of the CE model in capturing the energy-structure relationship of Al–Si disorder in K-feldspar. Moreover, the disordered configurations show a strong correlation between the total energy and the number of Al–O–Al bonds. The total energy increases with an increasing number of Al–O–Al bonds. The energy difference between structures with the same number of Al–O–Al bonds is due to variations in their local atomic arrangements. It is noted that the ground-state structure does not contain any Al–O–Al bonds. However, at high temperatures, such bonds are expected to form. To estimate their concentration at the melting temperature (1500 K), we performed Monte Carlo simulations of the annealing process in feldspar using a trained CE model. The system is annealed gradually through a temperature decreasing from 3000 to 1500 K, followed by trajectory sampling at 1500 K. A large supercell containing 2080 atoms was initialized and a canonical ensemble of 1000 configurations was generated. The total energy of the system was monitored every 100 Monte Carlo steps and was found to converge with an energy variation of approximately 1.5 eV.

The resulting distribution of Al–O–Al bonds from the sampling trajectory is shown in Fig. 2(b). The concentration of Al–O–Al bonds at 1500 K can be estimated from the ensemble-averaged number of Al–O–Al bonds in the sampled configurations $\langle f_{\text{Al-O-Al}} \rangle = \frac{1}{N_{\text{snap}}} \sum_{k=1}^{N_{\text{snap}}} \frac{N_{\text{Al-O-Al}}^{(k)}}{N_{\text{O}}}$, where N_{snap} is the number of sampled configurations, $N_{\text{Al-O-Al}}^{(k)}$ is the number of Al–O–Al bonds in the k th configuration, and N_{O} is the total number of oxygen atoms in the supercell. We find that $\langle f_{\text{Al-O-Al}} \rangle = 0.042\%$, corresponding to a concentration of $1.80 \times 10^{19}/\text{cm}^3$, which is in the same order of magnitude of

the most favorable native defects existing in feldspar crystal (see next section).

B. Intrinsic defects

Defect formation energies for native defects

The defect formation energy of a point defect is calculated as

$$E_{\text{f}}(D^q) = E(D^q) - E_{\text{perfect}} - \sum_i n_i \mu_i + q(\epsilon_{\text{VBM}} + \Delta\epsilon_{\text{F}}) + E_{\text{corr}}[D^q]. \quad (1)$$

$E(D^q)$ is the total energy of a supercell containing a defect D with charge state q . E_{perfect} is the total energy of a perfect supercell, ϵ_{VBM} is the energy of the valence band maximum (VBM), and $\Delta\epsilon_{\text{F}}$ is the Fermi level shift with respect to VBM. $E_{\text{corr}}[D^q]$ is the correction term for the finite-size supercell effect, and the extended Freysoldt-Neugebauer-Van de Walle (FNV) scheme [28] was applied here. n_i is the number of removed ($n_i < 0$) or added ($n_i > 0$) i -type atoms and μ_i is its corresponding chemical potential. The defect formation energies of all possible native defects with their charge states calculated with the PBE functional are given in Supplemental Material Table S1 [26]. The most energy favorable defects were then selected and reevaluated at the HSE06 level. The defect formation energies evaluated at the HSE06 level for K-feldspar are presented in Fig. 3. The defect formation energies are calculated under two sets of growth conditions: Al- and Si-rich, O-poor and Al- and Si-poor, O-rich. Although the formation energies are generally lower under O-poor conditions, the overall trends remain consistent between the two conditions. The most stable defect at Fermi level positions near the middle of the band gap is the silicon antisite Si_{Al} . As the Fermi level shifts toward the conduction band, the potassium vacancy V_{K} and the aluminum antisite Al_{Si} become the energetically preferred defects. The energy favorable defect concentrations calculated at thermodynamic equilibrium for

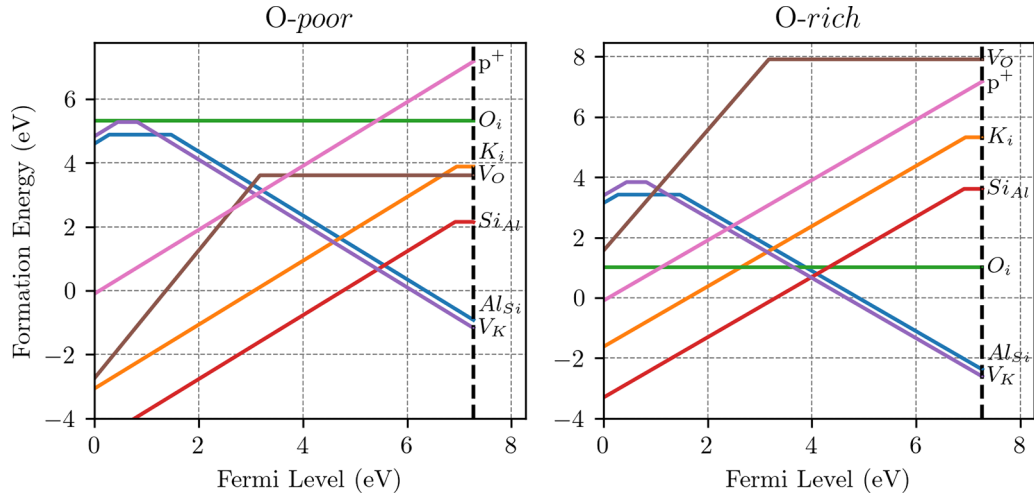


FIG. 3. Defect formation energies evaluated with the HSE06 exchange-correlation functional for K-feldspar. Two growth conditions were considered: Al- and Si-rich, O-poor on the left, and Al- and Si-poor, O-rich on the right. p^+ denotes the hole polaron.

the temperature at 1500 K are listed in Supplemental Material Table S3 [26]. We additionally calculated the defect formation energies for Na-feldspar, finding trends that closely mirror those of K-feldspar with the most stable defects being Si_{Al} , V_{Na} , and Al_{Si} . This is not a surprise since the electronic structure of two bulk crystals is very similar (see Supplemental Material Fig. S2 [26]).

C. Polaron localization

In this section, we examine the possibility of polaron formation in feldspar. The geometry optimizations initiated by adding either an electron or a hole reveal that an electron polaron cannot be stabilized, whereas a hole polaron readily localizes on bridging oxygen atoms. We identified the possible localization sites for the hole polaron and evaluated the corresponding trapping energies.

1. Preferred sites for a trapped hole

There are eight symmetry-equivalent bridging oxygens in the primitive cell, and their Ewald site energies can possibly inform *a priori* about which of the positions are most likely to stabilize a trapped hole. The Ewald energy for each equivalent O site in a unit cell is shown in Supplemental Material Table S2 [26], and indicates that a hole is unlikely to be trapped on O atoms bridging by two SiO_4 tetrahedra (Si–O–Si). This is further confirmed by performing a geometry optimization using the HSE06 functional: when a hole polaron is initialized on an Si–O–Si site, it cannot be stabilized and instead relaxes onto a neighboring Si–O–Al bridge. Consequently, four Oxygen sites (O_{Al}^1 , O_{Al}^2 , O_{Al}^3 , and O_{Al}^4) shared by one SiO_4 and one AlO_4 were considered. Here the subscript O_{Al} denotes an oxygen atom bonded to one Al and one Si atom, whereas the superscript numbers indicate the proximity ranking of these oxygen atoms to the Al atom in the conventional unit cell, with a superscript of “1” identifying the oxygen atom closest to the associated Al atom. The density difference of spin-up and spin-down electrons shown in Figs. 4(a)–4(c) suggests that the hole is localized predominantly on a single oxygen atom, with minor contributions from its neighboring O atoms.

The attempts to localize the hole on O_{Al}^1 always relaxes to O_{Al}^2 , which is consistent with the Ewald site energy of O_{Al}^1 being 0.5 eV lower than O_{Al}^2 and being the lowest among the four sites considered (see Table I).

Although the ground-state structure does not contain Al–O–Al bonds, these types of bridging oxygen are, from the electrostatic point of view (Ewald energy), the most favorable sites to trap holes. In order to verify this hypothesis, a disordered structure where Al and Si was swapped in the ground-state structure is generated to create such Al–O–Al bond. The projected density of states (PDOS) for the trapped hole on this Al–O–Al bond is shown in Fig. 5 and compared with the PDOS of the hole trapped on O_{Al}^2 in the ground-state structure. The density of states (DOS) level for the hole trapped on the Al–O–Al bridge is 1 eV deeper than that on O_{Al}^2 . This suggests that Al–O–Al bonds formed at high temperatures can act as efficient hole traps in feldspar.

2. Trapping energies of a hole polaron

The trapping energy E_{trap} of a hole polaron is calculated as the energy difference between a delocalized hole and a localized hole. A negative value of E_{trap} indicates that the localization is energetically favorable. The calculated trapping energies for the hole polaron localized on different O sites are summarized in Table I. The fact that O_{Al}^4 shows a favorable

TABLE I. Trapping energies E_{trap} (eV) for a hole trapped in oxygen sites calculated with the HSE06 functional. The Ewald energies E_{Ewald} (eV) are listed for reference.

Trapped site	E_{Ewald}	Trap depth (DOS)	E_{trap}
O_{Al}^1	−19.24	^a	^a
O_{Al}^2	−18.78	1.771	−0.240
O_{Al}^3	−18.09	1.678	−0.192
O_{Al}^4	−18.33	1.497	0.202
Al–O–Al	−15.54	2.703	−0.945

^aThe localization of a hole on O_{Al}^1 is not possible as it relaxes to a neighboring O_{Al}^2 site.

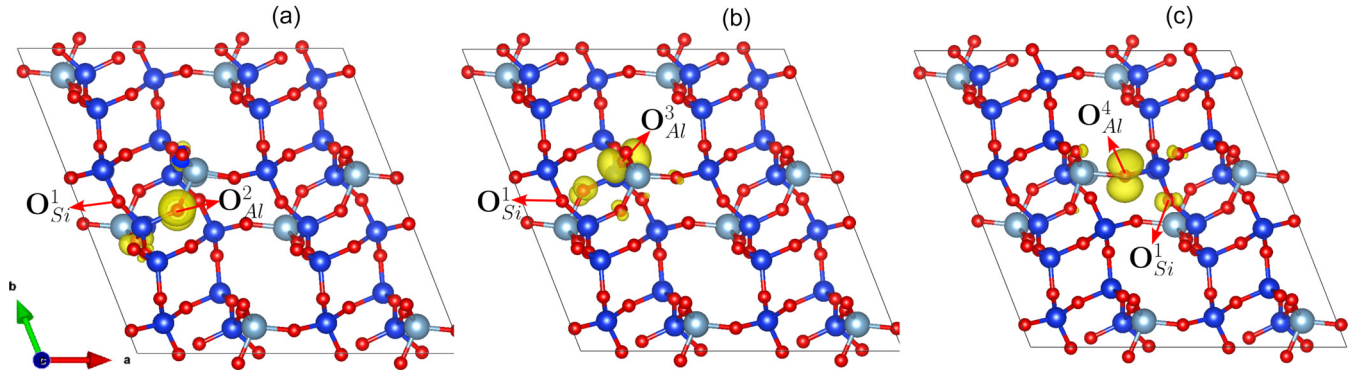


FIG. 4. The density difference between spin-up and spin-down electrons showing a hole can be localized in O_{Al}^2 (a) and in O_{Al}^3 (b) and O_{Al}^4 (c) in K-feldspar. The subscript O_{Al} denotes an oxygen atom bonded to one Al and one Si atom (Al–O–Si), whereas O_{Si} refers to an oxygen atom bonded to two Si atoms (Si–O–Si). The superscript numbers indicate the proximity ranking of these oxygen atoms to either an Al or a Si atom, with a superscript of “1” identifying the oxygen atom closest to the nearest Al or Si atom in the conventional unit cell. K atoms are not displayed for visual clarity.

Ewald energy but an unfavorable trapping energy is most likely due to the minor contributions of the neighboring O_{Si}^1 atom bridging two SiO_4 , which has the lowest Ewald energy among all O atoms, and no contributions on O_{Si}^1 are found for either O_{Al}^2 or O_{Al}^3 (see the density plot of the trapped hole in Fig. 4). O_{Al}^2 and O_{Al}^3 both show negative trapping energies, indicating that they can stably localize a hole polaron. Among all types of O bridging sites, the most favorable site for hole polaron localization is O bridging two AlO_4 (Al–O–Al) with a trapping energy of -0.945 eV. The migration barrier for the hole polaron between two neighboring O_{Al}^4 sites is 0.18 eV. This value is comparable to the trapping energies at the O_{Al}^2 and O_{Al}^3 sites, suggesting that the hole can thermally escape from O_{Al}^4 back to the valence band and subsequently become trapped at these alternative sites.

D. STE and its vertical emission energies

A self-trapped exciton is created when a trapped hole captures an electron that becomes semilocally bound via Coulomb interaction. We proceed to investigate the possible

STE configurations in feldspar based on the preferred hole localization sites identified in the previous section.

The trapping energy of a self-trapped exciton is defined as the energy difference between a delocalized electron-hole pair constrained at the ground-state geometry (corresponding to a vertical excitation) and the relaxed STE configuration, in which the excited state is allowed to relax to its preferred geometry. In an ideal description, the energy of a delocalized electron-hole excitation obtained from a Δ SCF calculation should coincide with the Kohn-Sham band gap. In practical supercell calculations, however, this condition is violated due to finite-size effects: the Δ SCF excitation energies are systematically smaller than the Kohn-Sham gap. This discrepancy originates from the artificial stabilization of the constrained delocalized excited state in finite supercells and becomes increasingly pronounced when hybrid exchange-correlation functionals are employed. As a result, this finite-size effect must be accounted for when evaluating STE trapping energies.

Following the convention in the literature [29], we define $\Delta E_{e-h}^{\text{artifact}}$ as the difference between the Δ SCF absorption energy computed with a given fraction α of exact Hartree-Fock exchange and the corresponding Kohn-Sham band gap. This

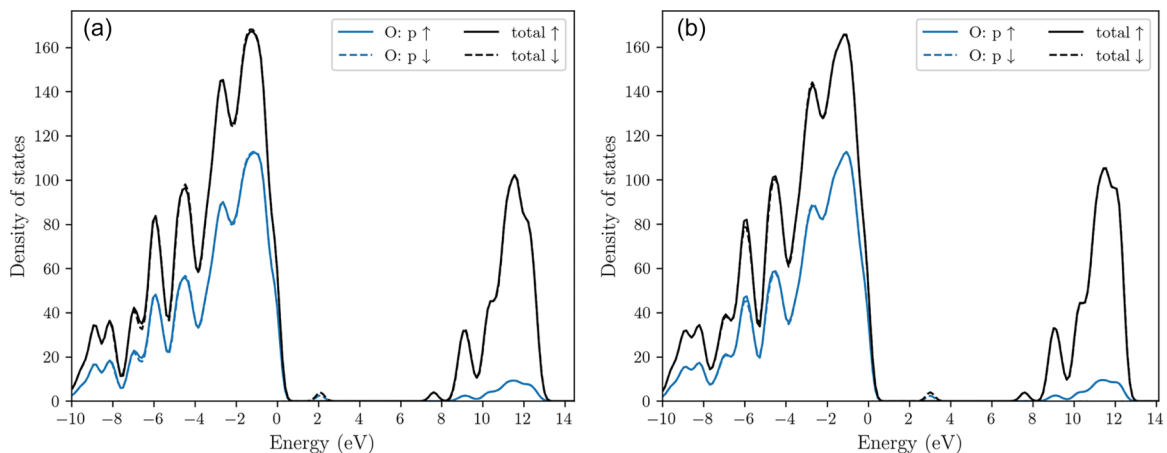


FIG. 5. PDOS for the system with the trapped hole on (a) O_{Al}^2 in the ground-state structure and on (b) O bridging two AlO_4 in the disordered structure. The geometry optimizations were performed with the HSE06 functional. See also the trap depth in DOS for all other O sites in Table I.

TABLE II. Trapping energies E_{trap} (eV) corrected for $\Delta E_{e-h}^{\text{artifact}}$ and vertical emission energies ϵ_{STE} (eV) for STEs in K-feldspar evaluated with the HSE06 functional. The experimental STE emission energy was taken from Ref. [15].

Trapped site	E_{trap}	ϵ_{STE}
O_{Al}^1	a	a
O_{Al}^2	-0.756	5.448
O_{Al}^3	-0.693	5.519
O_{Al}^4	-0.327	5.729
Expt.		5.348

^aThe localization of an STE on O_{Al}^1 is not possible as it relaxes to a neighboring O_{Al}^2 site.

quantity is negligible for semilocal functionals ($\alpha = 0$), but increases approximately linearly with α in hybrid functionals. For example, in a $3 \times 3 \times 3$ primitive supercell of LiF, $\Delta E_{e-h}^{\text{artifact}}$ reaches 2.81 eV for $\alpha=0.5$ using the PBE0 functional [29]. The magnitude of $\Delta E_{e-h}^{\text{artifact}}$ decreases systematically with increasing supercell size [29], confirming its origin as a finite-size effect. Physically, it reflects an artificial stabilization of the delocalized electron-hole state associated with the promotion of an electron from the valence band to the conduction band, whose magnitude depends on the fraction of exact exchange. Consequently, STE trapping energies computed in finite supercells are expected to be underestimated if this correction is neglected.

For the $2 \times 2 \times 2$ supercell and $\alpha = 0.385$ employed in this work, we obtain $\Delta E_{e-h}^{\text{artifact}} = 0.224$. All STE trapping energies reported here are corrected by this amount and summarized in Table II. After correction, all STE configurations exhibit negative trapping energies, indicating that they are energetically favorable and approximately 0.5 eV more stable than the isolated hole polaron reported in Table I.

The vertical emission energies associated with the STE recombination are also reported in Table II. The calculated emission energies decrease as the trapping energies increase, with the STE localized on O_{Al}^2 showing the lowest emission energy of 5.448 eV, which is in good agreement with the experimental value of 5.348 eV [15].

In addition, we calculated the STE emission energy for an STE localized on the O atom bridges two AlO_4 tetrahedra (Al–O–Al). The corresponding vertical emission energy is 4.453 eV (278 nm), which is nearly 1 eV lower than that of an STE localized on O_{Al}^2 sites. This emission may correspond to a previously unassigned ultraviolet luminescence band observed experimentally around 287 nm in K-feldspar [30].

E. Fe^{3+} luminescence mechanisms

In the experimental proposed mechanisms of Fe^{3+} luminescence in feldspar [14], Fe^{3+} may first capture either an electron or a hole to form Fe^{2+} or Fe^{4+} , respectively. In this section, we focus on the possibility of Fe^{3+} capturing a hole to form Fe^{4+} and if so, the associated trapping energy compared with that of capturing an electron to form Fe^{2+} . Here, we do not attempt to simulate the excited state of Fe^{3+} , as it requires more sophisticated methods employing multideter-

TABLE III. Trapping energies E_{trap} (eV) and trap depths in DOS (eV) for Fe^{3+} substituting an Al^{3+} site and subsequently capturing either a hole or an electron in K-feldspar, evaluated using the HSE06 functional. Here the subscript O_{Fe} denotes that the oxygen atom is bonded to the Fe atom, whereas the superscript numbers indicate the proximity ranking of these oxygen atoms to the Fe atom before the geometry optimization, with a superscript of “1” identifying the oxygen atom closest to the Fe atom.

Trapped site	Trap depth in DOS	E_{trap}
h ⁺ trapped in O atom bridging Fe^{3+}		
O_{Fe}^1	1.606	0.022
O_{Fe}^2	1.965	-0.332
O_{Fe}^3	1.854	-0.160
O_{Fe}^4	a	a
e ⁻ trapped in Fe^{3+}		
Fe^{2+}	3.737	-2.208

^athe hole is not localized on O_{Fe}^4 but relaxes to the nearest O_{Al}^2 bridging Al site.

minant wave functions, beyond DFT to accurately describe its multiplet electronic structure.

1. Formation of Fe^{3+} capturing a hole

We dope Fe^{3+} in K-feldspar by substituting one Al with Fe in a $2 \times 2 \times 2$ supercell. The system is then initialized with either an extra electron or an extra hole to simulate the formation of Fe^{2+} or Fe^{4+} , along with different spin configurations and magnetic moments. After geometry optimization, we find that Fe^{2+} can be stabilized, whereas Fe^{4+} consistently relaxes back to Fe^{3+} . This raises the question: if the extra hole does not reside on the Fe^{3+} site to form Fe^{4+} , where is it located?

The PDOS for the system initialized with Fe^{4+} is shown in Fig. 6 along with that of Fe^{3+} for comparison. It is clear in the PDOS that the extra hole is localized on a bridging oxygen atom composed of p orbitals, similar to the hole polaron discussed in previous sections, but with the peak position around 2 to 3 eV above VBM. The spin density difference plot (see Fig. 7) shows that the hole is localized on an O atom bridging Fe. This suggests that although Fe^{4+} is not stable in K-feldspar, the presence of Fe^{3+} can stabilize a hole polaron on its neighboring O site, forming an $(\text{Fe}^{3+} + \text{O}^-)$ metal-oxyl complex [31].

2. Trapping energies of Fe^{3+} capturing a hole or an electron

Table III summarizes the trapping energies for Fe^{3+} capturing either a hole or an electron. Note that finite-size corrections were necessarily applied to configurations that are not charge neutral, such as the Fe^{2+} state. The second nearest O_{Fe}^2 bridging Fe^{3+} shows a more favorable trapping energy than O_{Al}^2 in the pristine structure. The Fe^{3+} center further stabilizes the hole more strongly than the Al^{3+} , and its occupied d orbitals shift to lower energies relative to the Fe^{3+} in the absence of hole trapping in the bridging O atom, as shown in Fig. 6. E_{trap} for Fe^{3+} capturing an electron to form Fe^{2+} is -2.208 eV, making this process considerably more favorable than capturing a hole to form the exotic $(\text{Fe}^{3+} + \text{O}^-)$

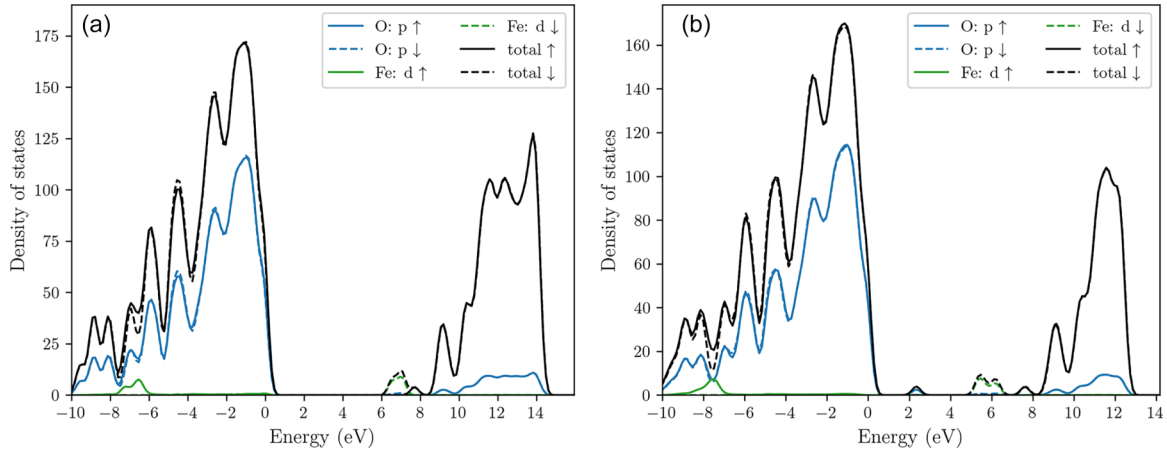


FIG. 6. PDOS for Fe doping in K-feldspar. Panel (a) shows the system with Fe^{3+} substituting an Al^{3+} site, while panel (b) corresponds to the same structure but initialized with the Fe^{4+} spin configuration. Geometry optimizations were performed using the HSE06 exchange-correlation functional.

complex with a trapping energy of -0.332 eV. Consistently, the corresponding trapping depth for Fe^{2+} is 3.737 eV, which lies much deeper in the band gap compared to the trap depth associated with a hole localized on an O site adjacent to Fe^{3+} with a value of 1.965 eV (see Table III).

The trapping energies in the above cases were evaluated for processes such as $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$, assuming that Fe^{2+} center is in its relaxed ground state. One may ask whether an e^- trapping by Fe^{3+} to form Fe^{2+} remains energetically favorable when the geometry is constrained to that of Fe^{3+} , rather than allowing full relaxation to the Fe^{2+} geometry, as illustrated in Fig. 8. In such case, the relaxation energy associated with the transition from the deformed configuration to the ground-state geometry of Fe^{2+} must also be taken into account. The relaxation energy ΔE_{relax} associated with Fe^{3+} capturing an electron and relaxing to Fe^{2+} optimized geometry is calculated to be 1.131 eV. As a result, E_{trap} for electron capture by Fe^{3+} under nonequilibrium conditions is -1.077 eV, confirming that Fe^{3+} remains a thermodynamically stable electron trap.

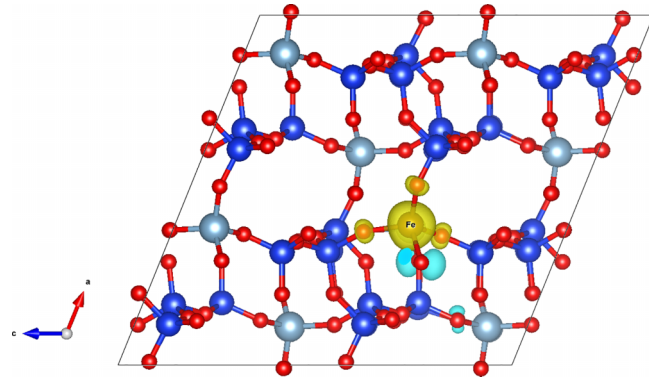


FIG. 7. Spin density difference plot for a $2 \times 2 \times 2$ supercell initialized as Fe^{4+} substituting an Al^{3+} site. The hole is localized on the oxygen atom bridging the Fe ion. Yellow and cyan represent spin-up and spin-down density difference, respectively. K atoms are not displayed for visual clarity.

3. Pathways to populate Fe^{3+} in excited state 4T_1

In summary, we hypothesized three different pathways leading to the population of Fe^{3+} excited states 4T_1 .

(i) Our calculations indicate that Fe^{3+} preferentially captures an electron from the conduction band to form Fe^{2+} . If the spin of the incoming hole is opposite to that of the trapped electron in Fe^{2+} , the system may relax back to the Fe^{3+} ground state, with the excess energy dissipated into the lattice via vibrations (phonons). In contrast, if the spin of the incoming hole is the same as that of the trapped electron in Fe^{2+} , the recombination can promote the system to the excited state 4T_1 , which subsequently relaxes radiatively to the Fe^{3+} ground state 6A_1 , giving rise to luminescence.

(ii) It is also possible for Fe^{3+} to stabilize a hole polaron on its neighboring O site, forming an $(\text{Fe}^{3+} + \text{O}^-)$ complex,

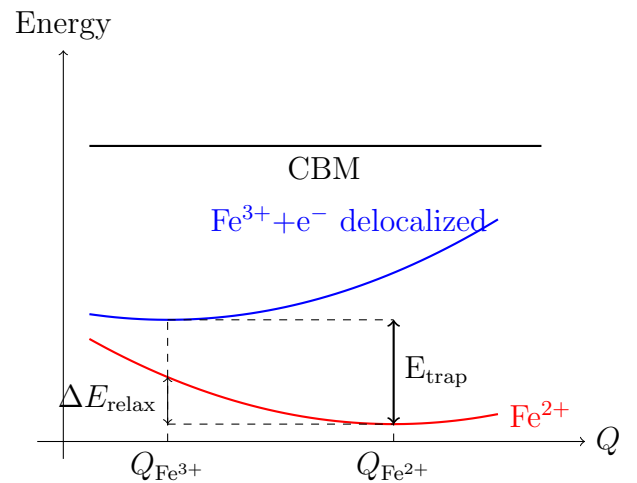


FIG. 8. Configuration-coordinate diagram illustrating electron capture by Fe^{3+} . The vertical transition at fixed lattice coordinate $Q_{\text{Fe}^{3+}}$, followed by relaxation to the equilibrium geometry $Q_{\text{Fe}^{2+}}$. This transition energy is labeled as ΔE_{relax} . The blue and red curves represent the potential energy surfaces of Fe^{3+} with an extra electron in the conduction band and Fe^{2+} , respectively.

which can then capture an electron to form a 4T_1 state, although this pathway is considerably less favorable than direct electron capture. In this case, the outcome again depends on the relative spin alignment during recombination: If the spin of incoming electron is opposite to that of the trapped hole, electron-hole annihilation leads the system return back to a 6A_1 state nonradiatively; if the spins are aligned, direct annihilation is blocked; instead, recombination promotes the Fe into a higher-energy multiplet state 4T_1 following the Hund's rule.

(iii) The third pathway involves an STE, composed of a hole polaron and a trapped electron, forming in the vicinity of Fe^{3+} . As discussed in previous sections, STEs can be stabilized on O_{Al}^x ($x=2,3,4$) in feldspar, and the ionization of an STE requires an energy of approximately 0.5 eV. We further evaluated the migration barriers for STE transfer between neighboring O_{Al}^4 sites and found a value of 0.231 eV, indicating that STEs are sufficiently mobile at high temperatures. This enables the STE to migrate toward the nearby Fe^{3+} center, where recombination can occur.

IV. CONCLUSIONS

In this work, we developed a cluster expansion model to accurately describe the Al-Si disorder in K-feldspar. We found that the total energy of disordered configurations scales linearly with the number of Al–O–Al bonds present in each structure. Using an annealing Monte Carlo search with the trained CE model, we identified the ground-state structure and estimated the concentration of Al–O–Al bonds to be at the same order of magnitude as that of the most stable point defects (Si_{Al} , V_{K} , and Al_{Si}) in K-feldspar at the melting temperature.

Regarding intrinsic luminescence in feldspar, we first identified stable oxygen sites for hole-polaron localization using the ground-state structure obtained from our CE model. Hole polarons are stabilized on oxygen atoms bridging Si–O–Al but not on Si–O–Si bridges. In the ground-state structure, the most favorable site for hole-polaron localization is the second-nearest oxygen bonded to Al(O_{Al}^2). While Ewald site energies generally predict favorable trapping sites, deviations arise from local electronic structure effects that cannot be anticipated without explicit DFT calculations. Holes that trapped at O_{Al}^2 can be thermally released with an energy of -0.240 eV. Importantly, Al–O–Al bonds formed at high temperatures are shown to be particularly efficient hole traps, with a trapping

energy of -0.945 eV. The vertical emission energy of a STE localized on O_{Al}^2 is calculated to be 5.448 eV, in good agreement with the experimental value of 5.348 eV. The emission energy calculated for an STE on Al–O–Al may correspond to a previously unassigned ultraviolet luminescence band observed experimentally around 287 nm in K-feldspar [30]. The resulting defect energetics and trapping characteristics provide a robust basis for future kinetic Monte Carlo simulations aimed at modeling charge transport and recombination dynamics in feldspar, thereby supporting the development of physics-based charge transport models that improve the reliability of luminescence dating using feldspar.

Finally, we elucidated the Fe^{3+} -related luminescence mechanism. Our results show that Fe^{3+} preferentially captures an electron to form Fe^{2+} ; subsequent recombination with a hole can populate the Fe^{3+} excited state 4T_1 responsible for the observed luminescence, provided the spin aligns with the trapped electron. In addition, the substitution of Fe^{3+} on the Al^{3+} site stabilizes a hole polaron on its neighboring O site and serves as an efficient hole trap even under lattice deformation, forming an $(\text{Fe}^{3+}+\text{O}^-)$ metal-oxyl complex. The O_{Fe}^2 site exhibits a trapping energy approximately 0.1 eV lower than that of O_{Al}^2 , indicating stronger hole stabilization near Fe site. While the $(\text{Fe}^{3+}+\text{O}^-)$ complex can also capture an electron to form 4T_1 , this pathway is considerably less favorable than direct electron capture by Fe^{3+} .

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DATA AVAILABILITY

The data that support the findings of this article are openly available [32].

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