

Article

Unraveling the Hf^{4+} Site Occupation Transition in Dy: LiNbO_3 : A Combined Experimental and Theoretical Study on the Concentration Threshold Mechanism

Shunxiang Yang ¹, Li Dai ^{1,*} , Jingchao Wang ² and Binyu Dai ³¹ School of Materials Science and Chemical Engineering, Harbin University of Science and Technology, Harbin 150080, China² No. 703 Research Institute, China State Shipbuilding Corporation Limited, Harbin 150080, China³ College of Chemistry, Beijing Normal University, Beijing 100875, China

* Correspondence: daili198108@126.com

Featured Application

This work provides a defect-engineering strategy for optimizing Dy-doped LiNbO_3 crystals via Hf^{4+} doping, enabling potential applications in two key areas: (1) visible-light-emitting devices (e.g., white-light LEDs or visible lasers), where Hf-tuned Dy^{3+} f - f transitions enhance luminescent efficiency; and (2) high-performance holographic storage media, as Hf-induced defect suppression improves optical homogeneity and photorefractive stability—critical for reliable data recording and retrieval.

Abstract

Precise control over defect structures is essential for tuning the functional properties of lithium niobate (LiNbO_3) crystals. Although the threshold effect of Hf^{4+} doping is well recognized, its underlying atomic-scale mechanism, especially in systems co-doped with luminescent rare earth ions, remains unclear. In this study, we combine experimental and theoretical approaches to elucidate the Hf^{4+} concentration-driven threshold behavior in Dy: LiNbO_3 crystals. A series of crystals with Hf^{4+} concentrations of 2, 4, 6, and 8 mol% were grown using the Czochralski method. Characterization through XRD and IR spectroscopy identified a threshold near 4 mol%, evidenced by an inflection in lattice constants and a pronounced blue shift of the OH^- absorption peak. UV–Vis–NIR absorption spectra revealed a systematic enhancement of Dy^{3+} f - f transition intensities, linking the global defect structure to the local crystal field of the optical activator. First-principles calculations showed that Hf^{4+} ions preferentially occupy Li sites, repairing antisite Nb defects ($\text{Nb}_{\text{Li}}^{4+}$) below the threshold, and incorporate into Nb sites beyond it, inducing structural reorganization. Electron Localization Function analysis visualized strengthened Hf–O covalent bonding in the post-threshold regime. This work establishes a complete atomic-scale picture connecting dopant site preference, chemical bonding, and macroscopic properties, providing a foundational framework for the rational design of advanced LiNbO_3 -based materials.



Academic Editor: Roberto Zivieri

Received: 24 November 2025

Revised: 13 December 2025

Accepted: 19 December 2025

Published: 23 December 2025

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Keywords: Hf: Dy: LiNbO_3 crystal; rare earth elements; defect structure; doping ions; first-principles calculations

1. Introduction

Lithium niobate (LiNbO_3 , LN) is a key ferroelectric material that continues to attract significant attention due to its outstanding electro-optic, nonlinear optical, and piezoelectric

properties [1,2], making it ideal for applications such as optical modulators, quantum circuits, and frequency converters [3–5]. Its ability to host a wide range of dopant ions further enhances its versatility [6,7], enabling customized materials for uses from holographic data storage to solid-state lasers [8,9].

Congruent LiNbO₃ (CLN, [Li]/[Nb] $\approx$ 0.946) is characterized by non-stoichiometry, leading to intrinsic defects such as lithium vacancies (V_{Li}^-) and antisite niobium (Nb_{Li}^{4+}), where Nb^{5+} occupies Li^+ sites [10,11]. While these defects facilitate doping, they also act as charge traps and scattering centers, often degrading performance by reducing optical damage resistance and impairing homogeneity [12,13]. Therefore, a major focus in LN research has been the strategic control of its defect structure to mitigate these drawbacks while enhancing desired functions. Two main strategies have been employed: doping with damage-resistant ions like Mg^{2+} , Zn^{2+} , In^{3+} , and Hf^{4+} [14–16], which at high concentrations replace Nb_{Li}^{4+} and repair defects, significantly improving photorefractive resistance, and increasing the [Li]/[Nb] ratio in the melt to reduce intrinsic defects and improve optical quality [17–21].

Rare earth (RE) doping of LiNbO₃ has also been widely studied to introduce laser and luminescent functions. Trivalent dysprosium (Dy^{3+}) is especially promising due to its strong yellow and blue emissions, useful for white-light-emitting diodes and visible lasers [22–24]. Dy^{3+} also exhibits long-lived intermediate energy levels suitable for up-conversion luminescence. Our previous work on Hf: Dy: LiNbO₃ showed that increasing the [Li]/[Nb] ratio enhances up-conversion efficiency [25], underscoring the importance of defect structure on Dy^{3+} performance. Hf^{4+} serves as an excellent co-dopant, outperforming Nb^{5+} in enhancing damage resistance and stability. Its larger ionic radius compared to Nb^{5+} improves lattice compatibility, while its lower charge and electronegativity minimize charge compensation needs and strengthen ionic bonding, leading to superior thermal and structural stability [6,7,26]. Although a concentration threshold for Hf^{4+} in LN systems is known [27,28], its impact on Dy^{3+} luminescence and the microscopic mechanism of Hf^{4+} incorporation—particularly its site preference and defect evolution across the threshold—remain inadequately explored in the Dy: LiNbO₃ system [25]. Key questions persist regarding how the Hf^{4+} threshold influences the local crystal field around Dy^{4+} and the atomistic nature of the defect transition.

To address these questions, we conducted a comprehensive study combining crystal growth, spectroscopic characterization, and first-principles calculations. We grew a series of Dy: LiNbO₃ crystals with Hf^{4+} concentrations of 2, 4, 6, and 8 mol% and used Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), X-ray diffraction (XRD), Fourier Transform Infrared (FT-IR) spectroscopy, and ultraviolet–visible–near-infrared (UV–Vis–NIR) absorption spectra to track structural, chemical, and optical changes. Building on our recent computational approach for Zn: Fe: Cu: LiNbO₃ [29], we constructed supercell models to calculate geometrically optimized total energies and electronic structures for different Hf^{4+} occupation scenarios. This combined methodology allows us to establish causation rather than mere correlation. Our findings not only confirm the Hf^{4+} threshold but also quantitatively connect macroscopic properties to a microscopic transition in Hf^{4+} site occupation—from defect repair at low concentrations to lattice modification at high concentrations. This work provides an atomistic explanation for the Hf^{4+} threshold effect in Dy: LiNbO₃, offering valuable insights for designing advanced LN-based photonic materials.

2. Experimental and Computational Methods

2.1. Crystal Growth and Preparation

Single crystals of Hf^{4+} -co-doped Dy: LiNbO₃ with nominal HfO₂ concentrations of 2, 4, 6, and 8 mol% (labeled Hf-2, Hf-4, Hf-6, and Hf-8) were grown along the ferroelectric

c-axis using the Czochralski method. The Dy^{3+} concentration was fixed at 1 mol% for all samples. High-purity (99.99%) Li_2CO_3 , Nb_2O_5 , HfO_2 , and Dy_2O_3 powders were weighed according to the congruent composition ($[\text{Li}]/[\text{Nb}] = 48.3/51.7$) and desired doping levels, then thoroughly ground and mixed. The mixtures were sintered at 750°C for 3 h and then at 1150°C for another 3 h in air to form polycrystalline LiNbO_3 . The resulting powders were melted in a platinum crucible in a single-crystal furnace (see the schematic setup in Figure 1). Growth parameters—temperature gradient, pulling rate, and rotation rate—were carefully optimized for each composition to ensure high optical quality and minimize defects. After growth, crystals were cooled slowly to room temperature at $50^\circ\text{C}/\text{h}$ to relieve thermal stress. They were then poled under direct current near the Curie temperature to form a single ferroelectric domain. Finally, wafers were cut from the central, homogeneous part of the boules and polished to optical grade on both sides for characterization. The resulting wafers were fully transparent and exhibited uniform coloration, indicating good optical homogeneity of the grown crystals. The growth parameters were carefully optimized for each Hf concentration. The optimization aimed to maintain a stable solid–liquid interface and avoid constitutional supercooling, thereby ensuring high optical quality and minimizing macroscopic defects. Across the studied concentration range, no significant instabilities such as pronounced defect clustering, interface breakdown, or melt stoichiometry shifts were observed. The final parameters were selected to yield fully transparent, optically homogeneous crystals with uniform coloration for all samples.

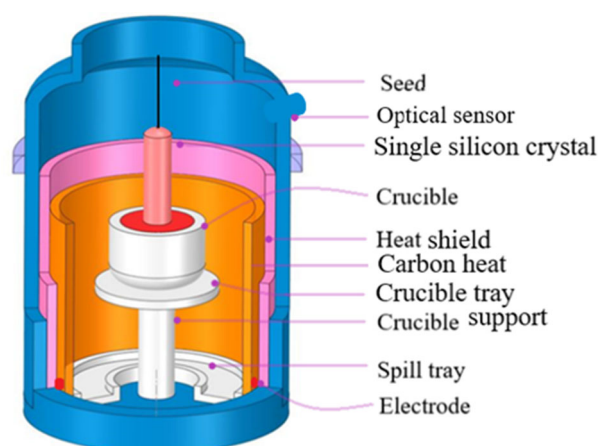


Figure 1. Schematic of the crystal growth setup.

2.2. Characterization Techniques

The actual concentrations of Hf and Dy ions in the as-grown crystals were determined by ICP-AES using an Optima 5300DV (Leeman, Sturtevant, WI, USA) instrument (estimated error $< 6\%$, controlled by standard solution calibration and repeated measurements). The effective distribution coefficient (K_{eff}), defined as the ratio of the ion concentration in the crystal (C_s) to that in the melt (C_l), was calculated to evaluate doping efficiency. The crystal structure and phase purity were characterized by XRD at room temperature using a Shimadzu XRD-6000 diffractometer (estimated error $\pm 0.04^\circ$, Shimadzu Corporation, Tokyo, Japan). Dopant-induced lattice distortions were assessed through systematic Rietveld refinement of XRD data. The meticulous refinement procedure ensured reliable extraction of the lattice constants. Critically, the systematic evolution of these parameters with Hf^{4+} concentration was unambiguous, as the changes observed were consistently greater than the precision of the measurement technique itself. The chemical bonding environment, particularly the configuration of OH^- groups which is highly sensitive to the local defect structure, was probed by FT-IR spectroscopy. Transmission spectra were

recorded in the wavenumber range of 400–4000 cm^{-1} using an Avatar-360 FT-IR Spectrometer (Niconet, Madison, WI, USA) with a resolution of 4 cm^{-1} . The wavenumber calibration was performed using standard samples with known OH^- absorption peaks. The observed blue shift of the OH^- peak is well above the instrumental resolution. To investigate the electronic transitions and the local environment of the Dy^{3+} ions, UV–Vis–NIR absorption spectra were measured at room temperature using a Varian Cary 5000 spectrophotometer (Agilent Technologies, Inc., Santa Clara, CA, USA) over the spectral range of 300–3000 nm. This professional spectral data processing method was employed to ensure that the information of Dy^{3+} absorption peaks extracted from the raw data is accurate and reliable. The systematic enhancement in the integrated intensity of Dy^{3+} f-f transition peaks across samples was reproducible and exceeded the measurement fluctuations.

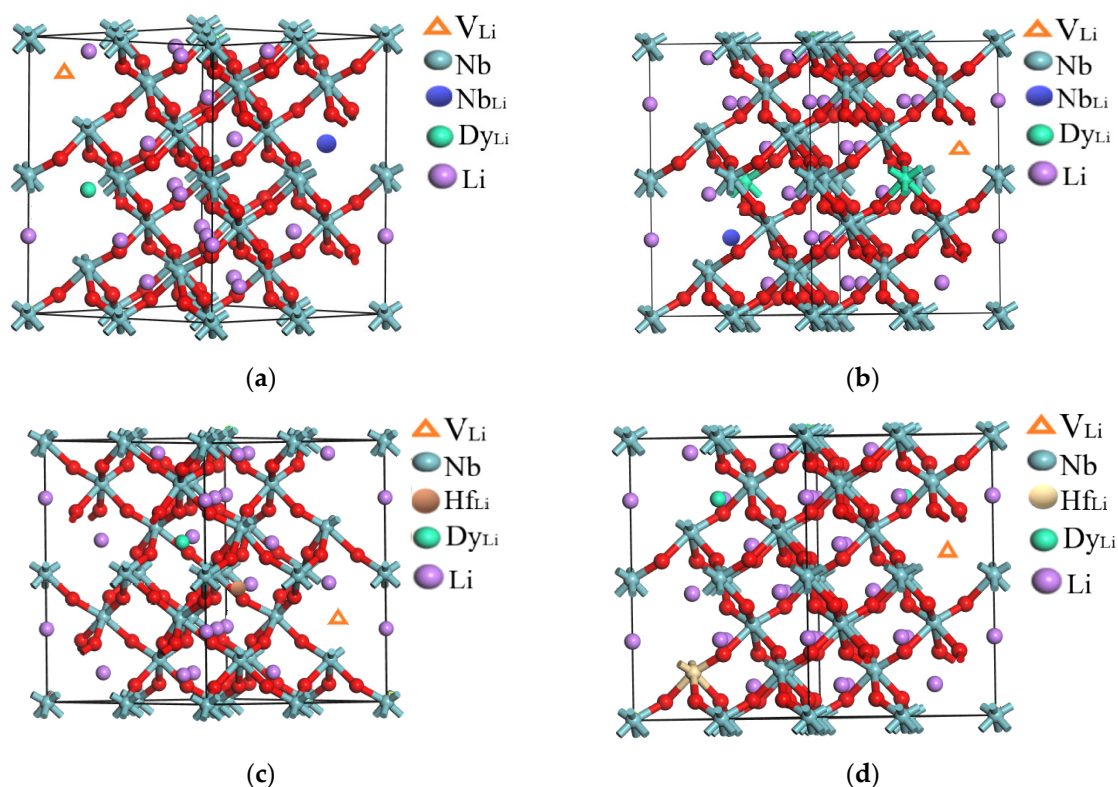
2.3. Computational Details and Model Construction

First-principles calculations based on density functional theory (DFT) were performed using the CASTEP module within the Materials Studio software package [30]. The computational parameters were consistent with our previously established and validated methodology for doped LiNbO_3 systems [31]. The exchange correlation functional was treated within the generalized gradient approximation (GGA) using the Perdew–Wang 1991 (PW91) formulation [32]. The choice of the GGA-PW91 functional is based on its successful application in our previous studies on doped LiNbO_3 systems [31] and its proven capability in describing geometric and electronic structure trends in such materials. To better describe the strongly localized 4f electrons of Dy^{3+} , a DFT+U correction with a Hubbard U parameter of 6.0 eV was applied to the Dy 4f orbitals. For Hf 5d states, which are more delocalized, no additional +U correction was applied, consistent with standard practice. While hybrid functionals or DFT+U could provide more accurate absolute band gap values for systems with localized 4f/5d states, the primary goal of this study is the qualitative comparison of relative stability, site preference, and electronic structure trends across different defect models. Test calculations confirmed that the key conclusion regarding Hf^{4+} site preference remains unchanged when using alternative functionals like PBE. The interactions between ionic cores and valence electrons were described by ultrasoft pseudopotentials [22,33,34]. A plane-wave basis set with a kinetic energy cutoff of 380 eV was employed. The Brillouin zone integration was sampled using a $3 \times 3 \times 1$ Monkhorst–Pack k-point mesh for the $2 \times 2 \times 1$ supercell. Convergence tests were performed with respect to the plane-wave cutoff energy and k-point sampling. The $2 \times 2 \times 1$ supercell (120 atoms) is a commonly adopted size in such studies and is sufficient for qualitatively discussing the site preference of single point defects. Geometry optimizations were conducted until the total energy, maximum force, maximum stress, and maximum displacement converged to thresholds of 1.0×10^{-6} eV/atom, 0.05 eV/Å, 0.1 GPa, and 1.0×10^{-3} Å, respectively.

A $2 \times 2 \times 1$ supercell of LiNbO_3 , containing 120 atoms, was constructed from the experimental trigonal structure (space group R3c) to model the doping configurations. While this supercell size corresponds to a specific doping concentration for a single substitution, the primary goal of our DFT calculations is not to quantitatively match the experimental threshold concentration, but to qualitatively unravel the underlying microscopic mechanism, specifically the site preference of dopant ions. To achieve this, a series of distinct defect models were constructed, each representing a plausible atomic-scale scenario during the doping process. The comparative analysis of their thermodynamic stability and electronic properties allows us to decipher the physical origin of the macroscopic threshold effect observed in experiments. Four distinct defect models were constructed (see Table 1 and their schematic structures in Figure 2):

Table 1. First-principles computational models used in this study.

Model	Samples	Model Structure
Model 1	Dy _{Li} : LiNbO ₃	Dy _{Li} ²⁺ -Nb _{Li} ⁴⁺ -6V _{Li} ⁻
Model 2	Dy _{Nb} : LiNbO ₃	Dy _{Nb} ²⁺ -Nb _{Li} ⁴⁺ -2V _{Li} ⁻
Model 3	Hf _{Li} : Dy _{Li} : LiNbO ₃	Hf _{Li} ³⁺ -Dy _{Li} ²⁺ -5V _{Li} ⁻
Model 4	Hf _{Nb} : Dy _{Li} : LiNbO ₃	Hf _{Nb} ²⁺ -Dy _{Li} ²⁺

**Figure 2.** Caption for computational models: (a) Model 1; (b) Model 2; (c) Model 3; (d) Model 4.

For each model, atomic positions and lattice vectors were fully relaxed. Geometrically optimized total energies were calculated to assess thermodynamic stability. Electronic structures (band structure, density of states) and the Electron Localization Function (ELF) were analyzed to interpret optical spectra and chemical bonding.

3. Results

3.1. Compositional Analysis

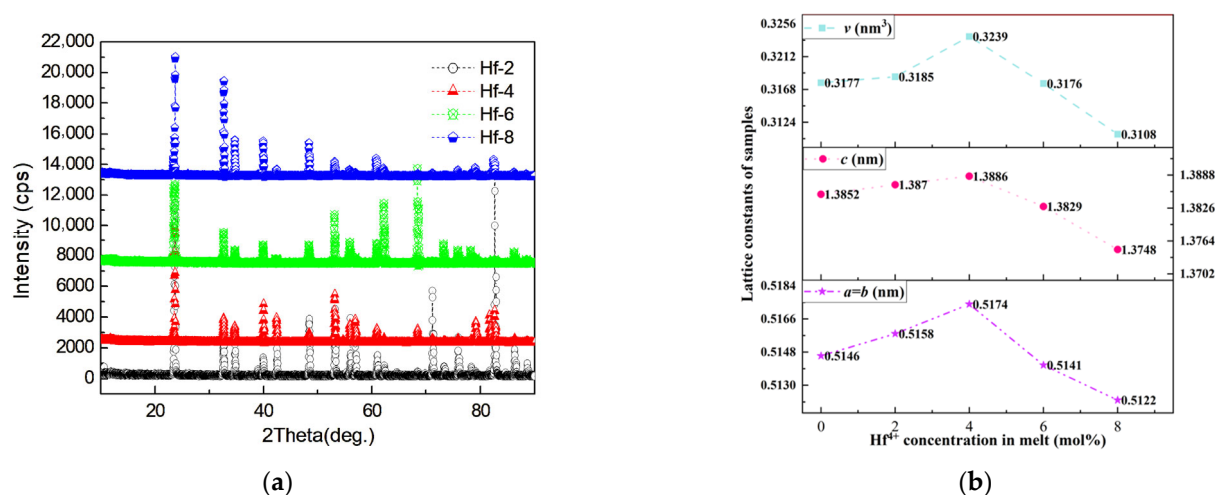
ICP-AES results for actual Hf⁴⁺ and Dy³⁺ concentrations are summarized in Table 2. Both dopants were successfully incorporated into the lattice. The effective distribution coefficient (K_{eff}) for both ions decreased monotonically with increasing Hf⁴⁺ concentration: the K_{eff} of Hf⁴⁺ decreases from 0.83 to 0.71, while that of Dy³⁺ decreases from 0.86 to 0.69. This concurrent decrease suggests non-ideal segregation behavior and indicates mutual interaction or competition between Hf⁴⁺ and Dy³⁺ during growth, likely due to their differing ionic radii and charges competing for limited lattice sites.

Table 2. Actual concentrations and effective distribution coefficients of Hf^{4+} and Dy^{3+} in grown crystals.

Samples	Hf^{4+} in Crystal	K_{eff} of Hf^{4+}	K_{eff} of Dy^{3+}
Hf-2	1.66	0.83	0.86
Hf-4	3.20	0.80	0.79
Hf-6	4.50	0.75	0.76
Hf-8	5.68	0.71	0.69

3.2. Structural Evolution and Threshold

Figure 3 presents the X-ray diffraction (XRD) patterns and the evolution of lattice parameters of Hf: Dy: LiNbO_3 crystals as a function of Hf^{4+} concentration. It can be seen from the XRD patterns that the diffraction peak positions of all Hf-doped samples are basically consistent with those of Dy: LiNbO_3 crystals without Hf doping, and no new impurity phase diffraction peaks appear. This indicates that the incorporation of Hf^{4+} does not change the crystal structure of LiNbO_3 , and the crystals still maintain a single-phase perovskite structure, with Hf^{4+} successfully solid-solved into the lattice. The diffraction peak intensities of samples with different Hf concentrations are different, which may be related to lattice distortion, change in grain orientation, or variation in crystallinity caused by Hf doping.

**Figure 3.** Structural characterization of Hf: Dy: LiNbO_3 crystals: (a) X-ray diffraction (XRD) patterns, and (b) evolution of lattice parameters with Hf^{4+} concentration.

Regarding the evolution of lattice parameters, as the Hf^{4+} concentration increases from 0 to 8 mol%, the lattice parameters, and unit cell volume show a trend of slight increase first and then decrease. When Hf^{4+} is incorporated into the lattice, it will replace Li sites or Nb sites, thereby causing lattice distortion. At low Hf doping concentrations, the lattice undergoes adaptive adjustment due to the stress generated by ion substitution, leading to a slight increase in lattice parameters; as the Hf concentration further increases, the lattice may undergo structural relaxation or adjustment of the distribution of doped ions, causing the lattice parameters to gradually decrease, which reflects the structural stability regulation mechanism of the crystal under high doping concentrations. In summary, based on the structural information provided by Rietveld refinement and the characteristic that the XRD peaks of all samples remain sharp without broadening, we believe that the observed non-monotonic evolution of lattice parameters is mainly due to the lattice strain and relaxation processes caused by changes in Hf^{4+} occupancy, rather than secondary factors such as macroscopic phase separation or defect clusters.

3.3. OH[−] Vibrational Spectroscopy

FT-IR spectroscopy provides a sensitive probe for local defect environments, particularly through the stretching vibrations of OH[−] groups. As shown in Figure 4, the OH[−] absorption peak in our crystals undergoes a systematic blue shift from approximately 3486 cm^{−1} (Hf-2) to 3498 cm^{−1} (Hf-8). For direct comparison, we measured a reference Dy: LiNbO₃ crystal (1 mol% Dy, without Hf doping), which exhibited its OH[−] absorption peak at 3483 cm^{−1} [35]. This value is characteristic of congruent LiNbO₃ and is assigned to the Nb_{Li}⁴⁺-OH_{Li}[−] defect complex. The minor shift to 3486 cm^{−1} in Hf-2 suggests that low-level Hf⁴⁺ doping has not drastically altered this primary defect environment. However, the significant and continuous blue shift at higher concentrations (Hf-4 to Hf-8) signifies a fundamental change. A higher wavenumber corresponds to a stronger O-H bond, typically resulting from the OH group being in a stronger local electric field. This is consistent with the formation of Hf_{Nb}[−]-OH_{Li}[−] complexes, where the negatively charged Hf_{Nb}[−] defect exerts a stronger attraction on the proton (H⁺) than the Nb_{Li}⁴⁺ defect does. The fact that the most pronounced shift occurs precisely around and above the 4 mol% concentration further corroborates the XRD findings, confirming that the threshold corresponds to the point where Hf⁴⁺ begins to incorporate into Nb sites in significant quantities.

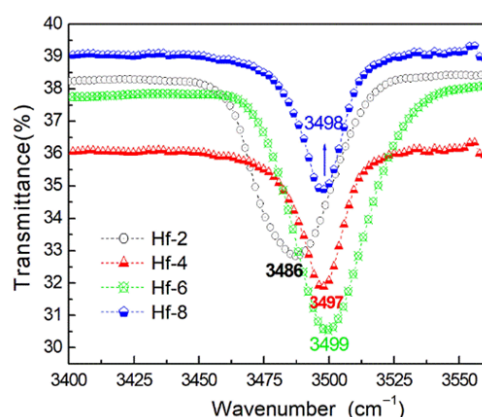


Figure 4. FT-IR spectra showing the blue shift of the OH[−] absorption peak.

3.4. Evolution of Defect Structures with Hf⁴⁺ Concentration

The synergistic analysis of compositional, structural, and vibrational data enables a coherent reconstruction of the defect structure evolution across the Hf⁴⁺ concentration series. This progression delineates a clear transition from a defect-compensating regime to one of lattice restructuring, centered around the identified threshold.

In the reference Dy: LiNbO₃ crystal (without Hf), the defect structure is dominated by the intrinsic Nb_{Li}⁴⁺-V_{Li}[−] clusters, as evidenced by the OH[−] peak at 3483 cm^{−1}. In crystals with lower Hf⁴⁺ content (Hf-2, 1.66 mol%), the doping architecture is primarily governed by the compensation of these intrinsic defects. The Hf⁴⁺ ions, driven by thermodynamic preference as confirmed by first-principles calculations, preferentially occupy the antisite niobium positions Nb_{Li}⁴⁺, effectively acting as defect repair agents. This incorporation forms Hf_{Li}³⁺ defect centers while leaving a significant population of the original Nb_{Li}⁴⁺-OH_{Li}[−]-V_{Li}[−] clusters largely intact. This is evidenced by the minimal deviation of the OH[−] absorption peak position (3486 cm^{−1}) from that of the reference crystal. The concomitant initial increase in lattice constants suggests that the incorporation of Hf⁴⁺ into these defect sites introduces a subtle lattice strain without yet triggering a major structural reorganization. As the nominal concentration approaches and surpasses 4 mol% in the melt (corresponding to an actual concentration of 3.20 mol% in the Hf-4 crystal), a fundamental shift in the doping mechanism occurs. The saturation of the preferred Nb_{Li}⁴⁺ sites forces Hf⁴⁺ ions

to incorporate into regular lattice sites. This marks the onset of the threshold behavior, characterized by the formation of self-compensated defect pairs such as $\text{Hf}_{\text{Li}}^{3+}\text{-Hf}_{\text{Nb}}^{-}$. The definitive signature of this transition is the pronounced blue shift of the OH^{-} absorption peak to approximately 3498 cm^{-1} , which signifies the dissolution of the original defect clusters and their replacement by new complexes where H^{+} is more strongly attracted to the negatively charged $\text{Hf}_{\text{Nb}}^{-}$ centers. The lattice parameters at this stage reach their maximum, reflecting the cumulative strain from Hf^{4+} incorporation in multiple sites. At supra-threshold concentrations (Hf-6 and Hf-8), the self-compensation mechanism becomes dominant. A greater proportion of Hf ions occupy both Li and Nb sites, leading to a more ordered and densely packed lattice structure. This increased structural coherence is directly observable in the sharpening of XRD peaks. The reversal in the trend of lattice constants, a contraction in both the a -axis and c -axis, signals the relief of initial strain and the establishment of a new, more stable structural equilibrium under the influence of extensive Hf^{4+} doping. The continuous decrease in the effective segregation coefficients for both Hf^{4+} and Dy^{3+} further underscores the increasing energetic cost and lattice-site competition at these elevated concentrations.

In summary, the defect architecture evolves from the baseline of the Dy: LiNbO_3 reference crystal, through a low-concentration regime dominated by the elimination of intrinsic antisite defects, across a critical threshold where site saturation prompts occupation of regular lattice sites, to a high-concentration regime characterized by widespread self-compensation and a consequent lattice contraction. This detailed pathway from defect repair to lattice restructuring provides a microstructural foundation for the observed macroscopic properties, firmly linking the Hf^{4+} concentration to the engineered crystal lattice.

3.5. Optical Absorption Properties

UV–Vis–NIR absorption spectra (Figure 5) reveal electronic transitions and the local environment of Dy^{3+} ions. The absorption coefficients for all characteristic Dy^{3+} f - f transitions (e.g., ${}^6\text{H}_{15/2} \rightarrow {}^6\text{F}_{9/2}$, ${}^6\text{H}_{13/2}$) increase systematically with Hf^{4+} concentration. Since the Dy^{3+} concentration is fixed, this enhancement must arise from increased oscillator strength, implying reduced local symmetry and higher covalency of Dy–O bonds due to Hf^{4+} -induced changes in the crystal field. In the UV region, the absorption edge of Hf-2 is at the longest wavelength, indicating the narrowest effective band gap. With increasing Hf^{4+} , the edge blue shifts, signaling band gap widening as Hf^{4+} eliminates defect-induced band-tail states. The Hf-2 sample, with the most residual $\text{Nb}_{\text{Li}}^{4+}$ defects, has the most band-tail states; Hf^{4+} incorporation cleans the band gap, leading to the observed blue shift.

Judd–Ofelt Analysis

To quantitatively assess the impact of Hf^{4+} doping on the local crystal field around Dy^{3+} ions, the Judd–Ofelt (J–O) intensity parameters (Ω_2 , Ω_4 , Ω_6) were derived from the absorption spectra and are listed in Table 3. The Ω_2 parameter, which is sensitive to local symmetry and covalency of the Dy–O bond, increases significantly with Hf^{4+} concentration up to Hf-6, then slightly decreases for Hf-8. This trend correlates with the Hf^{4+} site occupation transition and provides quantitative evidence for the modification of the Dy^{3+} local environment. The decreasing Ω_4/Ω_6 ratio further indicates changes in the crystal field symmetry. These J–O parameters substantiate the link between defect engineering via Hf^{4+} doping and the modulation of Dy^{3+} luminescence properties.

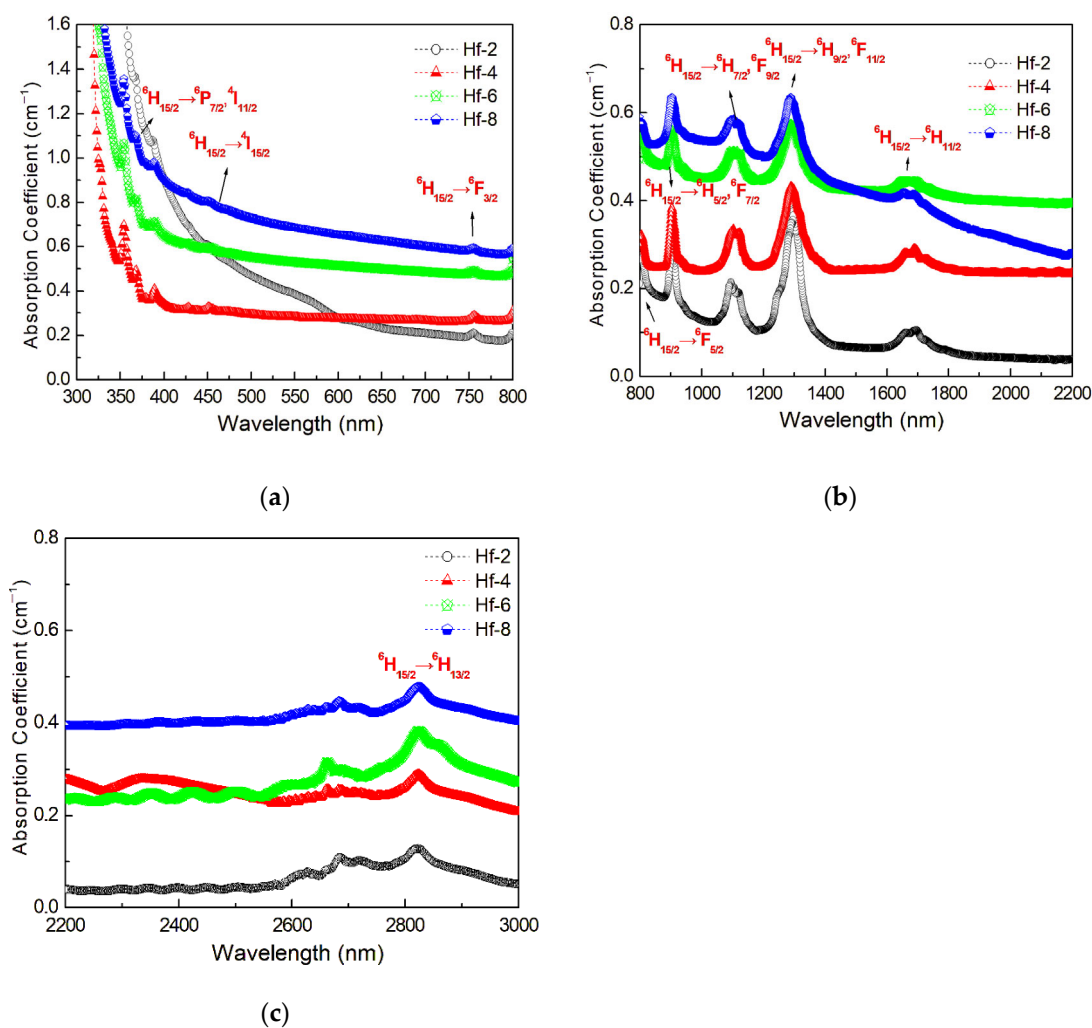


Figure 5. UV-Vis-NIR absorption spectra Hf: Dy: LiNbO₃: (a) UV-Vis region; (b) NIR region; (c) Mid-IR region.

Table 3. Judd–Ofelt intensity parameters (10^{-20} cm^2) of Hf: Dy: LiNbO₃ crystals.

Sample	Ω_2	Ω_4	Ω_6	$\chi (\Omega_4/\Omega_6)$
Hf-2	11.2461	4.5345	9.3785	0.4835
Hf-4	14.3257	4.8321	11.3426	0.4260
Hf-6	18.9328	5.9032	15.9842	0.3693
Hf-8	16.0324	4.3463	13.7327	0.3165

3.6. First-Principles Calculations

To establish an atomistic understanding of the threshold mechanism, we turn to first-principles calculations. The analysis of geometrically optimized total energies provides the thermodynamic driving force, while the electronic band structures and density of states reveal the consequent changes in the electronic structure that underpin the experimental optical phenomena.

3.6.1. Site Preference Energetics

To quantitatively compare the site preference of Hf⁴⁺ and Dy³⁺ ions, we calculated the total energy (after geometry optimization) for the four key models and compared them with the perfect LiNbO₃ supercell of equivalent size (120 atoms), with the results summarized in Table 4. A lower total energy indicates a more thermodynamically stable

configuration. Model 3 (Hf occupying Li site, Hf_{Li}) exhibits a significantly lower total energy than Model 4 (Hf occupying Nb site, Hf_{Nb}). This computationally confirms that Hf^{4+} has a strong thermodynamic preference for occupying Li sites over Nb sites. This fundamental preference rationalizes that Hf^{4+} ions naturally incorporate into the readily available Li sites (including the intrinsic defect $\text{Nb}_{\text{Li}}^{4+}$ sites), thereby eliminating the primary intrinsic defects. Meanwhile, the lower total energy of Model 1 (Dy occupying Li site, Dy_{Li}) compared to Model 2 (Dy occupying Nb site, Dy_{Nb}) confirms that Dy^{3+} itself preferentially occupies Li sites, establishing Models 3 and 4 as the relevant comparison for Hf^{4+} site preference. The relatively high total energy of Model 4 signifies that occupation of Nb sites is energetically costly and only occurs once the preferred Li sites are saturated.

Table 4. Geometrically optimized total energies of defect models and perfect LiNbO_3 .

Model	Description	E (eV)
Model 1	$\text{Dy}_{\text{Li}} + \text{Nb}_{\text{Li}}^{4+}$	−77,430.5
Model 2	$\text{Dy}_{\text{Nb}} + \text{Nb}_{\text{Li}}^{4+}$	−76,899.5
Model 3	$\text{Dy}_{\text{Li}} + \text{Hf}_{\text{Li}}$	−76,484.2
Model 4	$\text{Dy}_{\text{Li}} + \text{Hf}_{\text{Nb}}$	−75,694.0
Pure LiNbO_3	-	−73,461.4

3.6.2. Electronic Band Structures

The calculated band structures, presented in Figure 6, provide direct insight into the evolution of the electronic landscape with doping. Model 1, representing the baseline with intrinsic defects, exhibits a band gap of approximately 2.965 eV. Both its valence band maximum (VBM) and conduction band minimum (CBM) show relatively flat dispersion, indicative of large effective masses for both holes and electrons. This suggests low intrinsic carrier mobility, which is characteristic of the pristine, defect-containing lattice.

A dramatic change is observed in Model 3, where the band gap narrows significantly to 2.302 eV. This contraction arises primarily from a downshift of the CBM, which is consistent with the introduction of new electronic states from the Hf 5*d* orbitals, as seen in the PDOS. The reduced band gap directly correlates with the red shift of the absorption edge observed experimentally in low-Hf-concentration samples, indicating a reduced energy threshold for electronic transitions. For Model 4, where Hf^{4+} occupies a Nb site, the band gap is calculated to be 2.449 eV, an intermediate value between Models 1 and 3. This highlights the critical role of the dopant's crystallographic site in fine-tuning the electronic structure. It is important to note that while DFT calculations with GGA functionals are known to systematically underestimate the absolute band gap values, the relative trends in band gap evolution across different models are reliable and physically meaningful, which is the primary focus of our computational analysis. The different coordination environment of the Nb site leads to altered Hf 5*d*–O 2*p* hybridization, resulting in a less pronounced perturbation of the conduction band compared to Hf occupation of the Li site.

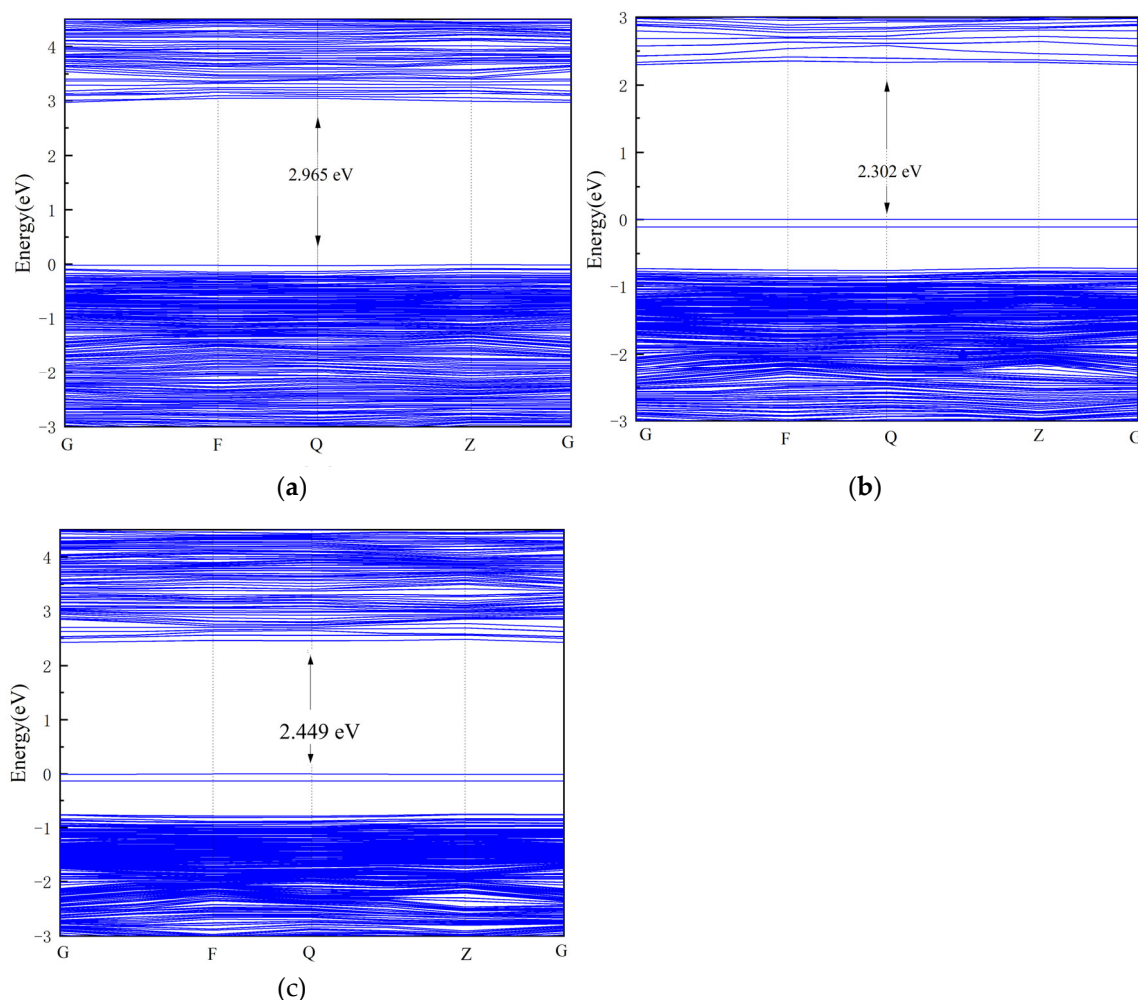


Figure 6. Band structures for (a) Model 1, (b) Model 3, and (c) Model 4.

3.6.3. Orbital and Bonding Analysis

The Partial Density of States (PDOS), which projects the total density of states onto specific atomic orbitals, provides detailed insight into the contribution of different elements to the electronic structure. A deeper analysis of the PDOS near the Fermi level (E_F) offers further insight, as summarized in Figure 7. Across all doped models (1, 3, and 4), the Dy^{3+} 4*f* orbitals give rise to sharp, highly localized peaks near E_F . This is a characteristic signature of the strongly localized nature of 4*f* electrons, which are largely insensitive to the local chemical environment changes induced by Hf doping. These states do not significantly contribute to band-edge physics but are crucial for the f-f optical transitions of Dy^{3+} . In Model 3, the Hf 5*d* orbitals contribute substantially to the lower portion of the conduction band, introducing new unoccupied states that are responsible for the observed band gap narrowing. In Model 4, the Hf 5*d* orbitals produce sharper and more intense peaks in the conduction band compared to Model 3. This is because the Nb site provides a more symmetric octahedral coordination for Hf^{4+} , leading to a more defined crystal field splitting of its d-orbitals and stronger Hf-O hybridization. This results in a more localized modification of the conduction band. The transition from the electronic structure of Model 3 to that of Model 4 underlines the significant electronic consequence of the Hf^{4+} site occupation transition at the threshold. It is not merely a structural change but an electronic restructuring that affects both the band gap and the nature of the conduction band states, with implications for optical absorption and charge transport.

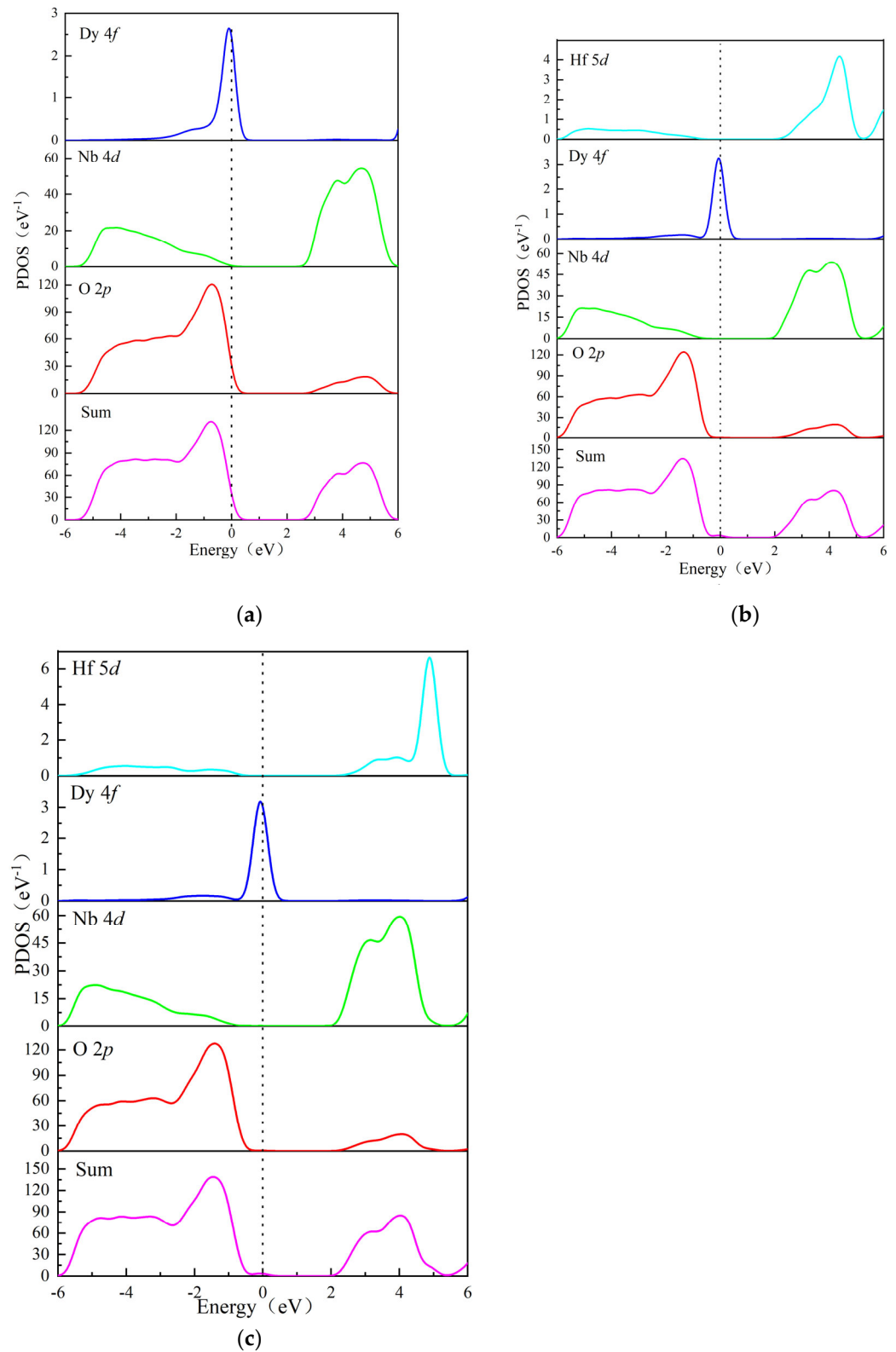


Figure 7. Partial and total density of states (PDOS and DOS) for Model 1 (a), Model 3 (b), and Model 4 (c).

To further corroborate the site-dependent bonding interactions revealed by the PDOS, we analyzed the Electron Localization Function (ELF), which provides a real-space visualization of electron localization and chemical bonding. The ELF plots for the key models are presented in Figure 8. In Model 3, the Hf atom is surrounded by regions of moderate

ELF enhancement (yellow-red), indicative of a covalent Hf-O interaction. Strikingly, in Model 4, the Hf atom exhibits significantly more intense and compact red ELF regions with its neighboring oxygen atoms. This unambiguous contrast demonstrates a stronger and more covalent Hf–O bond when Hf^{4+} occupies the Nb site, a direct consequence of the more favorable octahedral coordination environment. This real-space evidence solidifies our conclusion that the Nb site provides a more stable electronic configuration for Hf^{4+} , rationalizing the defect complex formation in the post-threshold regime and providing an electronic-scale basis for the stronger local electric field inferred from the IR spectra. The highly localized Dy 4*f* electrons were also consistently observed across all models, confirming their inert nature.

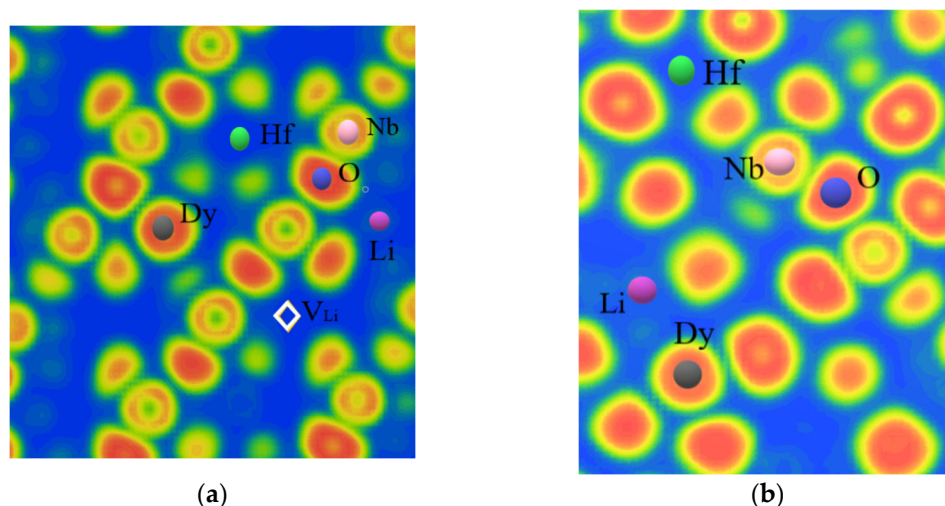


Figure 8. Electron localization function (ELF) distribution of Model 3 (a) and Model 4 (b).

The convergence of computational evidence, encompassing geometrically optimized total energies, electronic band structures, and electron localization, provides a unified and atomistically resolved model for the Hf^{4+} threshold behavior. The pronounced energy difference favoring Hf incorporation at Li sites over Nb sites fundamentally dictates the initial doping stage. This strong thermodynamic driving force leads to the selective occupation of Li sites, which necessarily involves the elimination of intrinsic defects. The consequent suppression of these defect states, directly observed in our PDOS and band gap calculations, offers a precise explanation for the blue shift of the optical absorption edge measured in crystals with moderate Hf doping.

The saturation of these preferential Li sites necessitates a change in incorporation mechanism at higher concentrations. The subsequent occupation of Nb sites by Hf^{4+} , a pathway governed by the considerably higher formation energy of Model 4, corresponds to the beginning of the structural modification regime. The distinct chemical environment of the Nb site, which our ELF analysis shows fosters a stronger, more localized Hf-O covalent bond, underpins the formation of stable defect complexes such as Hf_{Nb}^- . This altered electronic structure at the defect core is consistent with the markedly different local electric field probed by the blue-shifted OH^- vibrational mode. Thus, the suite of post-threshold phenomena, including lattice contraction and the evolution of absorption characteristics, can be traced to this thermodynamically compelled shift in the crystallographic site of Hf^{4+} ions.

4. Discussion

Our findings on the Hf^{4+} concentration threshold and site occupation transition in Dy: LiNbO_3 align with prior studies on doping effects in LiNbO_3 (e.g., Mg^{2+} , Zn^{2+}) doping) but extend this work by linking threshold behavior to rare earth (RE) ion luminescence—an underexplored area in previous research. Notably, while earlier Hf-doped LiNbO_3 studies confirmed a threshold, our combined experimental (XRD, FT-IR, UV–Vis–NIR) and first-principles (DFT, ELF) data clarify its atomic origin: Hf^{4+} prefers Li sites below 4 mol% (repairing $\text{Nb}_{\text{Li}}^{4+}$ defects) and shifts to Nb sites above, strengthening Hf–O covalency and modifying Dy^{3+} 's local crystal field. This modification is quantitatively corroborated by our Judd–Ofelt analysis, which shows a significant increase, followed by a slight decrease, in the Ω_2 parameter—highly sensitive to local symmetry and covalency—across the Hf^{4+} concentration series, aligning with the site occupation transition. This validates our core hypotheses and fills gaps in understanding RE-dopant interactions with Hf.

Broadly, this defect-engineering framework lays groundwork for deeper exploration of RE-doped LiNbO_3 's optical performance and applications. Subsequent work will build on this foundation: optimizing up-conversion luminescence (by leveraging Hf-tuned Dy^{3+} f–f transitions), enhancing holographic storage (via defect-suppressed optical homogeneity), and boosting photorefractive damage resistance (exploiting Hf-induced lattice stability). These extensions aim to translate lab-scale defect insights into practical advancements for photonic devices relying on RE-doped LiNbO_3 .

5. Conclusions

This study provides a comprehensive investigation of the Hf^{4+} concentration-driven threshold effect in Dy: LiNbO_3 crystals, linking macroscopic properties to atomic-scale mechanisms through combined spectroscopy and first-principles calculations. A clear threshold at ~4 mol% (3.20 mol% actual concentration in the crystal) was identified: ICP–AES confirmed doping gradients and competitive segregation; XRD showed an inflection in lattice parameters; FT-IR revealed a blue shift in the OH^- peak, indicating a new defect center; and UV–Vis–NIR spectra demonstrated enhanced Dy^{3+} f–f transitions and a blue-shifted absorption edge, signifying band structure purification.

The novelty of this work lies in its atomistic explanation: the threshold arises from a thermodynamically driven transition in Hf^{4+} site occupation. Below the threshold, Hf^{4+} prefers Li sites, repairing defects; above, it occupies Nb sites, modifying the lattice. Electronic structure calculations revealed that the band gap narrows in defect-rich models, while it widens with the incorporation of Hf^{4+} . ELF analysis visualized stronger Hf–O covalent bonding at Nb sites, rationalizing post-threshold defect stability and local electric fields. It is important to acknowledge the limitations of the DFT model, such as the systematic underestimation of absolute band gaps by the GGA functional and finite-size effects of the supercell on quantitative formation energies. However, these do not affect the qualitative trends and the physical mechanism of the site-preference transition, which is the central finding of this study.

In summary, this work establishes a multi-scale structure–property relationship—from atomic site preference and chemical bonding to electronic structure, macroscopic lattice parameters, and optical performance. This holistic understanding offers a framework for the rational design of doped functional crystals via targeted defect engineering.

Author Contributions: Conceptualization, S.Y., B.D. and L.D.; methodology, L.D.; software, J.W.; validation, S.Y. and L.D.; formal analysis, S.Y.; investigation, J.W.; resources, S.Y.; data curation, S.Y.; writing—original draft preparation, S.Y.; writing—review and editing, S.Y.; visualization, S.Y.;

supervision, L.D.; project administration, L.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Correspondence and requests for materials should be addressed to Li Dai. The data that support the findings of this study are available upon reasonable request from the authors.

Acknowledgments: This work was supported by the [Open Project Funds for the Key Laboratory of Space Photoelectric Detection and Perception (Nanjing University of Aeronautics and Astronautics)] under Grant [number NJ2020021-9]; [Natural Science Fund of Heilongjiang Province of China] under Grant [number LH2020E085]; and [Opening Project of State Key Laboratory of Crystal Material (Shandong University)] under Grant [number KF1906].

Conflicts of Interest: Author Jingchao Wang was employed by the company China State Shipbuilding Corporation Limited. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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