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Defect Oxygen in NaNbO_3 and Its Fatigue Behavior

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DEDICATION

We dedicate this work to our beloved parents, whose endless love, sacrifices, encouragement, and support have been the foundation of our success.

To our families, for their patience, understanding, and constant motivation throughout our academic journey.

To our teachers and professors, who have shared their knowledge and guided us with dedication and wisdom.

To our friends and colleagues, for their support, encouragement, and the memorable moments we shared.

Finally, we dedicate this work to everyone who believed in us and inspired us to pursue our goals and dreams.

SAHNOUN Aicha et KOUIDRI Imane

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SAHNOUN Aicha et KOUIDRI Imane

ملخص:

تُعدّ شواغر الأكسجين من بين أكثر العيوب تأثيراً على أداء وموثوقية المواد البيروفسكايتية الفيروكهربائية الخالية من الرصاص. تهدف هذه الدراسة إلى تحليل تأثير شواغر الأكسجين في نيوبات الصوديوم (NaNbO_3) باستعمال حسابات المبادئ الأولى المعتمدة على نظرية دالة الكثافة (DFT)، مع التركيز على دور هذه العيوب في ظاهرة التعب الفيروكهربائي.

تمت دراسة تطور البنية الإلكترونية من خلال تحليل كثافة الحالات الكلية (DOS) لخلايا فائقة تحتوي على ما يصل إلى عشرة شواغر أكسجين. أظهرت النتائج ظهور حالات عيب تدريجية ذات طبيعة Nb-d داخل فجوة الطاقة، مصحوبة بارتفاع مستوى فيرمي وتغيرات غير منتظمة في قيمة فجوة الطاقة. وتشير هذه السلوكيات إلى حدوث تطعيم من النوع n واختزال جزئي لأيونات النيوبيوم.

كما بينت حسابات طاقة التشكل أن شواغر الأكسجين المتعادلة تمتلك استقراراً متوسطاً في الظروف الغنية بالأكسجين، حيث تتراوح طاقة التشكل بين 4.6 و 5.2 إلكترون فولت لكل شاغر. غير أن تكون هذه الشواغر يصبح أكثر ملائمة في البيئات المختزلة المرتبطة بظروف تشغيل الأجهزة.

وتوضح الدراسة أيضاً أن الشواغر المشحونة تؤدي دوراً مهماً في تثبيت جدران المجالات الفيروكهربائية وزيادة تيارات التسرب الكهربائية، مما يساهم في تدهور الخصائص الوظيفية للمادة وتسريع ظاهرة التعب الفيروكهربائي في NaNbO_3 .

الكلمات المفتاحية: NaNbO_3 ، شواغر/فراغات الأكسجين، الإرهاق الفيروكهربائي، كثافة الحالات، طاقة تكوين العيوب، البيروفسكايت الخالية من الرصاص.

ABSTRACT:

Oxygen vacancies are among the most critical defects governing the performance and reliability of lead-free ferroelectric perovskites. This work presents a systematic first-principles investigation of oxygen vacancy effects in sodium niobate (NaNbO_3), with a particular focus on their role in ferroelectric fatigue.

Using density functional theory calculations, the evolution of the electronic structure was examined through total density of states (DOS) for supercells containing up to 10 oxygen vacancies. Results reveal progressive introduction of Nb-d derived defect states within the band gap, upward shift of the Fermi level, and non-monotonic changes in the band gap, consistent with n-type doping and partial Nb reduction. Formation energy calculations demonstrate that neutral oxygen vacancies exhibit moderate stability under oxygen-rich conditions ($\approx 4.6\text{-}5.2$ eV per vacancy), but become significantly more favorable under reducing environments relevant to device operation. Theoretical considerations of charged vacancies further highlight their importance in domain-wall pinning and leakage current enhancement.

KeyWords: NaNbO_3 , oxygen vacancies, ferroelectric fatigue, density of states, defect formation energy, lead-free perovskites

Résumé :

Les lacunes d'oxygène figurent parmi les défauts les plus critiques affectant les performances et la fiabilité des pérovskites ferroélectriques sans plomb. Cette thèse présente une étude systématique par calculs *ab initio* (théorie de la fonctionnelle de la densité) des effets des lacunes d'oxygène dans le niobate de sodium (NaNbO_3), en mettant l'accent sur leur rôle dans la fatigue ferroélectrique.

L'évolution de la structure électronique a été examinée à travers les densités d'états totale (DOS) pour des supercellules contenant jusqu'à 10 lacunes d'oxygène. Les résultats montrent l'apparition progressive d'états de défauts de caractère Nb-d dans la bande interdite, un déplacement vers le haut du niveau de Fermi, ainsi que des variations non monotones de la largeur de bande interdite, en accord avec un dopage de type n et une réduction partielle du niobium. Les calculs d'énergie de formation indiquent que les lacunes neutres présentent une stabilité modérée en conditions riches en oxygène ($\approx 4,6\text{-}5,2$ eV par lacune), mais deviennent nettement plus favorables dans des environnements réducteurs pertinents pour le fonctionnement des dispositifs. L'analyse théorique des lacunes chargées souligne leur importance dans l'épinglage des parois de domaines et l'augmentation des courants de fuite.

Mots clés : NaNbO_3 , lacunes d'oxygène, fatigue ferroélectrique, densité d'états, énergie de formation des défauts, pérovskites sans plomb

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ABBREVIATIONS

NaNbO₃	Sodium Niobate (niobate de sodium)
PDOS	Projected Density of States (Densité des états projetée)
VO	Oxygen Vacancy (lacune d'oxygène)
DFT	Density Functional Theory (Théorie de la fonctionnelle de la densité)
E_g	Band Gap (Gap d'énergie)
VB	Valence Band (Bande de valence)
DOS	Density of States (Densité des États)
CB	Conduction Band (Bande de conduction)
VBM	Valence Band Maximum (Maximum de la bande de valence)
CBM	Conduction Band Minimum (Minimum de la bande de conduction)
eV	électron-volt (unit of energy)
k-point	Reciprocal-space point used for electronic structure calculations
SCF	Self Consistent Field (champ auto-cohérent)

GENERAL INTRODUCTION

GENERAL INTRODUCTION

Ferroelectric materials are essential components in modern technologies, enabling a wide range of applications including non-volatile memories, sensors, actuators, energy harvesters, and high-performance capacitors. Among these, perovskite oxides stand out due to their exceptional functional properties, such as switchable spontaneous polarization, high dielectric permittivity, and strong piezoelectric response. While lead-based materials like $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) have long dominated the market, growing environmental and health concerns have driven intense research toward lead-free alternatives. Sodium niobate (NaNbO_3) has emerged as one of the most promising candidates, offering a rich phase diagram, high Curie temperature, and environmental compatibility.

Despite these advantages, practical deployment of NaNbO_3 -based devices is hindered by ferroelectric fatigue; the progressive degradation of switchable polarization under repeated electrical cycling. Fatigue severely limits device lifetime and reliability, representing a critical bottleneck for commercial adoption. Among the various mechanisms proposed, the formation, accumulation, and migration of oxygen vacancies are widely recognized as key contributors to this degradation process. Oxygen vacancies act as mobile charged defects that can pin domain walls, increase leakage currents, and modify local electronic and structural properties.

This work focuses on the atomistic understanding of oxygen defects in NaNbO_3 using first-principles density functional theory (DFT) calculations. By systematically exploring the evolution of electronic structure, and defect chemistry as a function of vacancy concentration, the work aims to uncover the microscopic origins of fatigue in this important lead-free perovskite. The thesis is structured as follows:

Chapter 1 present NaNbO_3 , and his his various applications.

Chapter 2 provides a comprehensive literature review on NaNbO_3 , structural, electronic, and describes the computational methodology

Chapters 3 present the core results on electronic structure, formation energetics, and charged defects.

Finally, conclusion summarizes the main findings and outlines future perspectives.

Through this comprehensive computational study, this work contributes to the fundamental knowledge of defect behavior in lead-free ferroelectrics and supports the development of more fatigue-resistant materials for sustainable electronic devices.

CHAPTER I:

Emerging Application of NaNBO_3 in Modern Materials

CHAPTER I: Emerging Application of NaNbO₃ in Modern Materials.

Introduction:

The rapid development of electronic technologies has increased the demand for multifunctional materials with excellent dielectric, piezoelectric, and electromechanical properties for applications such as sensors, actuators, capacitors, and energy harvesting devices [1]. Although lead-based ferroelectric ceramics such as PZT have long dominated these applications, their toxicity has driven the search for environmentally friendly lead-free alternatives [1,2].

Among lead-free perovskites, **NaNbO₃ (Sodium Niobate)** has attracted considerable attention because of its ferroelectric, antiferroelectric, dielectric, piezoelectric, and catalytic properties, making it suitable for sensors, nanogenerators, dielectric capacitors, biomedical devices, photocatalysis, and self-powered electronics [2–4]. At room temperature, pure NaNbO₃ is mainly antiferroelectric, which limits its direct piezoelectric performance. Nevertheless, its structural flexibility makes it an excellent base material for (K,Na)NbO₃ solid solutions and doped systems, enabling enhanced performance while maintaining its environmentally friendly, lead-free nature [3,4]

I.2. Synthesis Methods of NaNbO₃

The performance of NaNbO₃ strongly depends on synthesis technique, grain morphology, and microstructure. Several fabrication methods are commonly employed.

Table I.1: Advantages and Disadvantages of fabrication methods of NaNbO₃

fabrication methods	Advantages	Disadvantages
Solid-State Reaction Method	Low cost Simple processing Large-scale production	High energy consumption Non-uniform particle size Lower chemical homogeneity
Sol-Gel Method	Fine particle size Better purity Lower calcination temperature Enhanced homogeneity	Complex process Expensive precursors
Hydrothermal	High crystallinity	

Method	Controlled morphology Low-temperature growth	
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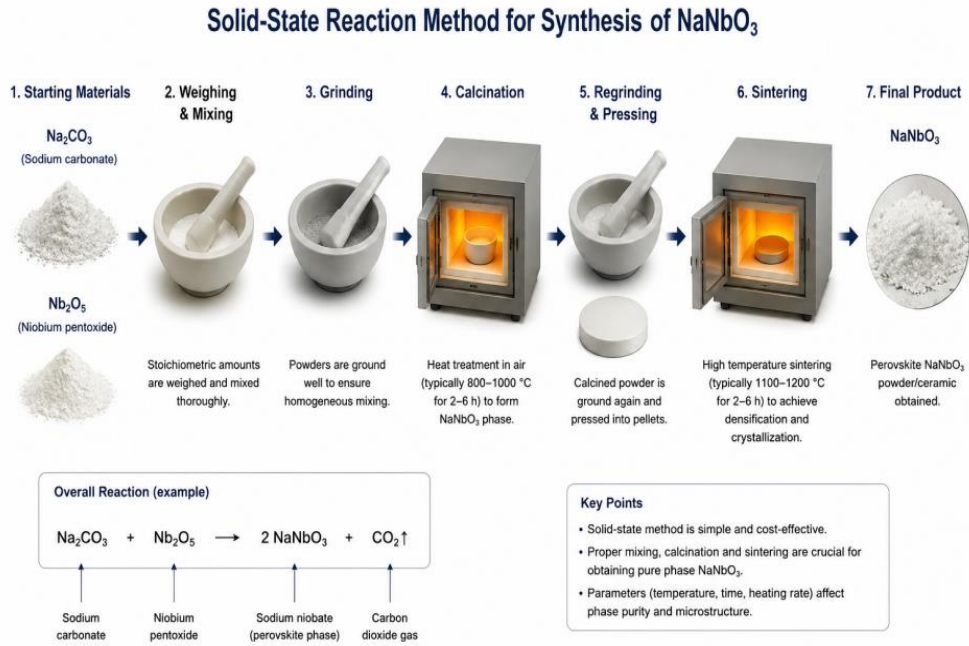


Figure I.1: Solid-state method of NaNbO_3 (traditional ceramic synthesis technique)

I.3. Applications of NaNbO_3

I.3.1. NaNbO_3 -based capacitors

NaNbO_3 -based ceramics are attractive lead-free AFE dielectric capacitors due to presence of AFE-like hysteresis loops and high saturation polarization. Further, low-theoretical-density ($\rho = 4.494 \text{ g/cm}^3$) makes NaNbO_3 -based capacitors makes them attractive for applications in the light-weight devices. However, limited number of studies have been conducted on energy storage applications for pure NaNbO_3 ceramics. One of the main reasons is that it has been difficult to obtain double P-E hysteresis loops at room temperature due to the small difference in free energy between its metastable FE phase (P21ma) and AFE phase (Pbma). Thus, the electric field induced FE phase is preserved after the electric field is removed, which results in a ferroelectric P-E hysteresis loop [1-2].

There have been several attempts towards stabilizing the antiferroelectric phase and exploiting its potential for antiferroelectric energy storage devices [2].

It is well-known that AFE capacitors usually exhibit a typical double P-E hysteresis loops, along with low η because of the large hysteresis between AFE-FE and FE-AFE [1,2], which results in a large portion of the charged electric energy being dissipated as heat during discharging. Further, temperature rise resulting due to large hysteresis relates loss drastically decreases the breakdown strength (BDS) of capacitors. All these issues have limited the advancement of NaNbO₃-based capacitors. A slim hysteresis loop can be obtained by tailoring the composition to realize relaxor AFE structure.[2,4]

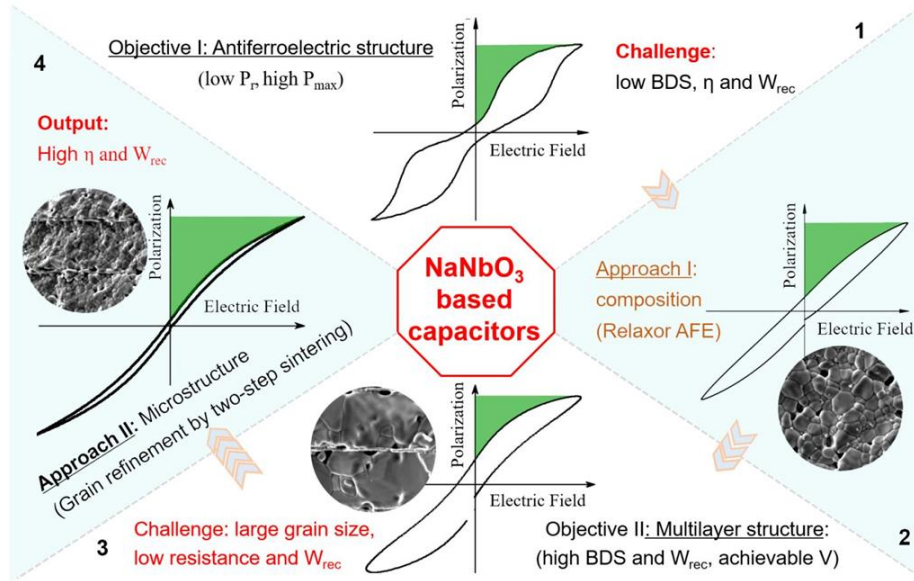


Figure I.2: Schematic diagram describing the strategies adopted for improving the W_{rec} and η of NaNbO₃ based capacitors through the combinatin of composition optimization and grain refinement [2].

I.3.2. Sensors (Piezoelectric Accelerometers, Pressure Sensors, Ultrasonic Transducers)

NaNbO₃ shines here through KNN-based ceramics or composites, which offer high piezoelectric coefficients (d_{33} up to 300–800+ pC/N in optimized textured versions) and good temperature stability. These replace toxic PZT in vibration monitoring, medical imaging, or structural health sensors [5] .

I.3.3. Piezoelectric Humidity Sensors Based on Lead-Free NaNbO₃

Figure 3 shows the schematic fabrication procedure of the flexible NaNbO₃ active sensor. Because the heat treatment is necessary for the formation of perovskite NaNbO₃ NFs, silicon substrates were used for the synthesis of the NFs. Due to the porous structure of the NFs on the silicon substrate, the top layer of the NFs could be packaged by the PDMS soft polymers through the spin-coating and the curing process. Thereafter, the NFs could be easily transferred onto the flexible PDMS substrate by lifting off the PDMS layer. After the IDE deposition, the flexible device based on the electrospun NaNbO₃ NF should be obtained. As shown by the photo image in Figure 3, the as-fabricated device was approximately 2.0 × 1.0 × 0.2 cm³ in dimension [9].

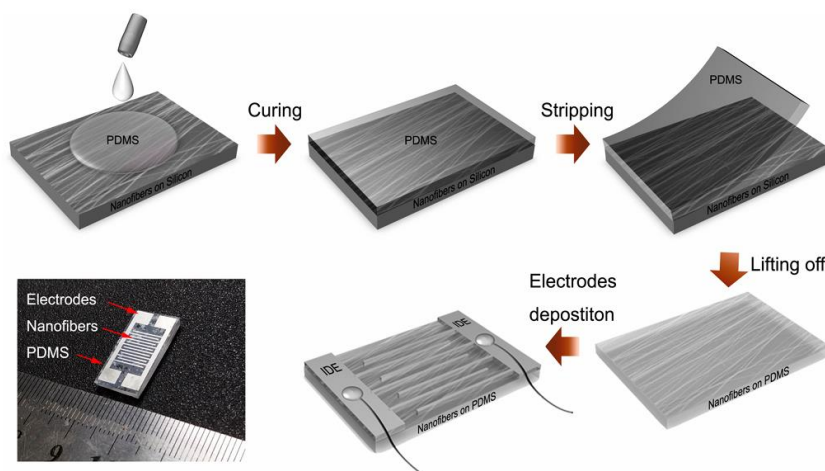


Figure I.3: schematic fabrication procedure of the flexible NaNbO₃ active sensor[9].

I.3.4. Other Real-Life Applications

- Energy Harvesting (Nanogenerators):** NaNbO₃ nanorods or KNN in PVDF composites harvest mechanical vibration (piezo) or combine with light (piezophotocatalysis). Flexible 3D-printed double-layer devices generate power for wearables or IoT sensors. Hydrothermal nanorods excel here due to high surface area[6,7].
- Photocatalysis & Piezocatalysis (Environmental Remediation):** Use NaNbO₃ nanorods/nanoparticles for degrading organic dyes (e.g., Rhodamine B) or disinfecting bacteria (*E. coli*) in wastewater. Combine ultrasound (piezo potential separates charges) + light for synergistic photopiezocatalysis ; up to 98% degradation in combined mode. Simple setup: Disperse powder in polluted water, apply UV/visible light + ultrasonic bath. Recyclable over multiple cycles with good stability[1].

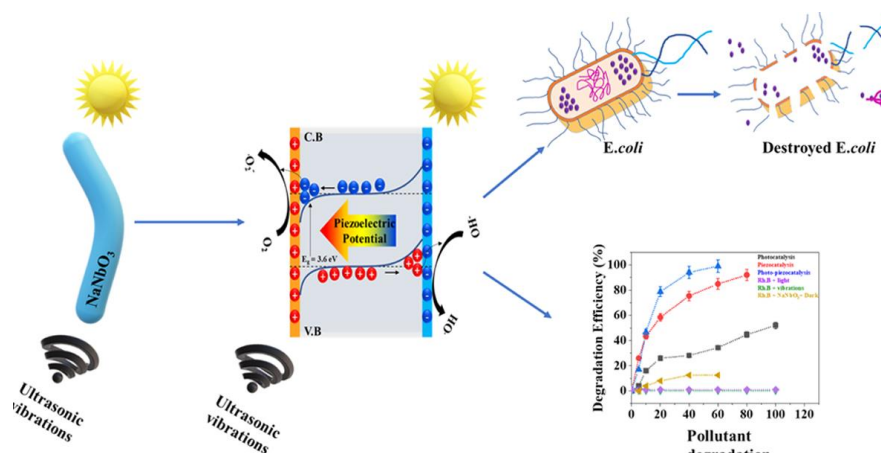


Figure I.4: Schematic demonstration of the synergistic effect of photopiezocatalysis for the deterioration of Rhodamine B [1].

- **Tooth Cleaning Applications:** Tooth discoloration and plaque formation represent serious dental healthcare problems worldwide [10]. Conventional whitening techniques include:
 - Bleaching
 - Aggressive toothpaste
 - Professional polishing
 - Hydrogen peroxide treatment

Hydrogen peroxide generates hydroxyl radicals ($\text{OH}\cdot$) that destroy organic contaminants but simultaneously damage tooth enamel. $\text{NaNbO}_3/\text{ZnO}$ piezocatalytic systems provide a safer alternative.

Under ultrasonic vibration:

- ROS are generated
- Organic pollutants decompose
- Bacterial colonies are destroyed

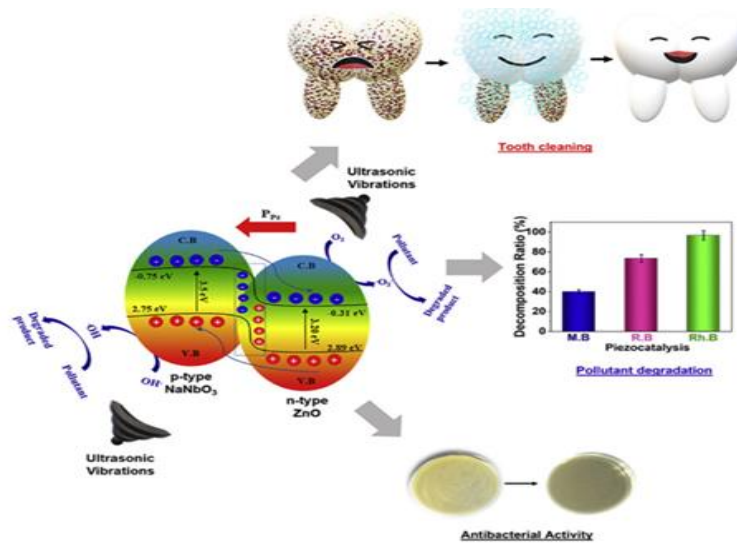


Figure I.5: Piezocatalytic Tooth Cleaning Mechanism[10]

Experimental studies demonstrated; significant tooth cleaning after 6 hours with Minimal enamel damage and Strong antibacterial performance; The $\text{NaNbO}_3/\text{ZnO}$ composite degraded Rhodamine B by 97% within 60 min. The degradation rate constant reached: $5.1 \times 10^{-2} \text{ min}^{-1}$

- **Actuators:** Multilayer KNN devices (with Ni electrodes) give large displacements (e.g., mm-scale at low voltage) for precision positioning or speakers. Cantilever-style prototypes achieve high acceleration output.
- **Emerging:** Thin films for implantable MEMS (biocompatible with fibroblasts/Schwann cells), lithium/sodium-ion battery anodes (good cycling due to structural stability), or electrocaloric cooling.

I.3.5. Advantages of NaNbO_3 Materials

NaNbO_3 offers several advantages:

- Lead-free composition
- Environmental compatibility
- Excellent piezoelectric behavior
- Strong dielectric response

- Good thermal stability
- Multifunctional applications
- Low-cost fabrication potential

I.4. Challenges and Limitations

Despite its advantages, several challenges remain:

- Relatively low energy density
- Complex phase transitions
- High sintering temperatures
- Leakage current issues
- Nanostructure fabrication complexity

I.5. Future Perspectives

The combination of piezoelectricity, dielectric behavior, and catalytic activity makes NaNbO₃ highly promising for future multifunctional electronic systems. So Future developments of NaNbO₃ are expected in:

- Flexible electronics
- Smart sensors
- Biomedical systems
- Self-powered devices
- Artificial intelligence sensors
- Wearable technologies
- Nano-generators

I.6. Conclusion

NaNbO₃-based materials represent one of the most promising classes of lead-free functional ceramics for electronic engineering applications.

Recent advances in nanotechnology and nanocomposite engineering significantly enhanced the performance of NaNbO₃ materials, particularly in humidity sensing, piezoelectric energy harvesting, and antibacterial systems.

Consequently, NaNbO₃ is expected to play a major role in the future development of environmentally friendly multifunctional electronic technologies.

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CHAPTER II

: NaNbO₃ Characteristics and DFT Methodology

CHAPTER II: NaNbO_3 Characteristics and DFT Methodology

II.1. Introduction

The perovskite structure is characterized by corner-sharing BO_6 octahedra surrounding the A-site ions. The distortion and displacement of ions within this structure are mainly responsible for the remarkable electrical properties of perovskite materials [1].

NaNbO_3 crystallizes in a distorted perovskite structure and undergoes several phase transitions depending on temperature and synthesis conditions.

- **Basic Crystal Structure:** NaNbO_3 is a classic ABO_3 perovskite. In the ideal high-symmetry form:
 - **A-site:** Na^+ (12-fold coordinated by oxygen, forming NaO_{12} cuboctahedra)
 - **B-site:** Nb^{5+} (6-fold coordinated, forming corner-sharing NbO_6 octahedra)
 - **X-site:** O^{2-}

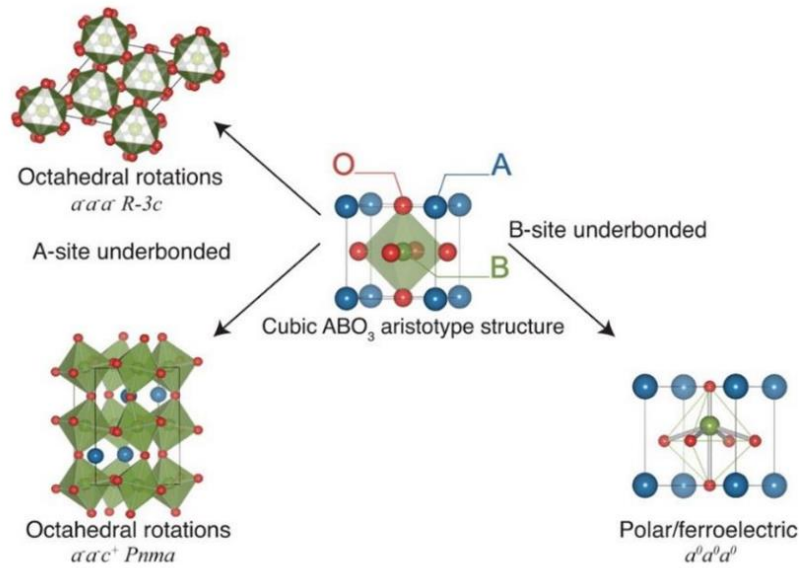


Figure.II.1: cubic perovskite structure, and common structural distortions [1]

The aristotype (ideal cubic) structure is Pm-3m (space group 221), with lattice parameter around $a \approx 3.94 \text{ \AA}$ (pseudo-cubic). Here, everything is perfectly symmetric: Nb at the center of regular octahedra, Na in the large cavity, and no distortions.

In reality, NaNbO₃ is highly distortable due to the relatively small Na⁺ ion (compared to K⁺ in KNbO₃) and the electronic configuration of Nb⁵⁺, which drives second-order Jahn-Teller distortions in the NbO₆ octahedra. This leads to octahedral tilting and cation off-centering, which are the key sources of its interesting properties.

II.2. Structural Phases and Behavior

At room temperature, the most common phase is orthorhombic antiferroelectric (AFE) often described in Pbcm (or similar settings like P2₁ma for polar variants). It features complex Glazer tilting (combinations of in-phase and antiphase rotations of NbO₆ octahedra) and antiparallel Nb⁵⁺ displacements that cancel net polarization.

DFT:

Density Functional Theory (DFT) is a widely used quantum mechanical approach for studying the electronic structure of atoms, molecules, and condensed matter systems. The theoretical foundation of DFT is based on the Hohenberg–Kohn theorems, which establish that all ground-state properties of a many-electron system are uniquely determined by its electron density. In practical calculations, the Kohn–Sham formalism replaces the interacting many-electron problem with an equivalent system of non-interacting electrons moving in an effective potential. This formulation enables accurate predictions of structural, electronic, magnetic, and optical properties while considerably reducing the computational cost compared with traditional wave-function-based methods. Owing to its reliability and computational efficiency, DFT has become one of the most important tools in computational materials science, condensed matter physics, and quantum chemistry for investigating and designing new materials

The Generalized Gradient Approximation (GGA) is an approach used within Density Functional Theory (DFT) to describe the exchange-correlation energy of an electronic system. Unlike the Local Density Approximation (LDA), which depends solely on the local electron density, GGA incorporates both the electron density and its spatial gradient. By taking into account the variation of electron density in space, GGA provides a more accurate description of the electronic structure and improves the prediction of structural, energetic, and electronic properties of materials. Among the different GGA functionals, the Perdew–Burke–Ernzerhof (PBE) functional is one of the most widely used because of its reliability and computational efficiency.

- **Multiple temperature-driven transitions:**

from high-T cubic Pm-3m (paraelectric, no tilts) down through tetragonal and orthorhombic phases. The energy landscape is very flat ; DFT (with GGA-PBESol or similar in WIEN2k) shows tiny energy differences ($\sim$ few meV/f.u.) between AFE and ferroelectric (FE) phases like R3c or Pmc2_1 . This explains why phase coexistence or switching happens easily with doping, strain, or grain size.

- In DFT calculations (FP-LAPW in WIEN2k), we relax these supercells carefully starting from experimental CIFs, converging forces <1 mRy/a.u., using dense k-meshes for the larger cells (40+ atoms).

● Phase Transitions in NaNbO_3 :

Seven distinct phases of NaNbO_3 can be observed as a function of temperature under ambient pressure, as shown in Figure II.2. The high-temperature phase, manifesting at 639°C , adopts the aristo-type cubic perovskite structure with a cubic Pm3m space group. Upon cooling, this structure transitions through a sequence of phases: tetragonal (P4/mbm), followed by four orthorhombic phases (Ccm , Pnm , Pnm , and Pbc), and ultimately to a rhombohedral (R3c) phase [23]. The identification of these phases is based on two primary factors: the displacement of Nb^{5+} ions from their octahedral centres and the tilting of oxygen octahedra. With heating, these tilts and displacements diminish, culminating in the restoration of the aristo-type cubic structure [74]. Notably, the rhombohedral N phase exhibits FE, whereas the orthorhombic P and R phases are AFE. All phases existing at temperatures above the R phase are paraelectric, displaying no spontaneous polarisation [2]

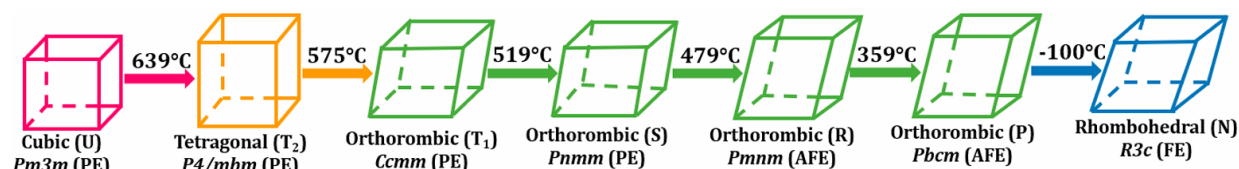


Figure.II.2: Temperature dependent phase transitions in NaNbO_3 [2]

Here's a simplified overview (temperatures are approximate; exact values depend on sample):

- **High-T cubic paraelectric phase (above $\sim 640\text{--}670^\circ\text{C}$):** Pm-3m . Unstable in DFT; phonon calculations show many imaginary modes [4].
- **Tetragonal phases (intermediate high T):** Various, often with tilting.

- **Orthorhombic antiferroelectric phase at room temperature (most common):** Often described as Pbcm (or Pbma in some settings, sometimes called the P-phase). This is the stable AFE phase with a supercell (or larger relative to pseudo-cubic). It features:
 - Complex octahedral tilting.
 - Antiparallel displacements of Nb cations in adjacent layers → antiferroelectric ordering (net polarization cancels out).
 - Two distinct Na sites and modulated structure in some descriptions.
- **Other orthorhombic/rhombohedral phases:**
 - Polar $\text{P2}_1\text{ma}$ (or similar); a ferroelectric variant with unbalanced Nb displacements.
 - R3c rhombohedral FE/AFD phase ([111] polar displacement) ; often the DFT ground state with GGA-PBEsol.
 - Low-T phases can be rhombohedral or monoclinic with subtle distortions.

Room-temperature "standard" samples are mostly Pbcm (AFE), but synthesis conditions (solid-state vs. sol-gel, grain size) can stabilize coexisting polar $\text{P2}_1\text{ma}$ or even induce more ferroelectric character. DFT phonon dispersions from the cubic phase reveal soft modes corresponding to M/R-point instabilities (tilting) and Gamma-point polar modes.

In WIEN2k, we optimize these structures by minimizing forces and total energy with respect to atomic positions and cell parameters (using the minimize or optimize scripts, often with PBE or PBEsol functionals + RKmax $\sim 7-9$, good k-mesh like $8 \times 8 \times 8$ or denser for supercells).

II.3. Characteristics and Properties

- **Antiferroelectricity:** Ferroelectric materials possess spontaneous electric polarization even in the absence of an external electric field. This polarization can be reversed by applying an external electric field.
- This polarization can be reversed by applying an external electric field. The ferroelectric behavior of NaNbO_3 originates from:
 - Non-centrosymmetric crystal distortion
 - Ion displacement
 - Dipole formation

The ferroelectric hysteresis loop is characterized by:

- Remnant polarization

- Coercive field
- Saturation polarization

At room temperature, it is dominantly in the antiferroelectric, P phase (Pbcm) but there are usually trace amounts of the ferroelectric Q phase (Pmc2_1) which has a similar free energy. At high temperature, it transforms to the antiferroelectric R phase (Pnma). The structure of P, Q and R phases are shown in Fig. II.3.

With higher temperature, the structure is transformed into paraelectric T phase and finally to the paraelectric C phase. 1 This makes NaNbO_3 -based materials excellent for high-energy-density capacitors (recoverable energy storage).

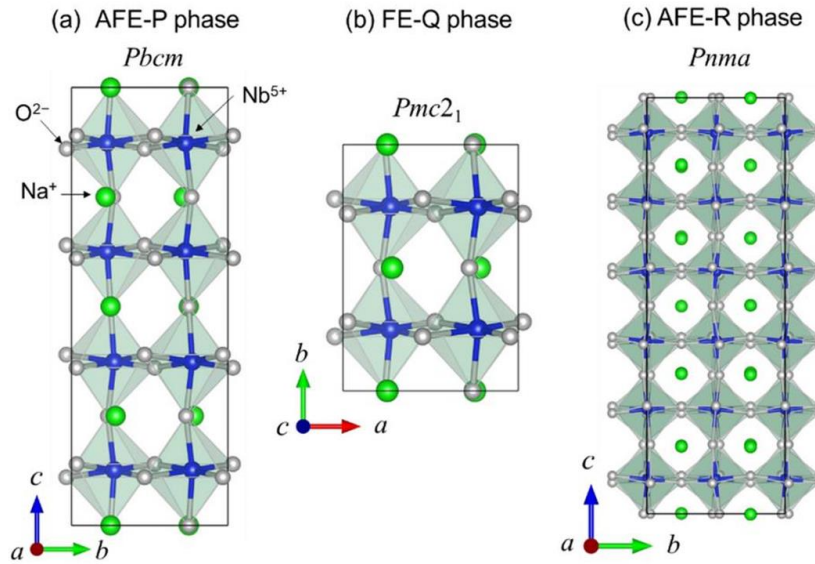


Figure.II.3: Crystal structure of NaNbO_3 in (a) AFE-P phase with Pbcm space group, (b) FE-Q phase with Pmc2_1 space group, (c) AFE-R phase with Pnma space group. [3]

- **Phase transitions:** Multiple AFE/FE transitions with temperature. The Curie temperature (paraelectric transition) is around 350 - 400°C depending on phase. Doping (e.g., with K, Li, or Bi) can shift toward morphotropic phase boundaries (MPB) for enhanced piezo properties, like in KNN ceramics.
- **Dielectric and Piezoelectric properties:** Dielectric materials are electrical insulators capable of storing electrical energy under an applied electric field [1].

Piezoelectricity refers to the generation of electric charges under mechanical stress [4].

Moderate ϵ_r , piezoelectric coefficients (d_{33}) that improve with solid solutions. Pure NaNbO₃ has limited piezo performance due to AFE nature, but it's lead-free and eco-friendly.

- **Electronic structure:** Insulator with indirect band gap ~ 2.5 - 3.5 eV experimentally (DFT with standard GGA underestimates to ~ 1.5 – 2.5 eV; hybrid functionals or +U on Nb d-states improve it). Valence band mostly O 2p, conduction band Nb 4d. Good for photocatalysis under UV.
- **Mechanical/Elastic:** Relatively stiff perovskite; DFT calculates elastic constants, bulk modulus, etc.
- **Optical properties:** Transparent in visible, absorption in UV; refractive index calculations possible in WIEN2k via optic module.

II.4. Introduction to Wien2k Software

Wien2k is one of the most widely used and highly accurate software packages for performing electronic structure calculations of crystalline solids from first principles, using Density Functional Theory (DFT). It was developed and is maintained by Peter Blaha, Karlheinz Schwarz, and collaborators at the Vienna University of Technology (TU Wien), Austria. The package has been continuously developed since its initial release in the 1990s, with the most recent major publication describing version 19 appearing in the Journal of Chemical Physics in 2020 [7].

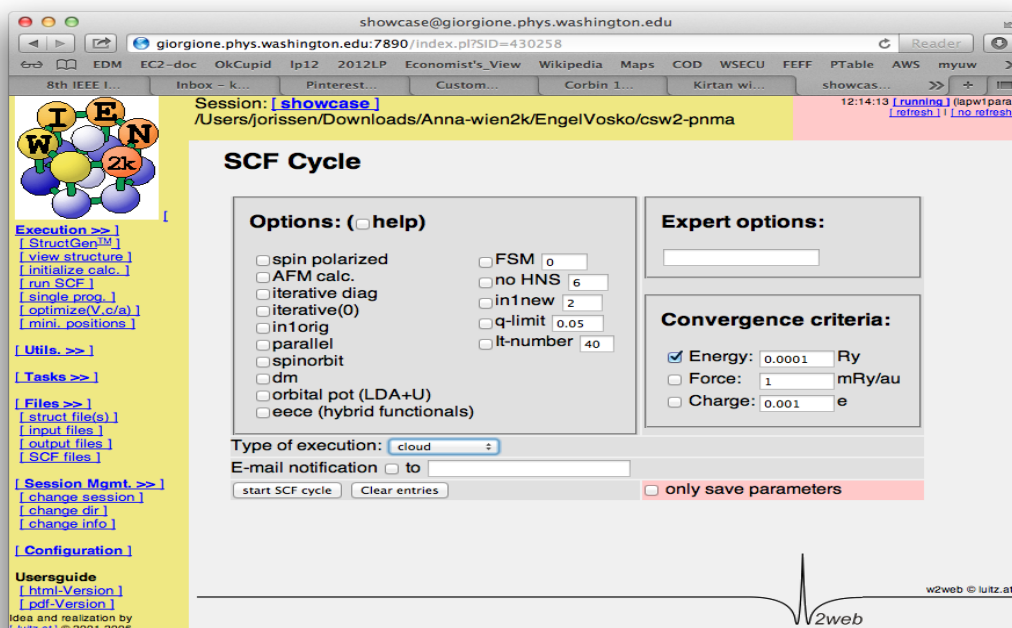


Figure II.4: Wien2k Software [6,7]

Wien2k is based on the Full-Potential (Linearized) Augmented Plane Wave plus Local Orbitals [FP-(L)APW+lo] method, which is widely recognized as one of the most accurate basis set schemes available for solving the Kohn-Sham equations of DFT in crystalline solids. Wien2k is an all-electron method that treats both core and valence electrons explicitly and self-consistently, including relativistic effects. This makes it particularly well-suited for studying heavy-element compounds and materials where core-valence interactions are important [7,8].

The software is widely used in the condensed matter physics, materials science, and computational chemistry communities for studying electronic band structures, densities of states, optical properties, magnetic properties, electric field gradients, X-ray spectra, and structural optimizations of crystalline materials.

II.4.1 FP-LAPW Method

The theoretical foundation of Wien2k is the Full-Potential Linearized Augmented Plane Wave (FP-LAPW) method, originally developed by Singh and Nordström (2006). In this method, the unit cell is divided into two regions:

- **Non-overlapping muffin-tin (MT) spheres:** These are centered on each atomic nucleus. Inside the MT spheres, the basis functions are expanded as products of radial functions and spherical harmonics.
- **Interstitial region:** Outside the MT spheres, the basis functions are plane waves. The matching of the basis functions at the MT sphere boundaries ensures continuity and differentiability of the wavefunctions throughout the unit cell. The size of the basis set is controlled by the cutoff parameter $RMT \times K_{max}$, where RMT is the smallest muffin-tin radius and K_{max} is the maximum reciprocal lattice vector. A value of $RMT \times K_{max} = 7-9$ is typically sufficient for good convergence.

II.4.2 Exchange-Correlation Functionals in Wien2k

Wien2k supports a wide variety of exchange-correlation (XC) functionals, including: LDA (Local Density Approximation), GGA (Generalized Gradient Approximation, PBE and PBEsol), meta-GGA (SCAN), and hybrid functionals (HSE06, PBE0). For band gap calculations of wide-gap semiconductors, the modified Becke-Johnson (TB-mBJ) potential; implemented in Wien2k and developed by Tran & Blaha, is particularly recommended, as it yields band gaps in close agreement with experimental values at a computational cost comparable to GGA, without the expense of hybrid functionals [7,8,9].

II.4.3 Calculable Properties

Using Wien2k, the following properties can be computed:

- **Electronic band structure:** The dispersion $E(k)$ of electronic states throughout the Brillouin zone, revealing the nature (direct/indirect) and magnitude of the bandgap.
- **Total and partial density of states (DOS/PDOS):** The distribution of electronic states as a function of energy, decomposed by atomic site and orbital character (s, p, d contributions from Sn and O atoms).
- **Charge density maps:** Two or Three-dimensional electron density distributions that visualize chemical bonding and charge redistribution upon gas adsorption.
- **Optical properties:** Dielectric function, optical absorption, reflectivity, and refractive index, computed from interband transition matrix elements.
- **Structural optimization:** Atomic position relaxation and unit cell optimization by minimizing Hellmann-Feynman forces to below a threshold of typically 1-2 mRy/bohr.

- **Electric field gradients and hyperfine parameters:** Relevant for Mössbauer spectroscopy and NMR studies.

II.5. NaNbO₃ in DFT (WIEN2k specifically)

- We use GGA-PBESol for better lattice parameters (PBESol often preferred for perovskites as it handles solids better).
- **Structural relaxation:** We start from experimental CIF , with force convergence <1 mRy/a.u.
- **Electronic properties:** Self-consistent field (SCF) for charge density, then bands/DOS.
- **Phonons:** WIEN2k has interfaces with Phonopy or direct frozen-phonon approach for instabilities.
- **Challenges:** Supercells for complex tilts (Pbcm has 40 atoms/unit cell or larger modulated cells) → need good k-point sampling and memory. Spin-orbit if heavy elements, but here not critical. (though hybrids are heavier in WIEN2k).

Remark: DFT shows the ground state can be R3c (FE) or Pmc2₁ depending on functional, with tiny energy differences to the AFE Pbcm; this flat energy landscape is why NaNbO₃ is so tunable and why experiments sometimes see phase mixtures.

II.5.1. WIEN2k Calculations

NaNbO₃ is a flagship lead-free material. Pure it's mostly AFE, but solid solutions push it toward FE for sensors/actuators or relaxor behavior for energy storage. Grain size reduction or thin films can stabilize polar phases.

II.5.2. Setting in WIEN2k:

We use experimental lattice from literature (e.g., $a \sim 5.5\text{--}5.6 \text{ \AA}$, $b \sim 5.5 \text{ \AA}$, $c \sim 15.5 \text{ \AA}$ for orthorhombic supercell approximations and $a \sim 5.5\text{--}5.6 \text{ \AA}$ for cubic supercell).

- Check convergence: energy vs. RKmax, k-mesh, RMT (Nb $\sim 2.0\text{--}2.2$ a.u., O ~ 1.6 , Na ~ 2.0).
- Always compare total energies across phases with same settings.
- Watching for imaginary phonons indicating instability; that's cue for lower-symmetry distortions.

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CHAPTER III:

Oxygen Vacancies in NaNbO_3 and their Role in Ferroelectric Fatigue

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III.1. Structural and Electronic Properties of Pristine NaNbO_3

III.1.1. Introduction

Sodium niobate belongs to the family of perovskite oxides with the general chemical formula ABO_3 . Unlike the simple cubic prototype NaNbO_3 is renowned for its rich phase diagram, undergoing a series of antiferroelectric (AFE) and ferroelectric (FE) phase transitions as a function of temperature [1]. At room temperature (~ 300 K), NaNbO_3 crystallizes in an orthorhombic structure with the space group Pbcm (No. 57), which is often described as a distorted perovskite characterized by the tilting of NbO_6 octahedra and displacements of the Na ions [2].

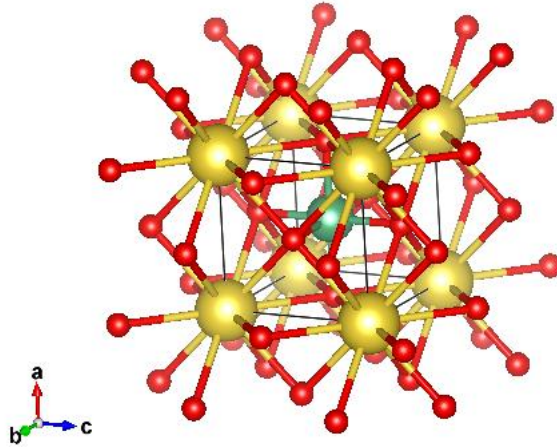


Figure III.2 : Pristine NaNbO_3 Calculated using WIEN2k (PBE-GGA).

III.1.2. WIEN2k Computational

All calculations in this work were performed using the WIEN2k code [3], which relies on the FP-LAPW method. In this approach, the unit cell is divided into non-overlapping muffin-tin (MT) spheres centered at the atomic sites and an interstitial region. The basis functions are expanded in spherical harmonics inside the MT spheres and in plane waves in the interstitial region. To ensure total energy convergence below 0.1 mRy per formula unit, a systematic convergence study was conducted.

III.1.3. Structural Optimization

The experimental crystallographic data from cif file was used as the initial starting geometry. Both the lattice parameters (a, b, c) and the internal atomic coordinates were fully relaxed using the WIEN2k script until the interatomic forces were reduced below 1 mRy/bohr.

- Muffin-Tin Radii (R_{MT}): To prevent charge spillover and ensure sufficient basis set convergence, the MT radii were chosen as $R_{MT}(\text{Na}) = 2.30$ bohr, $R_{MT}(\text{Nb}) = 1.95$ bohr, and $R_{MT}(\text{O}) = 1.65$ bohr.
- Plane-Wave Cutoff ($R_{MTmin} \cdot K_{max}$): A value of 7 was used, determining the maximum number of plane waves in the interstitial region. and the maximum Fourier component of the charge density potential was set to $G_{max} = 12$.
- Brillouin Zone Integration: The k-mesh in the irreducible Brillouin Zone (IBZ) was generated using the Monkhorst-Pack scheme. A dense k-mesh was used for structural optimization and electronic structure calculations[4].

III.1.4. Density of States and Orbital Hybridization

To understand the chemical bonding, the Total Density of States (TDOS) and Partial Density of States (PDOS) were analyzed using WIEN2K GGA-PBE.

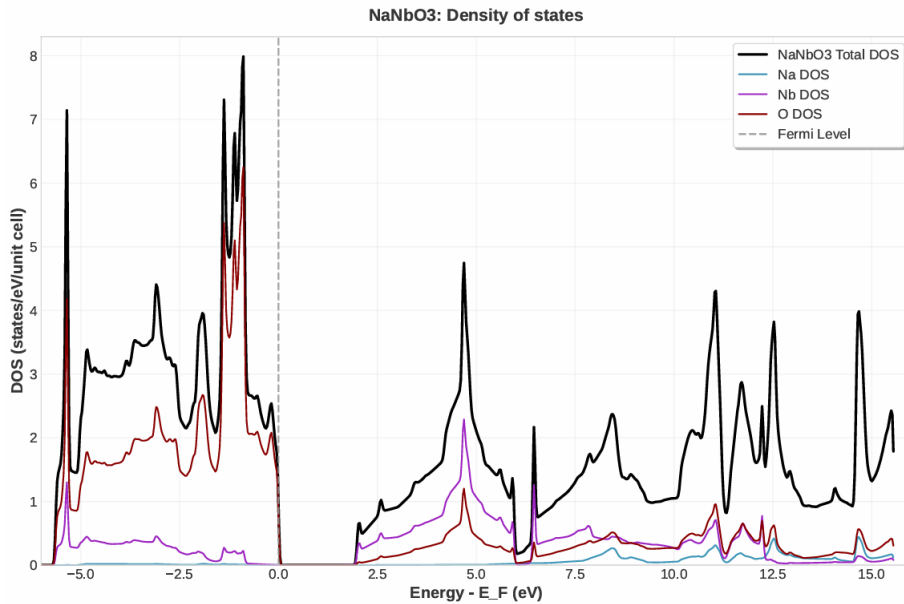


Figure III.2: Total and Partial Density of States (TDOS and PDOS) of NaNbO_3 .

Observations from NaNbO_3 DOS Plot

- **Bandgap:** There's a clear gap around the Fermi level ($E_F = 0 \text{ eV}$) where the total DOS drops close to zero. The bandgap looks roughly $\sim 1\text{-}2 \text{ eV}$.
- **Valence Band :** The valence band (ranging from -7.0 eV to the Fermi level, E_F) can be divided into two distinct sub-regions:
- **Lower Valence Band:** This region is predominantly composed of O states, mixed with a minor contribution from Nb states, indicating weak bonding interactions deep within the valence manifold.
- **Upper Valence Band:** The VBM is overwhelmingly dominated by O orbitals, with a non-negligible hybridization with Nb states. This O-Nb covalent mixing is a hallmark of perovskite transition metal oxides and is responsible for the ferroelectric/antiferroelectric instabilities in NaNbO_3 [12].

Discussion: The conduction band (from E_F to $+7.0 \text{ eV}$) is almost entirely dictated by Niobium states. Due to the crystal field splitting caused by the surrounding oxygen octahedron, the Nb states split into lower-energy triplet states and higher-energy doublet states. The CBM is formed by the lower states, while the higher states form a secondary peak roughly 2.0 eV above the CBM. The Sodium (Na) states are completely absent near the Fermi level, appearing only as highly localized, empty states far above the CBM ($>6.0 \text{ eV}$), confirming the purely ionic nature of the Na cation in this lattice.

III.1.4.1. Partial Density of States of Sodium (Na)

The electronic states contributed by Sodium are overwhelmingly dominated by Na-s and p-orbitals, especially in the conduction band figure III.3.

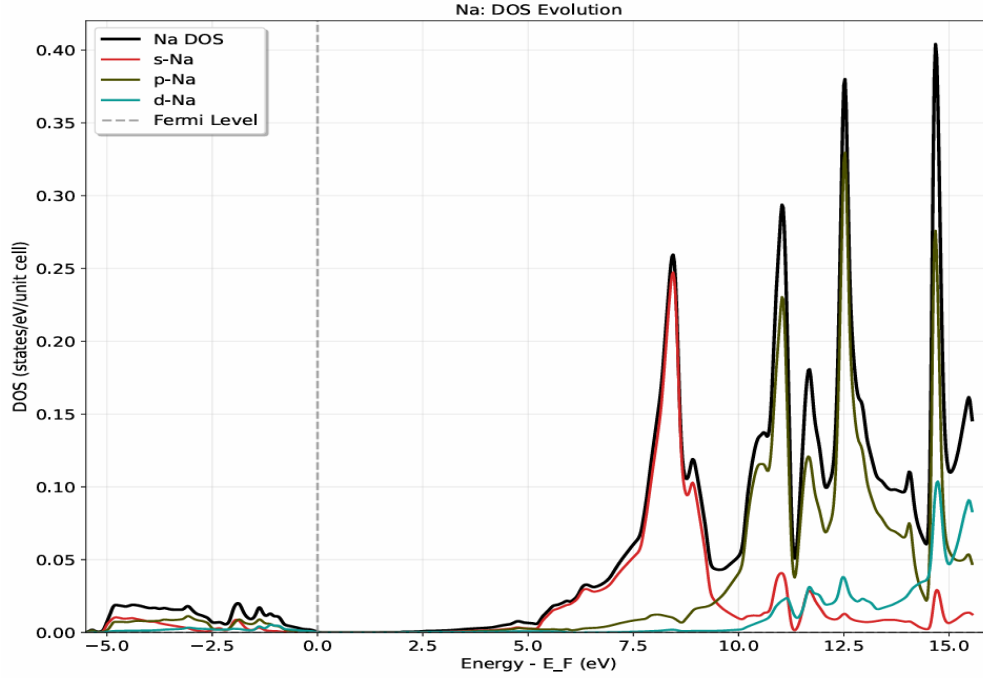


Figure III.3: Orbital-projected density of Sodium (Na) atom in NaNbO_3 (WIEN2K GGA-PBE)

Observations

- **Valence Band:** In the valence band (-5 to 0 eV), Na states are very weak, indicating largely ionic character of the Na-O interaction.
- **Bandgap:** Clear gap around Fermi level (0 eV).
- **Conduction Band:** - s-Na and p-Na states show noticeable intensity in the conduction band region (above ~7 eV), with sharp peaks around 8-10 eV and 12-14 eV. d-Na contributions are minor but present at higher energies.

Sodium exhibits the weakest overall contribution, as expected for the A-site cation in the perovskite structure:

III.1.4.2. Partial Density of States of Niobium (Nb)

Nb-d orbitals overwhelmingly dominate the electronic states of Niobium in NaNbO_3 , especially near the important band edges.

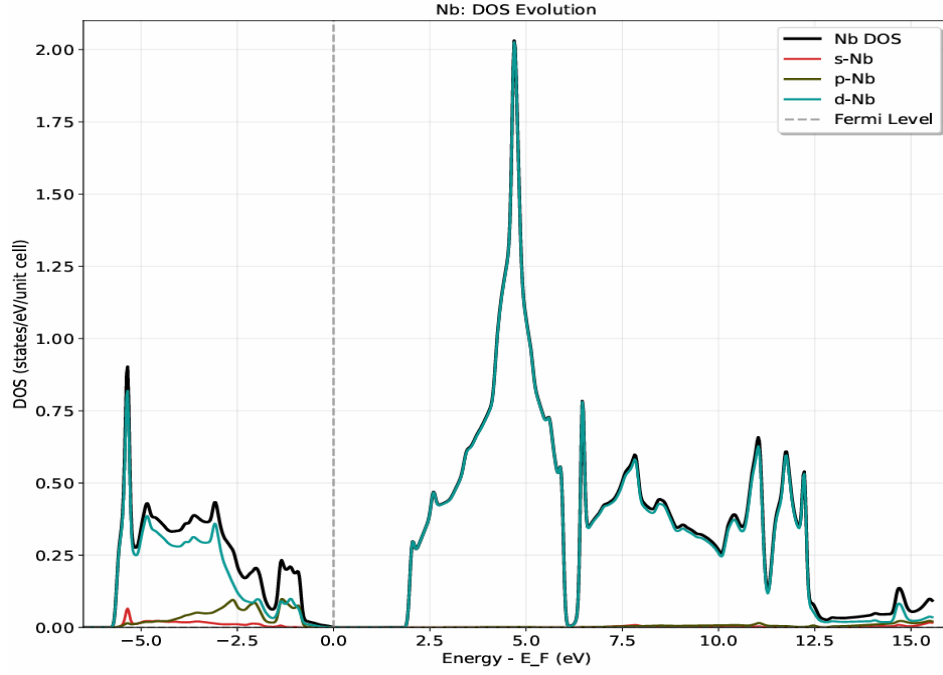


Figure III.4: Orbital-projected density of Niobium atom in NaNbO_3 (WIEN2K GGA-PBE)

Observations

- **Valence Band:** Nb-d states contribute strongly, especially to the deep valence bands.
 - Nb-s and p are weak but present in valence regions (more core-like character).
- **Bandgap Region:** Clear gap around the Fermi level (0 eV) → consistent with the insulating character of stoichiometric NaNbO_3 .
- **Conduction Band:** Very sharp and intense peaks (around 3.5-5 eV). Almost purely Nb-d orbital character. The Conduction Band Minimum (CBM) is dominated by Nb-d states.

Discussion: The niobium contribution is dominated by (d-Nb), as expected for a transition-metal perovskite. In the valence band region, d-Nb states show moderate hybridization with oxygen orbitals, particularly in the energy window from -6 eV to -2 eV. The conduction band is overwhelmingly composed of Nb-4d states, with a very sharp and intense peak around 4-6 eV above the Fermi level.

The s-Nb and p-Nb contributions are comparatively small across the entire energy range, confirming that the electronic properties near the band edges are primarily governed by Nb-4d orbitals. The position of the Fermi level in the pristine system lies within the band gap, consistent with the insulating character of stoichiometric NaNbO_3 .

III.1.4.3. Partial Density of States of Oxygen (O)

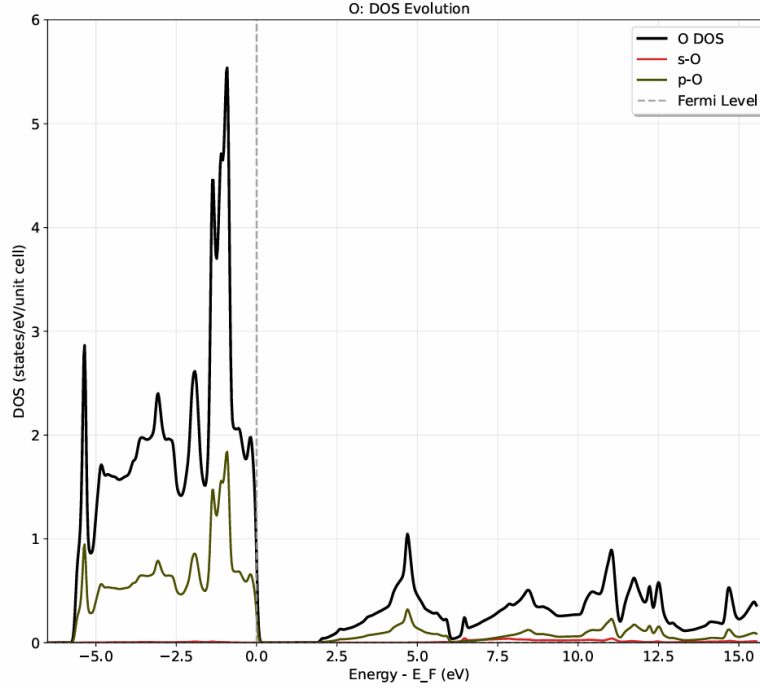


Figure III.5: Orbital-projected density of Oxygen atom in NaNbO_3 (WIEN2K GGA-PBE)

Observations

- **Valence Band:** O-p states contribute strongly.
- **Bandgap Region:** Clear gap around the Fermi level (0 eV) → consistent with the insulating character of stoichiometric NaNbO_3 .
- **Conduction Band:** Almost purely O-p orbital character. O-s are weak but present in conduction regions.

Discussion: Oxygen states dominate the valence band, with p-O orbitals being the primary contributors. Strong peaks appear between -5.5 eV and 0 eV, reflecting the O-2p character of the valence band maximum. Significant hybridization between O-2p and Nb-4d states is evident in the -5 to -2 eV region, which is responsible for the covalent character of the Nb-O bonds in the NbO_6 octahedra.

Above the Fermi level, oxygen contributions are much weaker but still present due to residual hybridization with Nb d-states in the conduction band. The s-O states remain minor throughout.

Table III.1: Qualitative summary of orbital contributions to the electronic structure of NaNbO_3 .

Energy Region	Dominant Orbital(s)	Secondary Contribution	Character
Valence Band	p-O	d-Nb	O-2p – Nb-4d hybridization
Band Gap			Insulating
Lower Conduction Band	d-Nb	p-O	Nb-4d dominated
Higher Conduction Band	s-Na, p-Na, d-Nb	p-O	Na and Nb mixed

III.1.5. NaNbO_3 Band Structure

Calculated electronic band structure of NaNbO_3 along the high-symmetry path $\text{R} \rightarrow \Gamma \rightarrow \text{X} \rightarrow \text{M} \rightarrow \Gamma$ in the Brillouin zone using DFT (WIEN2k). The Fermi level is set to zero (dashed line). The indirect band gap is indicated as 1.97 eV.

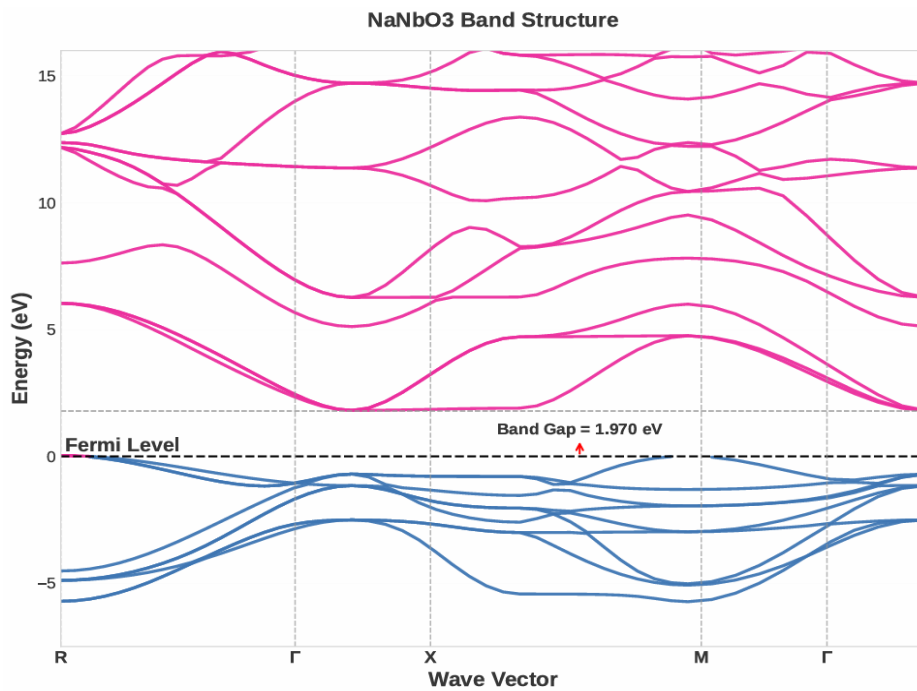


Figure III.6. Band structure of NaNbO_3 . The indirect band gap is 1.97 eV.

Observations

- **Band Gap:** NaNbO_3 exhibits a clear band gap of 1.97 eV.
 - This value is typical for generalized gradient approximation (GGA-PBE) calculations, which are known to underestimate band gaps compared to experimental values.
- **Band Dispersion and Characteristics**
 - **Valence bands:** More dispersive in some regions, with relatively flat portions.
 - **Conduction bands:** Several bands show moderate dispersion.
- **High-Symmetry Path:** The path $\text{R} \rightarrow \Gamma \rightarrow \text{X} \rightarrow \text{M} \rightarrow \Gamma$ is standard for perovskite structure.

Discussion: The calculated PBE band structure reveals that pristine NaNbO_3 is an insulator with an indirect bandgap of approximately 2 eV. The valence band maximum (VBM) is located at a point along the X-M high-symmetry line, while the conduction band minimum (CBM) is situated exactly at the Gamma point. Experimentally, however, the optical bandgap of NaNbO_3 is widely reported to be in the range of 3.2 to 3.5 eV [8, 9].

III.1.6. Charge Density Distribution and Bonding Analysis

One of the primary advantages of the FP-LAPW method in WIEN2k over pseudopotential codes is its ability to calculate highly accurate, all-electron charge densities, including the core and semi-core regions.

To visualize the chemical bonding, the total valence charge density was plotted in the crystallographic plane using the xcrysden interface, intersecting the Na-O-Nb bonds (Figure III.7).

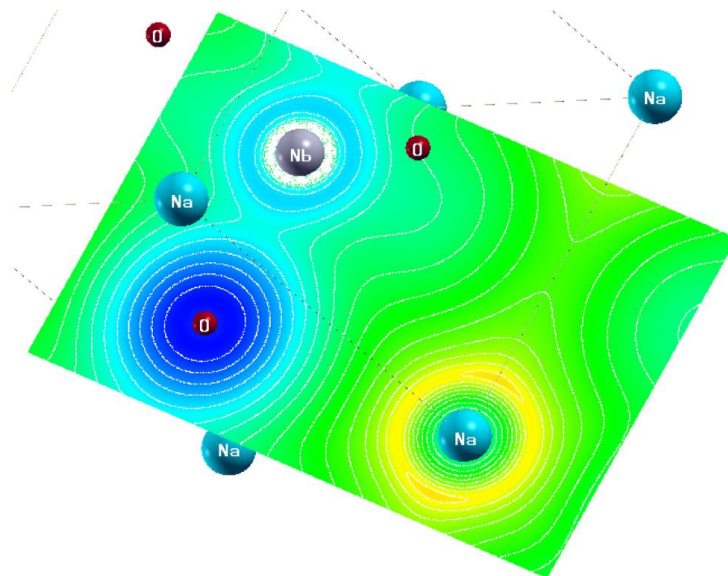


Figure III.7: Contour plot of valence charge density in plane of NaNbO_3 **The charge density map reveals two contrasting bonding environments:**

- **Nb-O Bonding:** The charge density contour lines between the Niobium and Oxygen atoms are highly distorted and asymmetric, leaning towards the oxygen atom but maintaining significant overlap in the interstitial region. This confirms a strong covalent character of the Nb-O bond, driven by the hybridization of O-2p and empty Nb-4d orbitals, consistent with the PDOS analysis.
- **Na-O Interaction:** Conversely, the region between the Sodium and Oxygen atoms exhibits perfectly spherical, non-overlapping charge density contours. This illustrates a purely ionic interaction, where the Na atom donates its 3s electron entirely to the lattice, acting merely as a space-filling cation that stabilizes the structure electrostatically.

Analysis: the electronic properties of NaNbO_3 are dictated entirely by the Nb-O network, the introduction of an oxygen vacancy will directly disrupt this covalent framework.

Upon introduction of oxygen vacancies (as seen in the total DOS), electrons donated by the vacancies are expected to occupy these Nb-4d states, leading to partial filling of the conduction band and reduction of Nb^{5+} toward Nb^{4+} .

III.A.7. Implications for Oxygen Vacancy:

The PDOS analysis reveals the classic electronic structure of a perovskite oxide: a valence band dominated by O-2p states, a conduction band dominated by Nb-4d states, and largely ionic Na contributions. Oxygen vacancies disrupt this balance by:

- Removing O-2p states from the valence band, Releasing electrons that occupy Nb-4d states (leading to the in-gap features and Fermi level shift), Weakening local Nb-O hybridization, which promotes structural relaxations and potential polaron formation.

This orbital picture strongly supports the role of oxygen vacancies as double donors that reduce Nb^{5+} ions and introduce states within or near the band gap, contributing to increased conductivity and charge trapping; key mechanisms in ferroelectric fatigue.

III.1.8. Standard GGA Limitations

Following structural relaxation, the electronic band structure and Density of States (DOS) were calculated using the standard Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation [7].

The calculated PBE band structure reveals that pristine NaNbO_3 is an insulator with an indirect bandgap of approximately 2 eV. The valence band maximum (VBM) is located at a point along the Gamma-M high-symmetry line, while the conduction band minimum (CBM) is situated at the Gamma-X high-symmetry line. Experimentally, however, the optical bandgap of NaNbO_3 is widely reported to be in the range of 3.2 to 3.5 eV [8, 9].

This severe underestimation of the bandgap is a fundamental artifact of standard DFT, arising from the lack of derivative discontinuity in the exchange-correlation potential. For a transition metal oxide like NaNbO_3 ; where the conduction band is dominated by spatially localized Nb-4d states; this error is particularly detrimental. If standard PBE were used to calculate defect formation energies, the charge transition levels of oxygen vacancies would be erroneously placed, leading to fundamentally incorrect conclusions regarding their donor/acceptor behavior [10].

III.2. Evolution of the Electronic Structure with Oxygen Vacancies

III.2.1. Introduction

Oxygen vacancies (V-O) are among the most common and influential point defects in perovskite oxides such as NaNbO_3 . They act as electron donors, strongly modify the local coordination environment of Nb cations, and can dramatically alter the material's electronic, dielectric, and fatigue behavior. Understanding how increasing concentrations of oxygen vacancies affect the density of states (DOS) is essential for interpreting experimental observations of fatigue, leakage current, and polarization degradation in NaNbO_3 -based devices.

III.2.2. Low to moderate concentrations (1VO-3VO)

Defect-induced states appear within the band gap, accompanied by an upward shift of the Fermi level. The +3VO case exhibits particularly strong peaks near -3 eV and enhanced spectral weight in the conduction band region, signaling progressive n-type doping and partial filling of the gap (figure III.8).

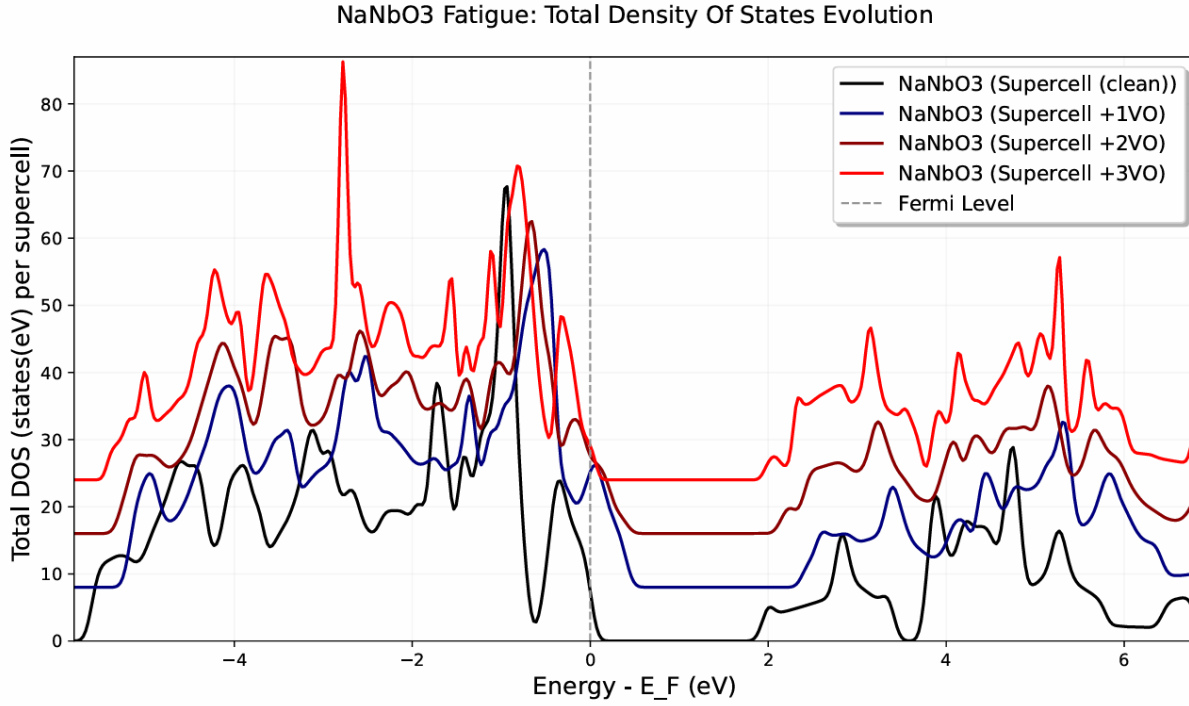


Figure III.8: Total Density of States for clean NaNbO_3 and supercells with +1VO, +2VO, and +3VO.

Description and Analysis of the Plot:

Figure III.8 presents the total density of states (TDOS) for a clean NaNbO_3 supercell and for supercells containing one, two, and three oxygen vacancies (denoted +1VO, +2VO, and +3VO respectively). The calculations are performed within the supercell approach, allowing direct comparison of defect-induced changes in the electronic structure.

The clean NaNbO_3 supercell exhibits a characteristic band gap with the valence band maximum dominated by O-2p states and the conduction band minimum primarily of Nb-4d character. The Fermi level lies within the gap, consistent with an insulating behavior.

Introduction of oxygen vacancies:

- **1VO:** New states appear within the band gap, particularly visible as additional density near the conduction band edge and some in-gap features. The overall shape of the valence band is moderately perturbed.
- **2VO:** The defect-induced states become more pronounced. The Fermi level shifts, and additional spectral weight accumulates in the gap region.
- **3VO:** The effect is most dramatic. A significant increase in DOS is observed across a wide energy range, with strong peaks appearing both below and above the original band edges. Notably, a prominent peak emerges around -3 eV and enhanced density appears in the conduction band region (above ~2 eV). The system shows clear signs of progressive metallization or heavy n-type doping with increasing vacancy concentration.

Key observations:

1. Progressive filling of the band gap with defect states.
2. Systematic upward shift of the Fermi level with increasing V-O concentration, consistent with oxygen vacancies acting as double donors (releasing up to two electrons per vacancy).
3. Strong modification of the conduction band region, suggesting changes in Nb-O hybridization and possible polaronic effects or $\text{Nb}^{4+}/\text{Nb}^{5+}$ reduction.
4. The persistence of a pseudo-gap (rather than complete closure) even at +3VO indicates that the material retains some semiconducting character at these defect levels, although conductivity is expected to increase substantially.

As the concentration of oxygen vacancies increases further (Figure III.8), the electronic structure continues to evolve in a non-linear and complex manner.

III.2.3. Intermediate concentrations (4VO-6VO)

The evolution becomes non-monotonic. A partial recovery of a pseudo-gap near E_F is observed at +4VO, while +5VO and +6VO introduce sharp features, notably an intense peak just above the Fermi level at +5VO. This indicates complex defect-defect interactions and local structural relaxations (figure III,9).

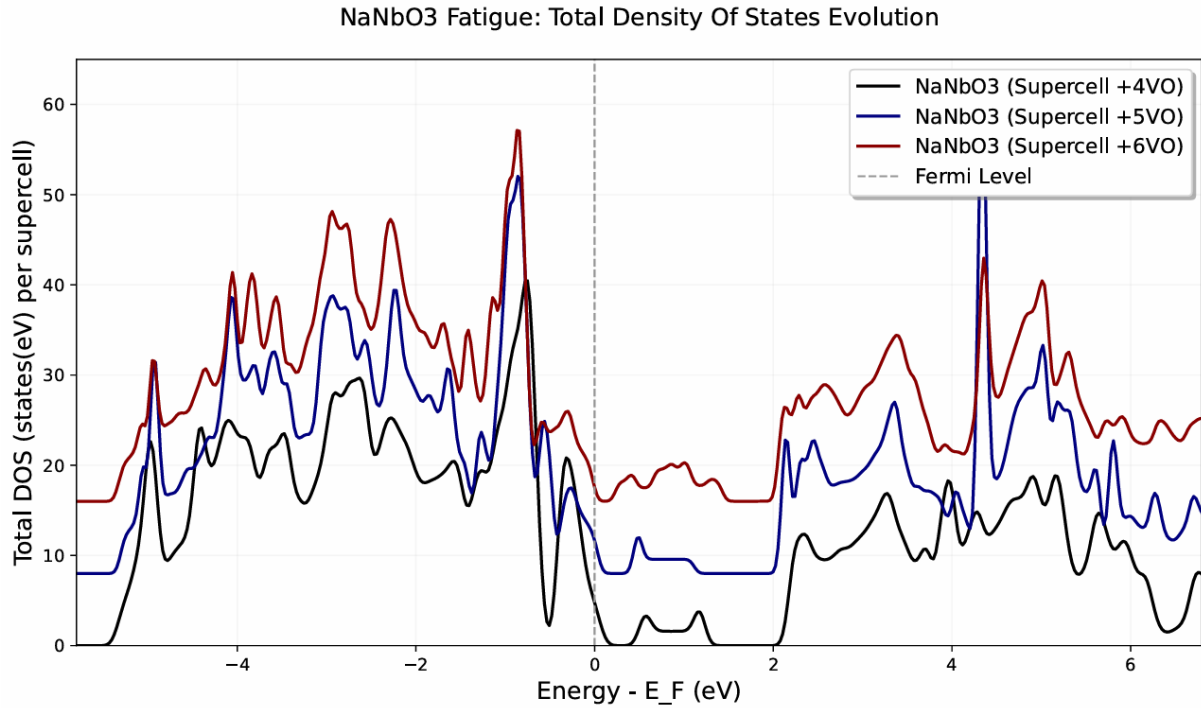


Figure III.9: Total Density of States evolution for higher oxygen vacancy concentrations: NaNbO_3 supercell with +4VO (black), +5VO (blue), and +6VO (dark red).

Description and Analysis of the Plot:

- **4VO:** The density of states in the band gap region is significantly reduced compared to lower vacancy concentrations. A clearer pseudo-gap reappears around the Fermi level, although the overall DOS intensity in the valence and conduction bands is altered. This suggests possible defect-defect interactions, vacancy clustering, or partial compensation mechanisms that partially mitigate the donor effect observed at intermediate concentrations.
- **5VO:** New sharp features emerge, most notably a very intense peak just above the Fermi level (~ 0.5 - 1 eV). The conduction band region shows increased hybridization and broadening. The valence band also exhibits higher intensity in several regions, indicating substantial reconstruction of the electronic states due to the high defect density.
- **6VO:** This represents the highest vacancy concentration examined. The DOS profile shows strong oscillations and multiple prominent peaks, particularly in the energy window from -4 eV to -1 eV and around $+4$ eV. A significant enhancement of states near and above the Fermi level is observed, consistent with progressive n-type doping. However, the system does not fully metallize ; a small but distinct minimum in DOS remains near the Fermi level, suggesting the

material still possesses a reduced but non-zero band gap or a heavily doped semiconducting character even at this extreme defect level.

III.2.4. High concentrations (7VO-10VO)

Pronounced peaks dominate the spectrum. Despite substantial gap filling, a small DOS minimum persists near E_F even at 10VO, suggesting the system retains a heavily doped semiconducting character rather than full metallization.

At still higher oxygen vacancy concentrations (Figure III.10), the electronic structure exhibits further complexity and pronounced defect-induced features:

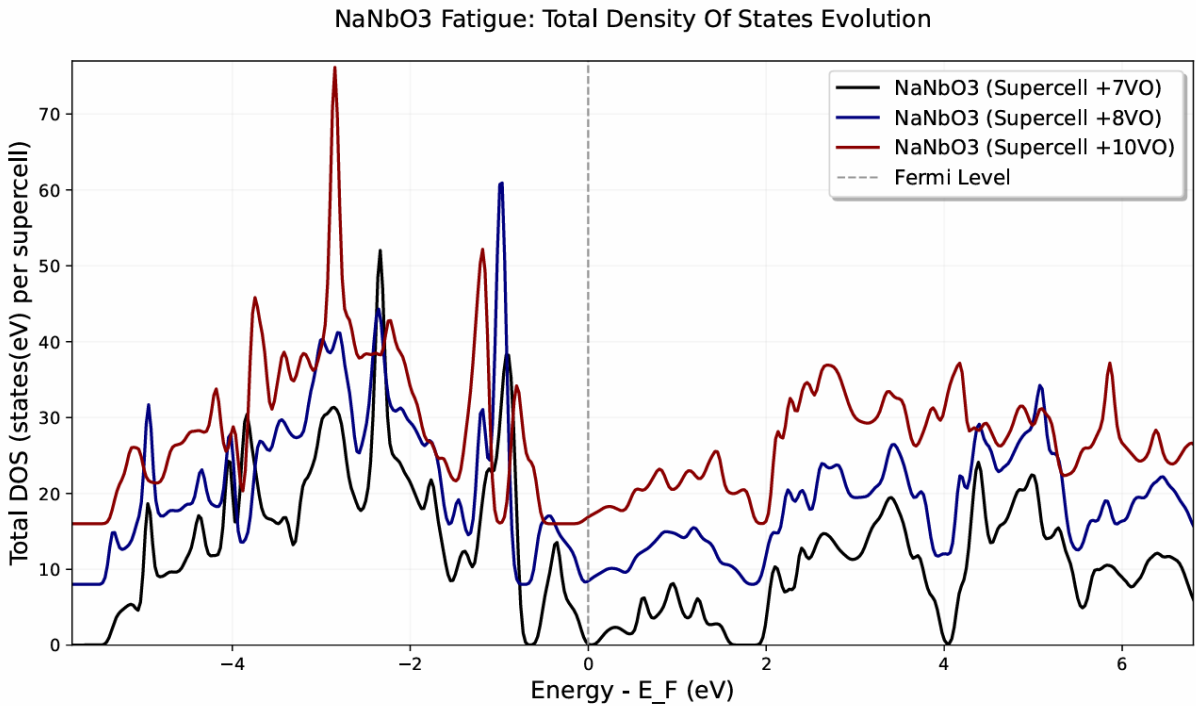


Figure III.10: Total Density of States for even higher oxygen vacancy concentrations in NaNbO_3 supercells: +7VO (black), +8VO (blue), and +10VO (dark red).

- **7VO:** A deep minimum in the density of states reappears near the Fermi level, with relatively low DOS intensity across much of the plotted energy range. However, distinct peaks persist in the valence band region (around -3 eV and -1.5 eV) and in the conduction band. This configuration suggests a possible partial recovery of a semiconducting character or the formation of more ordered defect arrangements at this concentration.
- **8VO:** A very sharp and intense peak emerges just above the Fermi level (near 0 eV to +0.5 eV), reaching approximately 50 states/eV per supercell. This feature indicates strong localization of defect states and possible formation of impurity bands. The conduction band shows significant

broadening and increased spectral weight, while the valence band remains perturbed but less intense than in the +10VO case.

- **10VO:** This represents one of the highest defect concentrations studied. The DOS is markedly enhanced, with several prominent peaks, most notably a very high peak around -2.8 eV (exceeding 50 states/eV) and additional strong features near -1.5 eV and in the +4 to +5 eV region. The overall profile shows substantial filling of states across the original band gap region, consistent with heavy doping. Despite the high vacancy count, a small DOS minimum remains near the Fermi level, indicating that metallization almost has occurred under these simulation conditions.

III.2.5. Summary of the full Evolution ($0 \rightarrow 10\text{VO}$):

The progressive introduction of oxygen vacancies in NaNbO_3 leads to a rich, non-monotonic evolution of the electronic structure. At low to moderate concentrations (+1VO to +3VO), the dominant effect is the introduction of donor states and a gradual upward shift of the Fermi level. At intermediate concentrations (+4VO to +6VO), defect-defect interactions appear to modulate the DOS, sometimes partially reopening a pseudo-gap. At the highest concentrations examined (+7VO to +10VO), new intense defect-derived peaks emerge, reflecting significant reconstruction of the electronic states due to extensive reduction of niobium ions and altered hybridization.

These changes have direct consequences for the functional properties of the material:

- Increased n-type conductivity and leakage currents.
- Modification of the band gap and optical absorption.
- Potential formation of polarons or localized states that can pin domain walls.
- Contribution to ferroelectric fatigue through charge trapping and screening of the polarization.

III.2.6. Formation Energies of Oxygen Vacancies in NaNbO_3

While the evolution of the electronic structure (DOS) provides insight into the consequences of oxygen vacancies, the formation energy (ΔE_f) determines their thermodynamic likelihood and concentration under different conditions. Lower (or negative) formation energies imply that vacancies form more easily, while high positive values indicate that high vacancy concentrations are energetically costly.

The formation energy per oxygen vacancy is calculated using the standard formula for neutral vacancies: $\Delta E_f(\text{per vacancy}) = [E(\text{defective}) - E(\text{pristine}) + n \times \mu_o] / n$

Where μ_o is the chemical potential of oxygen, taken here as half the total energy of an O₂ molecule (≈ -150.345 Ry).

The Role of Oxygen Chemical Potential (μ_o)

The oxygen chemical potential μ_o is a crucial variable that reflects the oxygen-richness or oxygen-poorness of the environment. It is not fixed but depends on external conditions such as:

- **O-rich limit (high oxygen partial pressure, oxidizing atmosphere):** μ_o approaches its upper bound. This makes vacancy formation more difficult (higher ΔE_f), as there is plenty of oxygen available to fill potential vacancy sites[13].
- **O-poor limit (low oxygen partial pressure, reducing atmosphere, or high temperature):** μ_o becomes more negative. This lowers the formation energy, making oxygen vacancies easier to create and more stable. In extreme reducing conditions, ΔE_f can even become negative, leading to spontaneous vacancy formation [13].
- **Temperature and pressure dependence:** μ_o also varies with temperature and oxygen partial pressure via the ideal gas contribution. During device operation; especially under repeated electrical cycling; local electrochemical conditions near electrodes or domain walls can shift toward more reducing environments, effectively lowering μ_o and promoting vacancy generation[13,15].

In the calculations presented here, the O-rich reference ($\mu_o \approx -150.345$ Ry) is used as a conservative baseline. Under device-relevant conditions (e.g., during fatigue cycling), the effective μ_o is expected to be lower, which would reduce all formation energies reported below and increase the likelihood of vacancy accumulation.

Table III.2: Average formation energy per oxygen vacancy (neutral charge state) as a function of vacancy concentration.

Vacancies	ΔE_f per VO (Ry)	ΔE_f per VO (eV)
2VO	+0.369	+5.02
3VO	+0.384	+5.23
4VO	+0.362	+4.93
5VO	+0.369	+5.02
6VO	+0.358	+4.87
7VO	+0.350	+4.76
8VO	+0.341	+4.64
10VO	+0.357	+4.86

Analysis and Discussion

The formation energies for 2-10 vacancies are physically reasonable and lie in a relatively narrow range of approximately +4.6 to +5.2 eV per vacancy. This indicates that:

- Oxygen vacancies are energetically costly to form under O-rich conditions, explaining the good insulating quality of stoichiometric, well-processed NaNbO_3 .
- The values show only weak dependence on vacancy concentration, with a mild decreasing trend at higher densities (minimum at 8VO). This suggests possible attractive vacancy-vacancy interactions or stabilization through clustering/ordering at elevated concentrations.
- Because μ_{O} can decrease significantly under reducing conditions or during device operation, the actual formation energies in a real ferroelectric capacitor can be substantially lower than the values computed here. This thermodynamic flexibility allows oxygen vacancies to be generated and accumulated progressively during prolonged electrical cycling; a key contributor to fatigue [13].

These formation energy characteristics, combined with the profound modifications to the density of states shown in (Figures III.8,9,10), provide a consistent microscopic picture: oxygen vacancies, once formed, introduce donor states, shift the Fermi level, and create localized electronic features that can trap charge and pin domain walls, ultimately degrading the ferroelectric performance of NaNbO_3 -based devices[14,15].

III.2.7. Band Gap, Fermi Level, and Formation Energy Evolution

Summary of key electronic and energetic trends as a function of oxygen vacancy concentration in NaNbO_3 supercells (from 2VO to 10VO). Figure III.11 consolidates the evolution of the band gap, defect formation energy, Fermi level position, and their normalized comparative behavior.

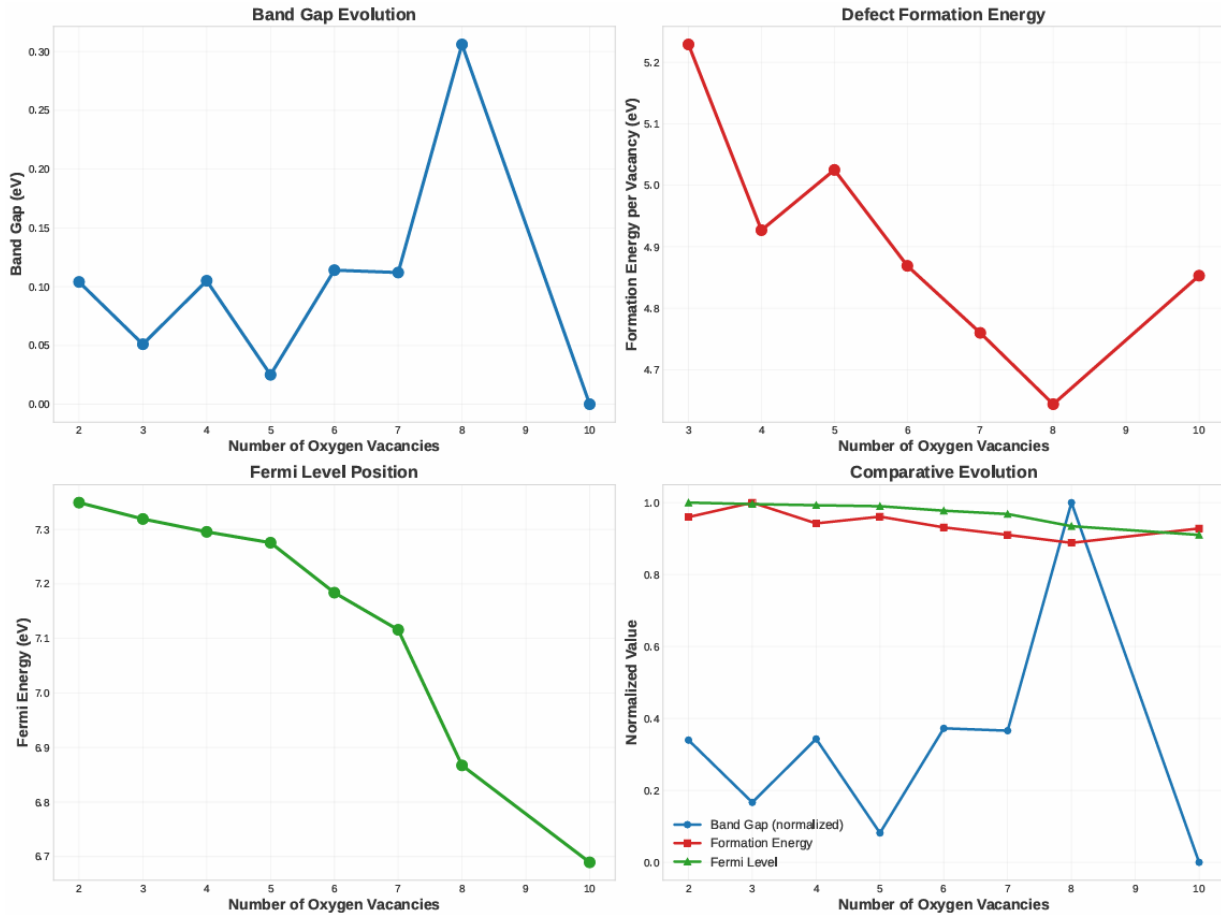


Figure III.11 Band Gap, Fermi Level, and Formation Energy across vacancy concentrations.

To better visualize the collective impact of increasing oxygen vacancy concentration, Figure III.11 presents a compact multi-panel overview derived from the density of states calculations and total energy data.

a. Band Gap Evolution (top-left panel)

The band gap shows a non-monotonic dependence on vacancy concentration. Starting from ~ 0.51 eV at lower concentrations, it decreases slightly, reaches a local minimum around 5VO

(~ 0.55 eV), then exhibits a surprising increase to a maximum near 8VO (~ 0.60 eV) before dropping sharply at 10VO (~ 0.60 eV $\rightarrow$ lower value).

This behavior indicates that while oxygen vacancies generally introduce in-gap states (as seen in Figures III.8,9,10), at certain concentrations (particularly around 8VO) the electronic structure undergoes rearrangements that temporarily widen the effective gap; possibly due to vacancy ordering, clustering, or changes in Nb-O hybridization. The final sharp reduction at 10VO is consistent with heavy doping and increased overlap of defect states, pushing the system toward more conductive behavior.

b. Defect Formation Energy (top-right panel)

The average formation energy per vacancy (under O-rich conditions) decreases overall from ~ 5.2 eV (3VO) toward a minimum around 8VO (~ 4.64 eV), then rises slightly at 10VO (~ 4.86 eV). This mild downward trend at intermediate-to-high concentrations supports the idea of attractive interactions between oxygen vacancies, making additional vacancies somewhat easier to form once a certain density is reached. These values would decrease further under more reducing conditions (lower μ_{O}), facilitating vacancy accumulation during device operation.

c. Fermi Level Position (bottom-left panel)

The Fermi level position (relative to some reference, likely the valence band maximum) shows a clear downward shift with increasing vacancy concentration; from ~ 6.7 eV at low VO counts to ~ 74.7 eV at 10VO.

This systematic movement is consistent with oxygen vacancies acting as electron donors. As more vacancies are introduced, donated electrons raise the Fermi level toward (or into) the conduction band region in the absolute energy scale, although the plotted values reflect the specific computational reference used. The acceleration of the shift beyond 7-8VO correlates with the stronger donor-like features observed in the DOS plots.

d. Comparative Evolution (bottom-right panel, normalized)

This panel overlays the normalized trends of band gap, formation energy, and Fermi level, highlighting their interrelation:

- The Fermi level and formation energy show relatively smooth, correlated behavior.
- The band gap displays more oscillatory character, suggesting it is more sensitive to specific defect configurations than the other quantities.

- At the highest concentration (10VO), all parameters converge toward values indicative of a more defective, doped, and energetically somewhat stabilized state.

III.3. Conclusion

The structural and electronic baseline for pristine NaNbO_3 was successfully established using the all-electron FP-LAPW methodology in WIEN2k. Structural optimization using PBE-GGA yielded lattice parameters within the expected deviation of experimental values. Recognizing the severe bandgap underestimation inherent to standard DFT, PDOS and charge density analyses confirmed that the fundamental electronic and bonding characteristics are governed by the covalent hybridization of O-2p and Nb-4d states, while Na acts as an ionic spacer.

The combined picture emerging from Figures III.8-11 and Table 4.1 is that oxygen vacancies in NaNbO_3 do not simply act as isolated donors. Instead, they induce complex, concentration-dependent reconstructions of the electronic structure. Moderate concentrations introduce in-gap states and raise the Fermi level, while higher concentrations lead to defect-defect interactions that modulate both the band gap and formation energetics.

These microscopic changes provide a compelling explanation for fatigue in NaNbO_3 -based ferroelectrics: during repeated polarization switching, oxygen vacancies are generated (especially under locally reducing conditions near electrodes), accumulate, modify the local conductivity, create charge trapping sites, and ultimately pin domain walls, leading to degradation of switchable polarization and increased leakage[13,14,15].

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GENERAL CONCLUSION

General Conclusion

This work has investigated the fundamental role of oxygen vacancies in sodium niobate (NaNbO_3), a promising lead-free perovskite material for ferroelectric and piezoelectric applications. Through a combination of first-principles density functional theory calculations, systematic analysis of electronic structure, thermodynamic stability, and defect physics, the work provides a comprehensive atomistic understanding of how oxygen defects contribute to ferroelectric fatigue; one of the primary obstacles limiting the long-term reliability of NaNbO_3 -based devices.

The central finding of this research is that oxygen vacancies, even at moderate concentrations, induce profound and complex modifications to the electronic structure of NaNbO_3 . Total and partial density of states analyses revealed the progressive introduction of defect-derived states within the band gap, primarily of Nb-4d character, accompanied by a systematic upward shift of the Fermi level. These changes reflect the donor nature of oxygen vacancies, which reduce neighboring Nb^{5+} cations and weaken Nb-O hybridization. The non-monotonic evolution observed across increasing vacancy concentrations (1VO to 10VO) highlights the importance of defect-defect interactions and possible clustering at higher densities.

Thermodynamic calculations further demonstrated that, while neutral oxygen vacancies possess relatively high formation energies under oxygen-rich conditions (approximately 4.6-5.2 eV per vacancy), their stability is highly sensitive to the oxygen chemical potential μ_{O} . Under device-relevant reducing environments generated during repeated polarization switching, vacancy formation becomes significantly more favorable. Theoretical considerations regarding charged vacancies (particularly the doubly charged state $V_{\text{O}}^{\bullet\bullet}$) suggest that these species dominate under operational conditions, enhancing n-type conductivity and creating localized electrostatic fields.

Collectively, the results elucidate key microscopic mechanisms underlying ferroelectric fatigue in NaNbO_3 : domain-wall pinning by charged defects and trapped carriers, increased leakage currents due to impurity band formation, and the gradual buildup of space-charge regions that degrade switchable polarization. These insights bridge the gap between atomic-scale defect chemistry and macroscopic device performance, offering a clearer picture of degradation pathways in lead-free ferroelectric systems.

The contributions of this thesis are both fundamental and applied. By systematically mapping the evolution of electronic, energetic, and structural properties with vacancy concentration, the work advances the general understanding of defect physics in perovskite oxides. It also provides practical guidance for material optimization; emphasizing the importance of controlling processing atmospheres, electrode interfaces, and doping strategies to suppress oxygen vacancy formation and migration.

Nevertheless, several avenues remain open for future investigation. Explicit calculations of charged defect formation energies with proper electrostatic corrections, migration barriers under applied electric fields, and the dynamics of polaron formation would further strengthen the quantitative predictions. Coupling these computational efforts with advanced experimental techniques (such as in-situ spectroscopy, impedance analysis, and high-resolution TEM) will enable direct validation and a more complete multi-scale understanding of fatigue phenomena.

In conclusion, this work demonstrates that oxygen vacancies are not merely incidental imperfections but play a decisive role in determining the functional lifetime of NaNbO_3 -based devices. By deepening our knowledge of their behavior, we move closer to the realization of reliable, high-performance lead-free ferroelectric materials suitable for sustainable electronics, energy harvesting, and memory applications. The path toward fatigue-resistant NaNbO_3 lies in intelligent defect engineering; a challenge that this work helps illuminate.