

Influence of donor and acceptor doping on conductivity in potassium niobate

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Lead-free ferroelectrics based on the (K, Na)NbO₃ solid solution have emerged as strong candidates to replace lead-containing ceramics due to their excellent piezoelectric and thermal properties. However, their practical application is hindered by high leakage currents and low ceramic density. Doping provides a strategy for enhancing material performance, highlighting the need for a deeper understanding of defect chemistry. For this purpose, we investigated the equilibrium of intrinsic defects and the doping behavior of Ca and Fe in the boundary phase KNbO₃. We have found all elements to be prone to vacancy formation. Moreover, Ca acts as a donor and leads to a large concentration of charge carriers and therefore larger electronic conductivity. On the other hand, Fe behaves as an acceptor and shows oxidation states ranging from 2⁺ to 5⁺, whose concentrations depend on the total Fe concentration. As a consequence, the number of charge carriers and the electronic conductivity are reduced.

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I. INTRODUCTION

Lead-free ferroelectrics have been researched for around 20 years as environmentally friendly and high-performance substitute materials for lead-containing ceramics [1–3]. In particular, their piezoelectric properties have been the central focus of research interest for actuator applications. So far, mixed systems based on (K_{0.5}Na_{0.5})NbO₃ (KNN), improved in 2004 by Saito *et al.* at Toyota [4], have proven to be promising material systems. They are characterized by a large piezoelectric coefficient d_{33} , excellent strain properties, a high Curie temperature T_C , and a high mechanical quality factor Q_m [2].

Despite optimized piezoelectric and ferroelectric properties, KNN is still rarely found in technical applications, with only a few exceptions. This is because the material typically exhibits high leakage currents and the ceramics often lack sufficient density [1,3,5]. Leakage currents arise from high grain boundary densities, internal surfaces in poorly sintered materials, and intrinsic defects or impurities that increase electrical conductivity. However, point defects also influence bulk and grain boundary diffusion, which is crucial for solid-state sintering. Therefore, a detailed understanding of the defect chemistry is essential for improving the material in terms of reduced leakage currents, improved sintering behavior, degradation, and aging.

Azadeh *et al.* [6] have studied the effect of Ca and Fe doping on the conductivity of KNN-based systems, observing

that Fe doping increases the conductivity of the system, while Ca doping leaves it unaffected. In general, they came to the conclusion that the impact of intrinsic defects on electrical properties exceeds the effect of extrinsic defects induced by doping. However, an accurate and quantitative study of the influence of donor and acceptor dopants on KNN systems is still missing. From a computational perspective, a perovskite system with more than three components presents several challenges, mainly due to the inability to capture site disorder effects with computational methods relying on periodicity, such as density functional theory (DFT). Körbel *et al.* [7,8] have addressed this four-component system using the Virtual Crystal Approximation, which replaces the two atom types of a binary system by one virtual atom type, which is created by mixing the properties (in this case the pseudopotentials that represent the atoms) in the required ratio. With this approach, they investigated the formation energies of vacancies and Cu and Fe substitutional defects. Although this method is optimal for systems that behave as ideal solutions, it cannot capture the effects of the short- and long-range site disorder typical of these perovskite systems.

In an effort to unveil the defect chemistry of the system with more than four components, we can gain important insights into the behavior of intrinsic and extrinsic defects by studying the two boundary phases, NaNbO₃ (NN) and KNbO₃ (KN). We have therefore decided to study the intrinsic and doped KNbO₃ system. Recently, we have looked at the defect chemistry of NN, finding that O and Na vacancies are present in large concentrations in the intrinsic regime [9]. Moreover, while NN is antiferroelectric, KN is ferroelectric at room temperature, as KNN [10].

Kotomin *et al.* [11] have investigated the formation energies of vacancies in KNbO₃, considering only their neutral charge state, and found that Nb vacancies show higher formation energies than K and O vacancies. Körbel *et al.* have studied the influence of Cu doping on the ferroelectric

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instabilities in KNbO_3 , by considering also the formation of defect complexes with Cu on Nb-site and oxygen vacancies [12,13]. To our knowledge, a detailed, quantitative study of the compensation mechanisms and defect thermodynamics in pure and doped KNbO_3 is still missing.

The paper is organized as follows: Section II describes the applied methodology of our calculations, Sec. III gives an overview of the presence of intrinsic and extrinsic defects, including their formation energies, charge transition levels, and doping behavior under various doping and quenching conditions, and Sec. IV summarizes the results of the present work and draws conclusions concerning majority charge carriers present in the systems.

II. METHODS

A. Computational details

All calculations were performed based on DFT using the Vienna *ab initio* simulation package (vaspP) [14–17]. The electronic wave functions were described using the projector augmented-wave method [18,19], which includes both valence and core states. The valence electron configurations of the projector augmented-wave datasets were K $3d^8 4s^1$, Nb $4d^{10} 5s^1$, O $2s^2 2p^4$, Fe $3d^{10} 4s^2 4p^2$, and Ca $3d^8 4s^2$. To study pure KNbO_3 , the exchange-correlation effects were treated using the Perdew-Burke-Ernzerhof [20] formalism of the generalized-gradient approximation. All defect calculations were performed for the room-temperature stable orthorhombic phase of KNbO_3 (*Amm2*, space group No. 38) using a $2 \times 2 \times 2$ supercell, containing 135 atoms. The *Amm2* phase shows dynamical instabilities at 0 K. In the presence of point defects, local structure relaxations can lead to artificially low formation energies when compared to a pure structure that lies on a saddle point on the potential energy surface. However, we calculated that the energy difference between the 0 K phase (*R3m*) and the room-temperature phase (*Amm2*) is only -0.14 meV/atom, meaning that these additional contributions are negligible when calculating the formation energies. The plane-wave basis set was expanded up to a 550 eV cutoff energy. The Brillouin zone integration was performed using a Γ -centered $6 \times 6 \times 6$ k mesh for unit-cell calculations and a $2 \times 2 \times 2$ k mesh for supercell calculations. The atomic positions were relaxed until the Hellmann-Feynman forces on each atom were below 0.05 eV/Å [21,22]. The density of states was calculated using a Γ -centered $12 \times 12 \times 12$ k mesh. We used the climbing image nudged elastic band method [23,24] to determine the saddle points required for calculating diffusion barriers, which imposes minimal constraints on the transition path. Transitions were limited to jumps between nearest-neighbor sites.

B. Defect thermodynamics

The formation energy ΔE_D^F of a defect D in charge state q is defined as follows [25–27]:

$$\Delta E_D^F = E_D - E_P + q(E_{\text{VBM}} + \mu_e) + E_{\text{corr}} - \sum_i \Delta n_i \mu_i, \quad (1)$$

where q represents the defect charge state, E_D is the total energy of the defective system, and E_P is the total energy

of the reference perfect cell. The third term expresses the dependence of the formation energy on the electron chemical potential (μ_e), where E_{VBM} is the valence band maximum (VBM) of the defect-free supercell, serving as the reference energy for μ_e .

E_{corr} accounts for the correction to the spurious electrostatic interactions between periodic defect images due to the finite supercell size. The correction scheme employed in this study follows the approach proposed by Kumagai and Oba [28]. The last term captures the dependence of the formation energy on the chemical potentials of the constituent elements. Here, Δn_i denotes the change in the number of atoms of type i between the defective and perfect cells. The chemical potential μ_i of element i is expressed as

$$\mu_i = \mu_i^{\text{ref}} + \Delta \mu_i, \quad (2)$$

where μ_i^{ref} represents the elemental reference chemical potential in its stable phase. These chemical potentials were derived from the Materials Project database [29,30], ensuring consistency with the computational parameters used in this work. A phase stability diagram for the orthorhombic phase of KNbO_3 was generated using the Pymatgen library [31,32].

A thermodynamic transition level corresponds to the electron chemical potential at which the formation energies of a defect in charge states q_1 and q_2 become equal. It is given by

$$\epsilon = -\frac{\Delta E_D^F(q_1) - \Delta E_D^F(q_2)}{q_1 - q_2}, \quad (3)$$

where $\Delta E_D^F(q_1)$ and $\Delta E_D^F(q_2)$ are the formation energies of the defect in charge states q_1 and q_2 , respectively, when μ_e is set at the VBM.

Under thermodynamic equilibrium, the defect concentration of species D in charge state q follows:

$$[D_q] = N_{\text{sites}} \exp\left(-\frac{\Delta E_{q,D}^F(\mu_e)}{k_B T}\right), \quad (4)$$

where q is the charge state, N_{sites} denotes the available lattice sites, and k_B is the Boltzmann constant.

The electron chemical potential (μ_e) in Eq. (1) is constrained by the charge neutrality condition:

$$n_e + n_A = n_h + n_D, \quad (5)$$

where n_e and n_h are the concentrations of electrons and holes, while n_D and n_A represent donor and acceptor defect concentrations, respectively. For multiple defect species (D) in various charge states (q), Eq. (5) can be rewritten as

$$\sum_{q,D} q[D_q] - n_e + n_h = 0. \quad (6)$$

Intrinsic carrier concentrations are obtained by integrating the density of states up to E_{VBM} for holes,

$$n_h = \int_{-\infty}^{E_{\text{VBM}}} D(\epsilon)[1 - f(\epsilon)]d\epsilon, \quad (7)$$

and from E_{CBM} onward for electrons,

$$n_e = \int_{E_{\text{CBM}}}^{+\infty} D(\epsilon)f(\epsilon)d\epsilon, \quad (8)$$

where $f(\epsilon, \mu_e) = [\exp(\epsilon - \mu_e)/k_B T]^{-1}$ is the Fermi-Dirac distribution.

In this work, these integrals were evaluated numerically using a Riemann sum over the computed density of states, following the implementation in Pymatgen [31]. The equilibrium value of μ_e was determined self-consistently by solving the charge neutrality equation at a fixed temperature, treating μ_e as the variable.

Materials such as functional oxides are often synthesized at high temperatures and quickly cooled down, which means that defects with low mobility installed at high temperatures (such as ionic defects) will still be present at low temperature. However, charge carriers have enough mobility to diffuse and equilibrate when temperature is decreased, meaning that quenched defects are allowed to equilibrate their charge states. The same argument can be applied to extrinsic defects, whose concentrations are fixed at the synthesis stage. The concentration of defect D in charge state q in fixed conditions can be calculated as follows [33]:

$$[D_q^{\text{fix}}] = [D_q] \frac{[s^{\text{fix}}]}{[s]}, \quad (9)$$

where $[D_q]$ is the concentration in equilibrated conditions, $[s]$ is the total concentration of element s (or a vacancy of the element) across all defect species in equilibrated conditions, and $[s^{\text{fix}}]$ is the total concentration of the same element in fixed conditions, which in practice might be a high-temperature concentration value arising from quenching, or the fixed concentration of a dopant. This approach allows one to keep the dependency of the defect charge state on temperature and electron chemical potential (μ_e).

C. Oxygen chemical potential

Defect formation energies are governed by the chemical potentials (μ_e and μ_i) of the reservoir, and for oxygen, this is directly related to its partial pressure. The oxygen chemical potential can be linked to temperature and partial pressure as follows [34,35]:

$$\mu_{\text{O}}(T, p_{\text{O}_2}) = \mu_{\text{O}}(T, p^0) + \frac{1}{2} k_B T \ln \left(\frac{p_{\text{O}_2}}{p^0} \right), \quad (10)$$

where k_B is the Boltzmann constant, T is the temperature, p^0 is the reference pressure, and p_{O_2} represents the oxygen partial pressure. As the reference state, we have chosen the computed energy of the O_2 molecule at 0 K, denoted as $\mu_{\text{O}}(0 \text{ K}, p^0)$. The temperature dependence $\mu_{\text{O}}(T, p^0)$ has been determined using thermochemical tables [36], following the approach in Ref. [35].

With this definition, the oxygen chemical potential can be derived from its partial pressure under experimental conditions. Alternatively, this formulation enables the evaluation of defect concentrations and the electron chemical potential as functions of the oxygen partial pressure, facilitating direct comparisons with experimental data.

TABLE I. Chemical potentials corresponding to experimental conditions of $T = 1358 \text{ K}$ and $p_{\text{O}_2} = 0.2 \text{ atm}$ and elemental reference values for each element. The values were generated starting from the K-Nb-O phase diagram containing the orthorhombic (*Amm2*) phase of KNbO_3 , with data from the Materials Project database [29,30] and processed with the Pymatgen library [31,32].

Element	$\Delta\mu$ (eV)	μ^{ref} (eV)
K	-1.82	-1.11
Nb	-7.74	-10.10
O	-1.59	-4.95
Ca	-6.50	-2.00
Fe	-3.23	-8.47

III. RESULTS AND DISCUSSIONS

A. Defect formation energies

In this study, we have computed the defect formation energies according to Eq. (1) with chemical potentials that reflect the experimental conditions in Ref. [6] ($T = 1358 \text{ K}$, $p_{\text{O}_2} = 0.2 \text{ atm}$), reported in Table I. The reference pure phase is orthorhombic KNbO_3 (*Amm2*, space group No. 38). The relaxed lattice parameters of the conventional unit cell are reported in Table II. Because of the finite size of the supercell, it is usually necessary to correct the unphysical electrostatic interactions between charged defect replicas. In our case, however, the computed ionic part of the dielectric constant is so large (802) that the defect charge is practically completely screened and this interaction becomes negligible. For each defect, we have computed all possible charge states, in order to obtain the charge transition levels [Eq. (3)], and to properly describe the contribution of each defect specie to the charge neutrality condition. The formation energies are reported in Fig. 1. K and O vacancies behave as expected with stable charge states of -1 and $+2$, corresponding to oxidation states of $1+$ and $2-$, respectively. Also Ca_K and V_Nb confirm our expectations in terms of charge states, with stable charges of $+1$ and -5 , respectively (oxidation states of $2+$ and $5+$). Interestingly, in terms of formation energies, V_Nb are comparable to V_K and V_O , especially when the Fermi level is above the middle of the band gap. This is not the case for the similar system NaNbO_3 , where the formation energies of Nb vacancies are much higher [33]. The most intriguing defect is definitely the substitution of Fe on the Nb site. In fact, the expected oxidation states for Fe are usually $2+$ and $3+$. However, in our case, Fe shows stable charge states in the band gap ranging from $+1$ to -3 , with several charge transition levels (represented by the stars in Fig. 1). Expressed in terms of oxidation states, it means that Fe shows oxidation states ranging from $6+$ to

TABLE II. Relaxed lattice parameters of the conventional unit cell of orthorhombic KNbO_3 (*Amm2*, space group No. 38), computed with the PBE functional [20].

Space group	Lattice parameters (Å)
<i>Amm2</i> (orthorhombic)	$a = 5.82, b = 5.86, c = 4.02$

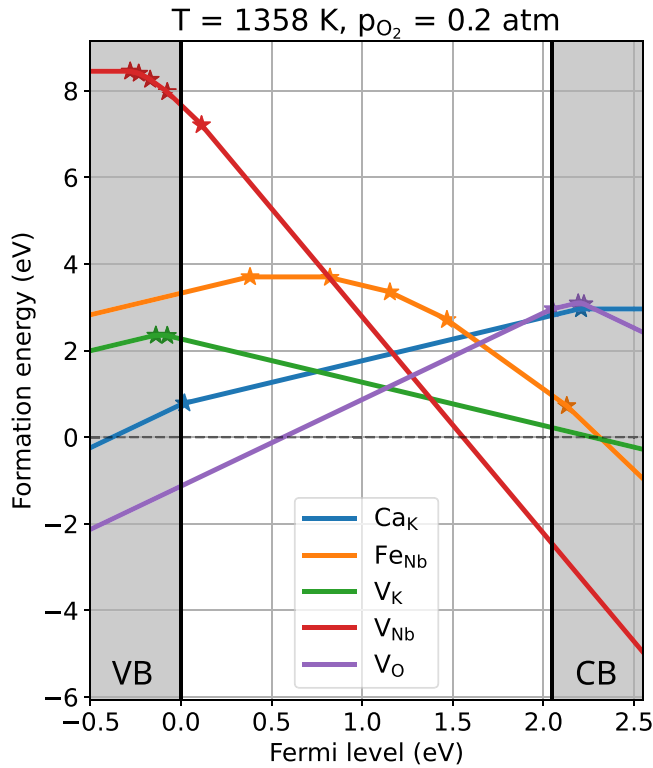


FIG. 1. Defect formation energies as a function of the Fermi level position, for thermodynamic conditions representative of the experimental conditions [6] (reported in Table I). The stars on the formation energy curves represent charge transitions. The slopes of the lines are equal to the charge states of the individual defects. The gray shaded areas represent (from left to right) the valence band and the conduction band, respectively. The black vertical lines represent the band edges.

2+, and its behavior depends on the position of the Fermi level. This highlights the fact that sometimes defects show unexpected features, depending on the system of interest. It is therefore clear the importance of considering all charge states and their dependence on the Fermi level position (as discussed in Sec. II B), without relying solely on common oxidation states. It is also important to note that this connection between charge states and oxidation states is not always appropriate, as one refers to the charge of the whole simulation cell and the other refers to the behavior of the single atomic species. To better understand this connection, one would need to determine where the charge is localized (or delocalized).

B. Influence of dopants on defect equilibrium

The calculation of formation energies provides the starting point for analyzing the defect thermodynamics. However, to quantify the defect concentrations and the position of the Fermi level, we need to solve the charge neutrality condition [Eq. (5)]. The formation energies reported in Fig. 1 assume the exchange of particles between the KNbO_3 system and a reservoir (Table I). This reflects the real scenario for intrinsic defects. On the other hand, the concentrations of extrinsic defects in the experiment are fixed at the synthesis stage. The implications are that the total concentrations of Ca_K and

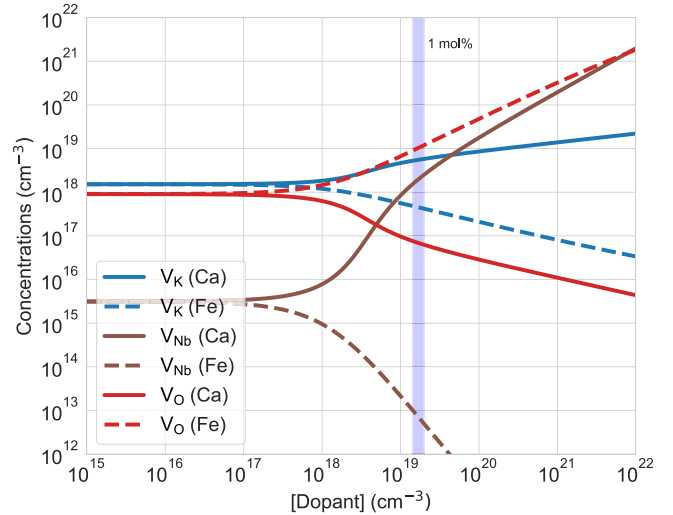


FIG. 2. Intrinsic defect concentrations as a function of the dopant concentration for Ca-doped and Fe-doped KNbO_3 . Since Ca on the K site is a donor, increasing the doping concentrations has the effect of promoting V_K and V_{Nb} , while demoting V_O . Doping with Fe has the opposite effect, since Fe on the Nb site is an acceptor.

Fe_{Nb} are fixed to the experimental dopant concentrations of 1 mol%, but their relative charges still depend on Fermi level and temperature, as discussed in Sec. II B. Moreover, with the goal of investigating the influence of dopants on the defect chemistry of KNbO_3 , it is useful to solve the charge neutrality and compute intrinsic defect concentrations as a function of the dopant concentration. Since the defect distribution is installed mainly at high temperature (see Sec. II B), we have chosen to evaluate the concentrations at the experimental sintering temperature of 1358 K. Figure 2 shows the concentrations of K and O vacancies as a function of the concentration of Ca and Fe. In the low-dopant concentrations regime, the intrinsic equilibrium dominates and the vacancy concentrations remain constant. Once the dopant concentration reaches approximately 10^{17} cm^{-3} , doping starts to be effective and the vacancy concentrations are altered. In particular, Ca acts as a donor and generates more K and Nb vacancies, while reducing the concentrations of O vacancies. On the other hand, Fe acts as an acceptor and has the opposite effect of decreasing K and Nb vacancies and promoting O vacancies.

As discussed in Sec. II B, ionic carriers are mostly frozen at room temperature. In contrast, electronic carriers are mobile and allowed to equilibrate. Therefore, when evaluating the Fermi level, we fix the distribution of ionic defects to the one installed at high temperature but evaluate the number of carriers and the ionic charges at room temperature [Eq. (9)]. Figures 3(a) and 3(b) show the Fermi level and total concentration of electronic charge carriers under quenched conditions as a function of the dopant concentrations, respectively. In the low concentration regime ($[\text{Ca/Fe}] < 10^{17} \text{ cm}^{-3}$), the Fermi level is close to the conduction band minimum (CBM), which makes the system an *n*-type semiconductor. The Fermi level shifts even closer to the CBM if we increase the concentration of Ca doping, since Ca on the K site is a donor. At room temperature, given the high concentration

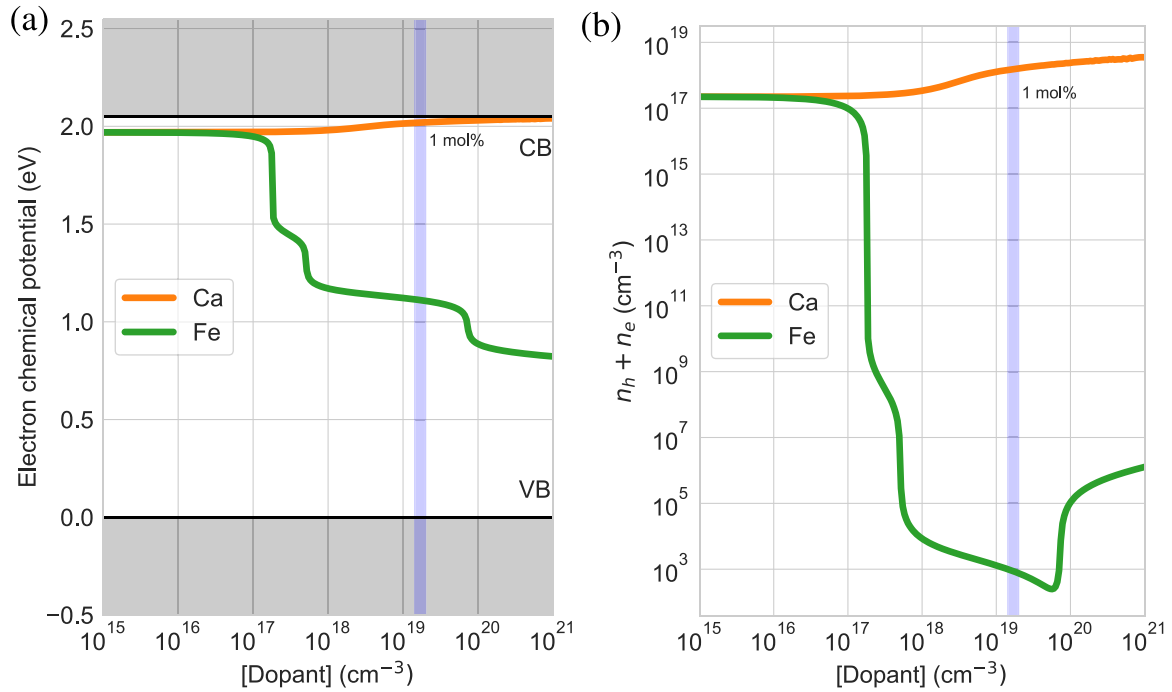


FIG. 3. (a) Electron chemical potential (μ_e , Fermi level) and (b) total electronic charge-carrier concentration (electrons+holes) in quenched conditions ($T = 1358\text{--}300\text{ K}$) as a function of the dopant concentrations. The defect distribution is computed at high temperature and kept fixed when solving charge neutrality at room temperature. At low concentrations (intrinsic regime) the system is n type, with the Fermi level being close to the CBM. Doping with Ca (donor) further increases the number of donors and increases the concentration of electronic charge carriers. Doping with Fe (acceptor) has the opposite effect of moving μ_e towards midgap and drastically reducing the number of carriers. The jumps in Fermi level induced with increasing Fe concentrations are caused by charge transitions of the Fe_{Nb} defect species.

of defects installed at high temperature, the Fermi level is pushed much closer to the band edges as compared to the high-temperature case, to compensate for the ionic charge. In fact, at lower temperatures, the distance from the band edges to the μ_e must be lower to generate sufficient electronic charges [Eqs. (7) and (8)]. This results in a relatively large concentration of electronic carriers, which in turn translates to increased electronic conductivity, as shown in Fig. 3(b). Doping with Fe leads to the opposite effect, because Fe on the Nb site is an acceptor. In fact, the Fermi level is shifted towards midgap by introducing Fe dopants. Moving further away from the band edges also results in a significantly lower concentration of electronic carriers. Moreover, when the Fe concentration is increased, the Fermi level shows several jumps. These are caused by the numerous charge transitions of Fe. Figure 4 shows the relative concentrations of all Fe charges as a function of the total Fe concentration. It is important to note that the superscript numbers in the legend are conceptually equivalent to the Kröger-Vink notation. We chose to represent them with numbers for more clarity given the multitude of charge states involved.

As discussed in Sec. III A, Fe_{Nb} shows several stable charge states, ranging from 0 to -3 , representing a range of Fe oxidation states from $5+$ to $2+$. At low concentrations, Fe_{Nb} is in charge state -3 (Fe^{2+}). Two charge transitions occur for concentrations between 10^{17} and 10^{18} cm^{-3} , with the increased concentrations of $\text{Fe}_{\text{Nb}}^{-2}$ and $\text{Fe}_{\text{Nb}}^{-1}$ (Fe^{3+} and Fe^{4+} , respectively). For higher Fe concentrations ($[\text{Fe}] > 10^{18}\text{ cm}^{-3}$) $\text{Fe}_{\text{Nb}}^{-1}$ becomes the dominant species (Fe^{4+}), while the -2 charge state decreases in concentration. The neutral charge

state appears for high concentrations, but does not exceed the concentration of the -1 charge state.

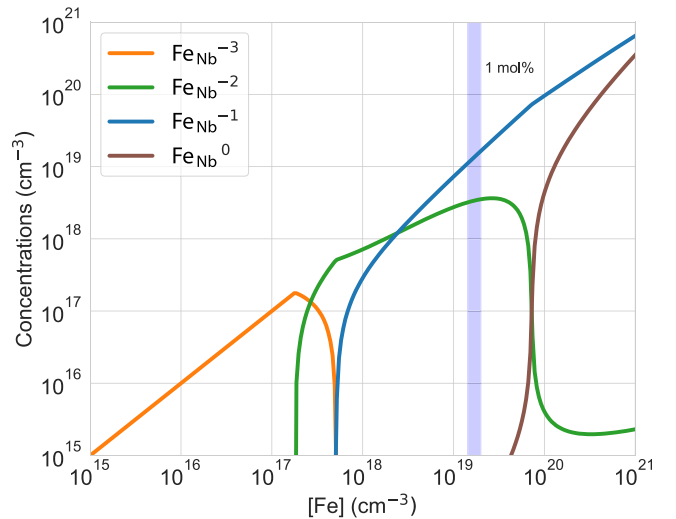


FIG. 4. Concentrations of charge states of Fe on the Nb site as a function of the total dopant concentration in quenched conditions ($T = 1358\text{--}300\text{ K}$). In the low concentration regime, the charge state -3 dominates (equivalent to Fe^{2+}). The charge state -1 (Fe^{4+}) dominates the high concentration regime, with increasing contribution of the neutral charge state (Fe^{5+}). In the middle, with concentrations between 10^{17} and 10^{18} cm^{-3} , two transitions occur with the contribution of charge state -2 (Fe^{3+}).

As briefly mentioned in the previous paragraph, the conductivity is directly proportional to the concentration of electronic charge carriers. According to the calculations in Fig. 3(b), doping KNbO_3 with Ca should have the effect of slightly increasing conductivity, since the total number of carriers increases with increasing Ca concentration. On the other hand, Fe doping has the opposite effect of drastically decreasing the carrier concentration. This is in contrast with the experimental conductivity measurements conducted by Azadeh *et al.* [6] on $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$, where Ca doping does not affect the conductivity, while Fe doping increases the conductivity until a concentration of 0.5% mol is reached. The nature of this discrepancy could be attributed to several factors.

Firstly, as mentioned in Sec. I, our target system is KNbO_3 , while the experimental system is a solid solution with K and Na, with the addition of other elements (Li and Ta) present in lower concentrations. The level of complexity of the experimental system could mean that the behavior of the dopants deviates considerably with respect to a simpler system like KNbO_3 . Additionally, it is possible that the actual concentration of intrinsic defects is much larger than the one we calculated for the bulk material and might overshadow the effect of the dopants. In fact, this material is prone to A-site nonstoichiometry due to alkali ion evaporation [6].

Secondly, when comparing the trends, we only consider the electronic contribution of the conductivity, while the measured conductivity reflects the sum of electronic, ionic, and (possibly) polaronic conductivities. However, since the mobility for electrons is larger than for ions, the electronic contribution should be dominant. Oxygen vacancies are amongst the most mobile ionic defect species in systems like perovskites, given the small size of oxygen ions. The mobility of ionic defects depends on their diffusion barrier, which we computed with the Nudged Elastic Band method (Sec. II A) to be 0.62 eV for a double-positively charged O vacancy. This value would not justify the fact that O vacancies are the main conduction mechanism, meaning electronic carriers should dominate. However, the experimental system is much more complex, with the presence of impurities and high-dimensional defects like grain boundaries. It is therefore possible that in such a complex system the concentrations, and especially the diffusion barriers, of O vacancies make ionic defects the dominant contribution to the conductivity.

Thirdly, while in this study we have only considered single defects, the presence of charged defect complexes can also influence the defect chemistry and the ferroelectric properties of the system [37–41]. Charged oxygen vacancies can in fact form defect complexes with the cations, especially when large defect concentrations are installed at the synthesis stage, which can be electrically active and affect the Fermi level and charge-carrier concentrations. Moreover, when these charged defects associate, they form dipoles that can interact with external electric fields and influence the dielectric properties. Lastly, the concentrations of the solid solution components in the material of interest are so high that they are at the edge of validity of our computational model. In particular, the defect thermodynamics in Sec. II B assumes that the concentration of defects is much smaller than the concentrations of lattice sites, so that it can be approximated to an ideal solution. In

this case, since the concentrations of defects are already of the order of mole percentages, it might be incorrect to assume that the defects do not interact with each other. This means that the higher the defect concentrations, the greater the inaccuracy of the computational model.

IV. CONCLUSIONS

The defect chemistry of intrinsic and extrinsic defects and the doping behavior in orthorhombic KNbO_3 doped with Ca and Fe have been determined using DFT. We found that all three types of vacancies show low formation energies at sintering temperature (1358 K) and atmospheric pressure. In addition, substitutional defects with Ca on the K site and Fe on the Nb site show comparably low formation energies, which explains how samples with concentrations of up to 1 mol % can be produced without secondary phase formation [6].

Moreover, we have determined the Fermi level, defect, and charge-carrier concentrations, by solving the charge neutrality equation for defect distributions installed at sintering temperature and charges equilibrated at room temperature (quenched conditions). We found that in the intrinsic regime the material is *n* type, with a large concentration of electrons (10^{17} cm^{-3}). Doping with Ca (donor) further increases the concentration of electrons. Doping with Fe (acceptor) moves the Fermi level toward midgap, thus drastically lowering the number of electronic carriers. Furthermore, we revealed that Fe can simultaneously display several oxidation states (from 2+ to 5+), where the dominant charge state depends on the Fe concentration.

Although these calculations provide important insight on the defect chemistry and doping strategies in KNbO_3 , there are still unanswered scientific questions. In fact, while in this study we have only considered single defects, the presence of charged defect complexes can also influence the defect chemistry and the ferroelectric properties of the system [37–41]. Additionally, it is not yet clear whether the doping behavior is identical in KNbO_3 and in the solid solution $(\text{K},\text{Na})\text{NbO}_3$. Moreover, The influence of the microstructure and their interaction with point defects is still to be addressed. In fact, defects can segregate to grain boundaries and form space-charge regions, which can influence the defect equilibrium and the mobility. This calls for further scientific research, oriented on the study of these complex ceramic solid solutions and higher-dimensional defects. Given the impossibility of addressing large systems with DFT, machine-learning potentials might offer a way to overcome these limitations and provide insight beyond point-defect thermodynamics.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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