

Microscopic Insights into the Reconstructive Phase Transition of KNaNbOF_5 with ^{19}F NMR Spectroscopy

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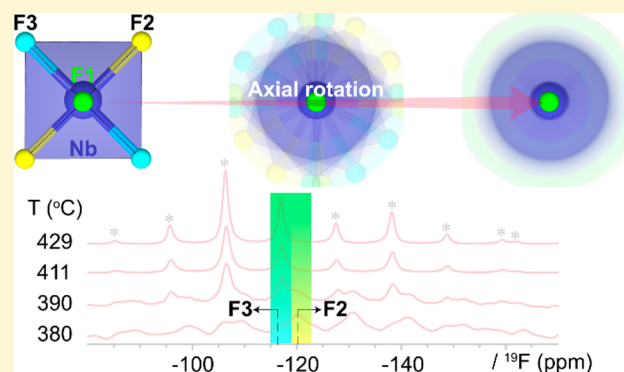
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ABSTRACT: The centrosymmetric polymorph of KNaNbOF_5 undergoes a reconstructive transition from a rare A-site vacancy ordered perovskite to a unique nonperovskite high-temperature phase. Previously, the high temperature phase was proposed to exhibit dynamical disorder with mixed occupancy of O and F on the anion sites owing to hopping rotations of the $[\text{NbOF}_5]^{2-}$ octahedra. Here, we utilize ^{19}F NMR techniques to assess the dynamic anion configurations through this reconstructive transition. We conclude from these measurements that the high-temperature phase exhibits $Cmcm$ symmetry with hopping rotations of the $[\text{NbOF}_5]^{2-}$ octahedra occurring only about the $F_{\text{apical}}\text{--Nb--O}$ axis of the octahedra such that there are no O/F mixed occupancy anion sites. We use these results to refine the microscopic description of the reconstructive transition and its driving force and examine changes

in the electronic structure of the d^0 oxyfluoride through the transition. Our work demonstrates the efficacy of ^{19}F NMR techniques combined with electronic structure calculations to understand thermodynamically driven changes in heteroanionic materials.



INTRODUCTION

Heteroanionic materials (HAMs) are an emerging class of designer materials in which functional properties can be tailored through insertion or exchange of a secondary anion.^{1,2} Among the breadth of properties that are accessible through anion engineering are nonlinear optical properties such as second harmonic generation,³ colossal magnetoresistance,⁴ metal–insulator transitions,⁵ and quantum phases.⁶ A major obstacle to achieving these anion-enabled properties lies in understanding how to control and characterize anion ordering in HAMs, as long-range anion order is a key factor in the appearance (or lack thereof) of many acentric functional properties.⁷ For example, anion ordering lifts inversion symmetry in $\text{Na}_3\text{MoO}_3\text{F}_3$, which is a necessary geometric requirement for ferroelectricity, piezoelectricity, and second harmonic generation. Anion disorder, likewise, can lead to unexpected responses as in $\text{Sr}_2\text{NiO}_3\text{F}$, whose low temperature spin-glass state arises in part due to the lack of anion ordering on the apical sites of the $[\text{NiO}_5\text{F}]^{7-}$ octahedra.⁸ Additionally, different anion configurations can effect electronic and optical properties such as the band gap, which in computational studies of CaTaO_2N , was found to vary up to 0.6 eV depending on the anion configuration.⁹ To that end, proper characterization of anion order is necessary to inform experimental synthesis and understand the origin of the macroscopic properties. Commonly utilized structural charac-

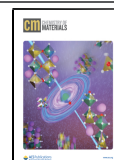
terization techniques such as X-ray and neutron diffraction, however, may not be sufficient to determine the anion order of heteroanionic materials, especially in oxyfluorides where the scattering lengths of O and F are comparable.^{1,2} Additional characterization techniques, such as IR, Raman, NMR spectroscopy, and electron diffraction are needed to accurately assess the extent of long-range and short-range order of multiple anions.

Specifically, ^{19}F NMR and powder X-ray diffraction (PXRD) have been used to synergistically determine the anion order in multiple oxyfluorides.^{10–16} Advanced NMR techniques can also reveal more detailed anion ordering information. For example, in $\text{Na}_3\text{W}_3\text{O}_9\text{F}_5$, ^{19}F and ^{23}Na MAS, $^{23}\text{Na} \rightarrow ^{19}\text{F}$ CP, and $^{19}\text{F} \rightarrow ^{23}\text{Na}$ HETCOR NMR experiments were performed to further refine the anion site order determined by powder XRD and Raman spectroscopy studies and provided additional insight into the ferroelectric-ferroelastic properties of the material.¹³ Additionally, NMR techniques have been used to study dynamic phenomena in oxyfluorides, such as dynamically

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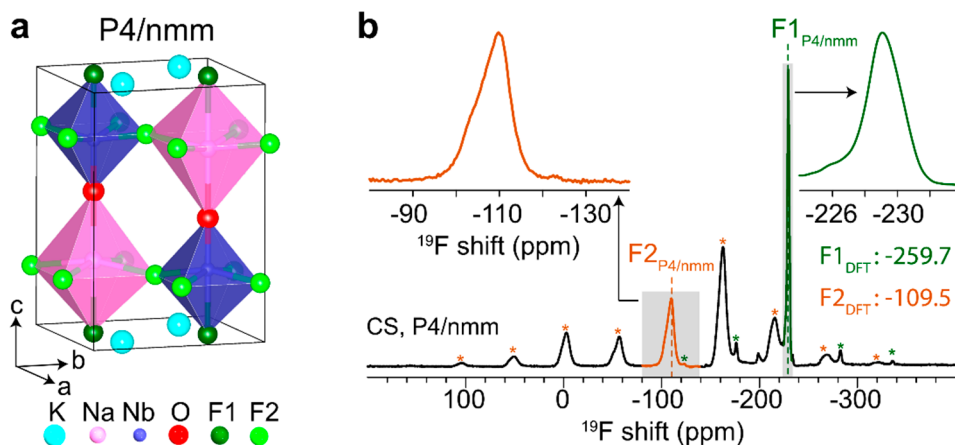


Figure 1. (a) Crystal structure and (b) high-resolution ^{19}F MAS (25 kHz) NMR spectrum of centrosymmetric (CS) KNaNbOF_5 ($P4/nmm$). In panel b, calculated ^{19}F NMR chemical shifts are also shown for reference. Asterisk (*) denotes spinning side bands.

disordered phases and order/disorder phase transitions.^{17,18}

For example, it was previously thought that the centrosymmetric to non-centrosymmetric phase transition in $\text{K}_3\text{WO}_3\text{F}_3$ from a disordered cryolite structure, $Fm\bar{3}m$, to the low temperature $I4mm$ phase was due to ordering of the anion sites. Using a combination of variable-temperature Raman and ^{19}F NMR spectroscopy, it was found that the anion sites remain disordered across the transition owing to fast reorientations of the fac- $[\text{WO}_3\text{F}_3]^{3-}$ octahedra.¹⁷

Here we use NMR techniques to examine the microscopic origins of an unusual reconstructive phase transition¹⁹ in the oxyfluoride KNaNbOF_5 . The room-temperature centrosymmetric variant of KNaNbOF_5 is an anion ordered elpasolite with ordered A-site vacancies. Upon heating from this tetragonal $P4/nmm$ structure, reconfiguration of the cation sublattice (and its associated vacant sites) occurs with rotations of nearly rigid $[\text{NbOF}_5]^{2-}$ octahedra breaking K/Na-ligand bonds. This complex choreography was proposed to rely on hopping rotations between six stable orientations of the $[\text{NbOF}_5]^{2-}$ octahedra, which effectively alter the O and F site order as seen from synchrotron powder X-ray diffraction (PXRD) measurements, and was proposed to yield a dynamically disordered high temperature (HT) phase with orthorhombic $Cmcm$ symmetry. Specifically, the dynamic disorder refers here to a state with an average structure consisting of a mixture of two phases distinguishable at the unit cell level with $Pbcm$ and $Pnma$ symmetry identified from molecular dynamics simulations. The $Cmcm$ structure forms a supergroup connecting these two phases. Using high-resolution and high-temperature ^{19}F magic-angle-spinning (MAS) NMR and density functional theory calculations, we show that HT phase is unlikely dynamically disordered between two phases and can be described with $Cmcm$ symmetry. We show that the rotational hopping of the $[\text{NbOF}_5]^{2-}$ octahedra is limited to rotations about the $F_{\text{apical}}\text{-Nb-O}$ axis of the octahedra, indicating that the HT phase does not show mixed anion-site occupancy, all anion sites are either 100% O or 100% F. Additionally, we connect the structural changes of the heteroleptic oxyfluoride units through the reconstructive transition to changes in the calculated electronic band gap. Last, we revise the model and driving force for the reconstructive transition in KNaNbOF_5 , arguing that it originates from only hopping rotations (orientational disorder) rather than O/F disorder on the anion sites.

RESULTS AND DISCUSSION

The crystal structure and high-resolution ^{19}F MAS NMR spectrum of centrosymmetric (CS) KNaNbOF_5 ($P4/nmm$) are shown in Figure 1. In CS KNaNbOF_5 (Figure 1a), two distinct F atoms are identified in the $[\text{NbOF}_5]^{2-}$ octahedra: the apical and equatorial fluorine atoms. The apical fluorine atom ($F1_{P4/nmm}$; notation of $F(\#)_{\text{space group}}$ is used to indicate specific fluorine anion sites in different phases of KNaNbOF_5 throughout) sits parallel with O along the c -direction or trans to O, whereas the equatorial fluorine atom ($F2_{P4/nmm}$) connects the $[\text{NaOF}_5]^{6-}$ and $[\text{NbOF}_5]^{2-}$ octahedra in the ab -plane.¹⁹ The ratio of site multiplicities between $F1_{P4/nmm}$ and $F2_{P4/nmm}$ is 1:4 with 100% site occupancy indicating anion order and resulting in the stoichiometry of 5 for the fluorine atom in the CS polymorph of KNaNbOF_5 .

The high-resolution ^{19}F MAS (25 kHz) NMR spectrum of the CS form of KNaNbOF_5 is shown in Figure 1b. Two ^{19}F isotropic NMR resonances, determined by recording ^{19}F NMR spectra at different MAS rates where isotropic resonances do not vary their positions with spinning (Figure S1), appear at -229.2 and -109.5 ppm, respectively. The ratio of the ^{19}F NMR spectral areal integral (including associated spinning side bands) of the resonances at -109.4 and -229.2 ppm is 1:4, which agrees well with the multiplicities of two fluorine atoms in the CS form of KNaNbOF_5 . Thus, the ^{19}F resonance at -229.2 ppm is assigned to the crystallographically distinct apical $F1_{P4/nmm}$ atom, and the ^{19}F resonance at -109.5 ppm is assigned to the equatorial $F2_{P4/nmm}$ atom. This assignment is also supported by DFT ^{19}F NMR calculations (Table S1).

The equatorial fluorine atom ($F2_{P4/nmm}$) showing a ^{19}F NMR resonance at -109.5 ppm presents a pronounced asymmetric line shape with an estimated full width at half-maximum (fwhm) of 4.3 kHz. Since the X-ray diffraction data²⁰ only reveals one type of local environment (Wyckoff site: 8j) for the equatorial fluorine atom, this wide distribution of ^{19}F frequencies is attributed to NMR interactions. In fact, $^{93}\text{Nb}\text{-}^{19}\text{F}$ J-coupling and residual $^{93}\text{Nb}\text{-}^{19}\text{F}$ dipolar coupling have been claimed and verified as the origin for this asymmetry in the ^{19}F signal of $\text{Cdp}_4\text{NbOF}_5$.¹⁶ In KNaNbOF_5 , the shorter Nb- $F2_{P4/nmm}$ bond (1.95 Å) makes the through-bond $^{93}\text{Nb}\text{-}^{19}\text{F}$ J-coupling more noticeable than that of the Nb- $F1_{P4/nmm}$ bond (2.15 Å), although the multiplet pattern is not resolved in either resonance likely due to residual broadening resulting from dipolar coupling interactions and relaxation.

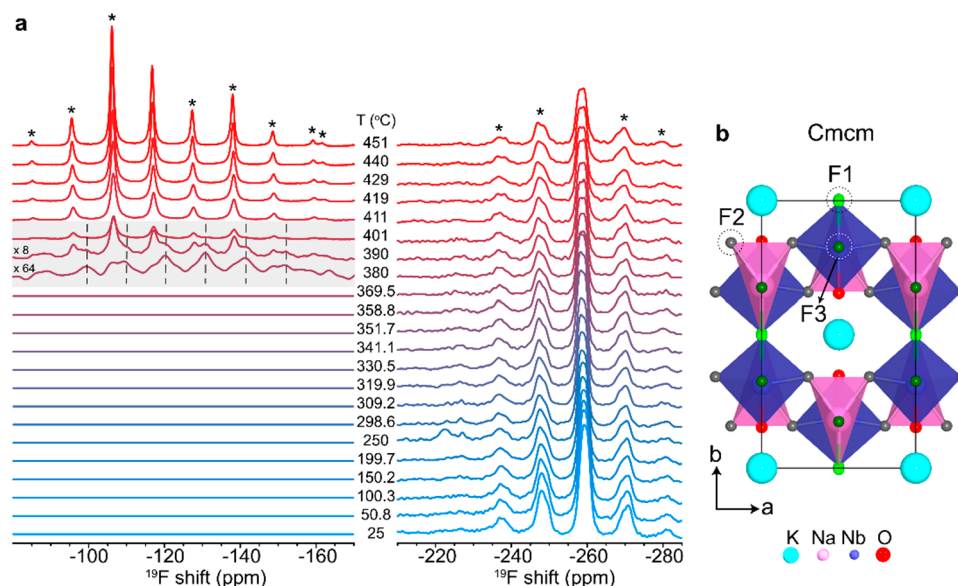


Figure 2. (a) In situ monitoring (heating process) of the phase transition in KNaNbOF_5 from the centrosymmetric (CS) phase ($P4/nmm$) to the high-temperature (HT) phase ($Cmcm$) by variable-temperature ^{19}F MAS (5 kHz) NMR. (b) Crystal structure of $Cmcm$ KNaNbOF_5 . Asterisk (*) denotes spinning side bands. Dashed lines serve as a guide-to-the-eye.

Note, the line broadening we observe is not relevant to understanding the reconstructive phase transition of KNaNbOF_5 and thus we do not assess it further.

To follow the structural changes in the $[\text{NbOF}_5]^{2-}$ unit during the CS \rightarrow HT phase transition, in situ high-temperature ^{19}F MAS (5 kHz) NMR is employed, and the summarized ^{19}F spectra following the heating process are presented in Figure 2 (the cooling process is shown in Figure S2). It is worth pointing out that this temperature-dependent ^{19}F NMR study was performed at a MAS rate of 5 kHz, due to hardware limitations for high-temperature NMR. Therefore, the spectra in Figure 2 show poorer resolution compared with spectra acquired at 25 kHz as shown in Figure 1. In the ^{19}F spectrum acquired at room temperature, one resonance appears at -259.2 ppm with a slightly asymmetric line shape, which agrees with the calculated shift of the apical fluorine ($\text{F1}_{P4/nmm}$) atom in CS KNaNbOF_5 (-259.7 ppm; Table S1). As a result, this -259.2 -ppm resonance is assigned to $\text{F1}_{P4/nmm}$. The asymmetric line shape for the -259.2 -ppm peak may arise from the J-coupling between Nb and the apical $\text{F1}_{P4/nmm}$. The large chemical shift anisotropy (CSA) of the ^{19}F resonance of equatorial fluorine atoms, $\text{F2}_{P4/nmm}$, renders the signal invisible at low spinning rates. To prove this, the magnitude of CSA is obtained by quantitatively simulating the high-resolution ^{19}F NMR spectrum of KNaNbOF_5 acquired at a fast MAS rate of 25 kHz (Figure 1b), and the CSA values of $\text{F2}_{P4/nmm}$ and $\text{F1}_{P4/nmm}$ ^{19}F resonances are 183.5 kHz and 21.9 kHz, respectively. The large shift anisotropy spreads out the ^{19}F signal of $\text{F2}_{P4/nmm}$ over a very broad range >180 kHz at low spinning rates, e.g., 5 kHz, resulting in extremely low sensitivity.

Upon increasing temperature to 369.5 °C, no noticeable changes in the chemical shift or line width can be seen in the ^{19}F spectra, except for minor short-range structural adjustments occurring at 250 °C, manifested in the appearance of small resonances at -223 ppm. Similar changes are observed for minor resonances near -211 ppm during the cooling process at a lower temperature of 199.7 °C (Figure S2).

Whether these structural adjustments are necessary before the phase transition takes place are not clear at this stage. Note that these structural changes should not interfere with the following discussion as we will show that at temperatures below 370 °C, no discernible phase transition can be traced. The unaltered line width of the $\text{F1}_{P4/nmm}$ resonance from room temperature to 369.5 °C implies negligible F-ion motion, suggesting improbable O/F site disorder in the $[\text{NbOF}_5]^{2-}$ unit within the low-temperature range.

At 380 °C, two ^{19}F resonances emerge at -120.2 and -116.7 ppm. According to DFT ^{19}F NMR calculations of different KNaNbOF_5 phases (Table S1), these two resonances originate from equatorial fluorine atoms (F2_{Cmcm} and F3_{Cmcm}) in the high-temperature phase ($Cmcm$). The emergence of these two ^{19}F resonances signifies the transition of KNaNbOF_5 from the centrosymmetric phase ($P4/nmm$) to the high-temperature phase ($Cmcm$). In these two phases, the local coordination of the apical fluorine atom, excluding site symmetry, is unchanged. The $\text{F1}_{P4/nmm}$ and F1_{Cmcm} can be viewed as the bridging atom between the Nb and Na polyhedra, and both atoms are trans to O as in the $[\text{NbOF}_5]^{2-}$ octahedra (Figures 1a and 2b). This similarity in the connectivity of the apical fluorine atom with Nb and Na in each corresponding polymorph results in the same ^{19}F chemical shift at -259.7 ppm. In contrast, the local environment of the equatorial fluorine atoms is substantially different because of the change in molecular geometry of the Na polyhedra from a distorted octahedron, $[\text{NaOF}_5]^{6-}$, to distorted trigonal bipyramid, $[\text{NaF}_5]^{4-}$, in the CS \rightarrow HT phase transition. The difference in local coordination of the equatorial fluorides in the HT phase leads to the formation of two distinct groups of equatorial fluorine atoms (F2_{Cmcm} and F3_{Cmcm}) as revealed by a small difference in ^{19}F NMR resonances (Figure 2).

As the temperature ramps up higher than 380 °C, the ^{19}F signals of the two equatorial fluorine atoms gradually merge, likely owing to fast F-ion exchange between them, rendering a sharp resonance at -116.7 ppm when the temperature reaches 450 °C. The averaged single ^{19}F isotropic shift of equatorial

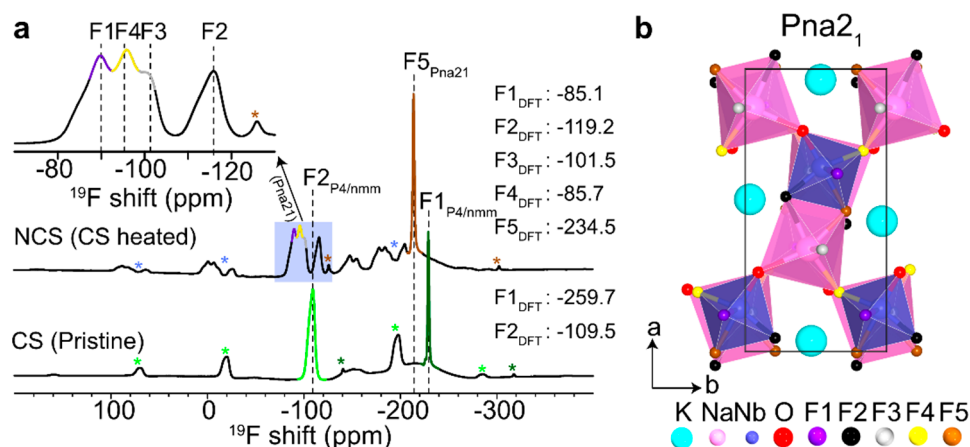


Figure 3. (a) High-resolution ^{19}F MAS (50 kHz) NMR spectra before and after heat-treatment on CS KNaNbOF_5 . (b) Crystal structure of noncentrosymmetric (NCS) KNaNbOF_5 ($Pna2_1$). In panel a, calculated ^{19}F NMR chemical shifts are also shown for reference. Asterisk (*) denotes spinning side bands.

fluorine atoms (F_{Cmcm}) at 450 °C is further verified as shown in Figures S3 and S4.

These findings indicate that the HT structure is not a dynamically disordered state between the previously proposed $Pnma$ and $Pbcm$ phases. The structures of the $Pnma$ and $Pbcm$ phases are shown in Figure S5 and both have an additional crystallographic fluorine site. DFT ^{19}F NMR calculations on $Pnma$ and $Pbcm$ phases suggest that isotropic ^{19}F NMR shifts (Table S1) of the equatorial fluorine sites resonate at -124.2 , -94.7 , and -93.6 ppm for $Pnma$ and -140.6 , -108.4 , and -84.8 ppm for $Pbcm$ (Table S1). However, these resonances are not experimentally observed. At 380 °C and above, we do not observe more than three peaks in the spectra or peaks greater than -110 ppm, indicating that the high temperature phase is likely only Cmcm .

Considering the fact that both the resonance position and line width of the apical fluorine atom ($F1_{\text{Cmcm}}$) are temperature independent, the motion-induced narrowing following the coalescence of the ^{19}F peaks (equatorial $F2_{\text{Cmcm}}$ and $F3_{\text{Cmcm}}$) suggests that the hopping rotations of the $[\text{NbOF}_5]^{2-}$ unit are restricted to rotations about the $F_{\text{apical}}\text{-Nb-O}$ axis (vide infra). This means that only the equatorial F atoms are allowed to swap positions and no O/F site disorder is possible.²¹ To further validate this statement, DFT ^{19}F NMR shift calculations on the HT phase (Cmcm) of KNaNbOF_5 is performed using an axial model, where the positions of the equatorial fluorine atoms are swapped, and a free rotation model, where the positions of one apical oxygen and one equatorial fluorine atom were swapped to mimic O/F site disorder. The result of this computational work is presented in Table S2. Examining individual F sites, the ones that change the most are F9 corresponding to the position of the apical oxygen, F1, which now is located trans to a F rather than O in the $[\text{NbOF}_5]^{2-}$ octahedra, and F11, which rests in an equatorial F position, but is now trans to an O in $[\text{NbOF}_5]^{2-}$. The apical F sites, F1 and F9, show downfield shifting to -133.1 ppm and -80.1 ppm, respectively, while the equatorial F11 shows upfield shifting to -166.4 ppm. Averaging over apical and equatorial sites, this manifests as a significant downfield shifting (larger ppm) in the averaged ^{19}F chemical shift of the apical fluorine atom (-204.5 ppm) in the free rotation model. In the case of axial rotations about the $F_{\text{apical}}\text{-Nb-O}$ axis, the exchange of equatorial fluorine atoms

does not shift the ^{19}F resonances, and the apical fluorine atom resonates with an average value at -221.2 ppm, which is more comparable to the experimental shift at -257.4 ppm (Table S1). Therefore, O/F site disorder (i.e., free rotations) is unlikely to occur in the HT form of KNaNbOF_5 since our experimental ^{19}F chemical shifts contradict the predicted chemical shifts in the presence of free rotations (hopping of the $[\text{NbOF}_5]^{2-}$ octahedra about six symmetry equivalent configurations).

During the cooling process (Figure S2), the sharp ^{19}F resonance (-116.7 ppm) at high temperature abruptly splits into two peaks as the temperature decreases to 380–370 °C, which is in line with the reduced F motion associated with the axial rotation of the $[\text{NbOF}_5]^{2-}$ unit. Below 370 °C, ^{19}F signals representing the equatorial fluorine atoms fade away due to an insufficient MAS rate for averaging the regained large CSA. High-resolution MAS NMR at 50 kHz is employed to determine the room-temperature phase after cooling.

High-resolution ^{19}F MAS NMR spectra acquired at a spinning rate of 50 kHz of the heat-treated KNaNbOF_5 after cooling to room temperature and the pristine CS KNaNbOF_5 are shown in Figure 3. In contrast to the spectrum for the CS form of KNaNbOF_5 , the ^{19}F MAS spectrum of the heated sample reveals five individual ^{19}F peaks (Figure 3a, top panel), indicating that CS \rightarrow HT transition is irreversible and a different phase of KNaNbOF_5 is obtained upon cooling, as previously observed in PXRD experiments.^{19,23}

The experimental ^{19}F chemical shifts (Table S1) agree moderately well with the computed shifts in the noncentrosymmetric (NCS) form of KNaNbOF_5 ($Pna2_1$).^{19,23} For the NCS form of KNaNbOF_5 (Figure 3b), five crystallographically distinct F sites are identified in the $[\text{NbOF}_5]^{2-}$ octahedra.²² The ratio of the multiplicities among $F1_{Pna2_1}$, $F2_{Pna2_1}$, $F3_{Pna2_1}$, $F4_{Pna2_1}$, and $F5_{Pna2_1}$ is 1:1:1:1:1, and the site occupancy is 100% (i.e., anion ordered) for all of five sites. The percentage of the ^{19}F NMR resonance areal integral (including spinning side bands) of the apical F ($F5_{Pna2_1}$) over the sum of the other four equatorial fluorine atoms ($F1_{Pna2_1}$ to $F4_{Pna2_1}$) is 19.4% ($\sim 1/5$) and the integral ratio among $F2_{Pna2_1}$, $F3_{Pna2_1}$, $F4_{Pna2_1}$, and $F1_{Pna2_1}$ (from small to large ppm) is 1.02:0.83:1.13:1.15, roughly consistent with the expected ratio of multiplicities in the NCS form of KNaNbOF_5 ($Pna2_1$). We therefore assign the structure of the heat-treated

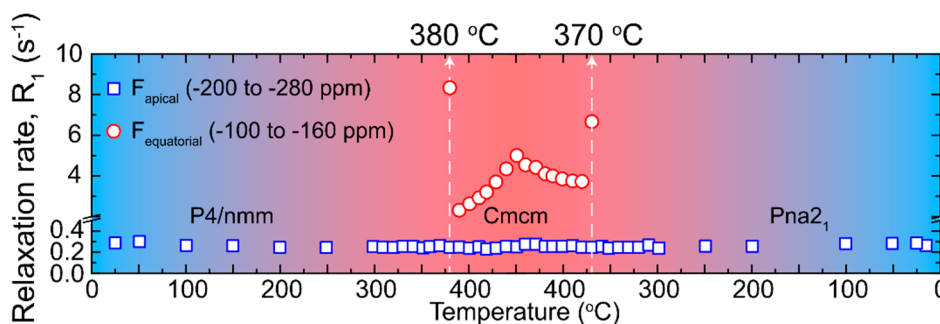


Figure 4. In situ ^{19}F NMR spin–lattice relaxation rate ($R_1 = 1/T_1$) measurements on the CS-to-HT phase transition upon heating (0 to 450 °C) and the HT-to-NCS transition upon cooling (450 to 0 °C) in KNaNbOF_5 .

sample to the NCS phase and confirm that cooling KNaNbOF_5 from high temperature leads to a polymorphic transition to the ground state noncentrosymmetric non-perovskite polymorph.¹⁹ We note that the $\text{F}_{\text{Pna}21}$ site (Figure 3b), which is axially opposite to O in the $[\text{NbOF}_5]^{2-}$ unit, presents the most upfield chemical shift (smaller ppm), and the rest of four equatorial fluorine atoms ($\text{F}_{\text{Pna}21}$ to $\text{F}_{4\text{Pna}21}$) share a wide distribution of chemical shifts in a range between -90 to -120 ppm. This is similar to what is observed in the CS structure, in which the apical fluorine atom ($\text{F}_{\text{P4/nmm}}$) resonates at the most upfield and the equatorial one ($\text{F}_{2\text{P4/nmm}}$) downfield at -109.5 ppm.

We now examine the possibility of dynamic O/F site disorder in the $[\text{NbOF}_5]^{2-}$ unit. Ion dynamics often induces fluctuation in local magnetic field, resulting in loss of spin coherence and thus changes in spin relaxation times. Therefore, NMR relaxometry is a sensitive tool for probing ion dynamics. *In situ* high-temperature ^{19}F spin–lattice relaxation time (T_1) measurements are performed on CS (P4/nmm) KNaNbOF_5 and the results are given in Figure 4. The T_1 times of the equatorial fluorine atoms ($\text{F}_{2\text{P4/nmm}}$, $\text{F}_{2\text{Cmcm}}$, $\text{F}_{3\text{Cmcm}}$; red circles in Figure 4) cannot be determined until 380 °C as their ^{19}F signals are unobservable due to large CSA. The T_1 values of the apical (-200 ppm to -280 ppm) and the equatorial (-100 to -160 ppm) F show significant difference. In particular, the relatively long T_1 times (slower relaxation rate $1/T_1$, blue squares) of the apical fluorine atoms ($\text{F}_{1\text{P4/nmm}}$ and $\text{F}_{1\text{Cmcm}}$) in both phases are independent of temperature throughout the entire measurement. The lack of changes in long relaxation time and no narrowing of the CSA with temperature for the $\text{F}_{1\text{P4/nmm}}$ and $\text{F}_{1\text{Cmcm}}$ resonances suggest very little motion is associated with $\text{F}_{1\text{P4/nmm}}$ and $\text{F}_{1\text{Cmcm}}$. Combined with evidence of no shift changes in these resonances, no static or dynamic O/F disorder occurs in the high temperature phase.

The reconstructive phase transition is revealed by a sudden jump in the relaxation rate (R_1) from 380 to 390 °C. The abrupt change in T_1 upon heating indicates structural modification and suggests the completion of the $\text{P4/nmm} \rightarrow \text{Cmcm}$ phase transition. The continuously shortened T_1 (increased relaxation rate $1/T_1$) from 390 to 450 °C, in conjunction with gradual reduction of CSA and narrowing of the isotropic resonance at -116.9 ppm (Figure S6), suggest increasing F exchange through axial rotations of the $[\text{NbOF}_5]^{2-}$ unit, which gradually averages out the CSA and the ^{19}F – ^{19}F dipolar couplings (Figure S6). On the cooling process, a reversible behavior is seen with a slower rate and smaller change in amplitude (Figure 4) likely due to different

transition pathways ($\text{P4/nmm} \rightarrow \text{Cmcm}$ vs $\text{Cmcm} \rightarrow \text{Pna}2_1$) as the axial rotations of the $[\text{NbOF}_5]^{2-}$ unit in the CS (P4/nmm) and NCS ($\text{Pna}2_1$) form of KNaNbOF_5 cannot be identical. At 370 °C, the sharp change in T_1 times indicates another structural modification responsible for the $\text{Cmcm} \rightarrow \text{Pna}2_1$ displacive phase transition. Based on the results of the *in situ* high-temperature ^{19}F T_1 measurements, the observed nature of dynamic disorder is confirmed as a result of rapid rotation in the $[\text{NbOF}_5]^{2-}$ unit about the axis of $\text{F}_{\text{apical}}\text{–Nb–O}$, and thus, no O/F anion disorder occurs in the high temperature phase.

Based on this understanding of the high-temperature structure and the associated thermally controlled structural dynamics, we propose a revised model for the reconstructive phase transition. Previously, the reconstructive transition was believed to be effectively driven by O/F site disorder induced by thermally driven octahedral hopping rotations among multiple symmetry equivalent orientations. Consequently, the anion disorder destabilizes the coordination environment of the K^+ and ordered vacant sites and leads to electrostatic interactions that cause them to attract.¹⁹ Given our results, it is clear that O/F disordering is not active in $\text{P4/nmm} \rightarrow \text{Cmcm}$ transition. We propose the hopping rotations alone are enough to destabilize the coordination environment of the K^+ ions and thus, the ordered A-site vacancies. Given that this type of ordered vacancy has only been observed in a few heteroanionic materials and not at all seen in homoanionic materials (i.e., oxides),²⁰ we expect that this type of vacancy ordering is generally unfavorable or perhaps stabilized by the O/F anion ordering. We expect that other known perovskites with ordered A-site vacancies, such as $\text{KNaMoO}_2\text{F}_4$ and KNaWO_2F_4 , may also show an irreversible reconstructive transition upon heating and a new phase upon cooling.

Last, our results are consistent with the minimum-energy-pathway (MEP) model for the reconstructive transition described previously (Figure S7a).¹⁹ The structure proceeds from the P4/nmm phase to a structure very similar to the Pbcm phase and then to HT Cmcm structure. Given the confirmation of O/F order in this structure, we can ascertain the electronic structure dependencies due to these structural changes through the reconstructive transition with reasonable accuracy. Despite the reconstructive nature of the transition from the CS to HT phases in KNaNbOF_5 , only minor changes in the calculated band gap are observed (4.32 and 4.30 eV, respectively). Interestingly, the band gap along the calculated MEP¹⁸ changes more as the $[\text{NbOF}_5]^{2-}$ octahedra rotate through the transition (Figure S7b). Upon detailed inspection of the electronic structure in Figure S7c and the structures along the MEP, we find that the changes in the band gap are correlated

with the change in the bandwidth of the F p states, except between points C and D. As the structure initially distorts away from the CS phase (point A), its behavior is similar to a displacive transition in which rotations of octahedra increases the band gap slightly, as expected for perovskite-like heteroanionic materials.²⁴ Further along the transition pathway, between points B and C, the structure no longer appears perovskite-like as the Na–F bonds begin to break as the rigid $[\text{NbOF}_5]^{2-}$ octahedra rotate. The band gap slightly decreases again, due to a widening of the F p states due to a change in orbital overlap with Nb. An increase in band gap between C and D occurs because the rigid $[\text{NbOF}_5]^{2-}$ octahedra and distorted Na-polyhedra move toward sharing an edge, which decreases the ligand-field splitting of the Nb orbitals. Finally, as the structure distorts toward the *Cmcm* phase, the Nb- and Na-polyhedra become corner sharing, increasing the ligand-field splitting and increasing the band gap.

In addition to the $[\text{NbOF}_5]^{2-}$ octahedra maintaining their rigidity and largely rotating about the *c*-axis throughout the transition pathway, the K^+ cations displace along the *b*-axis, effectively merging with the A-site vacancies and eliminating them. This essentially eliminates the perovskite-like structure observed in *P4/nmm* and transitions to a new unique structure type. Interestingly, after the transition, the K^+ ion forms two bonds to O and this coordination persists upon cooling through the reversible transition to the thermodynamic NCS ground-state phase (Figure S8). These K–O bonds are not seen in the CS polymorph.

CONCLUSION

Using high-resolution and high-temperature ^{19}F MAS NMR, we have confirmed the irreversible, reconstructive phase transition in KNaNbOF_5 from the CS *P4/nmm* polymorph to the HT *Cmcm* phase. In addition, we clarify some previously unobserved dynamic phenomena in the high temperature phase. We showed the HT structure is likely one phase, *Cmcm*, rather than a dynamically disordered phase consisting of *Pbcm* and *Pnma*, as proposed previously. Additionally, we showed that in the HT structure, the hopping rotations of the $[\text{NbOF}_5]^{2-}$ octahedra only occur about the $\text{F}_{\text{apical}}\text{–Nb–O}$ axis meaning that all of the anion sites are fully occupied by either F or O and hopping is only allowed between $\text{F}_{\text{equatorial}}$ sites. Based on these observations, we propose that the reconstructive transition in this perovskite with ordered A-site vacancies and ordered anions is driven by the axial rotations of the $[\text{NbOF}_5]^{2-}$ octahedra.

EXPERIMENTAL SECTION

Synthesis and Structure Confirmation of KNaNbOF_5 .

Caution: Hydrofluoric acid is toxic and corrosive and must be handled with extreme caution and the appropriate protective gear! If contact with the liquid or vapor occurs, proper treatment procedures should immediately be followed.^{25–27}

The reagents NaF (99%, Aldrich), KNO_3 (99.9%, Mallinckrodt), Nb_2O_5 (99.5%, Strem), and aqueous hydrofluoric acid (HF; 48% HF by weight, Aldrich) were used as received. All reactants were sealed in Teflon pouches as previously described.²⁸ The precursor Na_2NbOF_5 was synthesized hydrothermally via a previously published procedure²³ by combining 0.1344 g of NaF, 0.4254 g of Nb_2O_5 , and 1.2 mL of aqueous HF in a Teflon pouch. Six pouches were placed in a 125 mL Teflon-lined Parr pressure vessel filled with 42 mL of deionized water as backfill, and heated at 5 °C/min to 150 °C, held for 24 h, and slowly cooled to room temperature at 0.1 °C/min. The cooled products were left in the pouches at room temperature to crystallize

over 2 weeks. The product was then recovered in air via vacuum filtration.

The CS phase was synthesized with 0.0550 g (2.20×10^{-4} mol) of Na_2NbOF_5 , 0.0160 g (1.582×10^{-4} mol) of KNO_3 , and 0.12 mL (6.7×10^{-3} mol) of H_2O . The reagents were sealed in Teflon pouches and heated using the same procedure as for the Na_2NbOF_5 precursor. Both the CS and NCS products were left to crystallize in the pouches for 1–2 weeks to increase yield before recovery by vacuum filtration. Sample purity was confirmed by powder X-ray diffraction measurements on an Ultima IV X-ray diffractometer (Rigaku) with Cu radiation. Powder patterns were analyzed using MDI Jade (2010).

Solid-State ^{19}F NMR Experiments. The local ^{19}F environments in KNaNbOF_5 are examined by solid-state ^{19}F magic-angle-spinning (MAS) NMR operating at 470.5 MHz (11.75 T) on a Bruker Avance-III 500 spectrometer, which is equipped with a 2.5 mm Bruker HXY probe. ^{19}F spectra are obtained using a rotor-synchronized spin-echo sequence with a 90° pulse of 2 μs and a recycle delay of 100 s at a spinning rate of 25 kHz. In case of signals overlapping between spinning side bands and isotropic shifts, ultrafast MAS ^{19}F measurements are performed using a Bruker 1.3 mm Bruker HXY probe operating at 564.6 MHz (14.1 T) on a Bruker Avance NEO 600 spectrometer at a spinning rate of 50 kHz. ^{19}F spectra are obtained using a single pulse of 2.8 μs and a recycle delay of 100 s.

The reconstructive phase transition (*P4/nmm* to *Cmcm*) is investigated with in situ (heating and cooling) high-temperature ^{19}F MAS NMR on the CS (*P4/nmm*) phase KNaNbOF_5 . ^{19}F experiments are carried out using a LASMAS probe²⁹ operating at 470.5 MHz (11.75 T) on a Bruker Avance-III 500 spectrometer. ^{19}F spectra are collected from room temperature to 450 °C with rotor-synchronized spin-echo sequence using a 90° pulse of 6.9 μs and a recycle delay of 20 s at a spinning rate of 5 kHz. ^{19}F T1 relaxation measurements are performed with an inversion–recovery sequence to probe the behavior of F-ion dynamics. Prior to acquisitions of ^{19}F spectra, temperature calibration of the LASMAS probe is performed by linearizing the ^{79}Br chemical shift of KBr as a function of temperature (from room temperature to 700 °C).³⁰ After cooling, the heat-treated KNaNbOF_5 are subject to high-resolution ^{19}F MAS (25 or 50 kHz; 2.5 mm or 1.3 mm HXY probe) NMR to examine the ^{19}F local environments for phase identification. All ^{19}F spectra were calibrated with $\text{LiF}_{(s)}$ at –201 ppm. All ^{19}F spectra were analyzed and processed on Topspin (v4.0).

^{19}F NMR Shift Calculation. All of the calculations based on DFT were performed in the Vienna ab initio simulation package (VASP).³¹ The crystal structures of the CS and NCS phases were retrieved from ref 32. The structures of the HT phases (*Cmcm*, *Pnma*, and *Pbcm*) were retrieved from ref 19. The structure information on intermediate phases was obtained from group theoretical method and density functional theory (DFT) methods described in previous work.¹⁹ Projector-augmented-wave approach was used for electronic structure calculations with Perdew–Burke–Ernzerhof generalized-gradient approximation (PBE-GGA).^{33,34} A planewave cutoff of 500–550 eV and a k-point density of at least 500 per number of atoms in the unit cell were set until the total energy converged in all calculations. Before NMR shift calculation, the unit cell parameters were also relaxed. The chemical shifts were determined by magnetic shieldings using perturbation theory (linear response).^{35,36} The calculated shifts matched well with experimental shifts with a calibration factor of +15 ppm.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.0c01439>.

Analysis of ^{19}F NMR spectra and DFT calculation on ^{19}F NMR shifts for KNaNbOF_5 , electronic structure calculations of structures along the reconstructive transition path, and K^+ coordination (PDF)

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Notes

The authors declare no competing financial interest.

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