

How Lewis Acidity of the Cationic Framework Affects KNaNbOF_5 Polymorphism

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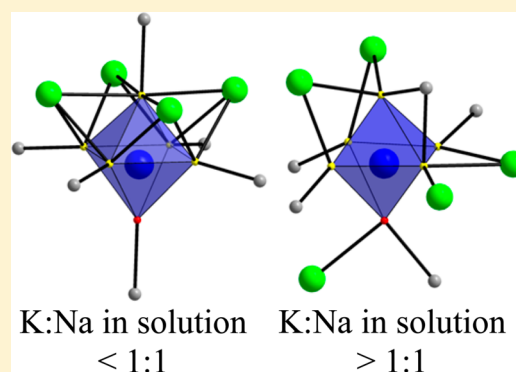
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S Supporting Information

ABSTRACT: The valence matching principle is used to explain the loss of inversion symmetry in the noncentrosymmetric (NCS) polymorph of KNaNbOF_5 in comparison to its centrosymmetric (CS) polymorph. The $[\text{NbOF}_5]^{2-}$ anion has five contacts to both potassium and sodium in the NCS polymorph, whereas in the CS polymorph there are only four contacts to potassium and six contacts to sodium. The lower average Lewis acidity of the cationic framework in the NCS polymorph relative to the CS polymorph reflects the loss of inversion symmetry. This lower average Lewis acidity is achieved during hydrothermal synthesis with a potassium-rich solution when the K:Na ratio in the reaction is greater than 1:1, as the Lewis acidity of potassium is lower than that of sodium. The contrasting coordination environments are manifested in secondary distortions that weaken the primary Nb=O interaction and lengthen the Nb=O bond in the NCS polymorph. An unusual heat-induced phase transition from the CS to the NCS polymorph was studied with in situ powder X-ray diffraction. The transition to the NCS polymorph upon cooling occurs through an intermediate phase(s).



INTRODUCTION

Noncentrosymmetric (NCS) materials are desired for their unique physical properties, but the stabilization of such materials is difficult to target. Understanding this stabilization is helpful for the design and synthesis of NCS phases. Noncentrosymmetric phases exhibit nonlinear properties such as second-harmonic generation (SHG), piezoelectricity, and/or pyroelectricity.¹ Strategies toward the synthesis of NCS materials are qualitative and focus on the use of acentric basic building units (BBUs), which often consist of elements with stereoactive lone pairs or d^0 metals subject to second-order Jahn–Teller (SOJT) distortions.^{2–5}

The incorporation of acentric BBUs does not alone guarantee an NCS structure. First, ligands of the BBU must be crystallographically ordered, which is not always achieved in oxide-fluoride compounds. Second, ordered building units must arrange without an inversion relation. Units with stereoactive lone pairs or SOJT active centers generally contain a polar moment, but an inversion center is usually electrostatically favored through an antiparallel arrangement of the polar units. Even if the units are oriented into a polar space group, the individual polar moments are often only partially aligned. According to Chen's anionic group theory, materials with a

greater alignment of individual polar moments will yield greater SHG efficiencies.⁶ Such alignment results in a polar space group. Knowledge of factors that can yield polar structures and align dipoles is important when attempting to synthesize new SHG materials.

The KNaNbOF_5 system is appealing for study, since both centrosymmetric (CS)⁷ and polar NCS polymorphs⁸ are known. This allows for direct comparison, since the identities of the cations are the same. Both polymorphs contain the $[\text{NbOF}_5]^{2-}$ polar anion. The $[\text{NbOF}_5]^{2-}$ dipoles are canceled in one of the polymorphs, resulting in a CS structure. The second polymorph, however, is polar because the $[\text{NbOF}_5]^{2-}$ dipoles are partially aligned. The synthetic conditions that influence the crystallization of one polymorph over the other can be determined. This system allows an acute understanding of stabilization of the NCS form.

A synthetic route is developed such that either polymorph could be made from the same combination of starting materials following the same heating profile. This new synthetic route is required to show that the polymorph that crystallizes from

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solution is controlled through variation of the K:Na ratio in the reaction solution. It is important to note that this ratio reflects the ratio within the reaction solution, not in the final product. The NCS and CS polymorphs both have the same stoichiometry. A K:Na ratio of greater than 1:1 results in the crystallization of the NCS polymorph, and a ratio below 1:1 results in the CS polymorph. This trend reflects the differences in coordination environments of the $[\text{NbOF}_5]^{2-}$ anion, which makes five potassium contacts in the NCS polymorph and four in the CS polymorph. This trend is explained through Pauling's second crystallographic rule (PSCR) and the valence matching principle. Pauling's second rule states that cations with the largest positive potential occupy sites that have the largest negative potentials.⁹ The valence matching principle states that stable structures form when the Lewis acidity of the cations closely matches the Lewis basicity of the anions. This principle was first applied to explain why certain stoichiometrically allowed silicates do not form¹⁰ and has since been extended to other oxides, oxyalts, and borates.^{11,12} These concepts can explain differences in the bonding network that result in breaking inversion symmetry in the NCS polymorph. Structural differences are also manifested in the strength of the secondary distortion.

The thermal stability of the two polymorphs is also examined. While heat-induced phase transitions typically result in an increase in crystal symmetry, a transition of the CS compound to the NCS polymorph was observed *ex situ*. This transition is investigated further with *in situ* powder X-ray diffraction (PXRD). Future *in situ* studies of this—and other—crystallization and precipitation processes could yield interesting results with regard to how one polymorph or another may form under similar but distinct synthetic conditions.

EXPERIMENTAL SECTION

Materials and Synthesis. *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.*^{13–15}

The compounds Nb_2O_5 (99.9% Aldrich), NaF (99%, Aldrich), KNO_3 (99.9%, Mallinckrodt), NaNO_3 (99.0%, Alfa Aesar), and aqueous hydrofluoric acid (HF) (48% HF by weight, Aldrich) were used as received. Deionized water was used in the syntheses. All reactants were sealed in Teflon (fluoro(ethylenepropylene), FEP) "pouches" as previously described.¹⁶ Four to six pouches were placed in a 125 mL Teflon-lined Parr pressure vessel filled with 42 mL of deionized H_2O as backfill. Pressure vessels were heated to 150 °C for 24 h and slowly cooled to room temperature at 0.1 °C/min. Products were left in the pouch at room temperature for an additional 24 h to promote crystallization. Pouches were opened in air, and the products were recovered via vacuum filtration.

The CS polymorph was synthesized with 0.0160 g (1.582×10^{-4} mol) of KNO_3 , 0.0550 g (2.20×10^{-4} mol) of Na_2NbOF_5 , and 0.12 g (6.7×10^{-3} mol) of H_2O . The NCS polymorph was synthesized with 0.0929 g (9.19×10^{-4} mol) of KNO_3 , 0.0496 g (1.98×10^{-4} mol) of Na_2NbOF_5 , and 0.12 g (6.7×10^{-3} mol) of H_2O . A space composition plot was created by keeping the sum of moles of potassium, sodium, and niobium approximately constant. Space composition plots with KCl , K_2SO_4 , K_2HPO_4 , K_2CO_3 , and K_3PO_4 as alternate potassium sources at similar molar ratios were also created.

Na_2NbOF_5 was synthesized through the reaction of 0.1344 g of NaF , 0.4252 g of Nb_2O_5 , and 1.2 mL of HF. Yields of Na_2NbOF_5 are increased by allowing the product to crystallize for 7 days before filtration.¹⁷

Powder X-ray Diffraction. Powder patterns of products identified in the space composition diagrams were recorded on a Rigaku

Geigerflex D/MAX-IA powder diffractometer. Samples were mounted on glass plate slides, and products were identified using Jade 5.0.

High-resolution *in situ* synchrotron powder diffraction data were collected using beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory, using an average wavelength of 0.412964 Å.¹⁸ Twelve perfect Si(111) analyzer crystals coupled to 12 Oxford-Danfysik LaCl_3 scintillators were scanned over a 2θ range of 0–26°, with data points collected every 0.002° 2θ and a scan speed of 0.02°/s. Samples were loaded into Kapton capillary tubes opened on both ends and capped with quartz wool on both ends. The Kapton capillary tube was then nested in a fused-silica capillary tube. The Kapton was used to prevent reactivity of the sample with silicon from the fused silica. The fused-silica capillary was needed to maintain the alignment of the sample at elevated temperatures, since Kapton loses rigidity at the higher temperatures used in our experiments. Samples were heated in a reaction flow cell as previously described.¹⁹ *In situ* powder diffraction data were collected under flowing argon. The capillary tubes were oscillated at approximately 10 Hz during the measurement to improve the transmission geometry powder averaging.

RESULTS AND DISCUSSION

Structural Comparison of KNaNbOF_5 Polymorphs. A structural comparison of the two KNaNbOF_5 polymorphs provides a better understanding of crystallization of one polymorph versus another. While both polymorphs contain the $[\text{NbOF}_5]^{2-}$ polar anion, the packing of these units and coordination environments of the potassium and sodium cations differ, leading to the two different space groups. The CS polymorph crystallizes in the space group $P4/nmm$, and the NCS polymorph crystallizes in the polar space group $Pna2_1$.

In both polymorphs, the $[\text{NbOF}_5]^{2-}$ unit coordinates to 10 cations. In the CS phase, each $[\text{NbOF}_5]^{2-}$ anion bonds to 6 sodium and 4 potassium cations, whereas in the NCS phase the $[\text{NbOF}_5]^{2-}$ anion bonds to 5 sodium and 5 potassium cations. Figure 1 shows the different coordination environments of the $[\text{NbOF}_5]^{2-}$ unit. This difference is accompanied by differences in cation coordination environments.

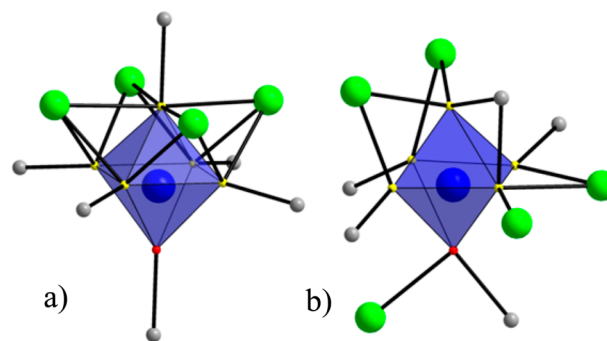


Figure 1. $[\text{NbOF}_5]^{2-}$ coordination environments of the (a) CS and (b) NCS polymorphs. Blue, yellow, red, green, and gray spheres represent niobium, fluorine, oxygen, potassium, and sodium atoms, respectively.

The sodium cation is octahedrally coordinated in both polymorphs. In the CS polymorph, this coordination is achieved through corner sharing with six different $[\text{NbOF}_5]^{2-}$ anions, as shown in Figure 2a. In the NCS polymorph, the sodium cation only coordinates to five $[\text{NbOF}_5]^{2-}$ anions. An octahedral environment around sodium is maintained in the NCS polymorph through edge sharing with one of the $[\text{NbOF}_5]^{2-}$ anions, creating the $[\text{NaNbO}_2\text{F}_8]^{6-}$ unit, as shown in Figure 2b. These acentric anionic units connect to

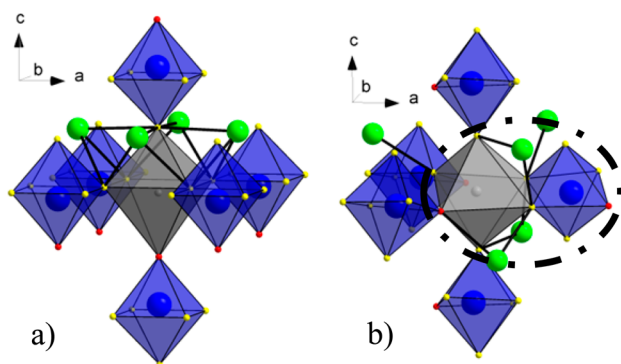


Figure 2. (a) The sodium coordination environment in CS KNaNbOF_5 . Sodium corner-shares with six $[\text{NbOF}_5]^{2-}$ units. (b) The sodium coordination environment in NCS KNaNbOF_5 . Sodium edge-shares with one $[\text{NbOF}_5]^{2-}$ unit and results in an $[\text{NaNbO}_2\text{F}_8]^{6-}$ unit (circled). Blue, yellow, red, green, and gray spheres represent niobium, fluorine, oxygen, potassium, and sodium atoms, respectively.

form a three-dimensional network that contains polar moments that are partially aligned along the c axis. A more detailed structural discussion has been previously described.⁸

The potassium cations coordinate to four and five $[\text{NbOF}_5]^{2-}$ anions in the CS and NCS polymorph, respectively, which reflects the greater number of potassium contacts to a given $[\text{NbOF}_5]^{2-}$ anion in the NCS polymorph. In the CS polymorph, four $[\text{NbOF}_5]^{2-}$ anions are arranged tetrahedrally around the potassium cation. This tetrahedral arrangement allows the potassium cation to face share with all four $[\text{NbOF}_5]^{2-}$ units to yield a total potassium coordination number of 12. Sterics associated with the incorporation of five $[\text{NbOF}_5]^{2-}$ anions in the NCS polymorph preclude face sharing. Therefore, the potassium coordination in the NCS polymorph is distorted and the potassium coordination number is reduced to 8. Figure 3 displays the differences in potassium coordination environments.

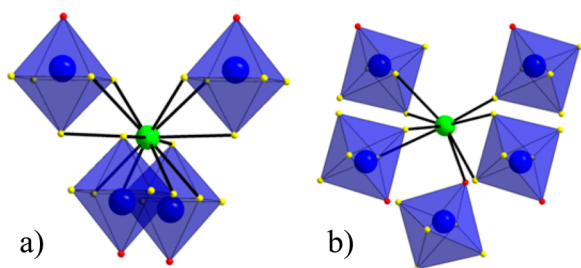


Figure 3. (a) The potassium coordination environment of CS KNaNbOF_5 . (b) The potassium coordination environment of NCS KNaNbOF_5 . Blue, yellow, red, green, and gray spheres represent niobium, fluorine, oxygen, potassium, and sodium atoms, respectively.

Valence Matching Principle. The valence matching principle states that a structure will be more stable when the Lewis acidity of the cation closely matches the Lewis basicity of the anion.¹¹ The Lewis acidity of a cation can be determined by dividing the atomic valence by the average coordination number. The Lewis acidity of sodium and potassium is calculated to be 0.17 and 0.13 valence units (vu) respectively.¹¹ The Lewis basicity of oxide-fluoride anions can be similarly determined. The valence contribution of the central cation to each oxygen/fluorine is subtracted from each anion's atomic valence. The differences are added and then divided by the

coordination number. The Lewis basicity of $[\text{NbOF}_5]^{2-}$ is calculated to be 0.17–0.20 vu. Structures are therefore expected to be more stable when $[\text{NbOF}_5]^{2-}$ bonds to sodium instead of potassium, since sodium and $[\text{NbOF}_5]^{2-}$ have more similar Lewis acid and base strengths.

The $[\text{NbOF}_5]^{2-}$ anion in the NCS polymorph bonds to an additional potassium cation and one less sodium cation in comparison to the CS polymorph. The bond network's average Lewis acidity is therefore slightly lower in the NCS polymorph. The average Lewis acidity of the bond network in the NCS polymorph does not match as closely to the Lewis basicity of $[\text{NbOF}_5]^{2-}$ as it does in the CS polymorph. This greater mismatch between Lewis acidity and basicity corresponds to a larger deviation of PSCR in the NCS polymorph.

Despite this greater deviation from PSCR, the NCS polymorph can be synthesized from a solution with KNO_3 and Na_2NbOF_5 as the reactants. In order for the $[\text{NbOF}_5]^{2-}$ anion to crystallize with the additional contact to potassium, a solution rich in potassium must be used. This concept is supported with the synthetic trends shown in Figure 4, which

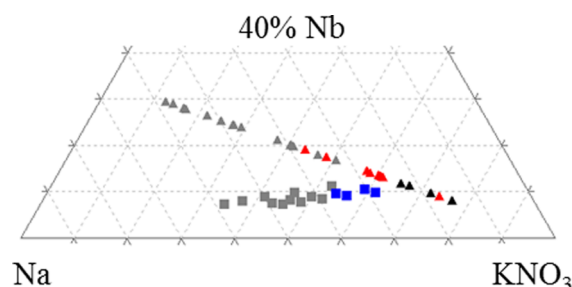


Figure 4. Space composition plot from mole fractions of K, Na, and Nb. Triangles represent reaction mixtures consisting of only KNO_3 and Na_2NbOF_5 . Squares represent reaction mixtures also containing NaNO_3 . Red, gray, and blue points contain the NCS, CS, and mixture of NCS and CS as products, respectively. Black points contain unknown phases.

demonstrates that the NCS polymorph is only achieved with reaction mixtures that have a K:Na ratio greater than approximately 1:1. A potassium-rich (relative to sodium) solution corresponds to a reaction mixture whose Lewis acidity is slightly lower, as potassium is less acidic than sodium, which ultimately leads to an NCS structure with a less acidic cationic framework. If there is an excess of dissolved potassium in the solution when the crystal nucleates and grows, a greater number of potassium contacts to the $[\text{NbOF}_5]^{2-}$ anion can be made, and the NCS polymorph can crystallize.

The sodium cation in the CS polymorph achieves an octahedral coordination environment through corner sharing with six different $[\text{NbOF}_5]^{2-}$ anions, as shown in Figure 2. Because only five sodium contacts are made to an $[\text{NbOF}_5]^{2-}$ anion in the NCS polymorph, the sodium cation must edge share with one of the $[\text{NbOF}_5]^{2-}$ units to achieve an octahedral coordination environment. The stability required to maintain a coordination number of 6 at the expense of edge sharing is driven by the valence matching principle; the Lewis acidity of sodium closely matches the Lewis basicity of $[\text{NbOF}_5]^{2-}$. The shared edge between sodium and an $[\text{NbOF}_5]^{2-}$ anion which forms the $[\text{NaNbO}_2\text{F}_8]^{6-}$ unit, shown in Figure 2b, contributes to breaking the inversion symmetry in the NCS polymorph.

The dipole moment of the $[\text{NbOF}_5]^{2-}$ anion is dictated by the direction of the $\text{Nb}=\text{O}$ bond. A given layer in the ab plane

of the CS polymorph has dipole moments aligned in the same direction, as can be seen in Figure 2a. Alternating *ab* layers have dipoles exactly canceling the dipoles in the layer above and below, which results in a CS structure. This pattern of alternating layers with exactly opposing dipoles is created since the octahedra with opposing dipoles are not tilted with respect to each other. The formation of the $[\text{NaNbO}_2\text{F}_8]^{6-}$ unit in the NCS polymorph results in tilting of the $[\text{NbOF}_5]^{2-}$ octahedra. This octahedral tilting results in partial alignment of the dipoles and creates a polar structure. The partial alignment of the dipoles and description of the polar structure has been described previously.⁸

The lower net acidity of the cationic network and the formation of the $[\text{NaNbO}_2\text{F}_8]^{6-}$ unit, however, does not alone guarantee the formation of an NCS structure. The related compound CsNaNbOF_5 is CS, despite the fact that cesium has a lower Lewis acidity than potassium, and CsNaNbOF_5 also contains the $[\text{NaNbO}_2\text{F}_8]^{6-}$ unit. The more covalent nature of the cesium bonds to O/F stabilizes a CS structure, as demonstrated through a comparison of the Born effect charges between CsNaNbOF_5 and the NCS form of KNaNbOF_5 .²⁰ While the valence matching principle cannot necessarily be universally applied to explain symmetry breaking in compounds that have related structures but different compositions, it can be used to explain the differences that exist within polymorphs of materials with the same composition, as in the case of KNaNbOF_5 .

Primary and Secondary Distortions. Early-transition-metal oxide-fluorides with the general formula $\text{M}^{\text{V}}\text{OF}_5^{2-}$ ($\text{M} = \text{V}, \text{Nb}, \text{Ta}$) or $\text{M}^{\text{VI}}\text{O}_2\text{F}_4^{2-}$ ($\text{M} = \text{Mo}, \text{W}$) are targeted for NCS materials owing to the enhanced primary distortion from the center of the octahedron experienced by the metal, which is a result of metal *d π* and oxygen *p π* orbital interactions.^{21,22} This distortion is enhanced by fluoride anions in positions away from the SOJT distortion. These inner-octahedral interactions can be affected by secondary distortions that result from interactions between the anions with the extended cationic network. Bonds between the oxide or fluoride ion and the surrounding cations cause the central M–O or M–F bond to lengthen to maintain atomic valence of the anion. Secondary distortions from the fluoride ligands can therefore enhance the primary distortion by lengthening the *trans* M–F bond, whereas secondary distortions with oxide anions will compete against the primary distortion by lengthening the M–O bond. The effect of alkali cation identity on these secondary distortions exhibited by $[\text{NbOF}_5]^{2-}$ has been discretely examined between Na/K and Na/Cs pairs in comparing the materials KNaNbOF_5 and CsNaNbOF_5 .^{8,20}

The different coordination environments of potassium and $[\text{NbOF}_5]^{2-}$ in the NCS KNaNbOF_5 polymorph that result from the deviation from PSCR is manifested in the secondary distortion of the out-of-center shift in the $[\text{NbOF}_5]^{2-}$ octahedron. Direct comparisons of the effect of secondary distortions can be made in this study, since the anion in which the primary distortion is observed and the cations that contribute to the differences in secondary distortion (i.e., potassium) are identical in the two polymorphs. The strength of the secondary distortions exhibited in the $[\text{NbOF}_5]^{2-}$ anion can be qualitatively compared using bond lengths. A shorter Nb=O bond will correspond to a weaker secondary distortion from the oxide and a stronger contribution of secondary distortions from the fluoride anions. The Nb=O bond length in the CS polymorph is 1.7179(14) Å. The Nb=O bond

length in the NCS polymorph is slightly longer at 1.745(5) Å. The difference in the Nb=O bond lengths can be explained by comparison of the secondary distortions through examination of the number of potassium contacts the oxide and fluoride ligands make. The sodium cations are not expected to contribute much to differences in secondary distortions between these two polymorphs, since each oxide and fluoride ligand make one contact to a sodium cation in both polymorphs. Therefore, the contribution of sodium to the secondary distortion should be roughly the same.

The oxide ligand does not make any potassium contacts in the CS polymorph, whereas one K–O contact is made in the NCS polymorph. This secondary distortion weakens the Nb=O bond and contributes to a longer Nb=O bond length in the NCS polymorph. In the CS polymorph, the axial F1 ligand makes four potassium contacts, while the equatorial F2 ligands make two contacts. In the NCS polymorph, the axial F1 ligand and equatorial F2 ligand make two contacts, and the remaining equatorial fluoride ligands each only make one potassium contact. These contacts can be viewed in Figure 1. Since the fluoride ligands overall make more potassium contacts in the CS polymorph, the $[\text{NbOF}_5]^{2-}$ anion in the CS polymorph experiences greater secondary distortions from fluoride ligands and thus contains longer Nb–F bonds and a shorter Nb=O bond. Potassium to oxide/fluoride bond lengths and bond valence sums^{23,24} are summarized in Tables 1 and 2.

Table 1. Bond Lengths (R_{ij} , Å) and Experimental Bond Valence Sums (V_j , Valence Units) for K in CS KNaNbOF_5

| K | R_{ij} | S_{ij} |
|-----------------------|-----------|----------|
| F1 (×4) | 2.9586(9) | 0.07 |
| F2 (×8) | 2.8492(4) | 0.10 |
| $V_j = \sum_j S_{ij}$ | | 1.08 |

$S_{ij} = \exp[(R_0 - R_{ij})/B]$, experimental bond valence in valence units of bond *ij*, R_0 is a constant dependent on bonded elements *i* and *j*, and $B = 0.37$.²³

Table 2. Bond Lengths (R_{ij} , Å) and Experimental Bond Valence Sums (V_j , Valence Units) for K in NCS KNaNbOF_5

| K | R_{ij} | S_{ij} |
|-----------------------|----------|----------|
| O | 2.834(5) | 0.15 |
| F1 | 2.638(4) | 0.17 |
| | 2.726(4) | 0.14 |
| F2 | 2.732(2) | 0.14 |
| F3 | 2.700(4) | 0.15 |
| | 2.826(4) | 0.10 |
| F4 | 2.822(5) | 0.11 |
| F5 | 2.853(4) | 0.10 |
| $V_j = \sum_j S_{ij}$ | | 1.06 |

$S_{ij} = \exp[(R_0 - R_{ij})/B]$, experimental bond valence in valence units of bond *ij*, R_0 is a constant dependent on bonded elements *i* and *j*, and $B = 0.37$.²³

The fewer potassium contacts made to fluoride ligands in the NCS polymorph is a direct result of spatial limitations that prevent face sharing with $[\text{NbOF}_5]^{2-}$ units, as described above. Figure 3 illustrates how the incorporation of a fifth $[\text{NbOF}_5]^{2-}$ unit to the potassium coordination sphere breaks the tetrahedral environment centered on potassium. This fifth $[\text{NbOF}_5]^{2-}$ unit is accompanied by a distorted potassium

coordination environment and lower symmetry, and results in five crystallographically unique fluoride ions (as opposed to two unique fluorides in the CS polymorph). Since the coordination number of potassium is lower in the NCS polymorph, potassium maintains its atomic valence in the NCS polymorph with shorter K–F bonds (see Tables 1 and 2). It is this decrease in potassium coordination number that results in fewer K–F contacts and weaker secondary distortions and ultimately results in a longer Nb=O bond in the NCS polymorph.

Synthesis of KNaNbOF₅ Polymorphs. The fact that KNaNbOF₅ exists in both CS and NCS polymorphs and that both polymorphs can be synthesized using hydrothermal techniques presents an interesting question as to what factors determine which phase ultimately crystallizes. While multiple synthetic routes have been reported for both polymorphs,^{7,8,25,26} a direct comparison to determine what factors control the formation of a given polymorph has not been published. One study does, however, report synthesizing both polymorphs in a single reaction.²⁵ The CS polymorph crystallizes first as blocks, followed by the NCS polymorph after longer periods of time. This study concludes that the CS polymorph is a kinetic product, since it is the first to crystallize.

A synthetic route was developed such that both polymorphs could be synthesized using the same reactants and heating profile, where the polymorph that forms is dictated by the K:Na ratio in the solution. A series of reactions that contained KNO₃ and Na₂NbOF₅ in water were conducted at 150 °C. Additional reactions were conducted with the addition of NaNO₃. A space composition plot from mole fractions of KNO₃, Na, and Nb is given in Figure 4. Reaction mixtures consisting of only KNO₃ and Na₂NbOF₅ are plotted as triangles, and all fall along a straight line corresponding to a 2:1 Na:Nb ratio fixed by the Na₂NbOF₅ precursor. Reactions deviating from this line were achieved through the addition of NaNO₃, which was chosen as the sodium source because the nitrate anion is already introduced in the system from KNO₃. Reaction mixtures containing NaNO₃ are plotted as squares. Figure 4 reveals an overall trend where a higher K:Na ratio, greater than about 1:1, favors crystallization of the NCS polymorph. The trend can be rationalized by examining the change in coordination environment of the [NbOF₅]²⁻ anion, depicted in Figure 1. In the CS phase, each [NbOF₅]²⁻ unit bonds to four potassium and six sodium cations, whereas in the NCS phase it bonds to five potassium and five sodium cations. The potassium sources KCl, K₂SO₄, K₂CO₃, K₂HPO₄, and K₃PO₄ were also used as alternatives to KNO₃ to confirm the synthetic trend. Both polymorphs were successfully synthesized using KCl and K₂SO₄, following a trend similar to that for KNO₃, where a K:Na ratio greater than 1:1 results in crystallization of the NCS polymorph. The CS polymorph can be synthesized using K₂CO₃, K₂HPO₄, or K₃PO₄. However, these basic salts did not yield the NCS polymorph even at high K:Na ratios. Experimental details are provided in the Supporting Information, and the results are summarized in Table S1.

The fact that the [NbOF₅]²⁻ anionic unit makes a greater number of potassium contacts in the NCS polymorph than the CS polymorph reflects the synthetic trend of a higher K:Na ratio yielding the NCS phase. This solution with a slightly lower Lewis acidity results in the less acidic cationic network found in the NCS structure. Analyzing the coordination environment of the [NbOF₅]²⁻ anion can therefore give insight as to how to synthesize the desired polymorph.

Heat-Induced Phase Transition. The thermal stability of both polymorphs was examined up to 400 °C. The fact that the NCS polymorph can be synthesized via a direct solid-state reaction between KF and NaNbOF₄ would suggest that the NCS polymorph is the thermodynamic phase.⁸ This is consistent with conclusions based upon crystallization rates previously reported.²⁵ The thermal stability of the CS polymorph was first examined by analyzing the product after heating to 400 °C. Interestingly, the CS polymorph transitions to the NCS polymorph. This may at first seem contrary to typical behavior, as symmetry typically increases upon heating.

In situ PXRD studies were conducted to probe this transition. Figure S1 (Supporting Information) shows the in situ PXRD of the CS KNaNbOF₅ polymorph upon heating to 400 °C and cooling to room temperature at a rate of 10 °C/min and reveals a number of transitions. The first prominent change upon heating occurs between 238 and 292 °C. A second prominent transition is observed between 349 and 393 °C. Upon cooling, two transitions are observed, the first between 393 and 337 °C and the second between 337 and 282 °C. The latter transition is the formation of the NCS polymorph. The phase observed at 400 °C is not the NCS polymorph of KNaNbOF₅. In fact, the NCS polymorph is not observed until the second phase transition upon cooling.

These in situ studies reveal that the CS polymorph does *not* directly transition to the NCS polymorph upon heating. The intermediates observed, however, are unknown structures. Attempts to index the intermediate phases have so far been unsuccessful; thus, it is unknown how many intermediate phases are present. It is likely that the intermediate phase(s) formed upon heating are CS since the initial phase is CS. Upon cooling, the intermediate phase(s) (likely CS) transitions to the NCS KNaNbOF₅ polymorph to follow typical phase transition behavior. The transition from the CS polymorph to the intermediate phase(s) is therefore irreversible.

The heating of the NCS polymorph was also studied via in situ PXRD. When this polymorph was heated to 400 °C and cooled to room temperature at a rate of 10 °C/min, the same intermediate transitions were observed as for the CS polymorph. Upon cooling, the intermediate(s) also transitioned to the NCS polymorph, indicating that the transition is reversible. It is important to note that the intermediate phase is metastable at 400 °C. Within 10 min at 400 °C, the intermediate phase(s) transitions to other undetermined phases. As such, the heating and cooling rate of either polymorph is crucial in order to observe the transition to the NCS phase. If the heating and cooling rates are lowered to 7.5 °C/min, alternate products are observed. Unlike the transitions observed from heating the KNaNbOF₅ polymorphs, the transition to these alternate products is irreversible; no transitions are observed when they are heated again. However, the intermediate phase(s) appears to be stable at 350 °C—after dwelling at 350 °C for 1/2 h, no decomposition products were observed and the sample transitioned back to the NCS polymorph upon cooling.

CONCLUSION

The primary distortion observed in [MO_xF_{6-x}]ⁿ⁻ units is often targeted to yield NCS materials. The deviation from PSCR in the NCS polymorph of KNaNbOF₅ that results from the greater difference between the Lewis acidity of potassium and Lewis basicity of [NbOF₅]²⁻ accompanies breaking inversion symmetry in the NCS polymorph. The additional potassium

contact made to $[\text{NbOF}_5]^{2-}$ in the NCS polymorph is accompanied by a loss of a sodium contact made. To compensate for the loss of a sodium contact, the valence matching principle drives sodium to share an edge with one of the $[\text{NbOF}_5]^{2-}$ groups to maintain an octahedral coordination. This results in the formation of the $[\text{NaNbO}_2\text{F}_8]^{6-}$ unit, which tilts the $[\text{NbOF}_5]^{2-}$ anions and creates a net polar moment. The coordination environment associated with the less acidic cationic framework of the polar structure can be synthetically achieved by increasing the K:Na ratio of the reaction mixture, since the Lewis acidity of potassium is less than that of sodium. The heat-induced phase transition of the CS to the NCS polymorph involved an intermediate phase(s) as the CS polymorph was heated. This phase then transitioned to the NCS polymorph upon cooling, following typical behavior.

■ ASSOCIATED CONTENT

📄 Supporting Information

Text, a table, and a figure giving the synthetic procedure of KNaNbOF_5 , a summary of products formed, and in situ powder diffraction of the CS KNaNbOF_5 polymorph upon heating and cooling. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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