



Investigations of Phase Transitions in KNaNbOF_5 with High-Temperature and High-Resolution ^{19}F Solid-State NMR

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Introduction

Phase transition pathways in heteroanionic polyhedra, KNaNbOF_5 , have been computationally predicted between $P4/nmm$ (CS), $Cmcm$ (HT), and $Pna2_1$ (NCS) phases.^[1] The experimental efforts suggest that O/F site disorders induced by rotation of NbOF_5^{2-} polyhedra are responsible for the phase transitions. Notably, the high-temperature $Cmcm$ phase, which exhibits dynamical disorders, plays a vital role in determining whether the transition pathway is reversible or irreversible. However, the correlation of dynamical disorders with the phase transition pathways has not yet been experimentally confirmed. Here, we employ *in situ* high-temperature and high-resolution ^{19}F NMR to establish the structure-property relationships in KNaNbOF_5 by monitoring the evolution of ^{19}F NMR spectra and ^{19}F ion dynamics through phase transitions.

Experimental

In situ ^{19}F MAS NMR experiments are conducted with a Bruker 7-mm laser-absorption MAS probe at 11.75T on a Bruker Avance-III 500 spectrometer from room-temperature to 451 °C at a spinning rate of 5 kHz. ^{19}F NMR spectra are obtained using a rotor-synchronized spin-echo pulse sequence. T_1 relaxation measurements are performed using a saturation-recovery pulse sequence. High-resolution ^{19}F MAS NMR measurements are performed with a 1.3mm HXY triple-resonance Bruker probe at 14.1 T on a Bruker Avance NEO 600 spectrometer. ^{19}F NMR spectra are acquired with a rotor-synchronized spin-echo pulse sequence at a spinning rate of 50 kHz. All ^{19}F NMR spectra are calibrated to 1M LiF at -203 ppm.

Results and Discussion

In situ ^{19}F NMR spectra of KNaNbOF_5 (CS) upon heating are shown in Fig.1. The high-temperature $Cmcm$ phase (-80 to -180 ppm) is detected at ~380 °C, which is consistent with the literature as evidenced by *in situ* PXRD.^[1] A merging of multiple ^{19}F environments with narrowing line-width is seen from 380 to 400 °C, suggesting fast F^+ exchange within NbOF_5^{2-} polyhedra, thus averaging out the Gaussian broadening from multiple local ^{19}F signals. The ^{19}F NMR spectra of pristine $P4/nmm$ (-200 to -300 ppm) phase show nearly negligible changes in line-shapes except for minor structural modifications at ~250 °C. Upon cooling, the ^{19}F NMR spectra (not shown) of the $Cmcm$ phase reduces and $P4/nmm$ phase restores the spectral intensity with stronger spinning side bands. The changes in spinning side bands indicate that the chemical shift anisotropy has changed; therefore, the orientation/geometry of NbOF_5^{2-} polyhedra has evolved before/after heating. The summary of *in situ* ^{19}F NMR T_1 relaxation time measurements of KNaNbOF_5 (CS) is given in Fig. 2. Several features can be seen: 1) $P4/nmm$ (CS) phase has relatively slow F^+ motions, indicated by T_1 independence of temperatures; 2) $Cmcm$ phase has a much shorter relaxation time, suggesting faster F^+ motions; 3) The sharp changes in T_1 times around T_c upon heating and cooling suggest phase transitions,^[2] which are in accordance with the computational predictions. High-resolution (50 kHz; not shown) ^{19}F NMR spectra of heated- KNaNbOF_5 (CS) confirms the formation of NCS phase, whose chemical shifts are verified by our DFT calculations.

Conclusions

We have successfully detected the phase transitions in KNaNbOF_5 using ^{19}F NMR. $Cmcm$ phase is detected by high-temperature ^{19}F NMR spectra and the phase transition is confirmed by T_1 relaxation measurements. High-resolution ^{19}F NMR spectra further support the CS → HT → NCS phase transition pathway. Two manuscripts are being prepared for submission on this work.

Acknowledgements

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References

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- [2] Rigamonti, A., Adv. Phys., **33**, 115–191 (1984).

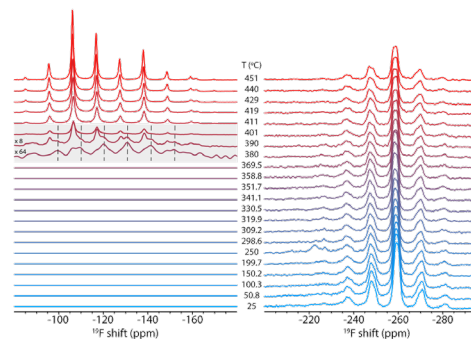


Figure 1. Variable-temperature ^{19}F NMR spectra of KNaNbOF_5 .

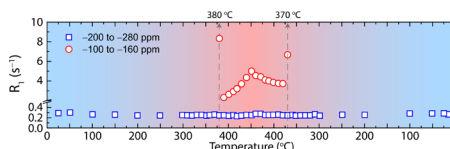


Figure 2. Variable-temperature ^{19}F T_1 measurements of KNaNbOF_5 .