

Topochemical Modulations from 1D Iron Fluoride Precursor to 3D Frameworks

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Abstract

Topochemical reactions are powerful pathways to modify inorganic extended structures, but the present approaches are limited by the degrees of freedom to tune the structural connectivity and dimensionality. In this work, we unveil a new topochemical bottom-up approach to tailor three-dimensional (3D) iron fluoride frameworks from the same one-dimensional (1D) $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ (IF) precursor upon reacting with iodide-based reagents (AI ; $\text{A}^+ = \text{Na}^+, \text{K}^+, \text{and } \text{NH}_4^+$). To elucidate their formation mechanism, a series of topochemical reactions is performed by varying the concentration of precursors, reaction temperatures and durations, and their corresponding products are analyzed through X-ray diffraction, nuclear magnetic resonance and Mössbauer spectroscopy techniques. Although the lower molar ratio of $\text{AI}:\text{IF}$ ($\approx 0.25:1.0$) produces the same hexagonal tungsten bronze (HTB)-type A_xFeF_3 , the topochemical reactions with higher $\text{AI}:\text{IF}$ ratios yield weberite- $\text{Na}_{1.95}\text{Fe}_2\text{F}_7$, tetragonal tungsten bronze (TTB)- $\text{K}_{0.58}\text{FeF}_3$ and pyrochlore- $\text{NH}_4\text{Fe}_2\text{F}_6$ phases. Our density functional theory calculations attribute the formation of iron fluoride phases to their thermodynamic stability. Moreover, kinetics also play an important role in enabling weberite and HTB fluorides with high purity, whilst the pyrochlore- $\text{NH}_4\text{Fe}_2\text{F}_6$ retains a minor HTB- $(\text{NH}_4)_x\text{FeF}_3$ impurity. Overall, the present work shows a new possibility of modulating the low-dimensional precursor to attain 3D frameworks with different structural arrangements *via* topochemical approaches.

Introduction

Chemical synthesis plays a central role in tailoring various classes of inorganic, organic and hybrid materials. Solid-state reactions, which are widely practiced from laboratory to industrial scale to produce inorganic materials, require high energy for the facile diffusion of reagents, thereby producing thermodynamically stable products. Although the recent progress in *in-situ* X-ray diffraction¹⁻⁴ and computational techniques^{5,6} have provided additional information regarding the formation mechanism of desired phases including metastable ones, the prediction of synthesis outcomes is still difficult as one cannot dictate the atomic diffusion processes occurring through conventional solid-state reactions. This situation is in stark contrast to organic synthesis, wherein molecular chemists employ retrosynthetic approaches to direct the atomic connectivity *via* solution-state sequential reactions for making targeted natural products, macromolecules and supramolecular structures. Further, organic crystals can be tailored using stereo- and regio-specific reactions between molecules confined in the lattice *via* crystal engineering approaches.⁷

While such direct control over atomic connectivity in extended inorganic structures is extremely challenging, soft chemical approaches, such as topochemical modulations, can modify cationic and/or anionic sub-lattices of a parent framework.^{8,9} So far, various classes of oxides,¹⁰ fluorides,¹¹ sulfides,¹² phosphates,¹³ and mixed-anionic frameworks¹⁴⁻¹⁶ have been synthesized using diverse topochemical approaches such as (de)intercalation, ion-exchange, dehydration, etc., which otherwise cannot be readily obtained through conventional solid-state reactions. Yet, the present topochemical approaches are restricted on two fronts: (i) the requirement of a thermodynamically stable phase first synthesized *via* solid-state synthesis, and (ii) the limited degrees of freedom for tuning the structural connectivity and dimensionality since the processes occur in sequential steps.

Recently, our group has demonstrated a novel topochemical bottom-up approach in which a one-dimensional $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ (IF) precursor is converted into 2D- NaFeF_4 and orthorhombic weberite 3D- $\text{Na}_2\text{Fe}_2\text{F}_7$ frameworks through the incorporation of a “structure-stabilizing agent”, NaF, into the host lattice.¹¹ Briefly, the formation of 2D- NaFeF_4 from $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ involves concurrent dehydration, ion-exchange between Na^+/F^- and H^+/OH^- groups, and condensation of F^-/OH^- groups. When the same reaction is carried out at higher temperature (230°C), the 3D- $\text{Na}_2\text{Fe}_2\text{F}_7$ framework forms through a minor rearrangement of the 2D framework upon topotactic fluoride deintercalation and iron reduction. It is worth noting that two other weberite polymorphs, monoclinic¹⁷ and trigonal $\text{Na}_2\text{Fe}_2\text{F}_7$ ¹⁸, were prepared through a high-temperature synthesis route, while the topochemical bottom-up approach enabled the manipulation of IF precursor lattice to produce orthorhombic- $\text{Na}_2\text{Fe}_2\text{F}_7$. A recent study highlighted the presence of orthorhombic, monoclinic and trigonal $\text{Na}_2\text{Fe}_2\text{F}_7$ polymorphs in the same sample prepared by high-energy ballmilling.¹⁹

Further, we have attempted to produce mixed-halide 2D- NaFeF_3Cl , - NaFeF_3Br , and - NaFeF_3I frameworks from an IF precursor by utilizing “NaCl/NaBr/NaI” as the corresponding structural-stabilizing agents (for details, see experimental). Whilst the X-ray diffraction (XRD) patterns (Figure 1a) collected on the products of the reactions between IF and NaCl or NaBr resemble that of NaFeF_4 , their corresponding energy-dispersive elemental mappings confirm the complete absence of chloride and bromide species (Figure S1). Further, the Fourier-transformed infrared (FTIR) spectra reveal the presence of OH^- anions (Figure S2a of the supporting information) in the samples. These observations suggest that the products of the reactions between IF and NaCl/NaBr belong to the $\text{NaFeF}_{4-x}(\text{OH})_x$ family of compounds. Interestingly, the reaction between NaI and IF at 130°C has been found to lead to 3D- $\text{Na}_2\text{Fe}_2\text{F}_7$ due to the redox activity of the I^-/I_2

redox couple,^{20–23} which opens new avenues to tailor 3D iron fluoride frameworks using iodide-based reagents. Previously, LiI and NaI reagents were used to synthesize Li- and Na-intercalated transition metal oxides through topotactic intercalation reaction.

Along those lines, herein, we report the direct formation of three different 3D iron fluoride frameworks from the same 1D-FeF₃·3H₂O precursor through the addition of iodide-based reagents (AI; A⁺ = Na⁺, K⁺, and NH₄⁺). We investigate their formation mechanisms and the underlying thermodynamic and kinetic factors using XRD, nuclear magnetic resonance (NMR) spectroscopy, and density functional theory (DFT) calculations.^{24,25} While the formation of 3D frameworks is dictated by the different knitting of 1D chains from the precursor, their phase purity is affected by temperature and reaction time of topochemical synthesis.

Results and Discussion

The reaction between AI and IF in 1:1 mole ratio was performed in tetraethylene glycol (TEG) solvent at 130 or 170°C for 6 h (see experimental section for details). Rietveld analysis of the powder XRD patterns collected on the products and the corresponding cell parameters are displayed in Figure 1b-d and Table S1-S3, respectively. As discussed earlier, the reaction between NaI and IF produces orthorhombic weberite-Na₂Fe₂F₇ (space group : *Imma*), whereas the reactions utilizing KI and NH₄I yield tetragonal tungsten bronze (TTB)-K_xFeF₃ (0.4<x<0.6)^{26,27} and pyrochlore-NH₄Fe₂F₆ phases, respectively.^{28,29} Note that pyrochlore-NH₄Fe₂F₆ sample contains a minor hexagonal tungsten bronze (HTB)-(NH₄)_xFeF₃ (0.2<x<0.4) impurity phase as well. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) analyses of weberite and TTB samples indicate compositions of Na_{1.99(5)}Fe_{1.99(9)}F₇ and K_{0.58(1)}Fe_{0.99(9)}F₃, respectively. Mössbauer experiments were performed on the weberite, HTB and pyrochlore samples to quantify the Fe³⁺/Fe²⁺ ratio (Figure S3a-c) and the corresponding fitting parameters are provided in Table

S4. While the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio (47:53) for the TTB sample almost matches that derived from the composition estimated with ICP, the higher Fe^{3+} content in the pyrochlore sample ($\text{Fe}^{3+}:\text{Fe}^{2+} \sim 68:32$) is probably due to the presence of the HTB impurity. Similarly, the weberite sample also shows a higher Fe^{3+} content ($\text{Fe}^{3+}:\text{Fe}^{2+} \sim 70:30$) than expected based on the ICP composition, due to the presence of an amorphous Na_3FeF_6 -type impurity as deduced from ^{23}Na nuclear magnetic resonance spectroscopy (NMR) measurement (Figure S3d). While the FTIR spectra of the products from NaI- and KI-based reactions show no signature of OH^- features (Figure S2b), the presence of NH_4^+ in the pyrochlore phase is confirmed by the features at 3250 and 1427 cm^{-1} (due to N-H stretching and N-H bending modes, respectively).³⁰ Further, scanning electron microscopy (SEM) analysis of the weberite, HTB and pyrochlore samples shows a significant reduction of their particle sizes compared to the IF precursor (Figure S5), which may be due to the dehydration reaction.³¹

To better understand the distribution of Na local environments in the weberite $\text{Na}_2\text{Fe}_2\text{F}_7$ sample, ^{23}Na solid-state nuclear magnetic resonance (ss-NMR) experiments were conducted. The presence of $\text{Fe}^{2+}/\text{Fe}^{3+}$ species in $\text{Na}_2\text{Fe}_2\text{F}_7$ (as well as in the other IF-framework structures discussed later) leads to strong paramagnetic interactions between the unpaired electron spins on Fe and the ^{23}Na nuclear spins under consideration and significant ^{23}Na NMR line broadening and large chemical shifts. Additionally, as ^{23}Na is a quadrupolar nucleus ($I = 3/2$), the resulting ^{23}Na NMR spectra are further broadened and shifted due to quadrupolar effects. The ^{23}Na solid-state NMR spectrum for NaI-IF weberite is shown in Figure S3d. The asterisks denote sidebands arising from the fast rotation of the sample during NMR data acquisition, which are suppressed in the overlaid ^{23}Na pj-MATPASS³² NMR spectrum. The pj-MATPASS spectrum consists of overlapping ^{23}Na resonances with chemical shifts in the range of 100 and 800 ppm, which are ascribed to several

^{23}Na local environments in weberite $\text{Na}_2\text{Fe}_2\text{F}_7$ at 7.35 T.¹⁹ An additional signal is observed near 1750 ppm, which we assign to Na nuclei in an amorphous Na_3FeF_6 impurity phase based on a previous report³³ and given that this compound is not observed by XRD. The presence of a small amount of amorphous Na_3FeF_6 impurity is consistent with the metastability of weberite- $\text{Na}_2\text{Fe}_2\text{F}_7$ and the presence of an adjacent, thermodynamically stable cryolite-like Na_3FeF_6 phase in the Na-Fe-F phase diagram.¹⁹

A fit of the quantitative ^{23}Na spin echo spectrum (Figure S4) provides additional insight into the total number of paramagnetic Na environments in the sample. The ^{23}Na spectrum can only be fit using a minimum of five components, as four components cannot capture the full intensity of the outer sidebands. Two of these five resonances arise from the two crystallographic Na sites in the amorphous Na_3FeF_6 impurity, and their chemical shifts ($\delta = 350$ and 1750 ppm) and intensity ratio (2:1) were fixed in the fitting procedure to match the previously reported spectral lineshape for this compound.³³ Their combined integrated intensities indicate that the Na_3FeF_6 impurity accounts for $5 \pm 2\%$ of the total Na molar content in the sample. The chemical shifts of the other three ^{23}Na resonances are consistent with Na species in $\text{Na}_2\text{Fe}_2\text{F}_7$ weberite structural variants. Yet only the orthorhombic variant is observed by XRD, with two crystallographic Na sites, which suggests the presence of a second, minor and poorly crystalline phase that cannot easily be observed by laboratory XRD. Overall, the ^{23}Na NMR results are consistent with the presence of a major orthorhombic $\text{Na}_2\text{Fe}_2\text{F}_7$ weberite phase, a minor amorphous Na_3FeF_6 impurity, and a minor and poorly crystalline $\text{Na}_2\text{Fe}_2\text{F}_7$ phase.

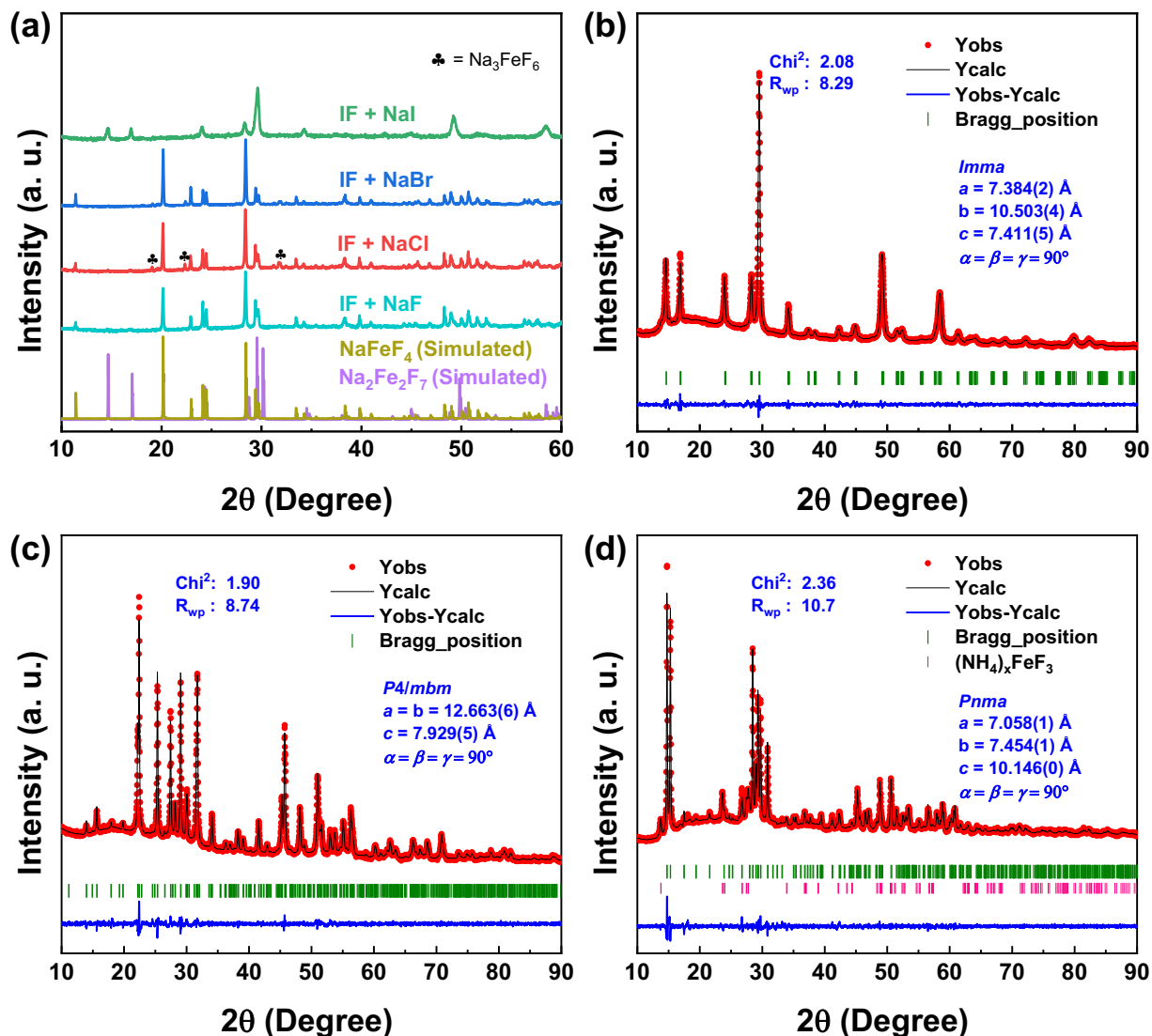


Figure 1: (a) Comparison of the XRD patterns collected on the products of reactions between IF and NaF/NaCl/NaBr/NaI. Rietveld analyses of the iron fluoride phases obtained by reacting (b) NaI, (c) KI, and (d) NH₄I with IF in a 1:1 molar ratio.

These results indicate that reactions initiated with the same IF:AI mole ratio (i.e., 1:1) produce three different iron fluoride compounds with different structural frameworks and A/Fe atomic ratios. While the modulations of the parent IF structure to the product structures can be rationalized by comparing their structural topologies (which will be detailed later), the remaining question is what thermodynamic and kinetic factors drive these topochemical reactions to yield different

products. To better understand this, we performed a series of topochemical reactions with varying Al:IF molar ratio, time, and temperature and studied their corresponding products *via* XRD. Firstly, we heated the IF precursor by itself (i.e., without Al) to 130°C in TEG for various time lengths from 1.5 to 6 h (Figure S6). At 1.75 h of reaction time, the XRD reflections corresponding to the IF precursor become weaker with little to no sign of a secondary phase. After 2 h at 130°C, however, the HTB-FeF₃·0.33H₂O phase starts to appear.^{34,35}

The formation of HTB-FeF₃·0.33H₂O from the IF precursor was further investigated through ¹H ss-NMR (Figure 2). The ¹H NMR spectrum of the IF precursor (Figure 2a) exhibits two paramagnetically-broadened signals centered at $\delta = -9$ and 188 ppm, with linewidths of 42 and 109 ppm, respectively, (summary of ¹H ss-NMR fits in Table S5) suggesting that the corresponding ¹H species are spatially close to Fe species. The sharper resonance at -9 ppm is attributed to isolated H₂O molecules in the IF framework (*i.e.*, not directly connected to FeF₆ octahedra),³⁴ and the broader resonance at 188 ppm is assigned to H₂O units occupying equatorial positions within the FeF_{6-x}(H₂O)_x (x between 0-4) chains, the latter being both closer and directly bonded to paramagnetic Fe species. The sharp signal at $\delta = 2$ ppm in the ¹H NMR spectra of HTB-FeF₃·0.33H₂O (Figure 2b) likely corresponds to isolated H₂O molecules now located in the large cavities of the HTB structure, leading to reduced paramagnetic broadening (and a slightly reduced shift) as compared to isolated H₂O molecules in the IF framework, while the broad signal at $\delta = 187$ ppm is similar to that observed for the IF and is therefore assigned to H₂O molecules within the FeF_{6-x}(H₂O)_x chains. The third broad signal centered at $\delta = 60$ ppm is hypothesized to also arise from coordinated H₂O, or perhaps OH⁻ units within the FeF_{6-x}(H₂O)_x chains, but in a slightly different local environment as compared to the H₂O molecules resonating at 187-188 ppm. Those

results overall indicate that the transformation of IF to HTB- $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ is driven *via* dehydration and condensation reactions.³¹

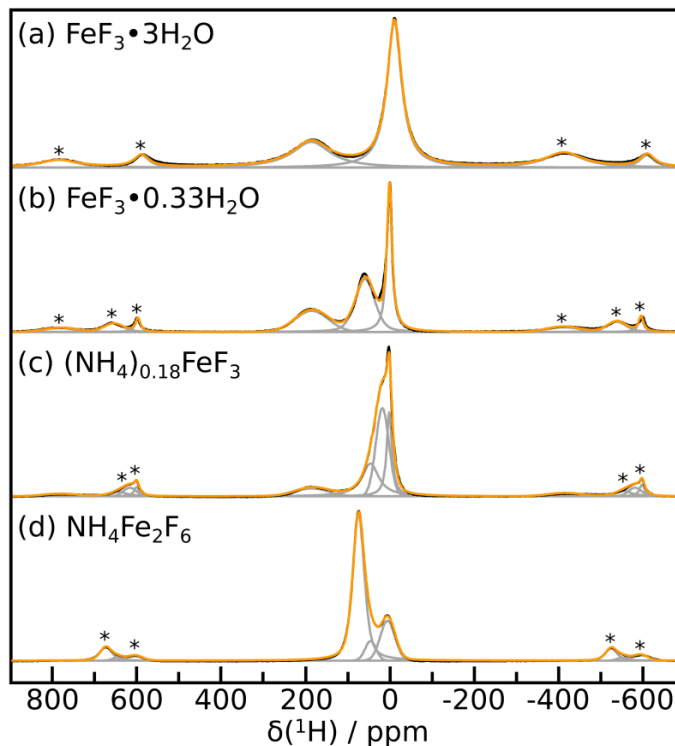


Figure 2: ^1H -NMR spin echo spectra collected on (a) $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$, (b) $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$, (c) $(\text{NH}_4)_{0.18}\text{FeF}_3$, (d) $\text{NH}_4\text{Fe}_2\text{F}_6$ along with fits of individual resonances. For each compound, the spectrum is shown in black, the overall fit in orange, and individual resonances in grey. Spinning sidebands are indicated by an asterisk (*).

Next, we studied the influence of the AI:IF molar ratio on the formation of the different 3D phases since the A/Fe atomic ratio decreases from weberite- $\text{Na}_2\text{Fe}_2\text{F}_7$, to TTB- K_xFeF_3 ($0.4 < x < 0.6$), to pyrochlore- $\text{NH}_4\text{Fe}_2\text{F}_6$. We carried out reactions between AI and IF precursors in different molar ratios at 130°C for 6 h and the corresponding XRD patterns collected on the reaction products are shown in Figure 3a-c. In the case of reactions between NaI and IF in a molar ratio of 0.25:1, HTB-type Na_xFeF_3 ($0.1 < x < 0.3$)³⁶ and weberite- $\text{Na}_2\text{Fe}_2\text{F}_7$ are formed. As the concentration of NaI is increased in the precursor mixture, the XRD peaks corresponding to HTB-type Na_xFeF_3

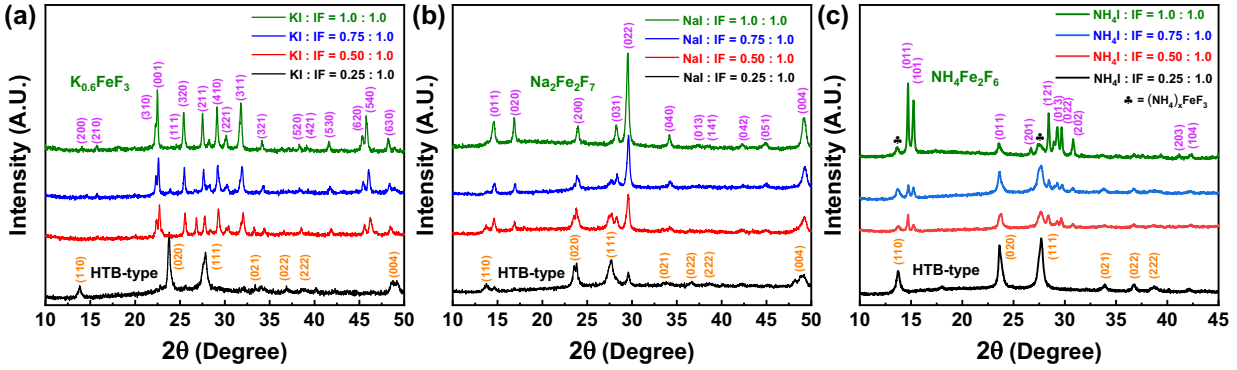


Figure 3: XRD patterns of iron fluoride phases obtained from the reactions between AI and IF with varied amounts of (a) NaI (b) KI and (c) NH₄I.

are reduced in intensity, whilst those corresponding to the weberite-Na₂Fe₂F₇ phase grow. Similar observations are noted for the KI and NH₄I-based reactions. At the lower KI:IF and NH₄I:IF ratio (0.25:1), HTB-type K_xFeF₃ and (NH₄)_xFeF₃ phases are produced whereas the reactions with higher concentrations of iodide reagents yield TTB and pyrochlore phases, respectively, but with minor HTB-type impurities. The formation of HTB-(NH₄)_xFeF₃ and pyrochlore-NH₄Fe₂F₆ is also monitored via ¹H NMR measurements (Figure 2). In the ¹H ss-NMR spectrum for HTB-(NH₄)_xFeF₃ (Figure 2c), a sharp signal at $\delta = 2$ ppm and a broader signal at $\delta = 187$ ppm (Table S5) are observed similar to HTB-FeF₃·0.33H₂O, suggesting the presence of similar ¹H environments in the cavities and within the FeF_{6-x}(H₂O)_x chains of the structure. The remaining signals at $\delta = 19$ and 47 ppm are tentatively assigned to NH₄⁺ units in the HTB framework. In the case of pyrochlore-NH₄Fe₂F₆ (Figure 2d), a dominant broad signal is observed at $\delta = 76$ ppm, which is likely associated with NH₄⁺ in the pyrochlore framework. The other two signals at $\delta = 7$ and 47 ppm (Table S5) are likely due to the remnant HTB-(NH₄)_xFeF₃ impurity phase in the sample on the basis of their chemical shifts. At this point an intriguing question arises: why can phase pure TTB and pyrochlore not be obtained despite utilizing excess AI?

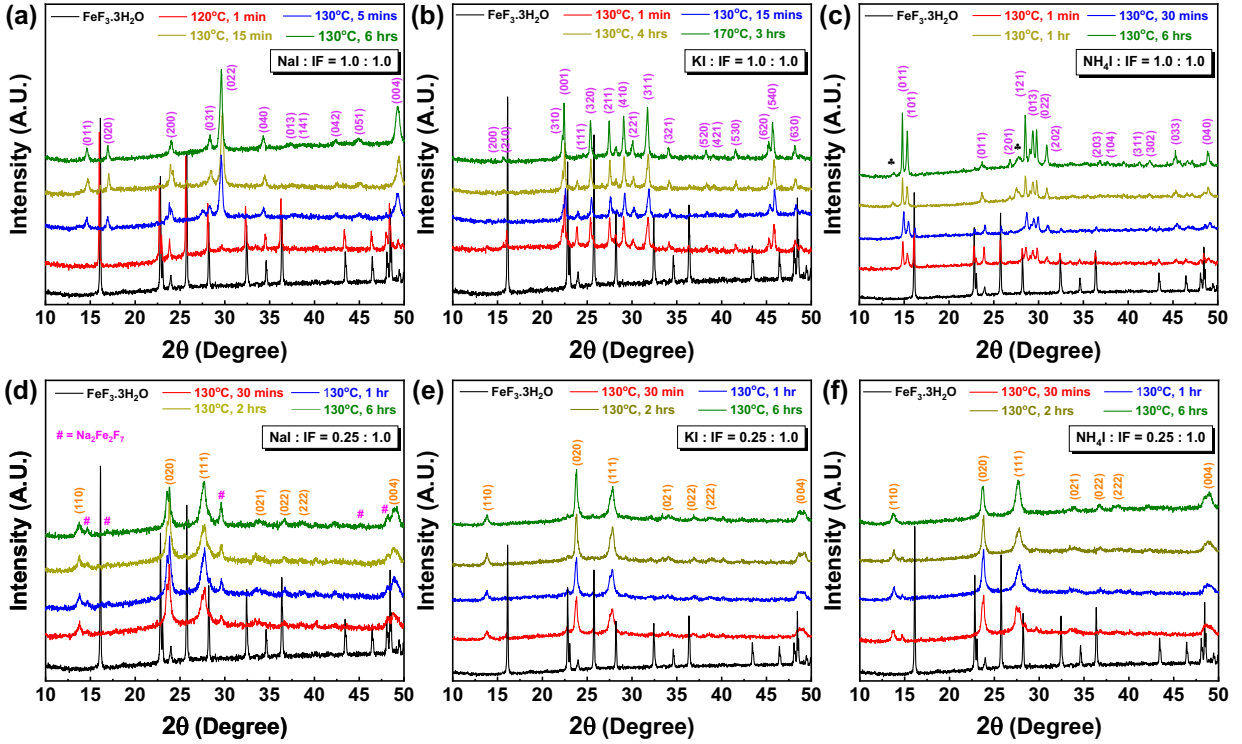


Figure 4: XRD patterns during the evolution of phases while heating IF with NaI, KI, and NH₄I in (a-c) 1.0:1.0 and (d-f) 0.25:1.0 ratios at different temperatures and time.

Further, we performed topochemical reactions at a fixed molar ratio of AI and IF at 130°C for different time durations. In the case of reactions with AI:IF $\approx$ 1:1, the appearance of weberite- $\text{Na}_2\text{Fe}_2\text{F}_7$, TTB- K_xFeF_3 and pyrochlore- $\text{NH}_4\text{Fe}_2\text{F}_6$ phases are noticed along with minor HTB-type phases within 1-5 mins (see Figure 4a-c). Whilst the phase purity of weberite- $\text{Na}_2\text{Fe}_2\text{F}_7$ is greatly improved upon extending the reaction time to 6 h, KI- and NH_4I -based reaction products still contained minor HTB- K_xFeF_3 and HTB- $(\text{NH}_4)_x\text{FeF}_3$, respectively. Notably, the phase purity of TTB- K_xFeF_3 is increased upon increasing the reaction temperature to 170°C (Figure S7); however, the same attempt with NH_4I and IF reaction was futile in improving the phase purity (Figure S8).

Additionally, we performed the reactions with AI:IF $\approx$ 0.25:1 (Figure 4d-f) under similar experimental conditions as previously described. In the case of the NaI/IF reactions, the product

collected after 30 min shows the formation of HTB- Na_xFeF_3 with weberite- $\text{Na}_2\text{Fe}_2\text{F}_7$ as a secondary phase. As the reaction time is increased to 6 h, the peak intensities of weberite- $\text{Na}_2\text{Fe}_2\text{F}_7$ increase at the expense of HTB- Na_xFeF_3 . On the contrary, the XRD patterns recorded on the products from KI/IF and $\text{NH}_4\text{F}/\text{IF}$ reactions (from 30 min to 6 h) show only the presence of HTB- K_xFeF_3 and $(\text{NH}_4)_x\text{FeF}_3$ phases. The estimated $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios from Mössbauer experiments suggest the composition of HTB phases as HTB- $\text{Na}_{0.03}\text{FeF}_3$, $-\text{K}_{0.05}\text{FeF}_3$ and $-(\text{NH}_4)_{0.16}\text{FeF}_3$ (Figure S9 and Table S4). To better understand the discrepancies among the formations of pure HTB- A_xFeF_3 phases, we performed another set of reactions in which HTB- A_xFeF_3 phases harvested after 1 hr were used as the precursors along with 0.75 moles of AI (Figure S10). Whilst the reaction of HTB- Na_xFeF_3 with additional NaI shows enhanced peak intensities of the weberite phase, no noticeable changes are observed for the KI- and NH_4I -based reactions. The conversion of HTB- Na_xFeF_3 to weberite- $\text{Na}_2\text{Fe}_2\text{F}_7$ can be ascribed to the greater thermodynamic metastability of the former, as discussed later in the manuscript.

To better understand the thermodynamic stability of iron fluoride compounds, DFT calculations were performed on the A-Fe-F phases of interest to this work. Figure 5 shows the energy above and below the convex hull (E^{Hull}) of various iron fluorides (*i.e.*, HTB, TTB, perovskite, AFeF_4 , pyrochlore, and weberite) within their respective ternary phase diagram, where blue, orange, and purple bars represent sodium, potassium, and ammonium-based iron fluorides, respectively. The horizontal dashed green line represents the rule-of-thumb of $E^{\text{Hull}} = 50$ meV/atom as a threshold for experimental synthesizability.^{37,38} The convex hull of each iron fluoride framework is depicted in Figure S17, while adjacent phases of stable iron fluoride frameworks and decomposition products of unstable or metastable iron fluoride frameworks are listed in Table S6 and S7 of the supporting information, respectively.

Based on our calculated convex hull, perovskite- NaFeF_3 (-11 meV/atom) and NaFeF_4 (-5 meV/atom) frameworks lie on the convex hull, where the negative E^{Hull} values indicate the formation energies from nearby stable phases in the chemical space, highlighting the stability of these frameworks, in good agreement with the perovskite phase being known as stable,³⁹ while the 2D NaFeF_4 framework is experimentally realized.^{11,40} In contrast, the E^{Hull} of weberite- $\text{Na}_2\text{Fe}_2\text{F}_7$ (16 meV/atom) and HTB- $\text{Na}_{0.25}\text{FeF}_3$ (32 meV/atom) phases are positive, indicating that they lie above the convex hull, while their magnitudes are within the range of tolerance limit of $E^{Hull} = 50$ meV/atom, which is expected to be stabilized at higher temperatures. Indeed, this agrees with our experimental finding that we successfully synthesized weberite- $\text{Na}_2\text{Fe}_2\text{F}_7$ phase at 130°C from IF by using NaI as a reducing agent. Note that our convex hull calculation suggests FeF_2 , NaFeF_4 , and Na_3FeF_6 as decomposition products, which aligns well with the observation of a small amount of Na_3FeF_6 impurity in the product of the reaction between NaI and IF (see Figure S2d). Notably, at higher temperatures, a phase exhibiting greater compositional, vibrational, and/or configurational degrees of freedom experiences a favorable increase in entropy compared to highly ordered phases. For instance, at higher temperature, the metastable weberite- $\text{Na}_2\text{Fe}_2\text{F}_7$ (16 meV/atom at 0 K) could potentially be stabilized over predicted stable, ordered competing phases like NaFeF_4 (-5 meV/atom at 0 K) due to its higher compositional and configurational degrees of freedom.

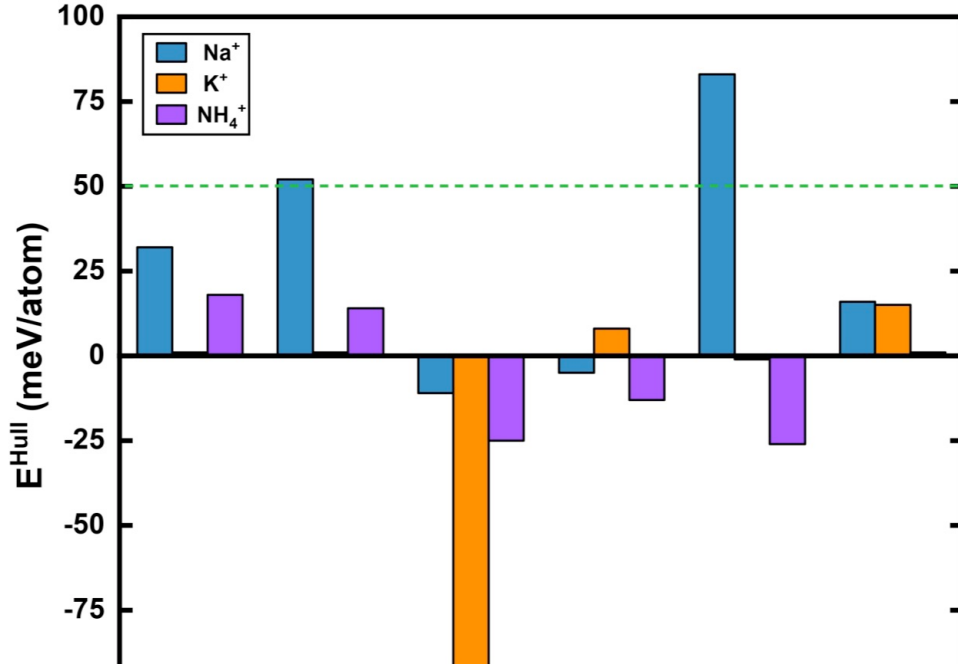


Figure 5. The energy above and below convex hull (E^{Hull}) of Na⁺, K⁺ or NH₄⁺ in a representative iron fluoride framework such as HTB, TTB, perovskite, AFeF₄, pyrochlore, and weberite, calculated from our ternary phase diagram. The blue, orange, and purple bars indicate sodium, potassium, and ammonium-based iron fluorides, respectively. The horizontal dashed green line represents the rule-of-thumb of $E^{Hull}=50$ meV/atom as a threshold for experimental synthesizability.³⁸

Similarly, the HTB-Na_{0.25}FeF₃ phase is observed during the reaction of IF precursor when using a low NaI mole fraction. Given its metastable nature, the addition of extra NaI in the reaction leads to its transformation to the weberite phase. On the contrary, the TTB-Na_{0.6}FeF₃ (52 meV/atom) and pyrochlore-NaFe₂F₆ (83 meV/atom) phases exhibit significantly higher E^{Hull} values, exceeding the synthesizability threshold of $E^{Hull}=50$ meV/atom suggesting the instability of these phases; evidently, we did not observe these phases during the synthesis of Na-based iron fluoride frameworks. Based on our 0 K convex hull, we infer that the TTB and pyrochlore Na-Fe-F phases are not likely to be stable and synthesized and will decompose to more stable phases. In the case of K-based iron fluorides, the perovskite-KFeF₃ phase unsurprisingly exhibits a large negative E^{Hull} value of -92 meV/atom, which lies on the convex hull indicating the higher stability of this

phase. In addition, the E^{Hull} of pyrochlore- KFe_2F_6 lies below the convex hull with a minimal E^{Hull} value of -1 meV/atom suggesting the stability of this phase as well. On the other hand, the E^{Hull} value for HTB- $\text{K}_{0.25}\text{FeF}_3$ (~1 meV/atom), TTB- $\text{K}_{0.6}\text{FeF}_3$ (~1 meV/atom), KFeF_4 (~8 meV/atom), and weberite- $\text{K}_2\text{Fe}_2\text{F}_7$ (E^{Hull} 15 meV/atom) phases are marginally positive, with these phases lying above the convex hull but within the tolerance of experimental synthesizability limit. Evidently, we have successfully synthesized the TTB- $\text{K}_{0.6}\text{FeF}_3$ framework from the reaction between KI and IF, while the HTB- $\text{K}_{0.25}\text{FeF}_3$ phase was also noticed during this reaction, both of which are only marginally above the convex hull (~1 meV/atom) and can be stabilized at room or higher temperatures. Although we predict KFeF_4 and $\text{K}_2\text{Fe}_2\text{F}_7$ phases to be metastable, they are not observed during the reaction between KI and IF, likely due to kinetic reasons.

Similarly, in the case of NH_4 -based iron fluorides, the pyrochlore- $\text{NH}_4\text{Fe}_2\text{F}_6$ phase is stable with E^{Hull} of -26 meV/atom, in line with our experimental observation. In addition, perovskite- NH_4FeF_3 and NH_4FeF_4 framework are also stable, despite not being observed in our experiments. The other NH_4 -containing phases are metastable with E^{Hull} of 18 meV/atom for HTB- $(\text{NH}_4)_{0.25}\text{FeF}_3$, 14 meV/atom for TTB- $(\text{NH}_4)_{0.6}\text{FeF}_3$ and 1 meV/atom for weberite- $(\text{NH}_4)_2\text{Fe}_2\text{F}_7$, suggesting that these phases may be encountered during high temperature synthesis reactions. Note that the (meta)stability of the HTB- $(\text{NH}_4)_{0.25}\text{FeF}_3$ phase is in good agreement with our experimental observation, where this phase is noticed during reaction between NH_4I at low mole fraction and IF, with the thermodynamic driving force to form the stable pyrochlore phase resulting in the reduction of the phase fraction of the HTB phase at higher temperatures and longer reaction times. However, the fact that the HTB impurity is never fully removed from our reactions may be attributed to kinetic reasons. Overall, our DFT-based thermodynamic stability investigation suggests that the observed structural variation of topochemically-synthesized iron fluorides upon

insertion of different cations can be largely attributed to the thermodynamic (in)stability of the respective frameworks.

Conclusions

In conclusion, the present study highlights the dependence of the formation of specific iron fluoride phases on the AI:IF precursor molar ratio, reaction temperature, and time. We show that lower AI:IF molar ratios (0.25:1) produce similar HTB-A_xFeF₃ iron fluoride frameworks, and increased AI (NaI, KI, NH₄I) concentrations lead to the formation of weberite, TTB and pyrochlore phases, respectively, due to their thermodynamic stability. Whilst high phase purity is achieved for the Na-weberite compound at relatively low temperature (130 °C), high-temperature annealing is necessary to produce phase-pure TTB-K_xFeF₃, indicating that kinetics play an important role in its formation. We note that all our synthesis attempts failed to form a pure pyrochlore phase, despite its thermodynamic stability. Importantly, the formation of weberite, TTB and pyrochlore phases occurs directly from the IF framework without the formation of intermediate HTB phases. Based on these observations, we tentatively propose the following formation mechanism of iron fluoride phases from the IF precursor:

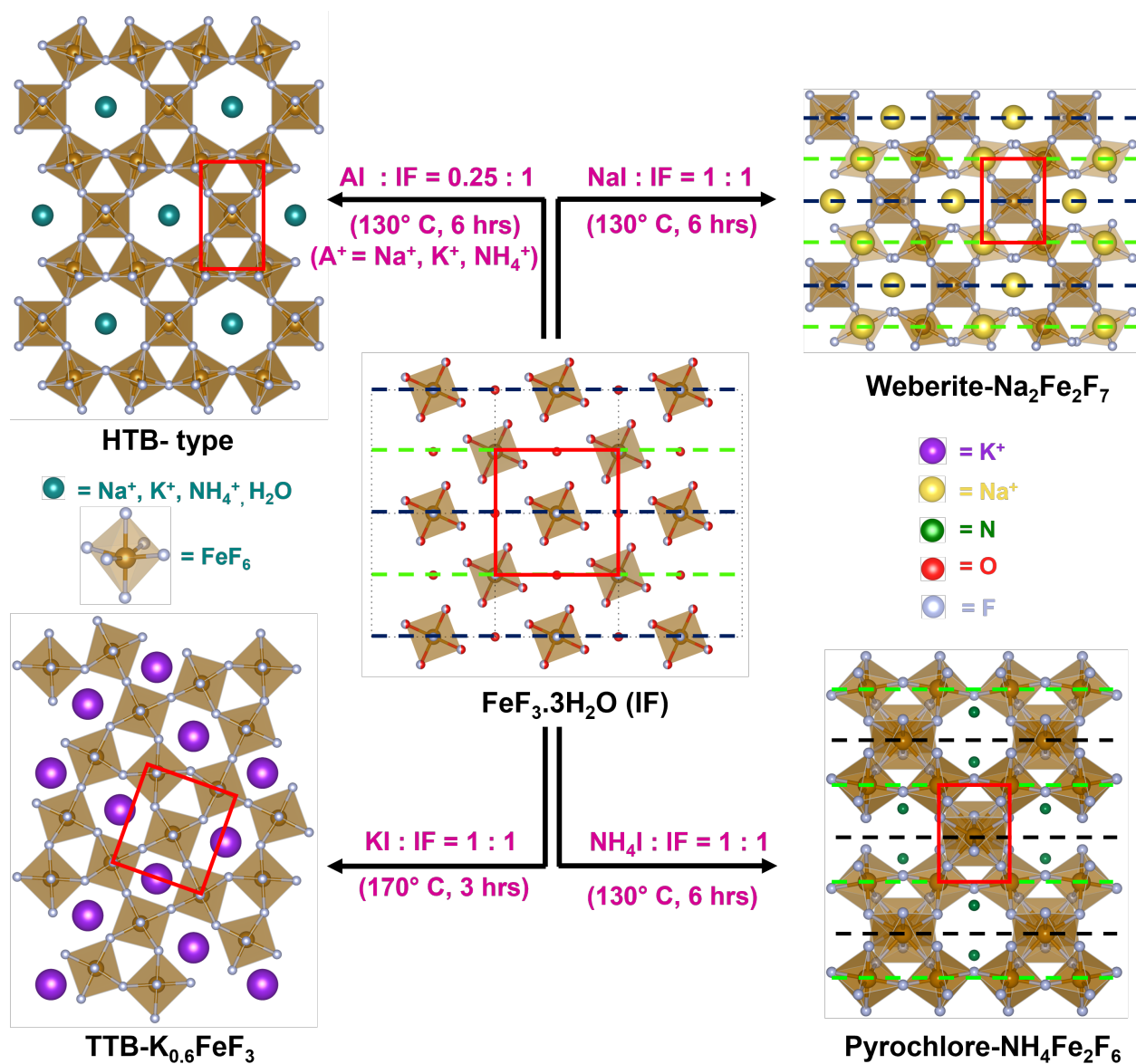


Figure 6: Mechanistic pathway and specific reaction conditions for the formation of various iron fluoride compounds from the IF-precursor with different AIs.

(a) The formation of HTB phases occurs *via* concurrent dehydration, ion-exchange and condensation reactions.³¹ As the topochemical reaction proceeds, each 1D chain $([\text{FeF}_6])_n$ and $[\text{FeF}_2(\text{H}_2\text{O})_4]_n$ ³⁴ in the IF framework knits with four other 1D chains to form hexagonal tunnels that are filled with A^+ cations. Similarly, the formation of the $\text{TTB-K}_x\text{FeF}_3$ phase can be described

as the condensation of 1D chains; however, the linkage of 1D chains in HTB and TTB phases are different, resulting in three different types of channels in TTB.

(b) Unlike the previous cases, the conversion of IF to weberite and pyrochlore phases requires more significant structural rearrangements. For the weberite phase, half of the 1D chains (indicated by blue dotted lines in Figure 4) in the IF framework break into individual FeF_6 units to pillar the remaining 1D chains (indicated by green dotted lines), resulting in the 3D weberite phase with Na-ions occupying the atomic positions of H^+ ions in H_2O . Similar transformations are required for the formation of pyrochlore but with the reknitting of broken individual FeF_6 units to produce chains that run parallel to $[1\ 0\ 0]$ and $[0\ 1\ 0]$ directions of the pyrochlore structure (Figure S18).

Experimental

Materials: Sodium fluoride (NaF, Alfa Aesar, 99.5%), Sodium chloride (NaCl, Alfa Aesar, 99.5%), Sodium bromide (NaBr, Alfa Aesar, 99.5%), Sodium iodide (NaI, Alfa Aesar, 99.5%), Potassium iodide (KI, Sigma Aldrich, 99%), Ammonium iodide (NH_4I , Sigma Aldrich, 99%), Iron (III) fluoride trihydrate ($\text{FeF}_3 \cdot 3\text{H}_2\text{O}$, Sigma Aldrich), Tetraethylene glycol (TEG, Alfa Aesar, 99%) were used for synthesis without further purification.

Synthesis: All the products were synthesized by solvothermal method. Firstly, 1:1 stoichiometric ratio of AI ($\text{A}^+ = \text{Na}^+, \text{K}^+ \text{ and } \text{NH}_4^+$) and $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ (IF) were taken in a Teflon-lined autoclave along with a 10 ml of TEG. The autoclave was then placed on oil bath and the mixture was continuously stirred at room temperature for several hours and then the temperature was increased gradually ($1^\circ\text{C}/\text{min}$) to certain temperatures, dwelled for different time durations, and cooled to room temperature. Reacting NaI with IF at 130°C for 6 hrs produces a pure weberite- $\text{Na}_2\text{Fe}_2\text{F}_7$ phase while for TTB and pyrochlore phase synthesis, the reaction temperature must raise to 170°C .

The same procedure is followed for the attempted synthesis of 2D-NaFeF₃(Cl/Br) frameworks where along with IF, NaCl, NaBr and was used and reacted at 150°C for 6 hrs. Next, the obtained product was centrifuged, washed with ethanol and acetone multiple times, and finally dried in vacuum oven at 60°C for 5 hours. The yield of each reaction was ~75% with respect to the amount of iron fluoride precursor used. The iron fluoride precursor and the formed products at different conditions were stored in a desiccator, or sometimes in glovebox to avoid any degradation or HF formation.

Materials Characterization. Powder X-ray diffraction of the samples was performed using a Cu K α_1 and K α_2 ($\lambda = 1.54056$ and 1.54439 Å, respectively) radiation in a Rigaku X-ray diffractometer. The structural refinements and Rietveld analysis are done with the help of FULLPROF suits. FESEMs were performed using a Zeiss, Gemini SEM 500, FEI Inspect F 50 operating at 10 kV. PIKE technologies GladiATR instrument was used to record the FTIR data.

¹H and ²³Na solid-state NMR spectra were collected on a Bruker Avance 100 MHz (2.35 T, ¹H Larmor frequency of 100 MHz) wide-bore NMR spectrometer and a 300 MHz (7.05 T, ²³Na Larmor frequency of 79.39 MHz) ultrawide-bore NMR spectrometer, respectively, at room temperature. The data were obtained at 60 kHz magic angle spinning (MAS) using a 1.3 mm double-resonance HX probe. ¹H and ²³Na NMR data were referenced against adamantane [(CH)₄(CH₂)₆, $\delta(^1\text{H}) = 1.8$ ppm] and sodium chloride solutions (NaCl, $\delta(^{23}\text{Na}) = 0$ ppm), respectively, and these samples were also used for pulse calibration. The data were processed using the Bruker TopSpin 4.0.8 software, and spectra were fitted using the DMfit software.⁴¹ ¹H spin echo spectra were acquired using a 90° radiofrequency (RF) pulse of 1 μ s and a 180° RF pulse of 2 μ s at 15.6 W with a recycle delay of 30 ms. ²³Na spin-echo spectra were acquired using a 90° radiofrequency (RF) pulse of 0.375 μ s and a 180° RF pulse of 0.75 μ s at 200 W. A recycle delay

between 1 to 50 ms was used, with exact values optimized to ensure that the entire ^{23}Na signal was fully relaxed between pulses. ^{23}Na pj-MATPASS (projected Magic-Angle Turning Phase-Adjusted Sideband Separation)³² isotropic spectra were also acquired using a 90° RF pulse of 0.375 μs at 200 W, with a recycle delay of 0.005 s.

^{57}Fe Mössbauer measurements were carried out in transmission mode with ^{57}Co radioactive source in constant acceleration mode using standard PC-based Mössbauer spectrometer equipped with WissEl velocity drive. Velocity calibration of the spectrometer is done with natural iron absorber at room temperature. The spectra were analyzed with NORMOS program. The obtained hyperfine parameters from the high field Mössbauer data are shown in Table S4.

Computational Methods

DFT calculations: Spin-polarized ground state total energies were calculated using DFT as implemented in the Vienna *ab initio* simulation package (VASP),^{42,43} with the usage of the frozen core projector augmented wave (PAW) potentials.⁴⁴ The elemental, binary and experimentally observed ternary iron fluoride structure, including the perovskite phase were obtained from the inorganic crystal structure database (ICSD),⁴⁵ with the exception of the weberite structure, which was obtained from.⁴⁶ Schematic of structures used in our calculations are given in **Figures S11-14**.

The structure of phases that were not observed during experimental synthesis are generated by inserting the cations of interest into an experimentally observed and well-known iron fluoride (*i.e.*, $\text{K}_{0.25}\text{FeF}_3$, $\text{K}_{0.6}\text{FeF}_3$, NaFeF_4 , $\text{NH}_4\text{Fe}_2\text{F}_6$, $\text{Na}_2\text{Fe}_2\text{F}_7$) structures obtained from ICSD, as illustrated in **Figure S11-S14**. For instance, ammonium and potassium-based weberite structures were obtained by substituting NH_4 and K at Na site of sodium-based weberite ($\text{Na}_2\text{Fe}_2\text{F}_7$). The same

approach is followed to generate other compositions as well. The perovskite KFeF_3 and NaFeF_3 were used to generate the cubic and orthorhombic perovskite polymorphs, respectively.

We used the Hubbard U corrected strongly constrained and appropriately normed (*i.e.*, SCAN+ U) exchange-correlation functional since prior studies have shown that it better predicts the experimental formation enthalpy of 3d transition metal oxides [3,4].^{47–49} An optimal U value of 3.6 eV is used for Fe in iron fluorides, which is obtained by fitting the DFT calculated oxidation energies of binary iron fluorides (*i.e.*, $\text{FeF}_2/\text{FeF}_3$) with that of experimental formation enthalpy (see **Figure S16**). We used a plane wave kinetic energy cutoff of 520 eV and a Gaussian smearing with a width of 0.05 eV to integrate the Fermi surface. For sampling the reciprocal lattice, a Γ -point-centered k -point mesh Monkhorst-Pack of at least $32/\text{\AA}$ density is chosen.⁵⁰ The ground state structural relaxation was performed by fully relaxing the atomic positions, cell shape, and cell volume, without any symmetry constraints, until the total energy and atomic forces were converged to 10^{-5} eV/atom and $|0.03|$ eV/ $\text{\AA}$, respectively. We considered both ferromagnetic (FM) and antiferromagnetic (AFM) orderings of iron fluorides to identify the correct ground state structure (see **Figure S15**).

To investigate the thermodynamic stability of experimentally observed iron fluoride frameworks (*i.e.*, HTB, TTB, AFeF_4 , pyrochlore, and weberite), we constructed a 0 K convex hull (A-Fe-F) using the pymatgen package,⁵¹ as demonstrated in **Figure S17**. For 0 K convex hull construction we considered all possible elemental (Na, K, N, H, F, Fe), binary (NaF , KF , NH_4 , FeF_2 , FeF_3), and ternary (Na_3FeF_6 , $\text{Na}_5\text{Fe}_3\text{F}_{14}$, K_2FeF_5 , $\text{K}_4\text{Fe}_3\text{F}_{12}$, $\text{K}_3\text{Fe}_3\text{F}_{19}$, $(\text{NH}_4)_2\text{FeF}_5$) configurations, whose ordered structures are available in the inorganic crystal structure database (ICSD). Note that the (in)stability of iron fluoride frameworks are also considered with respect to each experimentally observed polymorphs and the perovskite phase (*e.g.*, stability of $\text{Na}_2\text{Fe}_2\text{F}_7$ with respect to TTB-

Na_{0.6}FeF₃, HTB-Na_{0.25}FeF₃, NaFeF₄, pyrochlore-NaFe₂F₆, perovskite-NaFeF₃). After constructing the convex hull, we calculated energy above/below the convex hull (E^{Hull})⁵² to quantify the extent of stability or instability of phases (**Figure 3**).

ASSOCIATED CONTENT

Supporting Information

FTIR, Mössbauer, ²³Na-NMR and ¹H-NMR, FESEM, additional XRD data, crystal structures of different iron fluoride frameworks and the magnetic configurations of Fe atoms, reaction enthalpy variation with increasing U, convex hull using DFT. Table for structural details, E^{Hull} calculations, Mössbauer analysis, and ¹H NMR fitting parameters.

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Data availability

All the computational data presented in this study are freely available to all on our GitHub repository (<https://github.com/sai-mat-group/fe-fluorides-project>).

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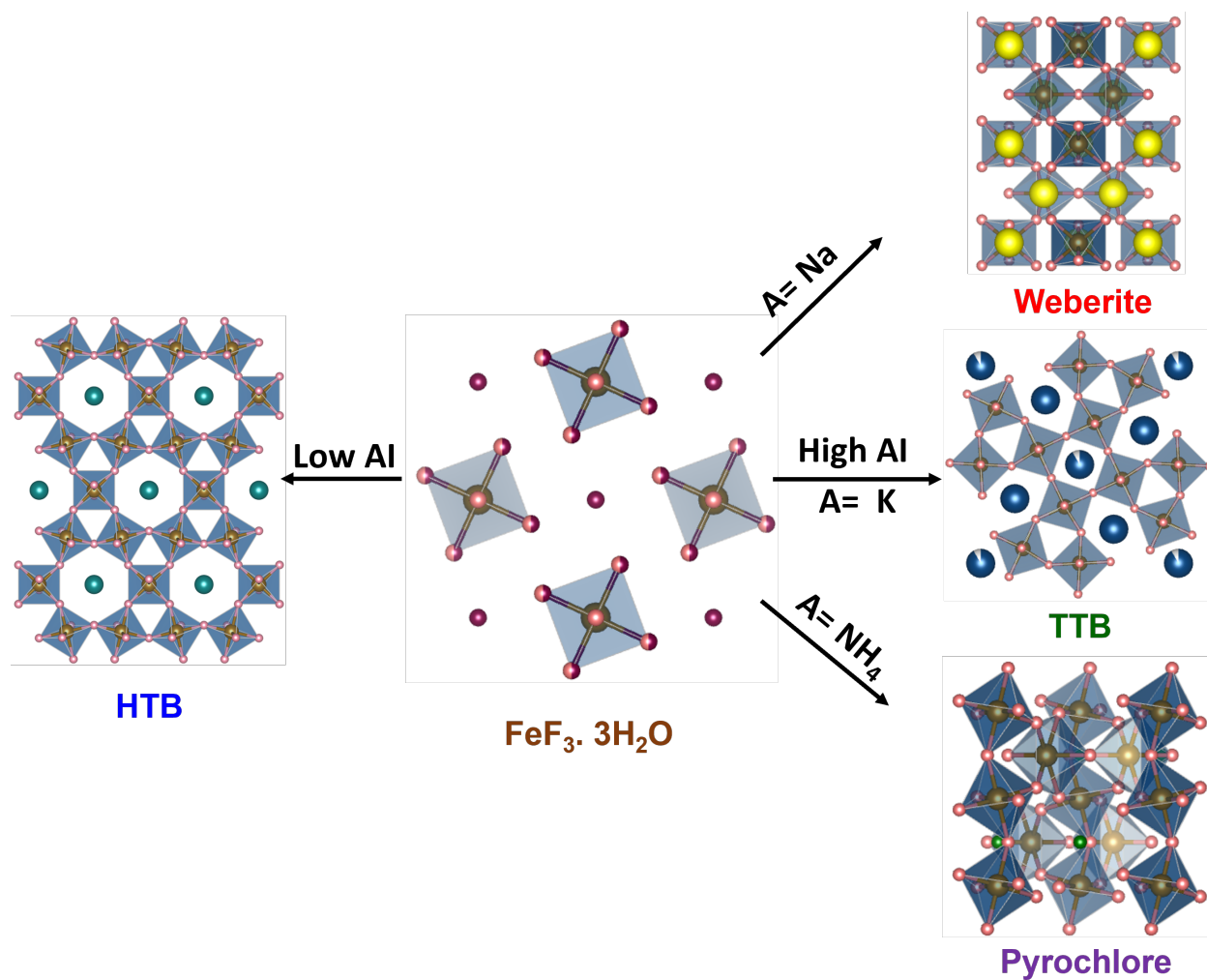
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TOC



Synopsis

A new topochemical bottom-up approach to synthesize 3D-iron fluoride frameworks from the same 1D- $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ precursor was demonstrated. The formation mechanism of the iron fluorides is elucidated through XRD, NMR and Mössbauer spectroscopy studies, which are further corroborated with DFT calculations.