Understanding the Fluorination of Disordered Rocksalt Cathodes through Rational Exploration of Synthesis Pathways


ABSTRACT: We have designed and tested several synthesis routes targeting a highly fluorinated disordered rocksalt (DRX) cathode, Li_{1.2}Mn_{0.4}Ti_{0.6}O_{2−x}F_{x} with each route rationalized by thermochemical analysis. Precursor combinations were screened to raise the F chemical potential and avoid the formation of LiF, which inhibits fluorination of the targeted DRX phase. MnF_{2} was used as a reactive source of F, and Li_{2}MnO_{4}, LiMnO_{2}, and Li_{2}Mn_{0.33}Ti_{0.66}O_{3} were tested as alternative Li sources. Each synthesis procedure was monitored using a multi-modal suite of characterization techniques including X-ray diffraction, nuclear magnetic resonance, thermogravimetric analysis, and differential scanning calorimetry. From the resulting data, we advance the understanding of oxyfluoride synthesis by outlining the key factors limiting F solubility. At low temperatures, MnF_{2} consistently reacts with the Li source to form LiF as an intermediate phase, thereby trapping F in strong Li–F bonds. LiF can react with Li_{2}TiO_{3} to form a highly lithiated and fluorinated DRX (Li_{4}TiO_{3}F); however, MnO is not easily incorporated into this DRX phase. Although higher temperatures typically increase solubility, the volatility of LiF above its melting point (848 °C) inhibits fluorination of the DRX phase. Based on these findings, metastable synthesis techniques are suggested for future work on DRX fluorination.

1. INTRODUCTION

The development of improved Li-ion batteries is essential to meet the growing demand for energy storage. Cathion-disordered rocksalt (DRX) materials are a promising class of cathodes with high energy densities that can exceed traditional layered cathodes such as LiCoO_{2} and Li[Ni, Mn, Co]O_{2} (NMC) without requiring the use of Ni or Co. In contrast to the ordered structure of layered oxides, DRX materials are characterized by disordered Li and transition metal ions within the face-centered cubic oxygen lattice, where facile Li diffusion can occur across a network of tetrahedral sites with low energy barriers. The disordered cation sublattice can host a variety of elements, creating the opportunity to use low-cost, redox-active transition metals such as Mn or Fe. Ionic substitution can also be carried out on the O sublattice; in particular, fluorination has been used to raise the capacity and improve the cyclability of DRX cathodes. Recent work on Mn/Nb-based DRX oxyfluorides demonstrated that capacity retention improves upon increasing substitution of O with F, suggesting that maximal fluorination is key to optimizing performance.

DRX oxyfluorides are conventionally made by solid-state synthesis with LiF as the single source of F. Because LiF contains highly ionic Li–F bonds with a large dissociation energy, the solubility limit between LiF and most lithium transition metal oxides is low. For DRX oxyfluorides with a composition of Li_{1.2}(Mn/Ti)_{0.4}O_{2−x}F_{x}, first-principles calculations indicate that only 5% O/F substitution (x ≤ 0.1) can be achieved at a synthesis temperature of 1000 °C. The solubility limit can be slightly improved for other compositions (e.g., through Mn/Ni replacement or increased Li content) but generally remains below 10%. In the place of traditional solid-state synthesis, high-energy ball milling can be used to increase F uptake into DRX materials. However, this method is not easily scalable as it requires high energy input and produces small sample quantities per batch. Moreover, ball milling reduces particle size and therefore cannot be used to make larger (e.g., micron-sized) particles that are sometimes desired for battery materials. Alternatively, organic fluoropolymers (e.g., PTFE) can be used as precursors for DRX oxyfluoride synthesis, potentially leading to a higher F content in the final products than those synthesized using LiF. Despite this improvement, the volatility of such fluorinating agents at moderate temperature (350 °C for PTFE) can be problematic, and LiF still appears as a secondary phase when attempting to make DRX compositions with greater than 10% O/F substitution.

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In this work, we evaluate several new synthesis routes targeting Li$_{2.2}$Mn$_{0.4}$Ti$_{0.5}$O$_{1.6}$F$_{0.4}$ and in the process clarify the specific reaction pathways that make high F uptake so challenging. Li$_{2.2}$Mn$_{0.4}$Ti$_{0.5}$O$_{1.6}$F$_{0.4}$ has a high theoretical TM capacity (≈260 mAh/g from Mn$^{2+/3+}$ redox), made possible by a substantial amount of O/F substitution (20%) that is well beyond the equilibrium solubility limit (5%) at 1000 °C. Preliminary sets were designed by optimizing the F chemical potential, maximizing the driving force to form the DRX phase, and minimizing the driving force to form any competing phases. MnF$_2$ is identified as a promising fluorination agent owing to its high F chemical potential, well exceeding that of LiF. However, we postulate that MnF$_2$ can improve F solubility only if it directly contributes to DRX formation rather than forming LiF as an intermediate phase, which would otherwise trap all F ions in strong Li–F bonds and lower the F chemical potential. Accordingly, several lithium metal oxides were tested as precursors to “lock in” Li and avoid LiF formation. Syntheses were monitored in situ using X-ray diffraction (XRD), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). Nuclear magnetic resonance (NMR) was also applied ex situ to characterize the synthesis products. Through a detailed analysis of the observed reaction pathways, we pinpoint several factors governing the synthesis of DRX oxyfluorides.

2. METHODS

2.1. Thermochemical Data. Formation energies calculated by density functional theory (DFT) were extracted from the Materials Project for all available entries in the Li–Mn–Ti–O–F chemical space, also including carbonates. These DFT-calculated energies describe the materials at 0 K and therefore do not include any finite temperature effects (e.g., vibrational or configurational entropy). We estimated the temperature-dependent Gibbs free energies for all solid phases using the machine-learned descriptor developed by Bartel et al., which can accurately model the effects of vibrational entropy. Except for the DRX phase, all materials are assumed to be ordered, and therefore, configurational entropy effects are neglected. For any gaseous species (O$_2$, CO$_2$, and CO) considered as possible reaction byproducts, free energies were calculated by summing DFT-calculated energies from the Materials Project with temperature-dependent experimental corrections from the NIST database. For both solid and gaseous phases, Gibbs free energies were calculated at 800 °C, a temperature commonly used for solid-state synthesis. A low partial pressure of 0.1 Pa was assumed for O$_2$, CO$_2$, and CO as all syntheses considered here are carried out under an Ar atmosphere. Reaction energies were calculated as the difference between the Gibbs free energy of the products and the reactants at 800 °C, normalized per atom of the product phase(s) formed.

To account for the impact of configurational entropy on the free energy of the targeted DRX phase, Li$_{2.2}$Mn$_{0.4}$Ti$_{0.5}$O$_{1.6}$F$_{0.4}$ we constructed a cluster-expansion Hamiltonian on the octahedral cation and anion sites of the rocksalt structure, following a similar procedure described in previous work. Pair interactions up to 7.1 Å, tetraplet interactions up to 4.0 Å, and quadruplet interactions up to 4.0 Å were included in the cluster-expansion formalism. All interactions were taken with respect to a baseline screened electrostatic energy defined by the formal charges of the ionic species (Li+, Mn$^{2+}$, Ti$^{4+}$, O$^{2-}$, and F$^-$). The effective cluster interaction (ECI) coefficients were fitted to DFT-calculated energies using an L$_2$-regularized least-squares regression approach designed to minimize the cross-validation error. Based on a fitting of energies from 653 distinct structures, we obtained a cross-validation error of 7 meV/atom. Canonical Monte Carlo simulations were carried out to obtain the internal energy of Li$_{2.2}$Mn$_{0.4}$Ti$_{0.5}$O$_{1.6}$F$_{0.4}$ as a function of temperature, from which the Gibbs free energy was calculated by integrating the heat capacity.

Our cluster-expansion calculations reveal that Li$_{2.2}$Mn$_{0.4}$Ti$_{0.5}$O$_{1.6}$F$_{0.4}$ is metastable with respect to phase segregation into Li$_x$Ti$_{0.5}$O$_{1.6}$F$_{0.4}$ and LiF. Based on the equilibrium phase diagram from Materials Project, the targeted DRX phase has an energy that is 25.3 meV/atom above the convex hull at 800 °C. This finding confirms recent reports that DRX materials generally have limited F solubility under equilibrium conditions and are therefore difficult to prepare using traditional solid-state synthesis. Nevertheless, several in situ studies have demonstrated that metastable intermediate phases can form during solid-state reactions when highly reactive precursors are used. Accordingly, we dedicate the next section to the identification of precursors that may lead to the formation of this metastable DRX phase (Li$_{2.2}$Mn$_{0.4}$Ti$_{0.5}$O$_{1.6}$F$_{0.4}$) with enhanced F solubility.

2.2. Precursor Screening. Our objective is to design new synthesis routes for DRX oxyfluorides by choosing alternative precursors that lead to enhanced F solubility. From equilibrium thermodynamics, the solubility limit of a particular species (i) in a host material occurs at the composition where the chemical potential of that species ($\mu_i$) is equal between the host and any competing phase(s). When $\mu_i$ is lower (i.e., more negative) in the competing phases than in the host, the system can lower its energy by placing species i in those phases rather than the host material, thereby reducing the solubility of i in the host. With respect to DRX oxyfluorides, LiF is the competing phase that limits F solubility owing to its large formation energy ($E_f$ ≈ −3.18 eV/atom) relative to Li and F. Because LiF remains stable at very low F chemical potential ($\mu_F$ ≥ −6.36 eV), it inhibits the fluorination of DRX materials when used as the only F source. Accordingly, to enhance F solubility, we only considered more reactive precursor sets with $\mu_F$ > −6.36 eV. These include transition metal fluorides that may replace or be used in conjunction with LiF as any fluoride mixtures are expected to form molten phases above their respective eutectic temperatures. In Figure S1, we show how the use of transition metal fluorides leads to increased $\mu_F$ relative to LiF.

Choosing starting materials with high $\mu_F$ is a necessary, though insufficient, condition to enhance F solubility in the final synthesis product. An additional requirement is to maintain high $\mu_F$ across any intermediate phases that form before the targeted DRX phase as solid-state reactions often go through a series of intermediate phases before forming the final product(s). Following this principle, LiF formation should be avoided if F solubility is to be improved. Our precursor search is therefore augmented with a second constraint that the thermodynamic driving force to form LiF from the starting materials is relatively weak. For each set, we identified the precursor pair with the largest (most negative) driving force ($\Delta G$) to form LiF; if $\Delta G$ < −250 meV/atom of product(s) formed, then that set is excluded from further consideration. This cutoff was chosen such that each precursor set is less likely to form LiF than the interfacial reaction between MnF$_2$ and Li$_2$O ($\Delta G = −255$ meV/atom). As will be demonstrated by our experimental results, avoiding a reaction between MnF$_2$ and the Li-containing oxide is critical to maintaining high $\mu_F$.

To screen precursors for Li$_{1.2}$Mn$_{0.4}$Ti$_{0.5}$O$_{1.6}$F$_{0.4}$, we conducted a cluster-expansion Hamiltonian on the octahedral cation and anion sites of the rocksalt structure, following a similar procedure described in previous work. Pair interactions up to 7.1 Å, tetraplet interactions up to 4.0 Å, and quadruplet interactions up to 4.0 Å were included in the cluster-expansion formalism. All interactions were taken with respect to a baseline screened electrostatic energy defined by the formal charges of the ionic species (Li+, Mn$^{2+}$, Ti$^{4+}$, O$^{2-}$, and F$^-$). The effective cluster interaction (ECI) coefficients were fitted to DFT-calculated energies using an L$_2$-regularized least-squares regression approach designed to minimize the cross-validation error. Based on a fitting of energies from 653 distinct structures, we obtained a cross-validation error of 7 meV/atom. Canonical Monte Carlo simulations were carried out to obtain the internal energy of Li$_{1.2}$Mn$_{0.4}$Ti$_{0.5}$O$_{1.6}$F$_{0.4}$ as a function of temperature, from which the Gibbs free energy was calculated by integrating the heat capacity.

Our cluster-expansion calculations reveal that Li$_{1.2}$Mn$_{0.4}$Ti$_{0.5}$O$_{1.6}$F$_{0.4}$ is metastable with respect to phase segregation into Li$_x$Ti$_{0.5}$O$_{1.6}$F$_{0.4}$ and LiF. Based on the equilibrium phase diagram from Materials Project, the targeted DRX phase has an energy that is 25.3 meV/atom above the convex hull at 800 °C. This finding confirms recent reports that DRX materials generally have limited F solubility under equilibrium conditions and are therefore difficult to prepare using traditional solid-state synthesis. Nevertheless, several in situ studies have demonstrated that metastable intermediate phases can form during solid-state reactions when highly reactive precursors are used. Accordingly, we dedicate the next section to the identification of precursors that may lead to the formation of this metastable DRX phase (Li$_{1.2}$Mn$_{0.4}$Ti$_{0.5}$O$_{1.6}$F$_{0.4}$) with enhanced F solubility.
Gibbs phase rule. Precursor sets that cannot be stoichiometrically balanced to yield $\text{Li}_1.2\text{Mn}_{0.4}\text{Ti}_{0.4}\text{O}_{1.6}\text{F}_{0.4}$ were excluded, allowing for gaseous byproducts including $\text{O}_2$, CO$_2$, and CO. These criteria produced a final list of 341 precursor sets that were considered promising for DRX oxyfluoride synthesis.

3. RESULTS

3.1. Conventional Precursors. To understand why highly fluorinated DRX cathodes are difficult to make using a conventional solid-state synthesis route, we first study the reaction pathway based on a standard mixture of LiF, TiO$_2$, $\text{Li}_2\text{CO}_3$, and MnO. In Figure 1a, XRD patterns are displayed for the synthesis products of these precursors when held at three different temperatures for 1 h: 700, 850, and 1000 °C. Each pattern was obtained after heating the precursors to the specified temperature under Ar flow followed by fast cooling to room temperature.

Upon heating the precursors to 850 °C, a clear change appears in the XRD pattern of the corresponding products. The diffraction peaks from MnO are diminished, while the LiF peaks grow, suggesting that higher temperatures increase the amount of MnO incorporated into the DRX phase but also extract LiF from it. This conclusion is further evidenced by a change in the DRX peak positions. The (002) peak exhibits a 0.5° shift toward lower 2θ, indicating a lattice constant increase of ~1.2% caused by the addition of Mn$^{2+}$ ions (85 pm radius).
and the loss of Li$^+$ ions (76 pm radius). This trend continues upon further heating to 1000 °C. The LiF signal becomes more intense, while the MnO signal is reduced to nearly zero. The DRX lattice constant also increases by an additional 0.3% relative to 850 °C. Interestingly, when the sample is held at 1000 °C for 12 h, the LiF peaks completely disappear. This leaves a pure DRX pattern that may lead one to believe that Li$_{1.2}$MnO$_{0.4}$Ti$_{0.4}$O$_{1.4}$F$_{0.4}$ was successfully made. However, the positions of the DRX peaks show only small changes (<0.1%) relative to the sample synthesized using a 1 h hold time at 1000 °C. We therefore suspect that LiF may not have been fully incorporated into the DRX phase, warranting further investigation by additional characterization techniques.

To gain insight into the behavior of LiF at high temperatures, we carried out TGA/DSC measurements on a sample of LiF held at 1000 °C for 5 h. In Figure 1b, the corresponding mass loss and heat flow curves are shown. A critical feature is identified at 848 °C, where an endothermic process occurs in accordance with the melting point of LiF. Immediately above 848 °C, the mass of the sample begins to decrease. Mass loss continues to occur as the sample is heated to 1000 °C. After 5 h at this temperature, only 35% of the starting mass remains. These findings reveal that LiF becomes volatile above its melting point when placed under flowing Ar, a necessary condition to avoid unwanted oxidation during the synthesis of Mn$^{3+}$-containing materials. We conclude that the DRX sample synthesized at 1000 °C appears pure not because LiF was successfully incorporated but instead because LiF evaporated from the system.

To verify the absence of LiF in the sample synthesized at 1000 °C for 12 h, NMR measurements were carried out on the corresponding product. In Figure 1c, we show the $^{19}$F NMR spectrum measured from this sample as well as a reference spectrum for LiF. Indeed, no LiF peak is found in the NMR spectrum ($\delta_{\text{iso}} = -204$ ppm) from the product synthesized from conventional precursors. Furthermore, the signal-to-noise ratio in the $^{19}$F NMR spectrum of our synthesis product is much lower than typically observed for DRX materials with a nominally high F content, synthesized by ball milling rather than by a traditional solid-state method. These findings support our conclusion that LiF is absent from the sample and that the synthesized DRX composition likely contains very little F because most of the LiF precursor evaporated during synthesis.

Our synthesis data illustrates that the targeted composition, Li$_{1.2}$MnO$_{0.4}$Ti$_{0.4}$O$_{1.6}$F$_{0.4}$, was not successfully obtained at any point during the heating process when using conventional precursors (LiF, TiO$_2$, Li$_2$CO$_3$, and MnO). Despite this finding, a highly fluorinated DRX phase with a nominal composition of Li$_2$TiO$_3$F was identified at 700 °C. Because MnO remains as a byproduct at this temperature, we hypothesize that heavy fluorination of DRX materials is attainable in the absence of the redox-active transition metal (Mn). To confirm this hypothesis, we carried out a separate synthesis experiment where a mixture of Li$_2$TiO$_3$ and LiF was heated at 800 °C for 8 h. This temperature was chosen below the melting point of LiF to avoid any volatility. In Figure 1d, the XRD pattern of the resulting synthesis product displays only peaks associated with the DRX phase, with no apparent impurity phases. The positions and intensities of the observed DRX peaks match those of a hypothetical solid solution between Li$_2$TiO$_3$ and LiF, assuming Vegard’s law. This result parallels our findings from the conventional DRX synthesis procedure and verifies that Ti-based DRX oxyfluorides can be heavily fluorinated if they do not contain Mn. From the perspective of cathode research, however, Mn is needed to enable a high reversible redox capacity over a practical voltage window (e.g., 2.3–4.6 V versus Li/Li$^+$). Therefore, we investigated whether MnO can be incorporated into the fluorinated DRX phase using a two-step synthesis procedure: Li$_2$TiO$_3$F was first synthesized, then mixed with MnO, and held at 800 °C for 16 h. Even after this long hold time, MnO peaks remain clearly visible in the corresponding XRD pattern (Figure S2). Hence, we conclude that MnO cannot be completely incorporated into the highly fluorinated DRX phase under reasonable temperatures and hold times.

3.2. Selection of Alternative Precursors. Based on the filters described in the Methods section, our computational search resulted in 341 precursor sets that are suspected to enhance F solubility. The full list of precursors and their properties are given in Table S1. To determine which of these sets warrant experimental investigation, we consider the tradeoff between two key metrics: the driving force to form Li$_2$MnO$_{0.4}$Ti$_{0.4}$O$_{1.6}$F$_{0.4}$ and the driving force to form LiF, hereafter denoted as $\Delta G_{\text{rxn}}$(DRX) and $\Delta G_{\text{rxn}}$(LiF), respectively. An ideal set of precursors should be sufficiently reactive such that DRX formation is favorable, $\Delta G_{\text{rxn}}$(DRX) < 0, and the magnitude of the associated driving force, $\Delta G_{\text{rxn}}$(DRX), is large. However, the precursors should not be so reactive as to produce LiF as an intermediate phase, which would lower $\mu_F$ and inhibit fluorination of the DRX phase. To succinctly represent this task, we frame it as a multi-objective optimization problem where the goal is to identify precursor sets occupying the Pareto front of $\Delta G_{\text{rxn}}$(DRX) and minimal $\Delta G_{\text{rxn}}$(LiF), assuming both are negative.

In Figure 2a, we present a scatter plot where each point represents a distinct precursor set and the axes show $\Delta G_{\text{rxn}}$(DRX) versus $\Delta G_{\text{rxn}}$(LiF). The red dashed line represents the Pareto front, which illustrates an optimal tradeoff between these two metrics. Five precursor sets are plotted in terms of their driving forces to form the targeted DRX phase (Li$_{1.2}$Mn$_{0.4}$Ti$_{0.4}$O$_{1.6}$F$_{0.4}$) versus the driving force to form LiF. Reaction energies are normalized per atom of product phase (DRX/LiF) formed. Three sets chosen to be investigated experimentally are listed in (b) and highlighted in red in panel (a).

$\Delta G_{\text{rxn}}$(DRX) versus $\Delta G_{\text{rxn}}$(LiF) for those sets. The red dashed line represents the Pareto front, which illustrates an optimal tradeoff between these two metrics. Five precursor sets are found to occupy the Pareto front—three of these are listed in Figure 2b and two in Table S1. Interestingly, all five precursor sets on the Pareto front contain MnF$_2$, which is a particularly promising fluorinating agent for several reasons. First and...
foremost, MnF₂ stabilizes F much less than LiF and is therefore suspected to raise the F solubility limit. This is quantifiable by comparing the lower bound on \( \mu_F \) where MnF₂ is stable (stable at \( \mu_F \geq -4.49 \text{ eV} \)) compared to LiF (\( \mu_F \geq -6.36 \text{ eV} \)) as well as other transition metal fluorides (e.g., TiF₃ is stable at \( \mu_F \geq -4.92 \text{ eV} \)). Second, MnF₂ places Mn in the proper oxidation state (Mn²⁺) to synthesize \( \text{Li}_2\text{MnO}_2\text{Ti}_4\text{O}_{12}\text{F}_0.4 \) without requiring any oxidation or reduction. Last, in comparison to TiF₃, MnF₂ has a weaker driving force to form LiF when combined with Li-containing precursors. For example, one may compare the following reactions with Li₂O:

\[
\text{MnF}_2 + \text{Li}_2\text{O} \to \text{MnO} + 2\text{LiF} \\
(\Delta G \approx -255 \text{ meV/atom})
\]

\[
2\text{TiF}_3 + 3\text{Li}_2\text{O} \to \text{Ti}_2\text{O}_3 + 6\text{LiF} \\
(\Delta G \approx -387 \text{ meV/atom})
\]

where the reaction energies are normalized per atom of the product phase(s) formed, ensuring a consistent comparison between reactions having different stoichiometries. The moderate reactivity of MnF₂ leads to a good balance between \( \Delta G_{\text{rxn}}(\text{DRX}) \) and \( \Delta G_{\text{rxn}}(\text{LiF}) \), which justifies its presence in all five precursor sets occupying the Pareto front. Of these five sets, one contains elemental Ti, which is difficult to work with owing to its ease of oxidation, while another has a weak driving force to form the targeted phase, with \( \Delta G_{\text{rxn}}(\text{DRX}) \approx -4.2 \text{ meV/atom} \). Accordingly, we exclude these two sets (listed near the top of Table S1) from further consideration. The remaining three precursor sets occupying the Pareto front were chosen to be investigated experimentally as they contain readily synthesizable precursors, are straightforward to handle, and have a strong driving force to form \( \text{Li}_2\text{MnO}_2\text{Ti}_4\text{O}_{12}\text{F}_0.4 \). These sets are summarized in Figure 2b and detailed in the following three paragraphs.

3.2.1. Set A: \( \text{Li}_2\text{MnO}_2 \text{ MnF}_2 \) and TiO₂. In this precursor set, MnF₂ is used as the single source of F. Because LiF is absent, there is a large driving force to form the targeted DRX oxyfluoride, with \( \Delta G_{\text{rxn}}(\text{DRX}) \approx -256.7 \text{ meV/atom} \). Another key component of this set is Li₂MnO₃, which has been previously synthesized²⁷ and is the only stable Mn²⁺-containing lithium manganese oxide reported in the Materials Project.²⁸ Because it contains Mn²⁺, Li₂MnO₃ can be used to synthesize \( \text{Li}_2\text{MnO}_2\text{Ti}_4\text{O}_{12}\text{F}_0.4 \) without requiring any oxidation or reduction. Moreover, Li₂MnO₃ has a less negative formation energy (\( E_F \approx -2.06 \text{ eV/atom} \)) than other lithium manganese oxides such as LiMnO₂ (\( E_F \approx -2.17 \text{ eV/atom} \)) and LiMnO₄ (\( E_F \approx -2.08 \text{ eV/atom} \)), where \( E_F \) is calculated relative to the elemental ground states (Li, Mn, and O₂). This also contributes to the large driving force for DRX formation from these precursors, although the reactivity of Li₂MnO₃ also leads to a moderately high driving force to form LiF through the following reaction:

\[
3\text{MnF}_2 + \text{Li}_2\text{MnO}_3 \to 6\text{LiF} + 4\text{MnO} \\
(\Delta G_{\text{rxn}} = -232.9 \text{ meV/atom})
\]

The magnitude of \( \Delta G_{\text{rxn}}(\text{LiF}) \) is less than that of \( \Delta G_{\text{rxn}}(\text{DRX}) \), but experimental synthesis with \( \text{in situ} \) characterization presented below will verify which occurs first.

3.2.2. Set B: \( \text{LiMnO}_2 \text{ Li}_2\text{TiO}_3 \text{ LiF, MnF}_2 \) and Mn. There are two F-containing precursors in this set, LiF and MnF₂, which form a eutectic system with a melting point of 600 °C.²⁷ We anticipate that this combination can provide both thermodynamic and kinetic benefits for oxyfluoride synthesis. Because the enthalpy of the mixture can be approximated as an average of LiF and MnF₂ just above its melting point (600 °C), this mixture has a higher F chemical potential (\( \mu_F = -5.73 \text{ eV/atom} \)) than pure LiF and should therefore be more reactive. The molten phase may also facilitate DRX formation by providing a medium for rapid diffusion of precursor atoms.³⁸ In addition to LiF, both LiMnO₂ and Li₂TiO₃ provide sources of Li for DRX synthesis. Because LiMnO₂ contains Mn³⁺ as opposed to the Mn²⁺ oxidation state needed for \( \text{Li}_2\text{MnO}_2\text{Ti}_4\text{O}_{12}\text{F}_0.4 \) synthesis, elemental Mn is introduced as a precursor to lower the average oxidation state (1 Mn²⁺ per 2 Mn³⁺). In contrast to Li₂MnO₃ as used in the previous precursor set, LiMnO₂ is more stable and therefore reduces the driving force to form LiF:

\[
\text{MnF}_2 + 2\text{LiMnO}_2 \to 2\text{LiF} + \text{MnO}_4 \\
(\Delta G_{\text{rxn}} = -73.3 \text{ meV/atom})
\]

The use of LiMnO₂ also leads to a weaker driving force for DRX formation, with \( \Delta G_{\text{rxn}}(\text{DRX}) \approx -91.7 \text{ meV/atom} \). Hence, the two sets described thus far sample two different extremes along the Pareto front, illustrating a tradeoff between \( \Delta G_{\text{rxn}}(\text{DRX}) \) and \( \Delta G_{\text{rxn}}(\text{LiF}) \).

3.2.3. Set C: \( \text{LiMnO}_2 \text{ Li}_2\text{TiO}_3 \text{ LiF, MnF}_2 \) and C. This precursor set is similar to set B, except Mn is now replaced with carbon to reduce Mn³⁺ (in LiMnO₂) to Mn²⁺ (in \( \text{Li}_2\text{MnO}_2\text{Ti}_4\text{O}_{12}\text{F}_0.4 \)) through evolution of CO₂ and/or CO. Precursor stoichiometries were also varied to accommodate the expected oxygen loss, leading to a greater proportion of MnF₂. When using this precursor set, the driving force for DRX formation can be tuned by the choice of synthesis conditions because the free energies of the gaseous CO/CO₂ byproducts are highly dependent on temperature. In contrast, the synthesis conditions have a comparatively negligible effect on the driving force to form LiF since no gaseous species participate in the reaction that forms LiF. Therefore, a high synthesis temperature and low partial pressure of CO/CO₂ (e.g., under flowing Ar) should be used to drive DRX formation. At 800 °C, for example, \( \Delta G_{\text{rxn}}(\text{DRX}) \approx -57.9 \text{ meV/atom} \). If this reaction is successful, then excess carbon may also be included as a means of \( \text{in situ} \) carbon coating, which is sometimes used to enhance the conductivity of electrodes.³⁹

3.3. Synthesis Experiments. 3.3.1. Set A: \( \text{Li}_2\text{MnO}_4 \text{ 2TiO}_2 \) and MnF₂. In Figure 3, we show XRD patterns measured from the synthesis based on a precursor mixture of \( \text{Li}_2\text{MnO}_4 \text{ 2TiO}_2 \) and MnF₂. At 200 °C, a pristine set of diffraction peaks associated with the precursors is observed, indicating that no reactions have yet occurred. Upon heating the sample to 400 °C, peaks for both MnF₂ and LiMnO₂ have completely disappeared. At the same time, new peaks associated with MnO and LiF have emerged, showing that MnF₂ reacted to form MnO and LiF between 200 and 400 °C according to eq 3. After this reaction has taken place, all F in the system is retained by the intermediate LiF phase, which we expect limits F solubility and precludes the formation of \( \text{Li}_2\text{MnO}_2\text{Ti}_4\text{O}_{12}\text{F}_0.4 \). Higher temperatures were explored to confirm this prediction.

A DRX phase is identified at 600 °C, accompanied by secondary peaks associated with a spinel-type phase. Relative to measurements at 400 °C, the MnO and TiO₂ peaks are
to a small amount of MnO. There is no detectable LiF at this temperature, even though its melting point (848 °C) has not yet been reached. This finding parallels our earlier results from the conventional DRX synthesis—highly fluorinated DRX materials can be made in the absence of Mn.

After reaching a final synthesis temperature of 900 °C, the amount of detectable MnO is diminished and the DRX peaks shift toward lower 2θ, suggesting incorporation of the large Mn²⁺ ions. However, we caution that these results should be interpreted carefully as the conditions may give rise to LiF volatility. As discussed earlier in the Results section (Conventional Precursors) and portrayed in Figure 1, LiF is extracted from the DRX phase at temperatures near 850 °C, above which it begins to evaporate under flowing Ar. It is therefore unlikely that the observed DRX phase in Figure 3 matches the targeted composition, Li₄Mn₂Ti₂O₈F₀.₄. In addition to the likely evaporation of LiF, a small amount of MnO remains even after the sample is held at 900 °C for 6 h. In conclusion, our synthesis trial based on Li₄Mn₂O₈, 2TiO₂, and MnF₂ was not successful because LiF formation occurred at low temperature (200–400 °C), well before the desired DRX phase could form. This negates the effect of starting with precursors that include a more reactive F source.

3.3.2. Set B: 2LiMnO₂₄, 4Li₃TiO₃, 2LiF, MnF₂, and Mn. In Figure 4, XRD patterns are displayed for the products resulting from reactions between 2LiMnO₂₄, 4Li₃TiO₃, 2LiF, MnF₂, and Mn when held at four different temperatures for 5 h: 700, 800, 900, and 1000 °C. The pattern measured at 700 °C consists of large diffraction peaks associated with TiMn₂O₆ in addition to minor LiF and DRX peaks. Past work indicates that TiMn₂O₆, sometimes written as Mn( TiMn)O₆, adopts a spinel structure where the tetrahedral 8a sites are predominantly occupied by Mn and the octahedral 16d sites are evenly occupied by Mn/
comprise the most reactive interface. According to eq 4, these reactants are expected to produce LiF and MnF$_2$. In Figure 5, the temperature, showing a non-linear contraction associated with Li$^+$ extraction. (d) The out-of-plane LiMnO$_2$ lattice constant is refined as a function of temperature, showing a non-linear contraction associated with Li$^+$ extraction. (d) Heating profile used during the synthesis procedure.

Since no XRD data is available below 700 °C, some thermodynamic analysis is required to understand which reactions might have led to the formation of TiMn$_2$O$_4$ as a dominant phase. For this task, we consider all possible reactions between pairs of precursors and identify the one with the largest driving force, $\Delta G$, following the principles developed in our previous work to predict synthesis pathways. For the current precursor set, LiMnO$_2$ and MnF$_2$ comprise the most reactive interface. According to eq 4, these reactants are expected to produce LiF and MnF$_2$. Assuming that this reaction occurs first, the spinel structure of Mn$_3$O$_4$ can provide a template for TiMn$_2$O$_4$ to form via an exchange of Mn/Ti ions between Mn$_3$O$_4$ and Li$_2$TiO$_3$. This process would also explain why a DRX phase forms at 700 °C since Mn/Ti mixing in Li$_2$TiO$_3$ leads to increased configurational entropy and favors a disordered rocksalt structure. Because all F ions are trapped within the highly stable LiF phase prior to the formation of the DRX phase, it is unlikely to be highly fluorinated. Hence, avoiding the LiMnO$_2$MnF$_2$ reaction (shown to occur <700 °C) is critical to oxyfluoride synthesis. The exact temperature and mechanism of this reaction will be discussed in the next section (precursor set C).

XRD patterns measured from the samples synthesized at 800 and 900 °C remain mostly unchanged with respect to 700 °C, which suggests that the intermediate phases (TiMn$_2$O$_4$, LiF, and DRX) are slow to react at temperatures below 900 °C. In contrast, when the sample is heated to 1000 °C, a new set of peaks associated with MnTiO$_3$ appear. Also, at this temperature, the DRX peaks disappear from the pattern, hinting at a transformation from DRX to MnTiO$_3$. The transformation may be caused by Li loss through Li$_2$O volatility, which is known to occur during DRX syntheses carried out at high temperatures, hence the use of excess Li$_2$O in conventional precursor mixtures. Some additional Li may also be transferred to TiMn$_2$O$_4$ between 900 and 1000 °C. Partial replacement of Mn$^{2+}$ (85 pm) by Li$^+$ (76 pm) in TiMn$_2$O$_4$ is evidenced by a small shift in its peak positions toward higher $2\theta$, indicating an ~0.3% reduction in the lattice constant.

In summary, the precursor mixture of 2LiMnO$_2$, 4Li$_2$TiO$_3$, 2LiF, MnF$_2$, and Mn did not produce the targeted composition, Li$_{1.2}$Mn$_{0.8}$Ti$_{0.4}$O$_{1.6}$F$_{0.4}$. More generally, our results demonstrate that elemental Mn is not a suitable precursor to synthesize DRX materials, which only ever appeared in minority amounts during the reaction sequence and were completely absent from the sample made at 1000 °C. Although our synthesis was carried out under an Ar atmosphere with nominally low O$_2$ content, we suspect that at least some of the metallic Mn precursor was oxidized before it could react with LiMnO$_2$ to reduce the average oxidation state to Mn$^{2+}$. This is evidenced by the final products being anion-rich, consisting predominantly of TiMn$_2$O$_4$ and MnTiO$_3$.

3.3.3. Set C: 2LiMnO$_2$, 3Li$_2$TiO$_3$, LiF, MnF$_2$, and C. In Figure 5a, we present the XRD patterns measured during the synthesis trial based on 2LiMnO$_2$, 3Li$_2$TiO$_3$, LiF, MnF$_2$, and C. In contrast to the previous synthesis procedures discussed, synchrotron radiation was used to monitor this route in situ.
allowing many XRD patterns to be captured with fine temperature resolution. Accordingly, the results are displayed as a heatmap where high (low) diffraction intensities are represented by bright (dark) coloring. We can use the heatmap to pinpoint reaction temperatures and estimate the relative amounts of all intermediate phases. In Figure 5b, the corresponding mole fractions are plotted as a function of time, and Figure 5d illustrates the relationship between time and temperature by showing the heating profile used during the synthesis procedure.

The first observed reaction initiates at 100 °C between MnF₂ and Li₂MnO₂, producing LiF and Mn₃O₄ according to eq 4. By refining the LiMnO₂ peaks, we identify a non-linear contraction in the out-of-plane lattice parameter (c), as shown in Figure 5c, which coincides with a decrease (increase) in the MnF₂ (LiF) peak intensities. This data suggests that Li extraction from LiMnO₂ occurs at temperatures as low as 100 °C, coupled with the oxidation of Mn⁴⁺ to Mn⁶⁺. The free Li⁺ ions facilitate a reaction with MnF₂, forming LiF. The reaction is complete below 500 °C, above which no MnF₂ is detected. Because this reaction occurs below the eutectic point of LiF–MnF₂ (600 °C), it precludes the formation of a more reactive fluoride melt, leaving LiF as the single fluorinating agent. The current results parallel our finding from precursor set B, where all MnF₂ was consumed below 700 °C, and further clarify the LiMnO₂–LiMnF₂ reaction temperature and mechanism. Considering that all F ions are again trapped in LiF, we expect that F solubility will be limited in the resulting DRX product.

The second reaction takes place between Mn₃O₄ and C, with reduction occurring at 700 °C to form MnO and CO₂ (and possibly CO) as follows:

\[
2\text{Mn}_3\text{O}_4 + C \rightarrow 6\text{MnO} + \text{CO}_2
\]

\[
(\Delta G_{\text{run}} = -182 \text{ meV/atom at 700°C})
\]  

(6)

The reduction of Mn₃O₄ leads to rapid formation of a DRX phase at 700 °C, in addition to a secondary MnO phase. Simultaneously, there is a large decrease in the amount of Li₂TiO₃ and LiF detected, and therefore, the DRX phase formed at 700 °C is likely to be highly fluorinated but deficient in Mn. Upon further heating to 932 °C, increasing incorporation of MnO into the DRX phase is evidenced by a decreased amount of MnO as well as a shift in the positions of the DRX peaks toward lower 2θ caused by lattice expansion. However, even after the synthesis procedure is completed and the sample is cooled to room temperature, the MnO byproduct remains apparent and comprises ~5% mole fraction of the DRX/MnO mixture. Although the downward trend in mole fraction of MnO (Figure 5b) might suggest that a pure DRX phase can be obtained with longer hold times, we again caution that MnF₂ to be retained until high temperatures where the DRX can form, thereby keeping MnF₂ high such that F solubility is improved in the final product.

We synthesized Li₃Mn₀.₃₃Ti₀.₆₆O₃ by heating a mixture of Li₂MnO₃ and Li₂TiO₃ to 900 °C for 8 h under flowing Ar. In Figure 6a, the XRD pattern of the resulting sample is shown.

![Figure 6](image-url)
synthesize Li$_{1.4}$Mn$_{0.4}$Ti$_{0.4}$O$_{1.6}$F$_{0.4}$, The XRD pattern of the resulting synthesis product is displayed in Figure 6b. A DRX phase does indeed comprise a majority weight fraction of the mixture; however, three impurity phases also appear in addition to leftover carbon: TiMn$_2$O$_6$, LiF, and MnO. These results point to the following side reaction:

$$\text{MnF}_2 + 2\text{Li}_2\text{Mn}_{0.33}\text{Ti}_{0.66}\text{O}_3 + \text{C} \rightarrow 4\text{TiMn}_2\text{O}_6 + 12\text{LiF} + \text{CO}_2 \quad (7)$$

Hence, LiF formation was not prevented by “locking in” Li$^+$ ions with a Mn$^{4+}$-based precursor. Even when a lower temperature of 400 °C was used, all MnF$_2$ was consumed to form LiF, further supporting the strong driving force and fast kinetics of the reaction.

4. DISCUSSION
In Table 1, we summarize the reaction pathways characterized in this work. Our characterization of DRX synthesis from

<table>
<thead>
<tr>
<th>precursors</th>
<th>temp (°C)</th>
<th>observed phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF, MnO, TiO$_2$, Li$_2$CO$_3$</td>
<td>700</td>
<td>DRX, MnO</td>
</tr>
<tr>
<td>LiF, Li$_2$TiO$_3$</td>
<td>850</td>
<td>DRX, MnO, LiF</td>
</tr>
<tr>
<td>Li$_2$Mn$_2$O$_3$, MnF$_2$, TiO$_2$</td>
<td>1000</td>
<td>DRX, LiF</td>
</tr>
<tr>
<td>LiMnO$_2$, Li$_2$TiO$_3$, MnF$_2$, LiF, Mn</td>
<td>800</td>
<td>Li$_2$TiO$_3$, MnF$_2$, LiF, Li$_2$MnO$_3$</td>
</tr>
<tr>
<td>LiMnO$_2$, Li$_2$TiO$_3$, MnF$_2$, LiF, C</td>
<td>700</td>
<td>TiMn$_2$O$_6$, LiF, DRX</td>
</tr>
<tr>
<td>LiMnO$_2$, Li$_2$TiO$_3$, MnF$_2$, LiF, C</td>
<td>1000</td>
<td>TiMn$_2$O$_6$, MnF$_2$, LiF, Mn</td>
</tr>
<tr>
<td>Li$<em>2$Mn$</em>{0.33}$Ti$_{0.66}$O$_2$, MnF$_2$, C</td>
<td>800</td>
<td>DRX, TiMn$_2$O$_6$, MnF$_2$, LiF</td>
</tr>
</tbody>
</table>

“The observed phases listed at each temperature include leftover precursors, intermediate phases, and final products. These are listed in order of decreasing weight fraction. All phases labeled “DRX” adopt a disordered rocksalt structure but may have different compositions.

conventional precursors (Li$_2$CO$_3$, TiO$_2$, MnO, and LiF) reveals several key reaction steps that dictate the composition of the final product. A highly fluorinated, but Mn-deficient, DRX phase forms at 700 °C, leaving MnO as a secondary phase that does not react until higher temperature. The existence of such a fluorinated DRX phase was verified through a separate experiment where Li$_t$TiO$_3$F was successfully synthesized from Li$_2$TiO$_3$ and LiF. These results confirm previous theoretical speculation that a high Li content and the use of d$^0$ elements (e.g., Ti) enhance F solubility in DRX materials, but incorporation of later transition metals (e.g., Mn) reduces F solubility due to the relatively weak bonds formed between Mn$^{4+}$F compared to Li$^{+}$-F. Although MnO can react with the highly fluorinated, Mn-deficient DRX phase at temperatures above 850 °C, it also leads to the removal of LiF from the DRX phase followed by evaporation of LiF from the sample. The volatility of LiF was confirmed by our TGA/DSC studies, which show that evaporation begins at 848 °C and becomes more rapid when held at higher temperatures, with only 35% of the starting mass remaining after 5 h at 1000 °C. Because much of the LiF precursor evaporates during synthesis, the resulting DRX phase has a lower F content than expected based on the precursor stoichiometry. This is further evidenced by a weak $^{19}$F signal from our NMR measurements on the final synthesis product.

As demonstrated by our computational search for new precursor sets targeting Li$_{1.4}$Mn$_{0.4}$Ti$_{0.4}$O$_{1.6}$F$_{0.4}$, there exist many possible synthesis routes that start with high F source such as MnF$_2$. In principle, these routes should lead to enhanced F solubility if the precursors directly contribute to DRX formation. However, our experiments show that this is not the case; DRX formation is always preceded by a series of intermediate phases resulting from reactions between precursor pairs. Importantly, the first reaction to occur in each synthesis route involves the formation of LiF, which negates the effects of starting from a more reactive F source and limits F solubility in any Mn-containing DRX phase formed at higher temperature.

The first reaction to take place in each synthesis path also dictates the temperature at which DRX formation proceeds. When Li$_t$MnO$_3$ is included in the precursor set, it reacts with MnF$_2$ to form LiF and MnO between 200 and 400 °C. Because MnO places Mn in the same oxidation state as the targeted phase (Mn$^{3+}$), no oxidation or reduction is required in later reactions. This enables the formation of a DRX phase at relatively low temperature (600 °C), though it competes with a secondary spinel phase (Li$_2$MnTi$_2$O$_6$) that requires further heating to consume. In contrast, when LiMnO$_2$ is included in the precursor set, it reacts with MnF$_2$ between 100 and 400 °C to form LiF and Mn$_2$O$_4$. Since Mn$_2$O$_4$ has a mixed oxidation

![Figure 7](image-url) Summary of the three major factors identified in this work that limit F solubility in DRX oxyfluoride materials synthesized by a solid-state approach.
state (Mn\textsuperscript{2+}/Mn\textsuperscript{3+}), it must be reduced before it can contribute to DRX formation, raising the required synthesis temperature. When a carbon precursor is used as a reducing agent, it successfully reduces Mn\textsubscript{2}O\textsubscript{4} at 700 °C and a DRX phase is formed shortly thereafter with only a minor MnO impurity phase. If Mn is alternatively used as a reducing agent, then it fails to react with Mn\textsubscript{2}O\textsubscript{4} and reduce the average Mn oxidation state to Mn\textsuperscript{2+}. Instead, an exchange reaction between Mn\textsubscript{2}O\textsubscript{4} and Li\textsubscript{2}Ti\textsubscript{4}O\textsubscript{7} replaces Mn\textsuperscript{3+} with Ti\textsuperscript{4+} to form a dominant spinel phase, TiMn\textsubscript{2}O\textsubscript{4}, in addition to a secondary DRX phase. These findings suggest that the competition between DRX and spinel phases can be controlled via the choice of reducing agent and synthesis temperature—stronger reducing agents (such as carbon) and higher temperatures favor DRX formation (1:1 cation–anion ratio), whereas weaker reducing agents and lower temperatures favor spinel formation (anion-excess).

Although none of our proposed synthesis routes were successful in forming the targeted composition, Li\textsubscript{1.2}Mn\textsubscript{0.8}Ti\textsubscript{0.4}O\textsubscript{1.6}F\textsubscript{0.4}, the results provide valuable insight into the factors that control DRX formation and inhibit their fluorination. Indeed, the importance of “dark” reaction data (i.e., failed syntheses) has been detailed in previous work, although negative results are rarely reported in the literature. Here, we demonstrate the utility of dark reaction data by using our results to identify three key principles governing F solubility in DRX oxyfluorides. These are illustrated in Figure 7 and discussed in the following three paragraphs.

4.1.1. Factor #1. Avoiding LiF is key to maintaining a high F chemical potential (\(\mu_F\)) and enhancing F solubility. Although MnF\textsubscript{2} was identified as a promising fluorinating agent, we find that it inevitably reacts with any Li-containing precursor (\(< 400 °C\)) to form LiF as an intermediate phase and inhibit their fluorination. Indeed, the importance of “dark” reaction data (i.e., failed syntheses) has been detailed in previous work, although negative results are rarely reported in the literature. Here, we demonstrate the utility of dark reaction data by using our results to identify three key principles governing F solubility in DRX oxyfluorides. These are illustrated in Figure 7 and discussed in the following three paragraphs.

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in the electrochemical properties of a DRX material with respect to an increase in its nominal F content is still insufficient evidence to prove enhanced fluorination. The expected increase in the nominal F content can be traced back to a greater LiF precursor stoichiometry. If significant LiF has evaporated from the sample, then the resulting DRX phase will be deficient in Li/F and excess in Mn. In turn, the electrochemical properties will be modified—not due to fluorination but from a higher Mn content.

In conclusion, to be confident in the composition of DRX oxyfluorides synthesized under gaseous flow, we suggest that short annealing times (<1 h) or low temperatures (<848 °C) should be used. Otherwise, additional characterization short annealing times (<1 h) or low temperatures (<848 °C) should be used. Otherwise, additional characterization techniques are needed to supplement XRD and confirm bulk thermodynamic ground state (LiF) that we show substantially limits F solubility in the DRX.

5. CONCLUSIONS
We have tested and analyzed several different synthesis pathways targeting DRX oxyfluorides to identify the main factors that limit their F solubility. Despite starting from a more reactive F source, LiF consistently forms via intermediate reactions between MnF2 and the Li-containing precursor, which lowers the F chemical potential and inhibits fluorination of the targeted phase. DRX materials with significantly increased F content (~25%) can be made if they do not contain Mn; however, this limits their usefulness as cathode materials since Mn provides the main redox capability. Higher temperatures enable increased Mn uptake, but this comes at the cost of LiF volatility, resulting in a DRX phase with a low F content. To synthesize DRX materials with both a high Mn and F content, it is necessary to explore alternative techniques for metastable materials synthesis where kinetic factors become dominant in the reaction mechanism, thereby avoiding the thermodynamic ground state (LiF) that we show substantially limits F solubility in the DRX.

Our findings demonstrate how failed experiments can still be useful to better understand materials synthesis, which often remains a “black box” process that must be optimized through trial and error. Several techniques enabling predictive synthesis have recently emerged.47–49 Yet none are universally applicable, and more tests are needed to identify their limitations. The theoretical methods used in this work rely on thermodynamics for the design of optimal precursors, yet they fail to capture more subtle effects related to kinetic factors. To improve upon the current approaches to synthesis design, new experimental data is needed. Although negative results are rarely reported in the literature, those reported here provide key insight into the challenges of fluorination. As such, we hope that our work sets a precedent for increased publication of failed synthesis data with concurrent interpretation of the results. This would not only contribute to an improved understanding of materials synthesis but also aid in the development of statistical models for synthesis outcome prediction.

6. EXPERIMENTAL DETAILS

6.1. Materials Synthesis. A conventional solid-state synthesis procedure was carried out using common precursors from previous work: LiF, MnO, TiO2, and Li2CO3. Stoichiometric amounts of these precursors, plus 10% excess weight of Li2CO3 to compensate for possible Li loss, were mixed in ethanol with five 10 mm and ten 2 mm stainless balls in a 50 mL stainless steel jar using a Retsch PM200 planetary ball mill at 300 rpm for 12 h. The resulting slurry was dried to form a powder, which was then pressed into a pellet using a 6 mm stainless steel die before heat treatment under an atmosphere of flowing Ar. Three synthesis temperatures were tested (700, 850, and 1000 °C), each with a 1 h hold time. A longer hold time of 12 h was also tested at 1000 °C. After heating, the samples were cooled to room temperature under Ar flow. The final products were manually ground in an Ar-filled glove box for subsequent characterization by XRD and NMR as described in the Characterization section.

6.1.1. Set A: Li4MnO4, MnF2, and TiO2. Because Li4MnO4 is not commercially available, we first synthesized it using a procedure outlined in previous work.37 Stoichiometric amounts of anhydrous Li2O and MnO were mixed in a high-energy SPEX mill (SPEX SamplePrep 8000 M) for 2 h. Stainless steel milling media were used in a 10:1 ratio of media to powder. The milled powder was recovered in an Ar-filled glovebox and pressed into pellets using a 13 mm stainless steel die. The pellet was annealed at 950 °C for 12 h under a flowing mixture of 96% Ar and 4% H2 in a tube furnace. The product was ground manually, and its purity was verified by XRD (Figure S2), which showed good agreement with past results. The DRX oxyfluoride synthesis was then carried out by mixing stoichiometric amounts of Li4MnO4, MnF2, and TiO2 with a mortar and pestle for 30 min in an Ar-filled glovebox. The resulting powder was recovered and used for temperature-dependent XRD measurements detailed in the Characterization section.

6.1.2. Set B: LiMnO4, Li2TiO3, LiF, MnF2, and MnO. Stoichiometric amounts of these precursors were sufficiently mixed for 12 h. The mixture was loaded into an alumina crucible and sealed inside a quartz tube under an Ar atmosphere. The vessel was then heated to the designated synthesis temperature with a ramp rate of 10 °C/min and annealed at that temperature for 4 h followed by a natural cool to room temperature. Four synthesis temperatures were tested (700, 800, 900, and 1000 °C). The final products were harvested by cutting the sealed tube, stored inside an Ar-filled glovebox, and ground into a powder that was then characterized by XRD.

6.1.3. Set C: LiMnO4, Li2TiO3, LiF, MnF2, and C. Stoichiometric amounts of these precursors, plus 5% excess weight of carbon, were mixed in ethanol with five 10 mm and ten 2 mm stainless balls in a 50 mL stainless steel jar using a Retsch PM200 planetary ball mill at 300 rpm for 12 h. The slurry was then dried and pelletedized before being sent to a beamline facility for in situ characterization by synchrotron XRD. A synthesis temperature of 932 °C was used under an atmosphere of flowing N2. A detailed description of the heating profile is given in the Characterization section.

Two additional synthesis procedures targeting Li2Mn0.66Ti0.33O2F0.44 were carried out with the following precursor sets: (1) Li2Mn0.66Ti0.33O2F0.44, MnF2, and C; and (2) Li2TiO3F and MnO. For set (1), Li2Mn0.66Ti0.33O2F0.44 was first synthesized by mixing stoichiometric amounts of Li2MnO4 and Li2TiO3 via wet ball milling, following the same procedure as described for precursor set C. The mixture was heated at 900 °C for 8 h under an atmosphere of flowing Ar followed by a natural cool to room temperature. The product was manually ground in an Ar-filled glove box and characterized by XRD. Next, stoichiometric amounts of Li2Mn0.66Ti0.33O2F0.44, MnF2, and carbon were mixed via wet ball milling and heated at 800 °C for 4 h under flowing Ar. The product was naturally cooled, ground in an Ar-filled glovebox, and characterized by XRD. For set (2), Li2TiO3F was first synthesized by mixing Li2TiO3 and LiF via wet ball milling and subsequently dried to form a powder, which was heated at 800 °C for 8 h in air. The product was naturally cooled, extracted, and ground into a powder. To synthesize Li2Mn0.66Ti0.33O2F0.44, stoichiometric amounts of Li2TiO3F and MnO were mixed following the same procedure as Li2TiO3F, followed by heating at 800 °C under an atmosphere of flowing Ar for 16 h. The product was naturally cooled, extracted in an Ar-filled glovebox, and characterized by XRD.

6.2. Characterization. Samples made from LiF, MnO, TiO2, and Li2CO3 were characterized by ex situ XRD using a Rigaku MiniFlex.
600 diffractometer with Cu Kα radiation ($\lambda = 1.54178\ \text{Å}$). The volatility of LiF during the synthesis procedure was studied by heating a pure sample of LiF powder at a rate of 5 °C/min to 1000 °C with a hold time of 5 h, while in situ TGA/DSC measurements were carried out using a Q600 SDT instrument. Solid-state NMR was also performed on the synthesis products of LiF, MnO, TiO₂, and Li₂CO₃ heated at 1000 °C for 12 h to check whether any LiF was present in the sample. These measurements were conducted using a wide bore Bruker BioSpin spectrometer ($B_0 = 2.35$ T, 100 MHz for $^1\text{H}$) equipped with a DMX 500 MHz console and a custom-made 1.3 mm X-broadband magic angle spinning (MAS) probe tuned to $^{19}\text{F}$ (94.1 MHz). Samples were packed in zirconia rotors in an Ar-filled glovebox and spun at $\nu_0 = 60$ kHz using dry nitrogen. $^{19}\text{F}$ chemical shifts were externally referenced against pure LiF powder, with $\delta_{	ext{LiF}}^{\text{(F)}} = -204$ ppm. $^{19}\text{F}$ NMR spectra were obtained using a rotor-synchronized spin echo sequence ($90°−\tau−180°−\tau$) with a 90° RF pulse of 0.35 μs, and data was averaged over 7168 transients with a recycle delay of 50 ms between scans. Additionally, isotropic $^{19}\text{F}$ NMR spectra were recorded using the projected magic angle turning phase-adjusted sideband separation (pi-MATPASS) pulse sequence, which effectively removes sidebands due to MAS. This experiment used the same 90° RF pulse as the $^{19}\text{F}$ spin echo. Results were averaged over 2000 scans with a recycle delay of 50 ms. Solid-state NMR data were processed using the Bruker TopSpin 3.6.0 software, and spectra were fitted using the DMfit software.

Ex situ XRD patterns of the synthesis products from sets A to C were measured using a Scintag XDS 2000, Bruker D2-Phaser, and Rigaku MiniFlex 600 diffractometer, respectively, each with Cu Kα radiation. For precursor set A, in situ XRD measurements were also performed by using a Malvern PANalytical X’Pert Pro MPD diffractometer (45 kV, 40 mA) equipped with an Anton Paar XRF-900 reaction chamber operated in 2° mode. During these measurements, a CuKα gas was used to purge the reaction chamber and avoid unwanted oxidation of the sample. Cu Kα radiation was used to collect XRD data at temperature intervals of 100 °C, ranging from 100 to 900 °C. A heating rate of 10 °C/min was used between each hold temperature, which was equilibrated for 1 min prior to data collection. For precursor set C, experiments were conducted with Beamline 28-ID-2 of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory. An X-ray wavelength of 0.1846 Å was used. The powder samples were pressed into pellets of 0.5 mm in thickness and 7 mm in diameter before loading into a Linkam TS1500 furnace. A two-dimensional X-ray detector (Perkin-Elmer XRD 1621), placed at 1493 mm from the sample, was used to collect XRD patterns during the heating procedure. A heating rate of 12 °C/min was used for temperature up to 600 °C followed by a heating rate of 3 °C/min up to 932 °C. For calibration based on thermal expansion, XRD patterns from a CeO₂ standard powder (NIST SRM 674b) were measured under the same conditions as the DRX samples.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acs.chemmater.2c01474](https://pubs.acs.org/doi/10.1021/acs.chemmater.2c01474).

Visualization of chemical potentials for different fluoride precursors, supplementary X-ray diffraction patterns, and a list of all precursor sets identified with computational screening ([PDF](https://pubs.acs.org/doi/10.1021/acs.chemmater.2c01474))

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Notes
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