SYNTHESIS AND CHARACTERIZATION OF SINGLE CRYSTALLINE METAL NITRIDE FLUORIDES

by
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METAL NITRIDE FLUORIDES

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ABSTRACT

There were two primary objectives for this thesis work, both of which are focused on inorganic nitride-fluoride (N-F) chemistry. The first objective was to prepare both previously known and new $\text{M}_2\text{NF}$ compounds in order to further elucidate the crystal chemistry of known phases, as well as to explore synthesis routes for new mixed metal compounds. The synthesis approach in all cases involved first preparing $\text{AMF}_3$ ($\text{A} = \text{NH}_4^+ \text{ or } \text{K}^+; \text{M} = \text{Cu}, \text{Mg}, \text{Co}$) perovskite-type fluorides as precursors. Modifications of known synthesis methods for these compounds led to very pure, dry precursor materials. Doubled cubic $\text{Ca}_2\text{NF}$ crystals prepared from a $\text{KCuF}_3$ precursor were analyzed via high resolution X-ray diffraction, from which it was learned that Frenkel defects thought to be present are actually a non-stoichiometric defect.

The second goal of this project was to synthesize new mixed metal nitride fluoride materials. Only two such materials have been reported in the literature, and one of these is a fluorine insertion compound. The most significant result from this part of the project was the successful preparation of a $\text{CaMgNF}$ phase related to rocksalt, but with quadrupled unit cell parameters due to ordering of cations and anions along the cell edges. This is the first bimetallic nitride-fluoride to be prepared that is a direct analog of an oxide.
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CHAPTER ONE
LITERATURE REVIEW OF INORGANIC NITRIDE FLUORIDE COMPOUNDS

1.1 Introduction

Inorganic nitride fluoride compounds have been a relatively unexplored area of inorganic chemistry. Many of the reported nitride fluorides can be viewed as "pseudo-oxides" in which one N\(^3^-\) (nitride) and F\(^1^-\) (fluoride) ion replace two O\(^2^-\) anions in an oxide analog, e.g. giving Mg\(_2\)NF as an analog of MgO. While thousands of oxides are known, fewer than forty inorganic nitride fluoride (N-F) phases have been reported. This is probably related to the difficulty in synthesizing metal nitride fluoride compounds in practice, despite the fact that their compositions are easily derived from any oxide formula in theory. As discussed below and later in this thesis, many of the metal N-F systems studied display a rich crystal chemistry relative to their oxide analogs.

1.2 Single-metal nitride fluoride: lanthanides, actinides, and transition metals

The first observation of N-F compounds was by Lavalle et al. (1966), who reported TcNF and ReNF as decomposition products of (NH\(_4\))\(_2\)TcF\(_6\) and (NH\(_4\))\(_2\)ReF\(_6\), respectively, at 300 °C. TcNF was reported as having a hexagonal structure with \(a = 5.98\) Å and \(c = 4.79\) Å, and ReNF as tetragonal with \(a = 5.88\) Å, \(c = 13.00\) Å. One year later, the formation of ThNF and ThN\(_x\)F\(_{4-3x}\) (0.94 \(\geq x \geq 0.79\)) was reported by Juza and Sievers (1968), as referenced by Morss (2006). The ThNF system was made by heating a 1:1 molar ratio of Th\(_3\)N\(_4\) and ThF\(_4\), while the phase ThN\(_x\)F\(_{4-3x}\) was prepared using an excess of ThF\(_4\) at 900 °C. ThNF was reported to have a rhombohedral structure with \(a = 7.13\) Å.
In addition, the compound ThNₓF₄₋₃ₓ was found to adopt a tetragonal structure related to the CaF₂ type structure with a = 4.06 – 4.148 Å and c = 5.845 – 5.839 Å.

Gunanda Waduge Chinthaka Silva reported in his dissertation (2009) the synthesis of ThNF. The product was made through thermal treatment of (NH₄)₄ThF₈ under ammonia at different temperatures up to 1100 °C. Gunanda showed that at 800 °C, 300 minutes were required to synthesize this product. However, at this temperature, unreacted ThF₄ was formed due to partial decomposition of (NH₄)₄ThF₈. The researcher also noticed that increasing the reaction temperature resulted in a significant decrease in reaction time, with heating the sample at 1100 °C for 15 minutes best for the ThNF formation. Heating (NH₄)₄ThF₈ for 300 minutes under NH₃ to 1000 °C for 75 minutes removed the fluorine content from the reaction, producing ThNF with ThO₂ impurities. This observation suggested that long heating at high temperatures generates a ThO₂ secondary chemical phase due to the oxygen produced by the quartz tube used as a heating region for the experiment. In conclusion, the refined lattice parameter of the ThNF rhombohedral unit cell was 7.1312 Å.

Further work on the Zr-N-F system was published some years later by Jung et al. (1973) who were the first to report the preparation of a wide range non-stoichiometric solid solution ZrNₓF₄₋₃ₓ (0.906 < x < 0.936) by ammonolysis of ZrF₄ at 580 °C. The group proposed an orthorhombic 27-fold superstructure (space group Cm2a; a = 5.374 Å, b = 5.368 Å, c = 5.186 Å) for ZrN₀.₉₀₆F₁.₂₈, with the subcell deduced from CaF₂ type. Subsequently, a study by Schlichenmaier et al. (1993) showed that this phase is, in fact, a nitride oxide fluoride Zr(N,O,F)ₓ (2.12 < x < 2.25). In this case, the compound was reported as monoclinic related to ZrO type. The structure was refined as containing
fluorine excess, and having a vernier-type structure. The authors were able to determine the structure of the phase via neutron powder diffraction as monoclinic with space group P112_1/b and lattice constants a = 5.1217 (3) Å, b = 2.1513(1) Å and c = 5.3669(3) Å, γ (gamma) = 90.128(6)°. In the same study, Schlichenmaier et al. (1993) also made ZrNF through ammonolysis of ZrF_4. With the help of electron diffraction and energy loss spectroscopy, the investigators indicated the phase possessed an isotype correlated to that of ZrO with space group P2_1/c, and lattice constants a = 5.227(3) Å, b = 5.026(2) Å, c_0 = 5.191(3) Å, β = 98.98(7)°.

The successful synthesis of ZrNF was reported by Zhua et al. (2004). The synthesized phase involved the reaction of ZrN powder and NH_4F as flux using a high-temperature, 1000 °C, and high-pressure method. All manipulations were carried out in an Ar-filled glove box because NH_4F is highly hygroscopic. The sample assembly was set in a pyrophyllite cube and subjected to a high pressure and high-temperature treatment using a cubic multi-anvil type apparatus. The Powder X-ray diffraction (XRD) pattern showed that the system contained a superstructure along a-axis as a function of composition related to ZrN_{0.906}F_{1.28}.

Koshina et al. (1966) published the synthesis of UN_xF_y, 0.94 ≤ x ≤ 1.00; 1.20 ≥ y ≥ 1.00, made from the reaction of UN treated with UF_4 at 1200 °C and another phase at a lower temperature, 950 °C. The lower temperature phase produced an orthorhombic structure with lattice parameters ranging from a = 5.632-5.643 Å, b = 5.602-5.610 Å, c = 5.712-5.707 Å, while the high temperature phase had a tetragonal lattice with a = 3.9515-3.948 Å, and c = 5.724-5.730 Å.
In 1972, the formation of a La-N-F compound was reported. This phase was synthesized from a mixture of LaN and LaF$_3$ in a 1:2 ratio for approximately one week at 1200 °C, or via ammonolysis of the fluoride at 900 °C (Tanguy et al. 1972) and appeared in a compositional structure of La$_{N_5}F_{3-3x}$ with $0.34 \leq x \leq 0.54$. The phase was found to have a cubic structure related to that of CaF$_2$, with anion vacancies and dislocation, and cell parameters ranging from 5.847-5.871 Å. Tanguy et al. (1972) also prepared Gd$_3$NF$_6$ by heat treatment of a 2:1 molar ratio of GdF$_3$ to GdN at 1000 °C, and reported that Gd$_3$NF$_6$ had a cubic structure related to CaF$_2$ with $a = 5.617$ Å.

Nine years following the work by Tanguy et al. on the La-N-F system, five Zinc-nitride fluorides were synthesized by Marchant and Lang (1981) in France. The formation of these five zinc nitride fluoride was done by heating a mixture of the fluoride and nitride of the metal. This manipulation yielded five phases as follows: $\alpha$-Zn$_2$NF, $\beta$-Zn$_2$NF, $\alpha$-Zn$_9$N$_4$F$_6$, $\beta$-Zn$_9$N$_4$F$_6$, and Zn$_7$N$_4$F$_2$. Debye-Sherrer patterns were employed to examine the five phases, however only two of the structural lattices were reported. The $\alpha$-Zn$_2$NF was found to have an orthorhombic unit cell with $a = 5.90$ Å, $b = 5.78$ Å, and $c = 6.53$ Å, and the $\beta$-Zn$_2$NF compound was found to be tetragonal with $a = 5.86$ Å, and $c = 6.53$ Å.

More recently, Lingampalli et al. (2016) reported the synthesis and some properties of Zn$_2$NF. First the authors synthesized the phase through thermal treatment-solid state reaction of Zn$_3$N$_2$ (precursor) with ZnF$_2$ in a 1:1 mole ratio. Observed in this study was Zn$_2$NF formed in two crystal systems: an orthorhombic structure at 500 °C, and a tetragonal system above 500 °C. For structural determination, the authors carried out Rietveld refinement of the powder X-ray powder diffraction process, and assigned
P4₁₂₁₂ (No.92) space group for the tetragonal system with cell parameters a = 5.873 Å and c = 6.532 Å. In addition, the researchers followed the same manner for the Zn₂NF orthorhombic structure. This structure was found to have sub-space group of P4₁₂₁₂ (P2₁₂₁₂₁, No. 19) with unit cell constants a = 5.850 Å, b = 5.892 Å, and c = 6.536 Å.

The authors also explored the physical properties of the phase based on electronic absorption spectra. The investigators reported the decrease in band gap of the phase due to presence of nitrogen content in the material. The band gaps are 2.8 eV for the tetragonal and 2.7 eV for the orthorhombic system. These band gaps are small compared to that of ZnO (3.2 eV). These values are in correlation to those obtained theoretically based on exchange-correlation energy functional calculations of Perdew-Wang (PW) within a Local Density Approximation (LDA). In addition to what was mentioned above, the most interesting investigation of the study is the photocatalysis of the phase. The researchers tested both zinc oxynitride fluoride and the pure Zn₂NF phases for hydrogen generation from water. It was reported that Zn₂NF phases exhibit more photocatalytic activity than a zinc oxynitride fluoride system under visible light irradiation. Concluded in this analysis is how nitrogen presence can change band gaps of materials, and thus its physical and chemical properties.

The synthesis of TiNF proposed by Wüstefeld et al. (1988) involved the reaction of (NH₄)₂TiF₆ with equivalent amounts of NH₄Cl at 400 °C, under an inert atmosphere, for 12 hours to form (NH₄)₂TiF₂:NH₄Cl adduct. The adduct (NH₄)₂TiF₂:NH₄Cl was then thermally decomposed at 280 °C under an inert gas, followed by ammonolysis to yield a light green powder identified as TiNF. The researchers were able to identify the structure of the system which turned out to be isostructural with the anatase phase of TiO₂,
showing random distributions of nitride and fluoride ions on the anion sites with the space group I4$_1$/amd, and a = 3.7891Å, c = 9.4863Å (Inorganic Crystal Structure Database, No. 63711). Later, a study by Nukumizu et al. (2003), on the same phase cast doubt on the purity of the system. The study, referenced by Seibel et al. (2009) reported that the synthetic route of Nukumizu et al. (2003) leads to a composition of TiN$_{0.13}$O$_{1.78}$F$_{0.05}$ instead of TiNF, due to the silica reaction vessel which served as an oxygen source during the preparation. Seibel et al. (2009), reported that their attempts to prepare TiNF through careful synthesis via ammonolysis of (NH$_4$)$_2$TiF$_6$ in a dry, oxygen-free atmosphere in a stainless steel reaction tube resulted in no product, whereas reaction in a silica tube resulted in a green anatase-type phase of composition TiN$_{0.05}$O$_{1.89}$F$_{0.06}$.

Thus the phase is better described as an N-F co-doped oxide rather than a nitride-fluoride.

### 1.3 Single-metal nitride fluorides: Alkaline Earth metals

Most of the work on the inorganic N-F chemistry reported to date is related to M-N-F compounds with M= Mg, Ca, Sr, and Ba. One of the earliest reports of “pseudo-oxide” nitride fluoride compounds was by Andersson in 1970 in a study reporting the synthesis of three powder phases of magnesium nitride fluoride: Mg$_3$NF$_3$, L-Mg$_2$NF, and H-Mg$_2$NF. Structural determinations were performed via powder X-ray diffraction, and compared to that of MgO rocksalt-type structure. Thus, Mg$_3$NF$_3$ showed a structure similar to the MgO cubic structure (but with a cation vacancy), where magnesium is coordinated octahedrally to four fluoride and two nitride ions at identical distances of 2.108 Å, nitrogen is in octahedral coordination to six cations, and fluorine is centered in a square configuration attached to four cations. Andersson indicated the phase had space group Pm-3m with a = 4.216 Å. The structure of L-Mg$_2$NF was described with anion
positions analogous to that of MgO, but the ordering of the anions within the Mg$_2$NF structure caused doubling along one of the dimensions of the cubic MgO structure. As a result, the L-Mg$_2$NF sample was indexed as tetragonal, with space group I4$_1$/amd, \( a = 4.186 \, \text{Å}, \ c = 10.042 \, \text{Å} \). Andersson described L-Mg$_2$NF as intermediate between the sodium chloride and zinc blende (with zinc four-coordinated) structures, where magnesium is coordinated to three nitrogen and two fluorine atoms, with a sixth long bond to a fluorine atom, forming a square pyramid. The H-Mg$_2$NF sample was indexed as isostructural to MgO at temperatures between 1250 °C and 1350 °C.

More recently Brogan et al. (2012) reported their preparation and structural analysis of Mg$_3$NF$_3$ and Mg$_2$NF, which confirmed the earlier work by Andersson discussed above, with the Mg$_2$NF compound reported here equivalent to Andersson’s (1970) L-Mg$_2$NF phase. The compounds were prepared by reaction of Mg$_3$N$_2$ and MgF$_2$ at 1050–1150 °C and structures were quantified via Rietveld analysis of X-ray and neutron powder diffraction data. Mg$_3$NF$_3$ is cubic (space group: Pm-3m) and has a structure related to rock-salt MgO, but with one cation site vacant as discussed above. Structural analysis of this system indicated that Mg is positioned on the 3c (0, 1/2, 1/2) site with the (0, 0, 0) site of the rock-salt structure vacant. This makes magnesium octahedral, connecting with two nitride anions and four fluoride anions. The N$_3^-$ ions are positioned on the 1b (1/2, 1/2, 1/2) site, and F$^-$ ions are at the 3d (1/2, 0, 0) site. Mg$_2$NF is tetragonal (space group: I4$_1$/amd) and has an anti-LiFeO$_2$ related structure, where F$^-$ occupies the equivalent Fe$^{3+}$ position, N$_3^-$ occupies the Li$^+$ position and Mg$^{2+}$ is located on the equivalent anion (O$_2^-$) position. The analysis reveals that the Mg$^{2+}$ cation is bonded to three N$_3^-$ and two F$^-$ ions, giving a square pyramidal coordination. As
discussed above, a long Mg-F interaction is present, giving Mg a pseudo-octahedral coordination, although the long interaction is essentially non-bonding.

Ehrlich et al. (1971) reported the synthesis of three systems of metal nitride fluoride: Ca$_2$NF, Sr$_2$NF, and Ba$_2$NF. Sr$_2$NF and Ba$_2$NF were made by a 3 to 1 molar ratio of metal to metal fluoride under nitrogen gas, and a 4 to 1 molar ratio for Ca$_2$NF. The mixtures were treated with an argon flow at 1000 °C for 24 hours, followed by a nitrogen flow for 24 hours at 1000 °C, 950 °C, and 700 °C for calcium, strontium and barium respectively (Ehrlich et al., 1971). The Ca$_2$NF product had a light yellow color, although colors of the other two phases were not reported. The products were characterized using Debye-Scherrer powder X-ray diffraction, which indicated the presence of both the MF$_2$ and M$_2$NF phases (where M = Ca, Sr, or Ba). Ehrlich et al. reported that all three systems had the rocksalt-type structure, similar to their respective MO oxide analog phases. The unit cell parameters for Ca$_2$NF, Sr$_2$NF, and Ba$_2$NF were reported as a = 4.937 Å, 5.368 Å and 5.691 Å, respectively.

Following this treatment, Galy et al. (1971) reported the synthesis of a series of Ca$_2$O$_{2x}$N$_{1-x}$F$_{1-x}$ compounds over the range from x = 0 to 1. The pure Ca$_2$NF phase was prepared by a stoichiometric reaction of Ca$_3$N$_2$ and CaF$_2$ at 900 °C for 24 hours, while the oxynitride fluoride phases were synthesized at 1000 °C by appropriate mixtures of CaO with the Ca$_2$NF product. Powder X-ray diffraction revealed all of the synthesized compounds had the rocksalt-type structure. Galy et al. (1971) reported that, as expected, the unit cell parameter increases as x decreases in these phases, i.e. as nitrogen content increases. For the pure Ca$_2$NF compound, they reported a unit cell parameter of a = 4.937 Å. Interestingly, Strozewski (2007) prepared a Ca-N-O-F single crystalline sample
by reaction of CaO and CaF$_2$ with Ca metal in N$_2$ gas, and used single crystal X-ray diffraction (data collected at room temp.) to quantify the structure as rocksalt-type with a = 4.938(9) Å, which is very close to the value of a = 4.937 Å for Ca$_2$NF reported by Ehrlich et al. (1971) discussed above. A carefully prepared Ca$_2$NF sample prepared by Strozewski yielded a rocksalt-type phase with a = 4.986(11) Å (diffraction data collected at 100 K), and the X-ray structure plot for this sample is shown in **Figure 1.1**. These results suggest that the Ca$_2$NF compounds reported by both Ehrlich et al. (1971) and Galy et al. (1971) are actually likely to be Ca-N-O-F phases.

**Figure 1.1** Structure plot from single crystal X-ray diffraction data for rocksalt-type Ca$_2$NF (Strowzeski, 2007).

Nicklow et al. (2001) published a paper reporting the synthesis of a single crystalline Ca$_2$NF that is isostructural with L-Mg$_2$NF reported by Andersson (1970) and Brogan et al. (2012) discussed above. The ‘L-Ca$_2$NF’ phase was prepared from a mixture consisting of a 3:1 molar ratio of calcium and calcium fluoride treated under nitrogen gas and heated to 1000 °C. The single crystalline product was yellow in color and air sensitive, and X-ray diffraction data indicated a tetragonal unit cell with space group I4$_1$/amd, and unit cell parameters a = 4.901 Å and c = 10.516 Å. Relative to the Ca$_2$NF
rocksalt-type phases discussed above, the c-axis in L-Ca$_2$NF is approximately doubled due to ordering of N and F atoms along that direction, as indicated in Figure 1.2.

In addition to the rocksalt- and L-Mg$_2$NF-type phases observed in Ca$_2$NF system as discussed above, a third phase for Ca$_2$NF was reported by Jack et al. (2005). This is isostructural with a doubled cubic Sr$_2$NF phase reported by Wagner (2002) with space group (Fd-3m) and $a = 4.9841\text{Å}$, showing ordering of N and F atoms along all three cell directions. Like the Sr analog (structure discussed below) optimal refinement of the single crystal X-ray data for Ca$_2$NF required positioning F atoms on tetrahedral interstitial lattice sites, which was treated as a Frenkel defect in the model. As will be discussed in Chapter 5, however, synthesis and detailed structural analysis of high resolution X-ray diffraction data of doubled cubic Ca$_2$NF within the present study has shown that this is not actually a Frenkel defect. The X-ray structure plot for doubled cubic Ca$_2$NF is shown in Figure 1.2. Note that Ca$_2$NF is only nitride fluoride system to date in which all three of rocksalt-, L-Mg$_2$NF, and doubled cubic-type phases have been observed.
Figure 1.2 Structure plots from single crystal X-ray diffraction data for two Ca$_2$NF phases. Left: tetragonal L-Ca$_2$NF (Nicklow et al., 2001), in which N and F atoms are ordered along the c-axis; and Right: doubled cubic Ca$_2$NF (Jack et al., 2005), in which N and F atoms are ordered along all three axes. F2 is an interstitial fluoride ion at a tetrahedral site.

Wagner (2002) synthesized single crystals of Sr$_2$NF by heating a melt of a 3:1 mole ratio of Sr: SrF$_2$ in a nickel crucible under a flow of ultra-high-purity N$_2$ gas to 1000 °C. Two different colored crystals were observed - brownish yellow and dark red. These are isomorphic to the doubled-cubic Ca$_2$NF phase discussed above. Both crystals are cubic with space group Fd-3m, and with unit cells that are approximately doubled along all three cell-axes relative to rocksalt-type Sr$_2$NF. As mentioned, this structure results from ordering of N and F atoms along all three cubic cell dimensions. X-ray analysis for the brownish yellow crystal showed a cell parameter of a = 10.6920(45) Å, and for the dark red crystal, a = 10.7655(20) Å. It was reported that refinement of both samples
revealed fluorine atoms located in interstitial tetrahedral sites of the lattice, and this was interpreted as a Frenkel defect. As mentioned above, results from the present study (see Chapter 5), suggest that this is not the case. These new results also provide a mechanism accounting for the different colors observed in the isostructural Sr$_2$NF crystals reported by Wagner, which will be further discussed in Chapter 5.

Siebel and Wagner (2004) reported the synthesis and structure determination of single crystalline Ba$_2$NF. The phase was prepared from heating a mixture of KCuF$_3$ and barium metal to 900 °C under a flow of nitrogen gas. The crystal was dark violet and highly air-sensitive. X-ray data revealed that the Ba$_2$NF phase is isostructural with rock-salt type BaO, with space group Fm-3m and cell parameter, a = 5.6796 (19) Å, Z =2. This value is slightly lower than the value of a = 5.691 Å reported by Ehrlich et al. (1971) discussed above, although it should be noted that single crystal X-ray data for the Siebel and Wagner sample was collected at 100K, whereas the Debye-Sherrer powder data collected by Ehrlich et al.(1971) was likely collected at room temperature. Thus thermal expansion could account for the larger unit cell of the latter sample.

Bailey et al. (2011) more recently published their study of a powered black/gray Ba$_2$NF phase prepared via a reaction of barium subnitride (Ba$_2$N) with barium fluoride at 725 °C for five days under the flow of argon, followed by slow cooling. The researchers employed powder X-ray and neutron diffraction methods to determine the structural features of the system. Samples were found to contain a mixture of phases, with the predominant one being a layered hexagonal phase with space group R-3m showing the anti-α-NaFeO$_2$ structure, as observed in other alkaline earth nitride halides, M$_2$NX, where M = Ca & Sr and X = Cl & (Br Bowman et al., 2005 & 2006). The unit cell parameters
(from refinement of neutron diffraction data) were reported as $a = 4.0242(2)$ Å and $c = 19.975(1)$ Å, and Bailey et al. also noted that this is the first nitride-fluoride phase known to crystallize in a layered hexagonal system. The two other phases observed in the sample consisted of rocksalt-type $\text{Ba}_2\text{NF}$ and unreacted $\text{BaF}_2$. The $\text{Ba}_2\text{NF}$ rocksalt-type component was found to have cell parameter $a = 5.7945(6)$ Å (room temp data collection), which is larger by at least 0.1 Å than both unit cells for isostructural $\text{Ba}_2\text{NF}$ phases previously reported by Ehrlich et al. (1971) and Seibel and Wagner (2004) discussed in the previous paragraph. This suggests that these two previously reported phases may contain oxygen impurity.

As this thesis is concerned largely with synthesis and characterization of alkaline earth nitride-fluoride phases, all phases reported to date in the $\text{M-N-F}$ ($\text{M} = \text{Mg, Ca, Sr, and Ba}$) systems are summarized in Table 1.1 below.
Table 1.1 Summary of previously prepared metal nitride fluoride compounds

<table>
<thead>
<tr>
<th>Oxide Analog (rocksalt)</th>
<th>Nitride-Fluoride</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>tetragonal</td>
</tr>
<tr>
<td>MgO</td>
<td>a, b L-Mg$_2$NF</td>
</tr>
<tr>
<td>CaO</td>
<td>c L-Ca$_2$NF</td>
</tr>
<tr>
<td>SrO</td>
<td>e Sr$_2$NF</td>
</tr>
<tr>
<td>BaO</td>
<td>f, h, i Ba$_2$NF,</td>
</tr>
</tbody>
</table>

*aAndersson (1970);  bBrogan et al. (2012);  cNicklow et al. (2001);  dJack et al. (2005);  eWagner (2002);  fEhrlich et al. (1971);  gStrozewski (2007);  hSeibel & Wagner (2004);  iBailey et al. (2011).*

1.4 Bimetallic nitride fluorides

Very few bimetallic nitride fluoride compounds have been reported in the literature.

Headspith et al. (2009) synthesized Ce$_2$MnN$_3$F$_{2-d}$ from the ternary nitride Ce$_2$MnN$_3$ via fluorine insertion using fluorine gas in the low temperature range 95-115°C. The fluorinated phase Ce$_2$MnN$_3$F$_{2-d}$ was found to have a tetragonal symmetry (P4/nmm; a = 3.8554(4) Å and c = 13.088(4) Å from neutron powder diffraction data, which also revealed a fluorine deficiency. Rietveld refinement of PXRD data showed that manganese ions are housed in distorted MnN$_5$F octahedra, with manganese moved from the ideal unit cell position roughly about 0.4 Å. This asymmetric environment for
manganese is due to ordering of N and F at the octahedral apical sites along the c-axis of the unit cell.

Stoltz et al. (2005) reported the synthesized phase of metastable Na₃ZrNF₁₋ₓ (x=0.3). The phase was prepared by the reaction of recrystallized β-ZrNCl with excess NaF at 350-400 °C for 10 days in vacuo with intermediate grinding. The researchers obtained both X-ray and neutron diffraction data for the phase’s structure determination. Several models were found that refined to one of the three space groups P6₃/mmc, R-3m, and P-3m1, with the best fit of data pertaining to P6₃/mmc. The optimal structural model is related to the layered ZrNCl-type structure, but with sequential F-Zr₂N₂-F layers arranged in a two-layer repeat unit vs. the three-layer repeat unit for β-ZnNCl. Between the F-Zr₂N₂-F layers is an interlayer of sodium and fluorine atoms showing partial occupancies and disorder, with sodium atoms in pseudo-octahedral sites. These arrangements give a double-layer hexagonal lattice with unit cell parameters a = 3.660(4) Å and c = 18.14(2) Å.

1.5 Theoretical studies of inorganic nitride fluorides

A study on magnesium nitride fluoride was reported by Fang et al. (2003), who used Density Functional Theory (DFT) within the Generalized Gradient Approximation (GGA) to show the chemical bonding and the effect of anion presence on electronic properties of the system. Calculated lattice parameters and interatomic distances for Mg₃NF₃ and L-Mg₂NF were compared to experimental values (discussed earlier) reported by Andersson (1970), and showed an agreement to within 1.5%. Band gap energy calculations showed a decrease in band gap with increasing nitrogen content, as expected. Thus, Fang et al. reported a decreasing trend in band gap energies, Eg, in proceeding from insulating MgF₂ with Eg = 6.8eV, direct semiconductor Mg₃NF₃ with
Eg = 3.6 eV, indirect semiconductor L-Mg$_2$NF with Eg = 2.1 eV, to semiconductor Mg$_3$N$_2$ with Eg = 1.6 eV.

Betranhandy and Matar (2005) proposed a possible new SiNF system via a theoretical study based on density functional theory in its local density approximation. Models for starting structures were built using a geomimetism principle, basically referring to the use of known mineral structures as a starting point for the calculations. The investigators demonstrated several structural manipulations on different systems, with a model based on the TiOCl-type structure proving to be the best fit. Here, the researchers substituted silicon and nitrogen for titanium and oxygen, respectively, while keeping the fluorine at the chlorine position within the starting lattice. This ionic placement resulted in a crystal structure of SiNF with an orthorhombic structure of space group Pmmn, with lattice constants a = 2.761 Å, b = 3.573 Å, and c = 6.688 Å.

Betranhandy and Matar (2005) pointed out the crystal structure of SiNF can be viewed as stacking of Si-N planes along the c-axis, with F planes positioned between them, as shown in Figure 1.3. The compound is expected to be an insulator with covalent character for Si-N bonds and ionic bonding for Si-F. The band gap for the proposed SiNF model is calculated to be roughly 6 eV, which is surprisingly large considering the presence of nitrogen in the system, but is likely related to the TiOCl layered-type structure. Another study on the same phase by Page et al. (2006) indicates the chance of the SiNF existence is good based on the small total energy per unit formula, which is 0.6 eV. Finally, Betranhandy et al. (2005) proposed synthetic routes for the system, specifically either solvothermal process or silicon nitride treated with the flow of fluorine gas or HF, as well as from a mixture of Si$_3$N$_4$ and SiF$_4$ suggested by Page at el. (2006).
More recently, Matar (2012) reported a theoretical study of TiNF demonstrating that this system would likely exist as a distorted anatase-type structure, predominately covalent Ti-N bonds and ionic Ti-F bonds. TiNF is predicted to be a semiconductor with a band gap of about 2 eV. This study was addressed on atom re-distributions based on geometry optimizations using ultra soft pseudo potentials within density functional theory. After atom distribution, the author noticed that the ions are arranged along the c-axis as Ti, N, F, Ti, F, N, and Ti, N, F producing a periodic pattern, and consequently the phase crystallizes in a tetragonal system. The phase obeys the group to subgroup relationship in terms of space group determination, that is, going from $I4_1/amd$ (No.141) to $I-4m2$ No.119 to $Imm2$ (No. 44).

In 2014, Matar published a theoretical study on CrNF as a hypothetical nitride-fluoride analog of CrO$_2$. Based on an initial model derived by ordering nitrogen and fluorine atoms on oxygen positions of rutile-type CrO$_2$, an MgUO$_4$-type ground state structure was obtained for CrNF from Density Functional Theory computations. The
transition from the tetragonal rutile-type structure to orthorhombic MgUO$_4$-type in going from CrO$_2$ to CrNF is related to CrN$_3$F$_3$ distorted octahedra present in the latter phase. Matar conducted this theoretical research as a desire to better understand this mixed ion compound and the possible properties it might have. For example, CrNF was predicted to behave as a soft ferromagnet as opposed to CrO$_2$, which is a hard magnetic material. The study also proposed possible methods to synthesize CrNF, namely: (1) the ammonolysis of chromium fluoride precursor such as the method used on ZrF$_4$ for obtaining ZrNF (Jung et al., 1973) discussed earlier, or (2) using fluorinated fluxes on CrN, following a high pressure, high temperature method similar to that used in the preparation of ZrNF from ZrN by Zhu et al. (2004), discussed earlier.
CHAPTER TWO

METHODOLOGY AND INSTRUMENTATION

This Chapter consists of information on the chemicals and experimental methods used. A brief introduction to the instrumentation used in analyzing the samples will also be included. Section 2.1 consists of details on the general experimental procedure employed and gases used in this research. A description on each technique used in this project is given in Section 2.2.

2.1 Synthetic methods

The basic syntheses approaches used in this work consisted mainly of standard ceramic methods or precursor routes to prepare single crystals of targeted products from the melt. These techniques will be summarized below.

2.1.1 Standard ceramic methods

This technique involves heating stoichiometric mixtures of sample starting materials in the solid state to high temperatures (~900-1600 °C) under air, Ar, N₂, NH₃, or other reaction atmospheres. For example, for preparation of the phase CaMgNF in this study, one of the reactions used was:

MgF₂ + Mg + 2 Ca + N₂ \rightarrow 2 \text{CaMgNF}

Here the precursors were easily purchased in pure form. Typically, this method is used to carry out solid state reactions to yield powder products. In our case, the reaction was heated to a high enough temperature to melt the reaction mixture; details of the reaction conditions will be discussed later. Slow cooling from the melt then permitted growth of single crystals for subsequent structure analysis, and is further discussed in the next section.
2.1.2 Crystal growth from the melt

This method requires heating the solid state reaction mixture to high enough temperatures such that all reactants melt. If reactant melting temperatures are too high, a flux may be used, which is a relatively low melting powder that essentially serves as a kind of solvent for the reactants. A disadvantage of this approach is that flux material is sometimes found in the crystalline products. Crystal growth requires very slow cooling (5 to 20 °C/hr in our case) to balance nucleation and growth – too fast, nucleation dominates and powder forms, too slow and growth dominates and crystals may be too large and possibly twinned. Note that the latter case is less of a problem with X-ray diffraction analysis software currently available for crystal structure analysis. Finally, knowledge of the phase diagram (if known) is very useful in predicting whether or not a given set of reaction conditions will be successful. For congruently melting phases, which maintain the same composition of the solid upon melting, one can expect the desired phase upon slow cooling. Incongruent melting materials solidify in different compositions from the melt, possibly preventing crystallization of the desired phase. Here, knowledge of the phase diagram is needed to design an alternate route for the synthesis.
2.1.3 Precursor method via co-precipitation

The precursor method applies to target reactions for which synthesis of one or more precursors is required for the reaction. This technique was employed in many of the preparations listed here, notably for reactions using KCuF₃, NH₄CoF₃, and NH₄Cu₀.₅Co₀.₅F₃ perovskite-type fluorides as precursors. Preparation of the fluoride precursors were carried out via co-precipitation of KF or NH₄F with the appropriate transition metal nitrate at room temperatures. Throughout this project, the procedure used involves first dissolving starting materials in alcohol, then mixing the dissolved materials together and allowing then to sit for a while to precipitate. The co-precipitation method maximizes the blending of beginning materials to get optimum products.

2.2 Equipment

For the work related to synthesizing perovskite-type fluoride, the starting materials and products of the reaction are air or moisture-sensitive. These materials, therefore, were handled under an inert atmosphere. This was achieved through the use of both glove bags, and a glove box shown in Figure 2.1.
2.2.1 The glove box and glove bag

The MBRAUN glove box operates with a permanent nitrogen atmosphere. This atmosphere is circulated, passing over molecular sieves and copper based catalysts, to remove moisture and oxygen. The glove box contains oxygen and moisture sensors and levels are maintained at O₂ ≤ 0.1 ppm and H₂O ≤ 0.1 ppm. Access into and out of the glove box is achieved via transfer ports on the side of the instrument. These ports have two doors, one external and one internal, so that air from outside can be replaced with nitrogen prior to entering the glove box chamber. The ports are evacuated using a rotary pump and refilled with nitrogen gas. This evacuation procedure is repeated several times to reduce the amount of air entering the system.
On the other hand, the glove bag is a smaller transparent chamber made of polyethylene. This chamber is used to keep the starting materials from coming in contact with moisture. It has two openings; one allows the operator to enter chemicals inside the bag and can be sealed with a zipper-lock, the other opening can be attached to a furnace in order to load the chemicals into the furnace. It has also small holes where gas pipes are inserted.

2.2.2 Tube furnaces

There is one type of furnace with different tubes used in the preparation of the materials described here: a tube furnace.

As the name applies, a tube furnace is comprised of a long rounded tube, serving as a heating section surrounded by the heating element and thermal insulation. A reaction tube is commonly inserted into this furnace, in order to accommodate the reaction mixture. Two different tube furnaces were used to best suit the requirements of each reaction: Thermolyne 59300, and Mellen, NACCI series 3x-12. The maximum operating temperature of these furnaces is 1700 °C and 1200 °C, respectively. These tube furnaces were employed under N₂ or NH₃ atmospheres in the preparation of nitride-fluoride compounds.

2.2.2.1 Reaction under N₂ gas

The reaction of metal nitride fluoride syntheses was carried out under an argon and nitrogen flow with experimental set-up shown in Figure 2.2 below.
This (Thermolyne 59300) consists of an Inconel reaction tube, which is a free oxygen provider and can be sealed from the air via a lid with two caps. The Inconel tube is a nickel-chromium alloy and typically is used for high-temperature purposes. In this way, the starting materials can be loaded in a nickel crucible and inserted in the tube from the glove bag, under an argon flow. Once the starting materials are removed from the glove bag, the tube is sealed on both sides and attached to argon and nitrogen cylinders. This ensures there is no air present in the system.

2.2.2.2 Reaction under NH$_3$ gas

When the reaction of solid materials took place under ammonia flow, the experimental set-up shown in Figure 2.3 was used.
Figure 2.3 The tube furnace used for ammonia reactions (Mellen, NACCI series 3x-12)

For ammonolysis reactions using this furnace (Mellen, NACCI series 3x-12), a Molybdenum tube was used as the heating zone, which can be sealed from the atmosphere through caps placed on each end of the tube. Molybdenum is known for tolerance at high temperatures and it is resistant to corrosion. This is optimal during an ammonia reaction, as ammonia is known for its corrosive properties. Through the ammonia reactions, low temperatures, below 400 °C, were used. This condition is suitable for the Molybdenum tube. In air Molybdenum starts to convert to molybdic oxide which sublimes above 400 °C. In this setting, the reagents can be manipulated inside the glove bag under a flow of argon, then sealed and transferred to the Molybdenum tube. Following that, the sealed Molybdenum tube is connected to the argon and ammonia supply.
2.3 Instrumental methods

2.3.1 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (HI-RET GA 2950) is a technique where the sample is subjected to a controlled temperature program in a controlled atmosphere. The mass of the sample is a function of temperature as heated. The TGA instrument consists of a sample pan, made mostly out of aluminum, which is placed on a precision balance. The pan is located in a furnace and is heated with a mass of a sample during the experiment. Inside the furnace is a thermocouple to measure the temperature inside the furnace in each step of the heating process. A sample gas provides an inert environment by flowing over the sample and exiting through an exhaust. After the experiment is completed, the thermogravimetric analysis curve appears on the computer screen from left to right: Y axis represents weight loss, X axis displays a range of temperatures. The descending thermogravimetric analysis curve indicates that a weight loss occurred. The TGA curve gives information on a number of features such as chemical composition, reactivity, and thermal stability. TGA was used in this work to determine the thermal stability and the decomposition temperature of perovskite-type compounds made in this project. Figure 2.4 below is a picture of the instrument used, which is, a TA HI-RET GA 2950.
2.3.2 Focused Ion Beam technique

A JEOL JIB-4500 Focused Ion Beam (FIB)/Scanning Electron Microscope (SEM) equipped with an EDAX Apollo XV Energy-Dispersive Spectrometer was used in this work mainly for compositional analysis of some of the samples prepared herein. The FIB/SEM is comprised of a vacuum column, a metal ion source, a sample holder, and a detector. The FIB technique uses a beam of ions, usually gallium, which can be operated at a low or high current beam. The ion beam, going through the vacuum column that contains a set of lenses and apertures, strikes the sample surface, generating many species including sputtered atoms, secondary electrons, and secondary ions. These ion species are collected by a detector to form an image of the sample. In addition to the imaging technique, the FIB/SEM is capable of cutting cross sections, performing elemental and
phase composition maps, and etching. At the end of an experiment, some analyses are done on the computer to show a profile of elemental composition of a sample. **Figure 2.5** depicts a FIB column.

*Figure 2.5* Schematic presentation of FIB system. (Brucherseifer, “SEM/ FIB”).
2.3.3 Powder X-ray Diffraction (PXRD)

PXRD is the most common diffraction technique used in solid state laboratories, and plays part in this project. The main instrument used in this project is a Rigaku Miniflex II powder diffractometer. Figure 2.6 shows a schematic of the PXRD technique. A specimen S in the form of a flat plate is supported so that rotations about the axis labeled O are possible; this axis is perpendicular to the plane of the page. The X-ray beam is generated at point T, and the intensities of diffracted beams are detected with a counter labeled C in the figure.

![Diagram of an X-ray diffractometer](image)

**Figure 2.6** Schematic diagram of an X-ray diffractometer; T = x-ray source, S = specimen, C = detector, and O = the axis around which the specimen and detector rotate. (Callister, 2007)

The creation of X-rays during this technique is generated within an electron gun housing a metal cathode which emits electrons that are accelerated towards an anode. When the cathode electrons strike a sample, electrons from inner shells of the sample atoms are ejected, creating holes. These vacancies are occupied when electrons
from a higher shell fall into them, releasing electromagnetic radiation in the form of X-rays. The processes are pictured in Figure 2.7

![Energy level diagram for copper metal showing transitions that generate X-rays. (Dinnebier and Billinge, 2009)](image)

**Figure 2.7** Energy level diagram for copper metal showing transitions that generate X-rays. (Dinnebier and Billinge, 2009)

As the sample holder moves at constant angular velocity, a recorder automatically plots the diffracted beam intensity versus the diffracting angle $2\theta$, which is measured experimentally. **Figure 2.8** shows a diffraction pattern for a powdered specimen.

![Diffraction pattern for a powdered sample. (Callister, 2007)](image)

**Figure 2.8** A diffraction pattern for a powdered sample. (Callister, 2007)
2.3.4 Single-crystal X-ray Diffraction (single-crystal XRD)

Single-crystal XRD was used in this work for structure analysis of the crystalline materials prepared. Two instruments were utilized: a Bruker D8 QUEST with Mo source, and a Bruker Prospector with Cu source. The Prospector diffractometer features high brightness Cu IµS Incoatec microsource with Quasar MX optics; an Apex II CCD area detector; kappa 4-axis goniostat; and variable temperature capabilities (Oxford cryostream 700, 80-400 K). Its powder XRD plugin feature allows multicrystalline X-ray data collection from very small or air sensitive samples (in capillaries or in reflective mode). The Bruker Quest features high a brightness Mo IµS Incoatec microsource; 100 cm$^2$ Photon 100 CMOS (Complimentary Metal Oxide Sensor) detector; Helios optics; kappa 4-axis goniostat, and variable temperature capabilities (Oxford cryostream 700 plus, 80-500 K). Its core feature is the new COMS technology, allowing the detector to operate continuously and shutterless leading to substantially faster data collection times. The main use of this instrument is for high resolution data collection and determination for charge intensity.

The research reported in this thesis benefited greatly from the availability of these well-equipped X-ray diffractometers. The crystals made through this research tend to be air-sensitive and very small. For these reasons, preparation of the crystalline samples for single-crystal X-ray diffraction is challenging. Crystals of optimal size for our samples (usually containing Ca and Ba) are typically a few tenths of a nm in largest dimension.
The single-crystal X-ray diffractometer primarily consists of an X-ray generator, a sample holder (Goniometer Head), an X-ray detector, and a cryostream, enabling flow of nitrogen over the sample for sample protection from air, as well as low-temperature (100 K) data collection. X-rays are generated inside a cathode ray tube by a filament to yield electrons, which are then accelerated to an anode (either Cu or Mo for our instruments) by providing a voltage difference. For data collection, the crystal is first mounted on goniometer head, where adjustments can be made to center the crystal in the appropriate position, making an alignment in any desired orientation. **Figure 2.9** features the components of a single-crystal X-ray diffractometer, specifically, the Bruker Quest instrument used in this work.

![Figure 2.9 Photograph featuring the main components of single-crystal X-ray diffraction, specifically, the Bruker Quest instrument used in this work.](image)
Upon interacting with the crystal, X-rays are diffracted from crystalline lattice planes, giving rise to a diffraction pattern. The X-ray diffraction data is collected as the intensity of scattering at any angle, and can be calculated by the combination of wave destructive and constructive interference of X-rays from each atom existing in the crystal. From the scenario above, a crystal structure determination can be obtained (Guinier, 1994). The angular deviation from the direct unscattered beam can be used in measuring the spacing of the reciprocal lattice and thus the spacing of crystal lattice. These spacings can be used to identify the size and the shape of the unit cell. In addition, the intensity of diffracted beams determines the position of atoms within the unit cell. Finally, a structure determination is done by matching the observed intensity pattern to the calculated one from a postulated model.

Constructive interference occurs when the phase difference between successive reflected beams is an integer number of the wavelengths. In all other cases, the interference between the beams is destructive. The condition under which constructive interference occurs is given by Bragg’s Law:

\[ n \lambda = 2dsin\theta \]  

(1.1) Guinier (1994)

where \( n \) is an integer, \( \lambda \) the X-ray wavelength, \( d \) the spacing between lattice planes, and \( \theta \) angle between the incident radiation and the planes of atoms.
Figure 2.10 Derivation of the Bragg equation. \( d \) is the spacing between parallel atomic planes and \( \theta \) the angle between these planes and the incident radiation. http://www.brucherseifer.com/html/sem_fib.html. [10/8/2011].

After the specimen is mounted on a sample stage, a preliminary set of frames are automatically collected for determination of the unit cell. Reflections from these frames are indexed to choose the reduced primitive cell and measure the orientation matrix. The primitive unit cell is then refined using least-squares analysis and converted to the proper crystal system and Bravias lattice (Putnis, 1992). Finally, a strategy for data collection is determined, and the data set is collected, integrated, and corrected for absorption prior to structure solution and refinement.
CHAPTER THREE

STATEMENT OF THE PROBLEM

There are two primary objectives in this work, both of which are focused on inorganic nitride-fluoride (N-F) chemistry - a vastly under explored area of materials research. For example, fewer than 50 N-F compounds have been reported compared to tens of thousands of known oxides. As previously mentioned, most of the studies to date have centered on the \( \text{M}_2\text{N}_x\text{O}_{(2-2x)}\text{F}_x (\text{M} = \text{Mg, Ca, Sr & Ba}) \) systems. Relative to oxides, mixed anion N-F as well as N-O-F materials offer the advantage of smaller band gaps due to the presence of nitrogen, yet enable greater flexibility in terms of choice of cations and their possible range of oxidation states relative to nitrides. These factors, coupled with the relatively lowered symmetry possible due to anion ordering in N-F or N-O-F compounds, suggest enhanced dielectric, magnetic, and/or optical properties for these materials. Note however that this project is focused on synthesis and crystal structure investigations of the proposed compounds.

The first objective was to prepare known and new \( \text{M}_2\text{NF} \) compounds in order to further elucidate the crystal chemistry of known phases, as well as to explore synthesis routes for new mixed metal compounds. For example, the role of oxygen has been questioned in inorganic N-F systems in general Strozewski (2007), and this work has investigated its role in the doubled cubic \( \text{Ca}_2\text{NF} \) system. A focused ion beam/scanning electron microscope equipped with EDXS was used to confirm the oxygen absence, and fluorine & nitrogen content of single crystalline samples.
A new M-N-F compound that was targeted was Co$_2$NF. The synthesis approach for all of the target compounds involved first synthesizing AMF$_3$ (A = NH$_4^+$ or K$^+$; M = Cu, Mg, Co) perovskite-type fluorides as precursors. Modifications of known synthesis methods for these compounds led to very pure, dry precursor materials. The fluoride precursors were typically reacted with appropriate metals in nitrogen or ammonia, depending upon ability of the metal to reduce nitrogen gas. Thus a specific goal of this project was to explore in depth the use of perovskite-type fluorides in the synthesis of M-N-F compounds, and based on the results of this work, explore these materials for further use as precursors in the preparation of bimetallic N-F compounds.

The second goal of this project was to synthesize new mixed metal nitride fluoride materials. Only two such materials have been reported in the literature, and one of these is an F insertion compound. Compounds targeted in this project include CaMgNF, BaCaNF, and CaCoNF.

Of interest was the preparation of the first perovskite N-F compound, particularly due to the importance of perovskite-related compounds in many applications, including high temperature superconductors and colossal magneto resistive materials. Note however that based on results of M-N-F synthesis from perovskite-type fluorides, this route to make mixed metal N-F compounds was not further pursued.

Also of interest was the preparation of mixed metal analogs of M$_2$NF rocksalt-type compounds, and the impact on crystal chemistry of features such as cation positioning or ordering in the lattice. Use of standard ceramic methods led to synthesis of an ordered Ca-Mg-N-F rocksalt-related phase, which is the first such mixed metal N-F compound to be prepared.
CHAPTER FOUR
SYNTHESIS OF PRECURSORS AND METAL NITRIDE FLUORIDES

This section includes discussion on the synthesis of metal nitride fluorides from mainly two methods: a precursor method and standard ceramic methods. The syntheses of metal nitride fluoride compounds are tedious. Many previously prepared metal nitride fluorides are air-sensitive, and furthermore, the starting materials had to be treated under an inert atmosphere. In this project, the same scenario was employed to prevent oxygen presence before and during the process of forming the compounds.

4.1 Synthesis of precursors

4.1.1 The synthesis of KCuF₃ precursor

The first step in forming the prepared metal nitride fluoride phases was to make the precursors KCuF₃, NH₄CoF₃, etc. Previous methods used to prepare KCuF₃ included a hydrothermal technique and aqueous co-precipitation methods (Tyagi et al., 2009), which were good enough to yield the product. However, these experimental procedures raised concerns. In the hydrothermal technique, the formation of hydrofluoric acid (HF) was evolved. Not only does this acid possess corrosive properties, but it also results in non-stoichiometric products. In the case of these fluoride compounds synthesized from the aqueous procedure, substitution of hydroxyl ion for one fluoride ion leading to a composition of KM(OH)F₂ (M= Cu, Co, Mg) has been reported (Machin et al., 1963; Li et al., 2000). In the current project, the synthesis of KCuF₃ from a non-aqueous procedure was developed and performed as described below.
The formation of KCuF$_3$ was carried out based on a procedure reported by Langley et al. (1984), but was modified herein as described below. The modified procedure starts with first mixing 0.12 mole of a methanol solution of KF and 0.04 mole of dissolved anhydrous Cu(NO$_3$)$_2$ in methanol. Also the dissolving and mixing processes were carried out in a glove box to avoid contamination of the anhydrous methanol. The mixture inside the glove box was allowed to settle for 30 minutes to complete the precipitation process. Then the resulting precipitate was taken out of the glove box and filtered using a vacuum pump. The next step was to take a small amount of the sample for X-ray powder diffraction analysis. The X-ray diffraction powder pattern is shown in Figure 4.1

The chemical equation for the reaction is $3KF + Cu(NO_3)_2 \rightarrow KCuF_3 + 2KNO_3$.

![Figure 4.1](image)

**Figure 4.1** Powder X-ray diffraction pattern for the pre-purified KCuF$_3$ compound.
As can be seen from the powder pattern in Figure 4.1, the product from this reaction is not pure since it contains KNO₃. Consequently, a purification process was performed. The KNO₃ impurity in the synthesis of KCuF₃ was removed by a reflux process. First, the product was weighed, and placed in a rounded bottom flask, and based on that weight, an amount of ethanol was added. The impurity’s weight was treated as the total amount of the sample. That manipulation led to how much ethanol was needed for the process. The solubility of KNO₃ in ethanol is 0.3g/100g at 25 °C. The sample was kept in excess ethanol for 4-5 hours with stirring. After that, the rounded bottom flask containing (KCuF₃) was placed in a sand bath at 70 °C for 3-4 hours while stirring: KCuF₃ is intact at 70 °C. After the purification process the sample was loaded on an X-ray powder holder for analysis. X-Ray powder diffraction showed KNO₃ was removed by this method, as seen in Figure 4.2.
4.1.2 The synthesis of NH₄CoF₃ precursor

For synthesis of NH₄CoF₃, the following procedure was carried out: three moles of ammonium fluoride was dissolved in a minimum volume of methanol in a 600 mL Erlenmeyer flask. Excess NH₄F was used in order to have sufficient amount for the reaction. In a 400 mL Erlenmeyer flask, one mole of the appropriate anhydrous CoBr₂ was placed with a minimum volume of methanol. All of the manipulations were again carried out in a glove box due to the hygroscopicity of the product. The divalent metal bromide solution was added dropwise to the ammonium fluoride solution. Adding the solution dropwise allows for thorough mixing, which facilitates the reaction between the metal bromide and ammonium fluoride. After the precipitate settled to the bottom of the
Erlenmeyer flask, it was transferred onto 0.5 mm filter paper in a Buchner funnel for filtration and drying. The NH₄Br impurity was removed using the same method employed for KCuF₃, but using methanol instead of ethanol, as NH₄Br is readily soluble in methanol (solubility of NH₄Br in methanol: 12.33 g/100 g of methanol at 20 °C). The product was washed with methanol followed by acetone, and then was collected and placed in an oven over night at 60 °C. Finally, the dried product was stored in a 20 mL scintillation vial, and tape was placed around the vial lid to prevent moisture from getting into the sample. The overall chemical reaction for preparation of NH₄CoF₃ is:

\[
3\text{NH}_4\text{F} + \text{CoBr}_2 \rightarrow \text{NH}_4\text{CoF}_3 + 2\text{NH}_4\text{Br}
\]

**Figure 4.3** An X-ray powder diffraction pattern for the NH₄CoF₃ compound following initial purification.

The powder pattern above shows that the product still had some impurities i.e. CoF₂·0.5H₂O. This contamination was removed by repeating the same process
mentioned above. The powder pattern shown in Figure 4.4 indicates the effectiveness of the method.

![Coupled TwoTheta/Theta](image)

**Figure 4.4** An X-ray powder diffraction pattern for the NH₄CoF₃ compound after the second heating-purification step.

Thermogravimetric analysis (TGA) was carried out to determine the temperature of the NH₄CoF₃, and the results presented in Figure 4.5 showed that NH₄CoF₃ decomposed at about 250 °C.
Figure 4.5 Thermogravimetric analysis of NH₄CoF₃.

4.1.3 The synthesis of NH₄Co₀.₅Cu₀.₅F₃ precursor

Regarding the synthesis of NH₄Co₀.₅Ca₀.₅F₃, there are two steps to be completed. The first step aims to synthesize NH₄Cu₀.₅Co₀.₅F₃. The second step was to heat the synthesized NH₄Cu₀.₅Co₀.₅F₃ with calcium metal to carry out cation exchange. The product of the latter study was then to be reacted under ammonia gas to prepare CaCoNF.

The first attempt involved dissolving three moles of ammonium fluoride in a 600 mL Erlenmeyer flask. Then half a mole of each of anhydrous CuBr₂ and CoBr₂ was dissolved inside a glove box in a separate 400 mL Erlenmeyer flask containing methanol as a solvent. The cobalt and copper bromide compounds were blended in one
Erlenmeyer flask, then the ammonium fluoride solution was put on a stirring plate and the divalent metal bromide solutions were added dropwise to it. The mixture was kept stirring for thirty minutes, and then allowed to settle for ten minutes. The Erlenmeyer flask containing precipitate was removed from the glove box, the pinkish color precipitate was filtered and washed with methanol then followed by acetone, and was collected in a glass vial. The sample was kept at 60 °C in an oven over night. The next day a small amount of the sample was loaded on an X-ray sample holder and analyzed via X-ray powder diffraction, which revealed that (NH₄)₂Co₀.₅Cu₀.₅F₄ was prepared rather than the desired (NH₄)₂Co₀.₅Cu₀.₅F₃ phase. The powder pattern of the produced phase is shown in Figure 4.6.

Figure 4.6 An X-ray powder pattern of the produced (NH₄)₂Co₀.₅Cu₀.₅F₄ phase.
As can be seen in the powder pattern, although \( (\text{NH}_4)_2\text{Co}_{0.5}\text{Cu}_{0.5}\text{F}_4 \) is not present on the PDF database, product peaks were bracketed by peaks from \( (\text{NH}_4)_2\text{CoF}_4 \) and \( (\text{NH}_4)_2\text{CuF}_4 \), strongly supporting the presence of \( (\text{NH}_4)_2\text{Co}_{0.5}\text{Cu}_{0.5}\text{F}_4 \).

It was decided to go forward using \( (\text{NH}_4)_2\text{Co}_{0.5}\text{Cu}_{0.5}\text{F}_4 \) rather than \( (\text{NH}_4)_2\text{Co}_{0.5}\text{Cu}_{0.5}\text{F}_3 \) as a precursor, however the powdered phase was not yet suitable for the further step. It is clear from the powder pattern in Figure 4.6 that the sample contained impurities, which likely was mainly \( \text{NH}_4\text{F} \). Upon heating the sample with methanol at 60 °C for purification, using the same method mentioned above, the compound instead underwent a phase change, transforming into three mixed phases: \( \text{NH}_4\text{CuF}_3 \), \( \text{NH}_4\text{CoF}_3 \), and \( (\text{NH}_4)_2\text{CuF}_4 \) as shown below in Figure 4.7.

**Figure 4.7** X-ray powder pattern following heating of \( (\text{NH}_4)_2\text{Co}_{0.5}\text{Cu}_{0.5}\text{F}_4 \). The heating process caused a phase change for the compound.
This new compound is not ideal for the formation of the targeted compound. However, it shed light on a new approach for synthesis of NH₄Cu₀.₅Co₀.₅F₃. Apparently, not pre-heating the solution of transition metal salts prior to mixing with the NH₄F solution affects dissolution of the salts, and thus reaction outcome. The following provides description of the synthesis of NH₄Cu₀.₅Co₀.₅F₃ from a new approach. First, three moles of ammonium fluoride were dissolved in a minimum volume of methanol in a 600 mL Erlenmeyer flask. An excess amount was used in order to have a sufficient amount for the reaction. In another 400 mL Erlenmeyer flask, half a mole of anhydrous CuBr₂ was dissolved in a minimum volume of methanol. In a third Erlenmeyer flask, half a mole of anhydrous CoBr₂ was dissolved in methanol. The ammonium fluoride solution was placed on a hot plate and brought to a gentle boil. At the same time the copper bromide and cobalt bromide solutions were initially mixed together, and then brought to a gentle boil. Then the mixed divalent metal bromide solution was then added dropwise to the boiling solution of ammonium fluoride. Adding the solution dropwise allows for thorough mixing, which facilitates the reaction between the metal bromides and ammonium fluoride. The solution was kept in this condition for 30 minutes with a mild stirring. Then the solution was removed from the hot plate, and allowed to settle for 10 minutes. All the manipulations above were done in a glove box to avoid moisture presence. After the precipitate settled to the bottom of the Erlenmeyer flask, the precipitant was taken out of the glove box and then filtered and cleaned using the same procedure described before, the sample was washed with methanol followed by acetone. Finally, the product was dried over night at 60 °C, and then stored into a 20 mL
scintillation vial. Tape was placed around the vial lid to prevent moisture from getting into the sample. The reaction follows the chemical equation below.

\[
0.5 \text{CuBr}_2 + 0.5 \text{CoBr}_2 + 3 \text{NH}_4\text{F} \rightarrow \text{NH}_4\text{Cu}_{0.5}\text{Co}_{0.5}\text{F}_3 + 2 \text{NH}_4\text{Br}
\]

For the purpose of structure confirmation, X-ray powder was carried out. The powder pattern of \(\text{NH}_4\text{Cu}_{0.5}\text{Co}_{0.5}\text{F}_3\) is presented below. The pattern indicates that the final product is probably relatively rich in cobalt, and may even consist of a two phase mixture. The predominant phase is likely to be a cobalt-rich cubic phase, while the other is copper-rich and tetragonal like \(\text{NH}_4\text{CuF}_3\).

![X-ray powder diffraction pattern for \(\text{NH}_4\text{Cu}_{0.5}\text{Co}_{0.5}\text{F}_3\) compound.](image)

**Figure 4.8** X-ray powder diffraction pattern for \(\text{NH}_4\text{Cu}_{0.5}\text{Co}_{0.5}\text{F}_3\) compound.
**4.2 Synthesis of metal nitride fluorides**

**4.2.1 Magnesium nitride fluoride system**

In a glove bag filled with argon gas, the synthesized KCuF$_3$ and KMgF$_3$ compounds were each used as precursors in separate reactions, and mixed with magnesium metal (Alfa Aesar 98.8%). The mixtures were each placed in separate nickel crucibles, which were positioned centrally in a nickel boat, and transferred into the Inconel tube from the glove bag under argon gas. The samples were then each heated under argon gas to 850 °C, followed by cooling to 200 °C. After that, the system was reheated to 850 °C under a flow of nitrogen gas. This temperature was maintained for 4 hours followed by cooling to 70 °C. The gas was terminated and the crucible was removed from the tube and placed in an argon-filled glove bag for observation. Below are the chemical equations describing the attempted phases syntheses:

$\text{KCuF}_3 + 4\text{Mg} + \text{N}_2 \rightarrow 2\text{Mg}_2\text{NF} + \text{KF} + \text{Cu}$

$\text{KMgF}_3 + 3\text{Mg} + \text{N}_2 \rightarrow 2\text{Mg}_2\text{NF} + \text{KF}$

The heating program carried out for the reactions is listed below:

(R = Ramp function, L = Temperature level, and D = Dwell time)

Step 1: R1: step function, L1: 70 °C, D1: 0 hour

Step 2: R2 100 °C / hr., L2: 580 °C, D2: 1 hour

Step 3: R3100 °C / hr., L2: 200 °C, D2: 2 hour

The switch from argon gas to nitrogen gas was performed during Step 3 dwell.

Step 4: R4 55 °C /hr., L4: 850 °C, D4: 4 hours

Step 5: R5 20 °C /hr., L5: 200 °C, D5: 0 hour
Step 6: R6 step function, L6: 70 °C, D6: 0 hour
Step 7: END

4.2.2 Calcium nitride fluoride system

An ammonolysis method was conducted here to investigate preparation of Ca$_2$NF using this method. The following reaction was hypothesized:

\[ \text{KCuF}_3 + 4 \text{Ca} + 2\text{NH}_3 \rightarrow \text{KF} + 2\text{Ca}_2\text{NF} + 3\text{H}_2 + \text{Cu} \]

The calcium metal (Alfa Aesar 98.8%) was mixed with KCuF$_3$ in a nickel crucible inside the glove bag filled with argon gas, and then the crucible with the sample was inserted into a silica tube. The external wall of the tube opening was coated with high-vacuum grease, and was attached to a cap having two openings; gas inlet and gas outlet. The system was heated first under argon gas at 900 °C for 4 hours, and the sample was cooled down to 200 °C. After this step, the system was reheated to 900 °C under a constant flow of ammonia gas and then cooled to 70 °C. Ammonia gas (high-purity 99.999%, Praxair) flowed through the tube for 4 hours.

The heating program followed the same fashion stated in the previous section.

Step 1: R1: step function, L1: 70 °C, D1: 0 hour
Step 2: R2 80 °C /hr., L2: 900 °C, D2: 2 hours
Step3: R3 80 °C /hr., L2: 200 °C, D2: 4 hours

The switch from argon gas to ammonia gas was performed during step 3 dwell.

Step 4: R4 60 °C /hr., L4: 900 °C, D4: 4 hours
Step 5: R5 25 °C /hr., L5: 200 °C, D5: 0 hour
Step 6: R6 step function, L6: 70 °C, D6: 0 hour
Step 7: R6 END
Once the sample was cooled, the ammonia gas flow was terminated and the product was removed for analysis, and then observed under a microscope. Some heterogeneous samples consisted of chunks of white powder and colorless crystals with a few copper pieces. Some isolated colorless crystals were also found in the product mixture and one of these was submitted for single crystal X-ray diffraction analysis, and the results are discussed in Chapter 6.

4.2.3 Cobalt nitride fluoride system

Another ammonolysis reaction was carried out to make Co$_2$NF. The proposed synthesis of Co$_2$NF started from the synthesis of NH$_4$CoF$_3$. The synthesized NH$_4$CoF$_3$ was put inside a nickel crucible. The treatment was done inside an Argon-filled glove bag due to the oxygen and moisture sensitivity of the reactant. The crucible with sample was inserted inside a molybdenum tube and then heated up to the decomposition temperature of the precursor, 250 °C, under a flow of ammonia for 2 hours. Then the system was cooled down to 70 °C. Once the sample was cooled, the ammonia gas flow was terminated and the product was removed for analysis via X-ray powder diffraction. This approach yielded a negative result, NH$_4$CoF$_3$ was still intact under this temperature. Therefore, a different reaction condition was carried out in the same manner, but at a higher temperature, and the heating program is below.

Step 1: R1: step function, L1: 70 °C, D1: 0 hour
Step 2: R2 60 °C /hr, L2: 350 °C, D2: 2 hours
Step3: R3 25 °C /hr, L2: 70 °C, D2: 0 hour
Step 6: R6 step function, L6: 30 °C, D6: 0 hour
Once the sample was cooled, the ammonia gas flow was terminated and the product was removed for analysis. This new condition caused the complete decomposition of NH₄CoF₃ into a black powder.

4.3 Synthesis of bimetallic nitride fluorides

Bimetallic nitride fluorides possess two metals combined with fluoride and nitride ions. Such materials have not been widely studied, so very few publications were produced so far as discussed in Chapter 1. The reactions below describe the syntheses experiments for two bimetallic nitride fluoride compounds.

4.3.1 Calcium magnesium nitride fluoride

The synthesis was based on a thermal treatment of starting materials in the solid phase. The mixture of two moles of Ca metal (Alfa Aesar 98.8%), one mole Mg turnings (Alfa Aesar 99.98%), and one mole of MgF₂ (Alfa Aesar 99.9%) was carried out in an Ar-filled glove bag. These three compounds were weighed and loaded in a nickel crucible, and then inserted into the Inconel tube from the glove bag. The chemical reaction for the proposed targeted compound is written below:

MgF₂ + Mg + 2Ca + N₂ → 2CaMgNF

The mixture was heated first under first an argon flow and followed by a nitrogen flow using the following program (R = Ramp function, L = Temperature level, and D = Dwell time)

Step 1: R1: step function, L1: 70 °C, D1: 0 hour

Step 2: R2 80 °C /hr., L2: 1000 °C, D2: 4 hours

Step3: R3 80 °C /hr., L2: 200 °C, D2: 2 hours

The switch from argon gas to nitrogen gas was performed during step 3 dwell.
Step 4: R4 60 °C/hr., L4: 1000 °C, D4: 4 hours
Step 5: R5 15 °C/hr., L5: 200 °C, D5: 0 hour
Step 6: R6 step function, L6: 70 °C, D6: 0 hour
Step 7: END

Once the reaction was finished, the nitrogen gas flow was terminated. The crucible with the product was removed from the furnace tube and put into a glove bag filled with argon gas. A small amount of the sample was taken from the crucible and placed on a microscope slide containing mineral oil and observed under an optical microscope in order to select a single crystal for X-ray diffraction analysis.

4.3.2 Calcium barium nitride fluoride

Another thermal-treatment trial for attempting to make bimetallic nitride fluoride was conducted. The mixture of 2 moles of calcium metal (Alfa Aesar 98.8%), one mole barium metal (Alfa Aesar 99.2%) packaged in oil, and one mole of barium fluoride (Alfa Aesar 99.9%) was carried out in an evacuated glove bag to avoid contamination of the reactants. Prior to mixing, excess oil was wiped from the chunk of Ba using a polishing cloth, followed by placing the chunk in an Ar gas steam. Following that, the mixture was loaded in a nickel crucible, and then inserted into the Inconel tube from the glove bag. After the insertion process, the tube was sealed with a cap. Below is the chemical equation describing the targeted phase:

\[
\begin{align*}
N_2 \\
\text{BaF}_2 + \text{Ba}^+ + 2\text{Ca} & \rightarrow 2\text{BaCaNF}
\end{align*}
\]

Then the mixture was heated first under first an argon flow followed by a nitrogen flow using the following program (R = Ramp function, L = Temperature level, and D = Dwell time)
Step 1: R1: step function, L1: 70 °C, D1: 0 hour
Step 2: R2 80 °C/hr., L2: 1000 °C, D2: 4 hours
Step 3: R3 80 °C/hr., L2: 200 °C, D2: 2 hours
The switch from argon gas to nitrogen gas was performed during step 3 dwell.
Step 4: R4 60 °C/hr., L4: 1000 °C, D4: 4 hours
Step 5: R5 15 °C/hr., L5: 200 °C, D5: 0 hour
Step 6: R6 step function, L6: 70 °C, D6: 0 hour
Step 7: END

Once the reaction was finished, the nitrogen gas was turned off. The crucible with the product was then removed from the furnace tube and placed into a glove bag filled with argon gas. A small amount of the sample was taken from the crucible and placed on a microscope slide containing mineral oil and examined under an optical microscope.
CHAPTER FIVE
CRYSTAL CHEMISTRY OF DOUBLED-CUBIC Ca$_2$NF

5.1 Preparation of Ca$_2$NF single crystals

Ca$_2$NF single crystals for this work were grown from Ca metal (Alfa Aesar 98.8%) and KCuF$_3$ prepared according to the method described in Section 4.1.1. The overall reaction for the synthesis is: $\text{KCuF}_3 + 4\text{Ca} + \text{N}_2 \rightarrow 2\text{Ca}_2\text{NF} + \text{KF} + \text{Cu}$. First, 0.400 g of KCuF$_3$ was placed in a nickel crucible inside a glove bag filled with argon gas. The KCuF$_3$ sample was then inserted into an Inconel tube, and was heated over night at 140 °C to exclude any possible water presence. The next day, the KCuF$_3$ sample was taken out of the tube, and was mixed with 0.400 g of Ca metal in the same fashion. After that, the mixture was transferred into the Inconel tube, and was heated to 1100 °C for one hour under an argon flow. Next, the reaction was cooled down to 200 °C at a rate of 80 °C/h. Following sample cooling, there were two additional steps leading to completion of the reaction. In the first step, the dynamic gas flow was switched from argon to nitrogen and the reaction mixture was reheated to 1100 °C, and held there for four hours. Then the reaction was cooled down to room temperature at a rate of 25 °C/h. The final product was taken out from the tube to a glove bag filled with argon. The detailed furnace program used in the Thermolyne tube furnace is given below (R = Ramp function, L = Temperature level, and D = Dwell time):

Step 1: R1: step function, L1: 70 °C, D1: 0 hour
Step 2: R2: 80 °C/hr, L2: 1100 °C, D2: 4 hours
Step3: R3: 80 °C/hr, L2: 200 °C, D2: 2 hours
(The switch from argon to nitrogen gas was performed during Step3 dwell.)

Step 4: R4: 60 °C/hr, L4: 1100 °C, D4: 4 hours

Step 5: R5: 25 °C/hr, L5: 200 °C, D5: 0 hour

Step 6: R6: step function, L6: 70 °C, D6: 0 hour

Step 7: END

After the reaction was completed, the crucible was retrieved from the tube and placed inside the glove bag under a flow of argon. The product was placed on a microscope slide, and was covered with mineral oil to keep moisture away. The product was observed under an optical microscope to search for yellow crystals confirming presence of the Ca$_2$NF phase. Finally, the sample was submitted to Dr. Zeller (the YSU staff crystallographer) for single crystal X-ray diffraction analysis. The results from this analysis will be discussed below.

5.2 Single crystal X-ray data collection

The crystal selected for analysis was 0.17 mm in largest dimension. X-ray single crystal diffraction data was collected to a resolution of 0.4 Å resolution, but was cut off at 0.45 Å for refinement. A Bruker D8 QUEST single-crystal diffractometer equipped with a very fine electron beam, 2.4-kW sealed tube X-ray source (MoKα radiation, 0.71073 Å) operating at 50 kV and 40 mA was employed for this analysis. A full sphere of intensity data was collected in 1800 frames (width of 0.303 and exposure time of 10 seconds per frame). The diffractometer is equipped with the IμS microfocus X-ray Molybdenum source. It is ideally matched with high-performance multilayer optics and provides a small, high-intensity X-ray beam that is well suited for the smallest, and most weakly diffracting crystals. The diffractometer also has a state-of-the-art detector, i.e. a
PHOTON 100 detector with CMOS technology (Complimentary Metal Oxide Semiconductor). This detector is air-cooled, single-phase power, and as mentioned is equipped with CMOS sensors, so the blooming effect does not occur. CMOS sensors handle strong reflections significantly better than previous generation CCD detectors, and, in particular, improve the low-resolution data quality. The goniometer of the diffractometer is designed for the highest accuracy and precision, excellent alignment, and long-term reliability. The goniometer has the smallest error in the cross section of the instrument axes, thus minimizing the sphere of confusion. Even the tiniest microcrystal stays reliably centered during the entire data acquisition, promising optimal data.

Refinement of the X-ray data acquired from this high intensity diffractometer, coupled with compositional analysis via a Focused Ion Beam/Scanning Electron Microscope, afforded details of the crystal chemistry for the doubled-cubic \( \text{Ca}_2\text{NF} \) not attained in the previous study by Jack et al. (2005). However, prior to final structure refinement, the sample was taken directly from the X-ray diffractometer to an adjacent electron microscopy lab for compositional analysis. This experiment will be summarized next.

5.3 Compositional analysis

Compositional analysis was conducted using the dual Focused Ion Beam (FIB)/Scanning Electron Microscope (SEM) equipped with an EDAX Apollo XV EDXS system described in Section 2.3.2. FIB/EDXS analysis has been sought to identify whether or not there is oxygen present inside the core of the crystal, indicating synthesis of a Ca-N-O-F phase rather than a nitride fluoride, Ca-N-F. The analysis was first carried out on the surface of the mounted crystal, and then several layers of the crystal were cut
away to penetrate the lower levels. The data is shown in Figure 5.1. Not surprisingly, oxygen was detected on the crystal surface, which could have been incorporated during transport of the crystal from the X-ray diffractometer (where it had been kept under flow of N₂) to the vacuum chamber of the SEM. However, no oxygen was detected at the crystal core. Based on detection limits of the technique, it can be concluded that only trace amounts of oxygen are present, if any, in the region analyzed. Although only one core sampling region was analyzed, it represents roughly 10% of sample volume, and so the sample was treated as a pure nitride-fluoride material for the purpose of the structure refinement.
Figure 5.1 FIB images and EDXS data of Ca$_2$NF taken from different regions of the crystal. Carbon content is from the organic tape used on the sample holder. Left: Data from the surface shows presence of oxygen; Right: data from crystal core, no oxygen observed.
5.3 Structure description and analysis

A summary of refinement data is presented in Table 5.1. The space group of Fd-3m and unit cell parameter of 10.0301 (5) Å suggested early on that this sample was likely isostructural to the previously reported doubled cubic phase of Jack et al. (2005). The rocksalt-related structure consists of Ca atoms in a single crystallographic site in octahedral coordination to 3 F atoms and 3 N atoms, which in turn are each located on distinct crystallographic sites that are octahedrally coordinated to Ca. Ordering of these N and F atoms along the cell edges is responsible for the observed doubling of the unit cell relative to rocksalt-type Ca$_2$NF, as shown in Figure 5.2. As mentioned, after the octahedral Ca and N & F octahedral positions were assigned, it was necessary to refine excess electron density still present as F atoms in interstitial tetrahedral sites.

![Figure 5.2](image)

**Figure 5.2** A view of the unit cell for the final Ca$_2$NF structure. Ordering of N and F atoms along all three cell axes is evident. F2 atoms at interstitial sites are also shown. (Plot generated from crystal maker, 9.2.2, 645).
Table 5.1 Refinement data for doubled-cubic Ca$_2$NF

<table>
<thead>
<tr>
<th>Crystal data</th>
<th>Quest14mz237_0m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>CaN$<em>{0.4619}$F$</em>{0.6147}$</td>
</tr>
<tr>
<td>$M_r$</td>
<td>58.23</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Cubic, Fd 3$^-m$</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>100</td>
</tr>
<tr>
<td>a (Å)</td>
<td>10.0301 (5)</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>1009.06 (15)</td>
</tr>
<tr>
<td>Z</td>
<td>32</td>
</tr>
<tr>
<td>Radiation type</td>
<td>Mo K$_\alpha$</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>4.22</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>$0.17 \times 0.07 \times 0.05$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Data collection</th>
<th></th>
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<tbody>
<tr>
<td>Diffractometer</td>
<td>Bruker AXS D8 Quest CMOS diffractometer</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Multi-scan Apex2 v2014.1-1 (Bruker, 2014)</td>
</tr>
<tr>
<td>$T_{\text{min}}, T_{\text{max}}$</td>
<td>0.570, 0.752</td>
</tr>
<tr>
<td>No. of measured, independent and observed [I &gt; 2$\sigma$(I)] reflections</td>
<td>4544, 316, 315</td>
</tr>
<tr>
<td>Rint</td>
<td>0.035</td>
</tr>
<tr>
<td>$(\sin \theta/\lambda)_{\text{max}}$ (Å$^{-1}$)</td>
<td>1.106</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Refinement</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$R[F^2 &gt; 2\sigma(F^2)]$, wR(F$^2$), $S$</td>
<td>0.029, 0.068, 1.35</td>
</tr>
<tr>
<td>No. of reflections</td>
<td>316</td>
</tr>
<tr>
<td>No. of parameters</td>
<td>17</td>
</tr>
<tr>
<td>No. of restraints</td>
<td>2</td>
</tr>
<tr>
<td>$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}}$ (e Å$^{-3}$)</td>
<td>1.28, −1.45</td>
</tr>
</tbody>
</table>
Potential disorder of Ca atoms (displacement by less than 0.1 Angstrom) was ignored during refinement. However, appreciable disorder was observed for fluorine and nitrogen atoms at octahedral sites. Three different sites occupied by only fluorine were refined, all of which are partially occupied. The site with the highest occupancy is the F1 position, located at octahedral sites. Large displacement at this site, probably due to the nearby, partially filled interstitial fluorine (F2) site, resulted in treating the original F1 atoms as distributed between three positions: the normal F1 site, and two symmetry equivalent positions of F1B around F1, which are displaced by 0.575 Å on either side of F1 towards and away from F2, as shown in Figure 5.3. The F1B and F2 sites have occupancies that refined to essentially identical values, indicating that displacement of F1 to F1B occurs only when a nearby F2 position is occupied.
Figure 5.3 A view of one Ca coordination sphere (75% ellipsoids) in the doubled-cubic Ca$_2$NF structure. F2 is the interstitial F position, and F1 is the octahedral F1 site. The F1 atoms shift to F1B positions away from F2 when the F2 site is occupied. F3 shares the N1 octahedral site to compensate excess charge from F2 atoms. (Plot generated using the XP program within SHELXTL, v. 6.14.)

The displacement of F1 away from the occupied F2 site may be related to the short distance of 2.172 Å between F1 and F2. Thus in the presence of an atom at the F2 interstitial site, atoms at nearby F1 sites seem to be displaced away from F2 by 0.575 Å to the F1B position, resulting in a more favorable F2...F1B distance of 2.747 Å. The total fluorine count for the sites at F1, F2 and F1B for the whole unit, when refined without restraints, sums up to more than 16 atoms (i.e. more than expected for the idealized formula Ca$_2$NF, which would have an ideal unit cell formula of Ca$_{32}$N$_{16}$F$_{16}$). At the same time, a positive residual electron density at the nitrogen site (N1) indicates disorder.
of nitrogen with small amounts of fluorine (F3), as the presence of oxygen was ruled out by using SEM-EDS measurements.

As reported to us by Dr. Zeller (YSU Staff Crystallographer during this work), when freely refined, the excess of fluorine in the lattice in combination with replacement of some nitrogen by fluorine yielded a nearly charge balanced compound. To achieve exact charge balance, the charges for nitrogen and fluorine throughout the lattice were constrained to match the total charge from calcium, 64. To summarize, the number of sites of F and N atoms in the lattice are as follows:

F1: 16, F2: 8, F3: 16, F1B: 32, N1: 16

These numbers, multiplied by the occupancy factors and the charge of each atom (1 for fluorine, 3 for nitrogen) were constrained to 64, the charge of the sum of the Ca atoms per unit cell. As the occupancy for F2 and F1B are identical, their occupancies were treated together, thus their occupancy factor was multiplied by (8 + 32) = 40. This resulted in the following SUMP command: SUMP 64.0, 40.0 2, 16.0 3, 48.0 4, 16.0 5 (with 48.0 being 16.0 multiplied by 3.0, the negative charge of nitrogen). N1 and F3, which share a site, were constrained to have identical positions and thermal parameters. Their occupancies were constrained to sum up to unity. Subject to these constraints, occupancies refined to the following values:

F1: 0.61769(19), F2, F1B: 0.21315(8), F3: 0.07529(12), N1: 0.92469(7)

Thus, 7.5% of nitrogen in Ca₂NF is replaced by fluorine, and an additional 15% of excess fluorine is found throughout the lattice in interstitial sites for charge balance. The resulting formula is
$\text{Ca}_{32}\text{N}_{14.78}\text{F}_{19.67}$ for one unit cell, or $\text{CaN}_{0.4619}\text{F}_{0.6147}$, or $\text{Ca}_{2}\text{N}_{0.9238}\text{F}_{1.229}$. Application of the occupancy constraints resulted in a marginal increase of R value by 0.05%. In conclusion, the refined composition for one unit cell can be written as

$\text{Ca}_{32}(\text{N}_{14.78}\text{F}_{1.22})_{\text{N oct site}}(\text{F}_{16.00})_{\text{oct site}}(\text{F}_{2.44})_{\text{int. tetrahedral site}}$. Thus on average there are 2.44 F excess atoms at interstitial sites per unit cell, and 1.22 excess F atoms on average replacing N atoms in the lattice for charge balance.

Table 5.2 shows the Positional, Occupational, and Anisotropic and Equivalent Isotopic Displacement Parameters for the final refinement pertaining to the discussion above.

Table 5.2  Positional, Occupational, and *Displacement Parameters for $\text{Ca}_2\text{NF}$ Crystal Refinement

<table>
<thead>
<tr>
<th>Ele</th>
<th>Site</th>
<th>Occ</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>U11</th>
<th>U23</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>32e</td>
<td>0.17</td>
<td>0.5099</td>
<td>0.7401</td>
<td>0.5099</td>
<td>0.00511</td>
<td>0.00029</td>
<td>0.50990(2)</td>
</tr>
<tr>
<td>F1</td>
<td>16c</td>
<td>0.15</td>
<td>0.2500</td>
<td>0.7500</td>
<td>0.5000</td>
<td>0.01198</td>
<td>0.0007</td>
<td>0.0120(5)</td>
</tr>
<tr>
<td>F2</td>
<td>8a</td>
<td>0.05</td>
<td>0.3750</td>
<td>0.8750</td>
<td>0.3750</td>
<td>0.00745</td>
<td>0.0000</td>
<td>0.0074(1)</td>
</tr>
<tr>
<td>F3</td>
<td>16d</td>
<td>0.04</td>
<td>0.5000</td>
<td>0.5000</td>
<td>0.5000</td>
<td>0.00585</td>
<td>0.0001</td>
<td>0.0058(2)</td>
</tr>
<tr>
<td>F1B</td>
<td>32e</td>
<td>0.04</td>
<td>0.2831</td>
<td>0.7831</td>
<td>0.4669</td>
<td>0.01106</td>
<td>-0.0026</td>
<td>0.4669(5)</td>
</tr>
<tr>
<td>N1</td>
<td>16d</td>
<td>0.46</td>
<td>0.5000</td>
<td>0.5000</td>
<td>0.5000</td>
<td>0.00585</td>
<td>0.0001</td>
<td>0.0058(2)</td>
</tr>
</tbody>
</table>

*The anisotropic thermal parameter is expressed as exp \[-2\pi^2(h^2 a^2 U_{11} + k^2 b^2 U_{22} + l^2 c^2 U_{33} + 2hka*b*U_{12} + 2hla*b*U_{13} + 2Klb*c*U_{23})]\]; $U_{11} = U_{22} = U_{33}$ and $U_{23} = U_{13} = U_{12}$ for F2, F3, & N1; $U_{23} = -U_{13} = U_{12}$ for Ca; $U_{23} = U_{13} = -U_{12}$ for F1; and $-U_{23} = -U_{13} = U_{12}$ for F1B. U(eq) is defined as one-third of the trace of the Uij orthogonalized tensor. N(1) and F(3) share the 16d site; displacement parameters constrained to be equal.

5.4 Discussion

The key outcome of the work described in this chapter is the improved model explaining the crystal chemistry of the doubled cubic phase of Ca$_2$NF, and by extension, Sr$_2$NF. Researchers in our group have noted for some time that although doubled cubic
rocksalt-related crystals of M$_2$NF (M = Ca or Sr), have been observed many times in laboratory preparations, refinements in every single case revealed the presence of F atoms at tetrahedral interstitial sites. Until now, these have been interpreted as Frenkel defects, usually involving around 10% or more of F atoms moving from their octahedral lattice positions to interstitial sites. If the lattice is built only through ordering of N and F atoms, one should expect to see occasional crystals with no F atoms at interstitial sites. This work has provided a plausible explanation for why such a structure has not been observed. It appears that under proper conditions (e.g. cooling rate and local environment in the melt), crystals grow with N and F in distinct and alternately ordered lattice positions. During growth, some F atoms substitute onto N positions, creating a deficiency in negative charge which is compensated by excess F atoms being retained in the crystal at interstitial sites. It is possible that the ‘pure’ doubled cubic phase (with no interstitials) is somewhat higher in energy than the stoichiometric phase, and so is observed only when the energy is lowered by the extra bonds of interstitial F, which in turn only arise when excess F is present. Interestingly, rocksalt-type crystals are almost always found together with the non-stoichiometric doubled cubic phase, suggesting that these phases are very close in energy. Future work will explore computational methods to determine the relative energies of all three of these systems, i.e. non-stoichiometric vs. stoichiometric doubled cubic and rocksalt-type Ca$_2$NF.

This model also provides an explanation for the two colors of doubled cubic crystals observed in the Sr$_2$NF system (Wagner, 2002). A brownish-yellow (BY) phase was observed with $a = 10.6920(45)$ Å, and a dark red (DR) crystal was reported with $a = 10.7655(20)$ Å. A larger cubic unit cell implies relatively greater N content in the lattice,
and thus a smaller band gap. This fits with unit cell parameters and colors observed, e.g., the DR crystal should have the smaller band gap since all colors are absorbed except red, meaning relatively more N in the lattice and larger unit cell parameter, as observed. The BY crystal would be expected to have the larger band gap, absorbing only in the violet/blue region such that the yellow/brown color is observed, meaning a relatively smaller amount of N and smaller cell parameter, as observed. However, the refinement (Wagner, 2002) showed that the DR crystal also has higher F content relative to the BY crystal (1.85 vs. 1.68 F atoms per unit cell at interstitial sites, respectively). Thus, based on the model presented here that depends on F\textsuperscript{−} replacement of N\textsuperscript{3−} for charge balance, the DR crystal should have less excess F content than BY, and thus greater N content overall rather than the reverse case, which does not fit with the observed colors and cell parameters.

The explanation is that the DR and BY crystals likely have some oxygen present, with the BY crystal having relatively more. For example, if the excess charge from 1.68 F atoms at interstitial sites in the BY lattice is compensated by the replacement of one N\textsuperscript{3−} ion by O\textsuperscript{2−}, then there is a 1.68 N atom deficiency per unit cell in the BY sample. On the other hand, if the excess charges due to the 1.85 excess F\textsuperscript{−} ions at interstitial sites in the DR crystal are compensated only by F\textsuperscript{−} ions, then 0.925 F\textsuperscript{−} ions per unit cell replace 0.925 N\textsuperscript{3−} ions for charge balance. This leaves relatively more N atoms in the DR lattice compared to the oxygen-containing BY phase, making the non-stoichiometric defect model consistent with the experimental data for the Sr\textsubscript{2}NF system.

Although we have compensated for excess negative charge in the lattice by substitution of one F atom for N for each two interstitial F atoms present in the lattice, an
alternative mechanism is possible (as suggested above) by substitution of one O atom for N for each interstitial F site occupied. Of course, the complete absence of oxygen in our sample cannot be guaranteed. We assumed that EDXS data taken from one sampling area in the core of the crystal that was reached using a focused ion beam indicated lack of oxygen in the lattice overall during data collection, and that oxygen found on the surface was incorporated during crystal transport to the EM lab. Table 5.3 compares the atomic percentages for the sample calculated from EDXS measurements to those obtained from the X-ray refinement. The experimental calcium, nitrogen and fluorine contents were adjusted to a 100% scale for the calculation. It is seen that the numbers do not compare very closely, probably due to the small sampling region or even crystal orientation effects. However, it is clear from the data that the system has excess fluorine, and that only trace amounts of oxygen, if any, is present in the sampling region.

Table 5.3 Comparison between the experimental data from EDXS measurements and X-ray refinement data for doubled cubic Ca₂NF system

<table>
<thead>
<tr>
<th>Atomic % in Ca₂NF</th>
<th>EDXS Data</th>
<th>X-ray Refinement Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>40.46</td>
<td>48.16</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>27.43</td>
<td>22.25</td>
</tr>
<tr>
<td>Fluorine</td>
<td>32.10</td>
<td>29.59</td>
</tr>
</tbody>
</table>
As noted above, rocksalt-type Ca$_2$NF crystals usually coexist in the product mixture with the doubled cubic sample. It must be mentioned here that single crystal X-ray diffraction analysis of a rocksalt-type sample found in this study revealed that the crystal has a cell parameter of $a = 4.9786(5)$ Å. Although this value is higher than previously reported values (e.g., $a = 4.965$ Å reported by Galy et al., 1971), it is slightly lower than the largest cell parameter we have observed for this system, which is $a = 4.9841(13)$ Å (Strozewski, 2007). This suggests that a small amount of oxygen could be present in the rocksalt sample, and therefore in the overall system despite lack of detection of oxygen in the doubled cubic sample core.

As discussed in Chapter 1, many doubts were voiced in the past (Strozewski, 2007) about the impurity of synthesized metal nitride fluorides, especially in the case of rocksalt-type Ca$_2$NF, where a variety of samples with different cell parameters have been reported. Oxygen is easily incorporated in these reactions, e.g., by experimental set-up or starting materials used. However, several important points are noted about the synthesis of the calcium nitride fluoride system in this work. The first of these is the meticulous treatment done for making pure Ca$_2$NF by excluding oxygen from the reaction to the greatest extent possible. The KCuF$_3$ precursor was made through a co-precipitation process involving no aqueous solvent, all the starting materials were mixed in a glove bag under argon, and an oxygen free (relative to silica) Inconel tube was used during the heating process. Nevertheless, infiltration of a small amount of oxygen in the system cannot be ruled out. Finally, it is important to note that the non-stoichiometric defect model for Ca$_2$NF presented in this chapter applies equally well whether or not the system contains oxygen.
CHAPTER SIX

RESULTS AND DISCUSSION METAL NITRIDE FLUORIDE STUDIES

6.1 Single crystalline metal nitride fluorides

6.1.1 Attempted preparation of magnesium nitride fluoride

The novel synthesis approaches proposed for preparation a single crystalline of Mg$_2$NF described in Section 4.2.1 both failed. These approaches involve reacting KMgF$_3$ and KCuF$_3$, each with Mg under nitrogen gas. For the case involving use of KMgF$_3$ as a precursor, X-Ray diffraction analysis was carried out on the white powder produced, and detected the presence of unreacted KMgF$_3$ and MgF$_2$. Evidently, some of KMgF$_3$ decomposed into MgF$_2$ while no N$_2$ gas was reduced. In addition, the reaction between KCuF$_3$ and Mg metal under N$_2$ gas did not yield a positive result. KMgF$_3$ was preferentially formed through this heating process, and it appears that Mg did not reduce the N$_2$ gas to form the nitride ion. Evidently, Mg is not able to reduce N$_2$ gas under our reaction conditions. In powder form, Mg$_2$NF has been produced through reaction of Mg$_2$N$_2$ and MgF$_2$ (Brogan et al. 2012).

In some parts of the thesis an ammonolysis approach to synthesis metal nitride fluorides was carried out as a way to introduce N$_3^-$ to the system without the need to first reduce N$_2$. Some metals are not strong enough to reduce the nitrogen gas, and this is the approach that should be used in the future to produce Mg$_2$NF single crystals for the first time. This ammonolysis approach was extracted from the method proposed by Woodward et al. (1998), who stated that ammonium metal group 4 fluorides can be heated under ammonia gas, and would undergo several intermediate compounds. These
intermediate compounds then would release HF and finally the ammonium metal fluoride would transform into metal nitride fluoride as \text{M}^{IV}\text{NF}.

### 6.1.2 Attempted calcium nitride fluoride via ammonolysis

Ammonolysis was conducted in this work on the reaction of KCuF\textsubscript{3} with calcium metal under ammonia at 900 °C in a silica tube. The reaction process was outlined in section 4.2.2. This reaction, ammonolysis of Group 2 metal, mixed with fluorine compounds has not been previously reported to our knowledge. This reaction was carried out to determine whether or not Ca\textsubscript{2}NF, which is a known compound, could be prepared using this approach. If so, the approach would be promising for preparation of mixed metal N-F compounds. It was expected that Ca metal would reduce Cu\textsuperscript{2+} in KCuF\textsubscript{3} and react with NH\textsubscript{3} gas during this process. The reaction did not yield Ca-N-F; instead it produced a colorless single crystal of KCaF\textsubscript{3}, as verified by X-ray analysis which showed the unit cell matches KCaF\textsubscript{3}, orthorhombic with \textit{a} = 6.16 Å, \textit{b} = 6.18 Å, and \textit{c} = 8.71 Å. The findings of this study seem consistent with a study conducted by Ashcraft, (1982) who carried out several ammonia gas reactions, e.g. metal fluoride with ammonia gas, in an attempt to make metal nitride fluorides. All the attempted approaches toward this area of synthesis were unsuccessful. The failure of making Ca\textsubscript{2}NF from the current procedure could be due to KCaF\textsubscript{3} being more thermodynamically stable than Ca\textsubscript{2}NF, so that it forms preferentially. Indeed, more research and additional approaches are needed to prepare metal nitride fluoride compounds through ammonolysis. There might be a potential reaction leading to synthesis of Ca\textsubscript{2}NF under ammonia. First, one would synthesize KCaF\textsubscript{3}, and then would react the later under ammonia at the desired temperature. The reaction is shown below:
2 KCaF$_3$ + NH$_3$ → Ca$_2$NF + 2 KF + 3 HF

This reaction would need to be tested initially at different elevated temperatures in order to determine a desirable temperature where KCaF$_3$ completely decompose of CaF$_2$ and KF. At relatively low temperatures, the phase could react to an undesirable product such as K$_2$CaF$_4$. Future investigations of metal nitride fluorides from ammonia gas reactions should also focus on transition-metal nitride fluorides. These compounds would give interesting results, and a show variety of stoichiometry, due to different oxidation states possible.

### 6.1.3 Attempted preparation of cobalt nitride fluoride

Another ammonolysis reaction was carried out in an attempt to make Co$_2$NF. The synthesized NH$_4$CoF$_3$ was heated at 300 °C under ammonia for 2 hours inside a molybdenum tube as described in section 4.2.3. Powder X-ray diffraction (PXRD) was carried out on the black powered product, and indicated that this procedure did not yield the desired compound; rather unexpectedly it produced cobalt fluoride. It appears that ammonia gas did not provide the nitride ion. Another trial using a higher reaction temperature (450 °C) was performed. This new condition achieved the same product. It seems that cobalt fluoride is the most thermally stable compound for these reaction conditions. Further research looking at the impact of both desirable reaction temperature and duration of heating time may help determine whether this method would work. The selection of specific metals might result in a positive test. Different metals may have more affinity for nitride than for fluoride. Using alternative ammonium metal fluoride compounds such as (NH$_4$)$_2$MF$_4$ rather than NH$_4$MF$_3$ might also help this procedure to succeed. This assumption is theoretically drawn from the study conducted by Fuertes
(2014) who reported the synthesis of ZrNCl through the reaction of (NH₄)₂ZrCl₆ with ammonia. It is worth attempting whether this reaction thermally treated with ammonia can be achieved:

\[
\begin{align*}
(NH_4)_2CoF_4 & \rightarrow CoF_2 + 2NH_3 + 2HF \\
2 CoF_2 + NH_3 & \rightarrow Co_2NF + 3 HF
\end{align*}
\]

An advantage of this process is the formation of CoF₂ and NH₃ gas as intermediates during the course of the reaction.

Another proposed reaction that could be conducted to make Co₂NF is based on the work of Silva, (2009) who made ThNF from the reaction of ThO₂ with NH₄HF₂. Here, the proposed reaction involves reacting CoO with NH₄HF₂ at room temperature, leaving the reaction perhaps for a day to let CoF₂ form. Following this treatment, the ammonia saturated CoF₂ would be heated under a dynamic ammonia steam to form the desired product, the reaction is as follows

\[
\begin{align*}
CoO + NH_4HF_2 & \xrightarrow{R.T} CoF_2 + H_2O + NH_3 \\
2CoF_2 + NH_3 & \rightarrow Co_2NF + 3HF
\end{align*}
\]

Whether these assumptions are proven successful until experiments are conducted is difficult to ascertain with our experiments.

6.2 Single crystalline preparation of bimetallic nitride fluoride

6.2.1 MgCaNF system

The synthesis approach targeting MgCaNF was described in section 4.3.1. After the reaction was complete, a small amount of the product was selected in an argon-filled glove bag, and placed on a microscope slide containing mineral oil. The mineral oil protects the sample from atmospheric oxygen and moisture during the time takes to mount the sample on the X-ray diffractometer. Looking at the sample under an optical
microscope, a few bright yellow crystals were discovered in the product mixture. One of these crystals was selected and mounted on a Bruker Quest single-crystal diffractometer described in Chapter 2. The data (obtained at 100 K) showed the successful and unprecedented growth of a Ca-Mg-N-F phase. Although the sample was actually multicrystalline, low quality data analysis showed that CaMgNF crystallizes in space group Fm-3m. The refinement was conducted on 763 unique reflections, and the R value obtained was 0.0885. X-ray refinement showed that the structure consists of an ion ordering sequence of N-Ca-F-Mg-F-Mg-F-Ca-N along the cubic cell edges, resulting in a unit cell with a = 20.8074(57) Å, essentially quadruped relative to the M2NF rocksalt-type metal oxide phase, or doubled relative to the doubled-cubic Ca2NF described earlier. A structure plot is shown in Figure 6.1. Although a bimetallic N-F analog of rocksalt-type MO (M= Group II cation) appears to have been prepared for the first time, the lack of quality data acquisition due to the multicrystalline nature of the sample, quick decomposition of the crystals prepared, and small crystal size was an obstacle for complete structure determination. Thus the weak data collection of the phase generated an incomplete structure for the crystal.
Figure 6.1 A structure plot from weak single crystal X-ray diffraction data for the rock-salt CaMgNF system showing quadrupled ordering (relative to rocksalt-type cell) of ions along the cell axes.

The X-ray data obtained showed there are four calcium atoms and three magnesium atoms in the unit cell, these metals are connected to a range of ions with some distortion observed, resulting in peculiar coordination numbers for some metal positions. As seen in Figure 6.2 the calcium atoms are connected to a range of ions from four to six, and distortion in the coordination environments is apparent. The three magnesium atoms exist in only four and six coordination numbers. It should also be noted that some positions are disordered, as can be seen for the F3 position bonded to
Mg6. It must be emphasized again that data quality did not permit optimal structural refinement. Therefore, the metal coordination environments shown in Figure 6.2 may not be the correct ones.

![Figure 6.2 Coordination environments of the metals present in Ca-Mg-N-F system.](image)

The positional, occupational, and displacement parameters that were obtained from the refinement achieved are shown in Table 6.1. The refined composition is 
\[
\text{Ca}_{1.50}\text{Mg}_{0.81}\text{F}_{1.03}\text{N}_{0.84},
\]
which is not charged balanced due to the incomplete refinement.
Table 6.1 Positional, Occupational and Displacement Parameters for partial CaMgNF Crystal Refinement

<table>
<thead>
<tr>
<th>Ele</th>
<th>occup</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca1</td>
<td>1.00</td>
<td>0.1078</td>
<td>0.1078</td>
<td>0.2280</td>
<td>0.01272</td>
<td>0.0127</td>
<td>0.0106</td>
</tr>
<tr>
<td>Ca2</td>
<td>0.50</td>
<td>0.2500</td>
<td>0.0000</td>
<td>0.2500</td>
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<td>0.01176</td>
<td>0.0328</td>
<td>0.0332</td>
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<td>Ca4</td>
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<td>0.0000</td>
<td>0.0000</td>
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<td>0.04640</td>
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<tr>
<td>F1</td>
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<td>0.0000</td>
<td>0.0000</td>
<td>0.5000</td>
<td>0.0214</td>
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<td>F2</td>
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<td>0.184</td>
<td>0.3159</td>
<td>0.3159</td>
<td>0.04130</td>
<td>0.0413</td>
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</tr>
<tr>
<td>F3</td>
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<td>0.0000</td>
<td>0.1583</td>
<td>0.1583</td>
<td>0.02054</td>
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<td>0.0000</td>
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<td>0.0606</td>
<td>0.0605</td>
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<td>Mg1</td>
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<td>0.00802</td>
<td>0.0093</td>
<td>0.0092</td>
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<td>0.1398</td>
<td>0.3602</td>
<td>0.00450</td>
<td>0.0045</td>
<td>0.0045</td>
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<tr>
<td>Mg6</td>
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<td>0.0000</td>
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Selected interatomic distances, of the unit cell obtained from single crystal diffraction data of the system are summarized in Table 6.2. As expected, Mg-N and Mg-F bond distances tend to be significantly shorter than those for Ca-N and Ca-F.
Table 6.2 Interatomic distances for Ca-Mg-N-F phase; the left table shows the calcium coordination, the right one presents the magnesium environment.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance Å</th>
<th>Bond</th>
<th>Distance Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca1-N3</td>
<td>2.4698</td>
<td>Mg1-F2</td>
<td>2.1201</td>
</tr>
<tr>
<td>Ca1-F4</td>
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<tr>
<td>Ca2-N3</td>
<td>2.5203</td>
<td>Mg4-N3</td>
<td>1.8642</td>
</tr>
<tr>
<td>Ca2-F4</td>
<td>2.7111</td>
<td>Mg4-N4</td>
<td>1.9500</td>
</tr>
<tr>
<td>Ca3-N3</td>
<td>2.3219</td>
<td>Mg6-F1</td>
<td>2.2511</td>
</tr>
<tr>
<td>Ca3-N4</td>
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<td>Mg6-N4</td>
<td>2.5794</td>
</tr>
<tr>
<td>Ca3-F3</td>
<td>2.8314</td>
<td>Mg6-F3</td>
<td>2.6513</td>
</tr>
<tr>
<td>Ca4-N1</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Ca4-F1</td>
<td>2.6491</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca4-F2</td>
<td>2.6491</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca4-F5</td>
<td>2.6491</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is worthwhile to re-synthesize the phase in the future, and to obtain better crystals for data collection. The reaction between MgF₂, and Ca and Mg metals with N₂ gas appears to have been successful despite the expected preferential reduction of Mg²⁺ in MgF₂ by Ca. The more reasonable approach would appear to be reacting CaF₂ with Mg metal, but past experience in our lab shows that reduction of N₂ gas by Mg metal is difficult to achieve.

6.2.2 BaCaNF System

The reaction for preparation of BaCaNF was described in Section 4.3.2, and yielded four different colors of colored crystals: yellow, dark red, brownish, and black. A yellow crystalline sample was determined to be a known Ca₂NF phase, and so was not further investigated.

Upon analyzing a sample of the black crystal by X-ray single crystal diffraction, it was found to have lattice parameters of a = 9.28 Å, b = 16.07Å, c = 12.09Å and β = 107.45Å. These cell parameters of the crystal were very similar to the lattice parameters
of Ba$_2$Ni$_6$N$_7$ with $a = 9.487\,\text{Å}$, $b = 16.578\,\text{Å}$, $c = 12.137\,\text{Å}$, and $\beta = 107.05\,\text{Å}$. Gudat et al. (1991) synthesized their phase by reacting BaNiN and Ba$_3$N$_2$. However, the presence of nickel in the current system would be from use of the nickel crucible. Although our sample was not further analyzed here, it is likely that some Ca is incorporated in the structure, accounting for the smaller unit cell parameters for our phase relative to the literature values.

Unfortunately, a BaCaNF phase was not found in the product mixture. However, the reaction of the stoichiometric mixture of BaF$_2$ with Ca and Ba metals under N$_2$ gas resulted in another significant finding. A dark red crystal was mounted on the Bruker Prospector X-ray single crystal diffractometer under a flow of nitrogen, and a low temperature data collection was performed on the crystal at 100 K. Although crystal quality was again poor (multicrystalline and highly air sensitive sample), data analysis revealed the crystal belongs to the Ba-CN-N-F system, having a body-centered cubic lattice with $a = b = c = 11.1197(2)\,\text{Å}$ and space group Im-3. The incorporation of the carbon in the phase is likely from oil used to store the barium metal. Although it does appear that some Ca shares the Ba1 site (see below), note that this is only the second phase we are aware of that has been found in the Ba-CN-N-F system. Ramunno and Wagner (unpublished results) previously observed a well-refined phase of composition Ba$_{24}$(CN$_2$)$_{18}$N$_{1.5}$F$_{7.5}$, with space group R3 and cell parameters $a = b = 13.9733(7)\,\text{Å}$ and $c = 8.6875(5)\,\text{Å}$. This structure consists of interpenetrating chains of Ba-centered trigonal prisms, and is quite different than the structure observed here, despite the very similar reaction conditions for the previous sample compared to the current study. The main difference in the reactions is the presence of Ca in the reaction here.
Our refinement revealed two crystallographically distinct metal sites within the present structure. One of these is positioned at the unit cell corners and center, and was originally refined as a calcium position, however, the R value improved if it were refined as Ba instead. This was labeled the Ba1 site. Interestingly, this position appears to be at the center of a slightly distorted icosahedron, with the other metal position (fully occupied by Ba atoms) located at the 12 vertices of the icosahedron. This was labeled the Ba2 site. Note that at this point another refinement on the phase was performed for the sake of confirmation by Dr. Matthias Zeller (now staff crystallographer at the Dept. of Chemistry, Purdue University). This refinement was started from P-1, and gave a solution in I-3m. It was noticed in this analysis that the Ba1 site appears disordered between Ba and Ca, and we incorporated this finding into our refinement.

We found that the Ba2 atoms are coordinated to 6 atoms in a pseudo pentagonal pyramidal coordination, with bonds to 3 N1 and 2 F1 atoms in the pentagonal plane, and one questionable bond to a shared apical N2/F2 position at a distance of only 2.053 Å away and with a N2/F2-Ba2-petagonal planar angle of only about 46°. There is a longer non-bonded interaction to an N1 atom on the other side of the pentagonal plane at a distance of 3.218 Å. Note that the N1 atoms are also bonded to C atoms as part of the carbodiimide ion, \((CN_2)^2^-\). As shown in the structure plot in Figure 6.3, these carbodiimide ions bridge adjacent Ba2 atoms to each other.
Figure 6.3 Partial structure plot of $\text{Ba}_{24.5}\text{Ca}_{1.5}(\text{CN}_2)_{12}\text{N}_4\text{F}_{16}$. Bridging of $\text{Ba}2$ atoms through $\text{CN}_2^{2-}$ ions is evident. The $\text{N}2/\text{F}2$ atoms bonded to $\text{Ba}1$ are omitted. Projected approx. along [100]; the vertical axis is [001]. (Plot generated from crystal maker, 9.2.2, 445).

The $\text{Ba}1$ position appears to be octahedrally coordinated to six atoms refined as a mixed $\text{N}/\text{F}$ site (the $\text{N}2/\text{F}2$ position). However, as noted above, this position is too close to the nearest $\text{Ba}2$ atom (2.053 Å), and also goes non-positive definite when refined anisotropically. The $R$ value increased by over 1% when the position was removed. Dr. Zeller also did not find any bonds to the $\text{Ba}1$ position in his refinement. It is therefore concluded that the data quality is insufficient to complete the structure assignment; the data is simply too weak to reliably refine the ligands around the $\text{Ba}1$ site. Nevertheless,
the refined unit cell composition with the N2/F2 position refined (isotropically) is
Ba$_{24.5}$Ca$_{1.5}$(CN$_2$)$_{12}$N$_4$F$_{16}$. The R values for this refinement are $R_1$(all data) = 0.0713 and
$wR_2 = 0.1692$. Better crystals must be prepared in future work to achieve the structure.
Some interatomic distances of the Ba$_{24.5}$Ca$_{1.5}$(CN$_2$)$_{12}$N$_4$F$_{16}$ structure are summarized in

**Table 6.3**

**Table 6.3** Interatomic distances for the Ba-Ca-N-F phase.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distances (Å)</th>
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</thead>
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<tr>
<td>Ba1-N2/F2</td>
<td>2.7061</td>
</tr>
<tr>
<td>Ba2-N1</td>
<td>2.773, 2.893</td>
</tr>
<tr>
<td>Ba2-F1</td>
<td>2.919</td>
</tr>
<tr>
<td>Ba2-N2</td>
<td>2.053</td>
</tr>
<tr>
<td>C1-N1</td>
<td>1.2042</td>
</tr>
</tbody>
</table>

Although the synthesis approach implemented here produced the unexpected
Ba(Ca)-CN-N-F compound, the targeted BaCaNF phase was not achieved via this route.
As a result, a new synthesis process should be investigated in the future to prepare the
desired phase. A possible future route for preparation of BaCaNF would be initially
mixing CaF$_2$ with Ba$_3$N$_3$ using solid state reaction. For example, the phase could be made
according to the following reaction

$$2\text{CaF}_2 + \text{Ba}_3\text{N}_2 \rightarrow 2\text{BaCaNF} + \text{BaF}_2$$

Successful preparation of this product from solid state reaction could achieve
powdered phases; yet another possibility for future work leads to the synthesis of single
crystalline material. Observation of Ba-Ca- CN-N-F inferred a possible reaction
mechanism for the formation Ba-Ca-N-F. That would be the reaction of nitrogen gas with barium fluoride and calcium metal. This rocksalt analog would be accomplished according the following reaction:

\[
2 \text{BaF}_2 + 6 \text{Ca} + \text{N}_2 \rightarrow 2 \text{BaCaNF} + 2\text{Ca}_2\text{NF}
\]

The main target of this reaction is barium calcium nitride fluoride. However, some byproducts could be produced. For example, calcium nitride fluoride could be made through this route, as well as other products, such as calcium nitride or calcium fluoride.

It would also be of interest to investigate bimetallic nitride fluorides consisting of a transition metal with oxidation state of +2, such as MLNF, (Where M = Group II cation and L = transition metal with oxidation state of +2, e.g., Co²⁺, Mn²⁺, or Zn²⁺). The incorporation of a transition metal with a Group II metal might reduce the air sensitivity of the final product, since the alkaline earth metal nitride fluorides are moisture sensitive (Lingampalli et al., 2016). The synthesis could be achieved in two steps. The first step is to prepare ammonium transition metal copper fluoride with composition of (NH₄)₂MCuF₆; the second step is then to react the latter compound with one of the Group II metals under ammonia gas. The proposed reactions are summarized below:

\[
6\text{NH}_4\text{F} + \text{CoBr}_2 + \text{CuBr}_2 \rightarrow (\text{NH}_4)_2\text{CoCuF}_6 + 4\text{NH}_4\text{Br}
\]

\[
(\text{NH}_4)_2\text{CoCuF}_6 + \text{Ba} + \text{NH}_3 \rightarrow \text{BaCoNF} + \text{Cu} + 2\text{NH}_4\text{F} + 3\text{HF}
\]

The successful preparation of the bimetallic nitride fluoride from these routes would be significant in terms of the novel nitride-fluoride composition produced.
CHAPTER SEVEN
SUMMARY

This work investigated new syntheses routes for the preparation of both previously known as well as new metal nitride fluoride materials. Traditionally, solid state chemistry has explored the impact on material properties through cation substitutions in oxides. Much rarer (but becoming more pronounced in recent years) is the manipulation of anion compositions of oxides to modify properties of solid state materials. A major practical motivation for synthesis of metal nitride fluorides is that nitrogen decreases the band gap of this phase into the visible light region relative to analogous metal oxides. The substitution of fluoride ion along with nitride permits the cation/anion ration to be retained. Also relative to nitrides, nitride fluorides can form compounds with metal ions of a wider range of oxidation states.

As there has been some question of the purity of inorganic N-F compounds reported in the past, particularly related to oxygen content of the samples, one motivation of this work was to investigate ways to optimize conventional methods for preparation of pure metal nitride fluorides. This work focused on the use of perovskite-related fluorides (e.g. KCuF₃) as precursors in the preparation of M₂NF compounds, particularly Ca₂NF here. These fluoride precursors are typically prepared by co-precipitation of appropriate binary salts from aqueous solution, however a water-free method was developed here using methanol as the solvent. The use of an aqueous solvent results in partial substitution of hydroxide ions for fluoride ions in the precursor, which in turn introduces
oxygen into the final nitride-fluoride product. In addition to use of a non-aqueous solvent, careful treatment was implemented by performing the synthesis in a glove box with high purity argon or nitrogen environment. Finally, the high temperature reaction of precursor with Ca (or other) metal was performed using an Inconel tube. Silica heating tubes used in past reactions were often a primary source of oxygen contamination.

This study successfully yielded Ca$_2$NF from KCuF$_3$ and calcium metal under a flow of nitrogen. Although both rocksalt-type and doubled cubic Ca$_2$NF single crystalline samples were found in the product mixture, this work took advantage of the availability of a high intensity state-of-the-art X-ray diffractometer and a dual Focused Ion Beam (FIB)/Scanning Electron Microscope (SEM) instrument equipped with EDXS to elucidate the crystal chemistry of the doubled cubic $M_2$NF phase ($M = Ca, Sr$). In all past X-ray diffraction studies involving these phases in our lab, residual electron density is always present in the lattice as an interstitial tetrahedral site occupied by F atoms. Until now, these have always been refined as Frenkel defects. However, very high quality X-ray data in this study showed that F is actually present in excess at the interstitial site, rather than being present due to repositioning of a nearby F atom from an octahedral site. Furthermore, compositional analysis of the freshly exposed (by the FIB) inner core of a Ca$_2$NF sample in the SEM showed our sample to be a pure N-F phase. Thus a mechanism involving replacement of $N^3-$ by $F^-$ ions for charge compensation of the excess $F^-$ interstitial atoms was proposed, indicating that a non-stoichiometric rather than Frenkel defect is actually in operation. The mechanism also explains the different colors of doubled cubic Sr$_2$NF crystal that has been previously observed, although this requires presence of an oxygen impurity.
Attempts to prepare Mg₂NF in this study via the direct reactions of KMgF₃ and KCuF₃ (i.e. in separate reactions) with Mg metal under N₂ gas were not successful. Instead, unreacted KMgF₃ along with MgF₂ was found in the first reaction, and KMgF₃ and Cu metal for the second reaction. The phases produced are likely more thermodynamically stable than Mg₂NF. In addition, these results are consistent with the results from many past experiments in our lab of the inability to reduce N₂ gas using Mg metal.

This project was also concerned with the synthesis of metal nitride fluorides using ammonia as a nitrogen source. One benefit of employing this approach is that the reaction temperatures are typically lower than needed for nitrogen gas reactions. Also, NH₃ provides a source for N³⁻ ions for cases in which N₂ is not easily reduced, such as in reactions with Mg metal mentioned above. Two ammonolysis reactions were performed based on theoretical assumptions. One of these assumptions aimed at making cobalt nitride fluoride was based on a study by Woodward et al. (1998) involving reaction of ammonium metal fluorides with NH₃ to make the metal N-F compound. In this study, ammonolysis of NH₄CoF₃ to produce Co₂NF was unsuccessful. X-Ray powder diffraction identified the black powder product as CoF₂. Preparation of Co₂NF through this method was impossible indicating further work for different routes is required to obtain cobalt nitride fluoride.

A highlight of this project was the successful synthesis of a new bimetallic nitride fluoride, CaMgNF. To our knowledge, this is the first N-F compound prepared containing two different metals that is a direct analog of an oxide (rocksalt-type MO in
this case). The CaMgNF compound was produced from a mixture of MgF$_2$, Ca metal, and Mg metal, and was found to have space group Fm-3m with a cell parameter of 20.8074 (57) Å. Essentially, the lattice is quadrupled relative to rocksalt due to ordering of both cations and anions along cell edges. Unfortunately, the structure refinement is incomplete due to weak data from poor crystal quality. Nevertheless, the existence of the Ca-Mg-N-F composition is certain, and future work can focus on optimizing the reaction to produce higher quality crystals. This result will certainly open up research for several related systems, and expands the rich crystal chemistry observed in inorganic nitride fluorides in general.

Another bimetallic N-F compound targeted in this work was the preparation of BaCaNF through the reaction of BaF$_2$ with Ca and Ba metals under nitrogen gas. Although the target compound was not prepared, among the reaction products were dark red crystals that X-ray diffraction analysis revealed to be a new compound in the Ba(Ca)-CN-N-F system. The carbon originated from oil that the Ba was stored in. This is a body centered crystal with space group Im-3, and cell parameter 11.1197(2) Å. There are two metal positions in the structure, one of which is at the bcc (corners and body center) position. This metal lies at the center of a slightly distorted icosahedron with the other metal position located at the 12 vertices of the icosahedron. These Ba atoms are linked by carbodiimide ions (CN$_2$)$_2^-$ ions. The Ba atom at the bcc position is disordered with partial substitution of Ca. Again, weak data from poor crystal quality did not permit optimal refinement of the structure. In particular, it was not possible to unambiguously assign ligands to the Ba atom at the bcc position. The refined composition for the phase is Ba$_{24.5}$Ca$_{1.5}$(CN$_2$)$_{12}$N$_4$F$_{16}$. Of significance is that to our knowledge, this is only the second
metal carbodiimide phase to be prepared, with the other being prepared previously in our lab (unreported results).

Future attempts to prepare the BaCaNF phase must eliminate any appreciable source of carbon from the reaction, to avoid the preferential formation of carbodiimides. This could easily be accomplished by using barium metal stored under argon with the reaction used in this work. Alternatively, suggested synthesis routes presented in Chapter 6 could be implemented.
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