Preparation and Single-Crystal Structure Analysis of Ca_2NF

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Single-crystalline samples of Ca_2NF were prepared by heating a stoichiometric mixture of Ca metal and CaF_2 under N_2 to 1000°C, followed by slow cooling from the melt. The resulting Ca_2NF crystals were yellow in color, and highly air-sensitive. A single-crystal X-ray diffraction analysis indicated that the compound is isostructural with L-Mg_2NF, with tetragonal cell parameters $a = 4.9018(9)$ Å and $c = 10.516(3)$ Å, $Z = 4$, and space group $I4_1/amd$ (No. 141). X-ray refinement was carried out by full-matrix least-squares on F^2 on all data, to give $R_1 = 0.0426$ (all data) and $wR_2 = 0.0630$ for 12 parameters and 101 independent reflections. The final position assignments were analyzed via bond valence sum calculations. © 2001 Academic Press

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INTRODUCTION

Although ideal formulas of inorganic nitride–fluoride analogues of oxides are easily derived by replacing two O^{2-} ions of the oxide with NF^{4-}, less than 40 inorganic nitride–fluoride polycompounds have actually been reported. Of these studies, fewer than half reported structures based on quantitative methods, mainly involving powder diffraction techniques. The first of these was a paper by Andersson (1) in which structures of three magnesium nitride–fluorides, L-Mg_2NF, Mg_3NF_3, and H-Mg_2NF, were determined based on powder X-ray diffraction data that was analyzed using least-squares crystal-structure refinement calculations. L-Mg_2NF was described as having a structure intermediate between the rocksalt and zincblende types, with magnesium atoms in square pyramidal coordination. The high-temperature/pressure phase, H-Mg_2NF, was found to be isostructural with MgO, while the

structure of Mg_3NF_3 is reportedly related to that of MgO, except that 1/4 of the magnesium sites are empty in an ordered fashion.

The preparation of powder samples of Ca_2NF, along with Sr_2NF and Ba_2NF, has been previously reported by Ehrlich *et al.* (2), and based on a qualitative study using the Guinier powder X-ray diffraction method, they reported that all three of these compounds have the rocksalt structure like their analogous oxides. Galy *et al.* (3) also reported that Ca_2NF has a rocksalt-type structure, based on powder methods. In this study, we report on the preparation and single-crystal X-ray structure analysis of Ca_2NF. The only other single-crystal X-ray structures previously reported for inorganic nitride–fluoride compounds were for compounds in the Zr–N–F (4) and U–N–F (5) systems, although the Zr–N–F compound has since been reported (6) as an oxy nitride–fluoride with an incommensurate, compositely modulated structure.

EXPERIMENTAL

Sample Preparation

Single crystals were prepared by slow cooling from a melt consisting of a 3:1 mole ratio of Ca:CaF_2, reacting under a flow of ultra-high-purity N_2 gas. Initially, the reactants were mixed in a glove bag under inert atmosphere and placed in an Ni crucible. The crucible was then inserted into a silica tube that was sealed from air while allowing dynamic flow of inert gas. The reaction mixture was first heated to 1000°C under Ar for 1 h and then cooled to 200°C, at which point the gas flow was switched from Ar to N_2. Next, the reactants were heated to 1000°C for 4 h, followed by cooling at a rate of 15°C/h to 200°C, and finally to room temperature at 80°C/h. An abundance of yellow crystals were present in the final product mixture; these were

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assumed to be Ca$_2$NF crystals based on the fact that this was also the color of the Ca$_2$NF powder sample reported by Ehrlich *et al.* (2) The crystals were very air sensitive, as evidenced by the release of ammonia fumes within several minutes of exposure to air, and were therefore always handled in a glove bag under inert atmosphere. The sample selected for X-ray analysis was an irregular polygonal-shaped crystal, of approximate dimensions $0.24 \times 0.16 \times 0.09$ mm^3. The crystal was first mounted onto the tip of a small glass capillary, and then inserted into a larger silica capillary tube that was sealed under inert atmosphere to protect the crystal from air during the data collection.

Structure Determination

X-ray data were collected at Kent State University on a Bruker SMART 1k CCD single-crystal diffractometer equipped with a fine focus, 2.4-kW sealed tube X-ray source (Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A full sphere of intensity data was collected in 1800 frames using ω scans (width of $0.30°$ and exposure time of 10 s per frame).

Unit cell parameters could not be determined using reflections from 450 thresholded frames, indicating the possible presence of twinning. Attempts to index these reflections with GEMINI resulted in only one orientation matrix, which was assigned using 56 of 117 reflections. No related orientation matrix could be found from the remaining reflections. It was then hypothesized (and supported by later analysis) that the cause of the apparent twinning was that the sample was pseudo-polycrystalline in nature, consisting of a predominant single crystal surrounded by smaller crystallites in the capillary. In order to continue the analysis, the assigned orientation matrix was next used in SMART to determine the higher symmetry cell and to refine the unit cell parameters to a reciprocal lattice vector error of 0.003. The resulting refined cell was then used to integrate all data in SAINT, which in turn used 384 reflections to achieve the final parameters utilized in the ensuing structural refinement. Prior to structure solution and refinement, an empirical absorption correction was performed on the data files written by SAINT using SADABS, which also simultaneously corrected for other effects, such as absorption by the glass capillary. Refinement data, including the cell parameters, are summarized in Table 1, atomic coordinates and anisotropic and equivalent isotropic displacement parameters are listed in Table 2, and bond lengths and selected angles are given in Table 3.

RESULTS AND DISCUSSION

Refinement

As the unit cell parameters indicated a tetragonal structure, it was immediately evident that this sample of Ca$_2$NF

TABLE 1
Crystal Data Summary and Refinement Results for Ca$_2$NF

Structural formula	Ca$_2$NF
Formula weight	113.17
Color	Yellow
Crystal size (mm)	$0.24 \times 0.16 \times 0.09$
Space group	$I4_1/amd$ (No. 141, origin choice $\#2$)
a (Å)	4.9018(9)
b (Å)	4.9018(9)
c (Å)	10.516(3)
V (Å^3)	252.67(9)
Z	4
ρ_{calc} (Mg/m^3)	2.975
λ(Mo$K\alpha$) (Å)	0.71073
μ (mm^{-1})	4.197
θ range for data collection (°)	4.59 to 28.24
Limiting Indices	$-5 \leq h \leq 6$, $-6 \leq k \leq 6$, $-12 \leq l \leq 13$
No. of reflections collected	695
No. of independent reflections	101 ($R_{int} = 0.0894$)
No. of parameters	12
Refinement method	Full-matrix least-squares on F^2
Final R indices [$I > 2\sigma(I)$]	$R_1(F)^a = 0.0316$, w$R_2(F^2)^b = 0.0585$
Final R indices (all data)	$R_1(F)^a = 0.0426$, w$R_2(F^2)^b = 0.0630$
Goodness-of-fit on F^2	1.190
Largest diff. peak and hole	0.605 and -0.418 eÅ^{-3}

[a] $R_1(F) = \sum ||F_o| - |F_c||/\sum |F_o|$ with $F_o > 4.0\sigma(F)$.
[b] w$R_2(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ with $F_o > 4.0\sigma(F)$, and $w^{-1} = \sigma^2(F_o)^2 + (W \cdot P)^2 + T \cdot P$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$, $W = 0.0272$, and $T = 0.00$.

is not isostructural with CaO (rocksalt-type), as reported previously by Ehrlich *et al.* (2) and Galy *et al.* (3). However, the parameters are similar to those for L-Mg$_2$NF reported by Andersson (1), which are $a = 4.186$ and $c = 10.042$ Å. Also, analysis of the systematic absences suggested a space group of $I4_1/amd$, consistent with that reported by Andersson for L-Mg$_2$NF. Thus it is apparent that the Ca$_2$NF sample prepared in this study is isostructural with Andersson's L-Mg$_2$NF compound. The structure was determined using direct methods, and the three atomic positions expected by comparison to the L-Mg$_2$NF structure could be assigned immediately. Following the initial structure solution, the atomic positions, anisotropic displacement parameters, and occupancies converged after seven cycles of least-squares refinement on F^2.

From the occupancy factors given in Table 2, the empirical composition was found to be Ca$_{2.00}$N$_{1.05}$F$_{1.00}$, in good agreement with the ideal composition of Ca$_2$NF. The displacement parameters indicate some possible disordering (discussed later) of fluorine atoms along the c axis, but otherwise are typical.

Polycrystalline Nature of the Sample

To test the possible polycrystallinity of the sample, the 450 frames of data used in the single-crystal structure

TABLE 2
Positional, Occupational, and Anisotropic[a] and Equivalent Isotropic[b] Displacement Parameters ($\text{Å}^2 \times 10^4$) from Ca_2NF Final Refinement

Atom	Site	Occupancy factor	x	y	z	U_{11}	U_{22}	U_{33}	$U(\text{eq})$
Ca(1)	8e	0.2498	$\frac{1}{2}$	$\frac{3}{4}$	0.1032(1)	12(1)	10(1)	12(1)	11(1)
F(1)	4a	0.1245	0	$\frac{3}{4}$	0.125	14(2)	14(2)	40(4)	22(2)
N(1)	4b	0.1316	$\frac{1}{2}$	$\frac{1}{4}$	0.125	16(2)	16(2)	12(4)	15(2)

[a] The anisotropic thermal parameter is expressed as $\exp[-2\pi^2(h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$; $U_{12} = U_{13} = U_{23} = 0$.

[b] $U(\text{eq})$ is defined as one third of the trace of the U_{ij} orthogonalized tensor.

refinement, and containing both indexed and unindexed reflections, were analyzed as powder diffraction data. This "powder" analysis was accomplished by importing the 450 frames of unwarped data from the CCD system into a Bruker GADDS (General Area Detector Diffraction Software, GADDS) system, which is routinely used for powder diffraction at Youngstown State University. As GADDS is normally configured for a multiwire area detector, the system was calibrated for analysis of the CCD data by importing corundum powder data collected on the CCD system, and using it as a calibration standard. Following the calibration, all 450 frames of Ca_2NF single-crystal data obtained from the CCD system were integrated (from 3.0 to 175.1° in χ) in GADDS, and merged into a single powder diffraction pattern. The "powder" data was indexed using the TREOR program on Bruker's WIN-INDEX package (ver. 1.5), and cell parameters were refined using WIN-METRIC (ver. 2.1). All peaks could be indexed according to the final unit cell parameters: $a = 4.883(3)$ Å and $c = 10.5(1)$ Å, which are reasonably close within the given esd's to the cell parameters obtained from the single-crystal analysis listed in Table 1. The results of the powder analysis indicate that the Ca_2NF sample was a single-phase material, and did not decompose during the data collection. As the crystal appeared to be single crystalline when initially selected, it is quite possible that the polycrystalline nature of the sample was due to fracturing of the crystal while it was being

inserted into the silica capillary tube. Indeed, high susceptibility to mechanical damage was commonly observed in Ca_2NF crystals prepared from several different synthesis trials completed in this study.

Structure Description and Analysis

As mentioned, the present Ca_2NF compound is not isostructural with the samples reported by Ehrlich *et al.* (2) and Galy *et al.* (3) as having the rocksalt-type structure. If the Ca–N–F and Mg–N–F systems are taken to be analogous, then a possible explanation for this discrepancy is that these previously reported compounds are actually isostructural with the rocksalt-type Mg_3NF_3 phase reported by Andersson (1). In any case, the single-crystal analysis completed in this study unambiguously assigns a L-Mg_2NF-type structure to Ca_2NF, in which calcium is basically five-coordinated to three N^{3-} ions and two F^- ions, with a sixth longer, weak or nonbonded interaction to a F^- ion. The structure plot shown in Fig. 1 depicts this coordination environment for calcium.

The reason that the Ca_2NF composition does not have the rocksalt structure (at least at ambient pressure) is due to ordering of N and F atoms, causing an approximate doubling of the c axis relative to the cubic CaO-like structure. Also, the requirement that all Ca–N and Ca–F bond lengths be identical in the rocksalt structure is likely too rigid of a constraint for the Ca_2NF composition. In the L-Mg_2NF-type structure, the constraints are less rigid, and so the Ca–N and Ca–F bond lengths are nonidentical along the c axis. Note however that the Ca–N and Ca–F bond lengths in the a–b plane are necessarily identical, and also that the anions are approximately cubic closest packed. Thus the structure of Ca_2NF is actually closely related to the rocksalt type, except that the apical Ca–N bond length (i.e., along the c axis) of each "octahedral" unit is relatively shortened, while the Ca–F apical length is relatively elongated to the point that it is essentially a nonbonded interaction. Since alternating polyhedra have the short apex pointing in opposite directions, the repeat distance along the c axis is given

TABLE 3
Bond Lengths and Selected Angles for Ca_2NF

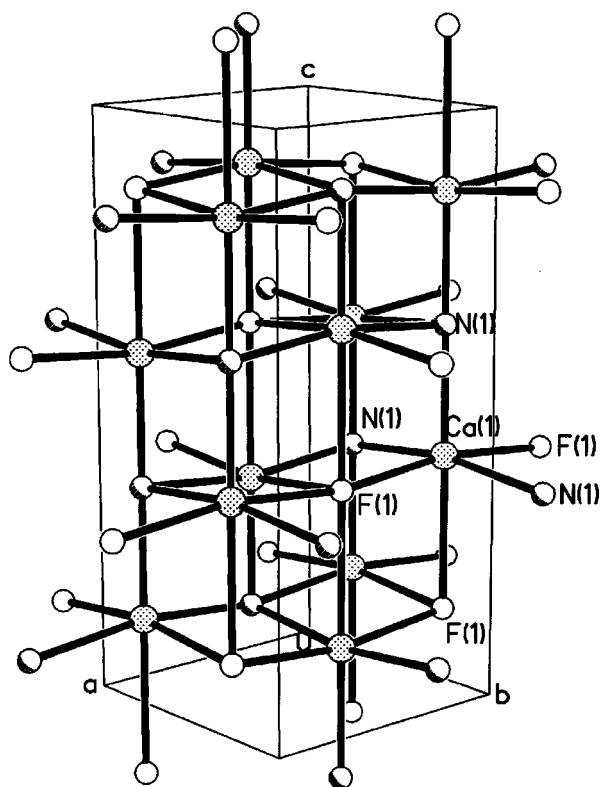| Bond or angle	Distances (Å) or angles (°)
Ca(1)–N(1)#1	2.4000(12)
2 Ca(1)–N(1)#2	2.4616(5)
2 Ca(1)–F(1)#1	2.4616(5)
[a]Ca(1)–F(1)#2	2.8579(13)
N(1)#1–Ca(1)–N(1)#2	95.34(2)
F(1)#1–Ca(1)–N(1)#2	89.504(5)

[a] Weak or nonbonded interaction.

FIG. 1. Structure plot for the final Ca_2NF structure; atoms are labeled for one Ca coordination sphere. Weak Ca–F interactions along the c axis are drawn as bonds.

meter might suggest that the F position, with no refinable positional parameters at the 4a site in the $I4_1/amd$ space group, actually represents an average position of a more complicated anion arrangement. Due to the similarity of X-ray scattering factors for N and F atoms, whether this is the case could best be revealed by neutron diffraction, in which the scattering factors for N and F are very different.

Bond-Valence Sum Analysis

Typically, a bond-valence sum analysis is performed as a reasonable method for checking the overall structure of a given inorganic crystalline solid. As described by Brese and O'Keeffe (8), the bond valence, v_{ij}, between two atoms i and j is given by the expression:

$$v_{ij} = \exp[(R_{ij} - d_{ij})/0.37],$$

where R_{ij} is a unitless empirical parameter characteristic of the atom pair forming the bond and d_{ij} is the experimental
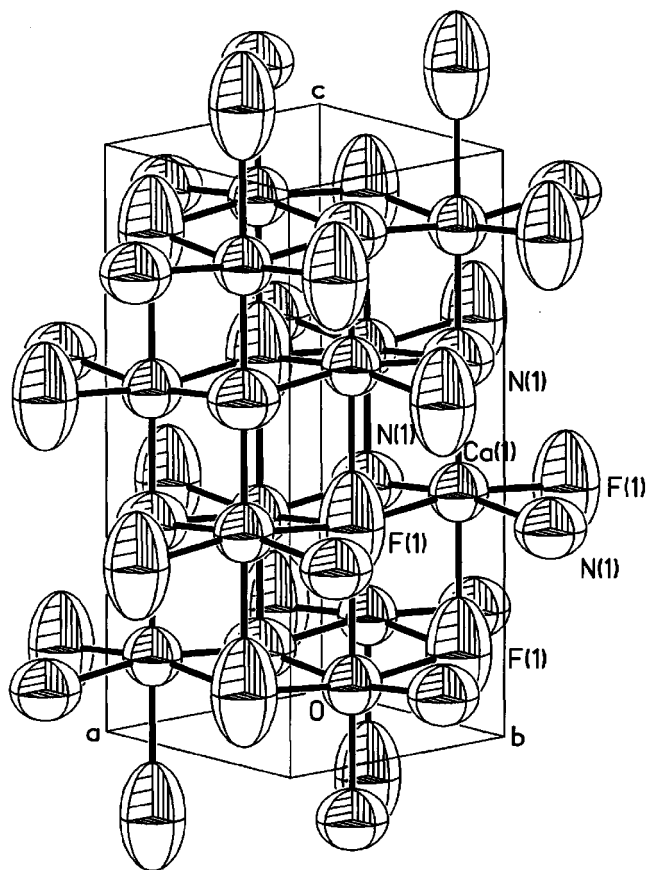
by the sequence F–Ca–N–Ca–F, or by the sum of two long Ca–F "bond" lengths and two short Ca–N bond lengths: (2×2.8579) Å $+ (2 \times 2.400)$ Å $= 10.516$ Å. If these bond lengths had identical magnitudes of 2.45 Å, and no anion ordering was present, the structure would be that of rocksalt. Alternatively, the structure could perhaps better be described as anti-$LiFeO_2$ type (7), but with a distorted oxygen (i.e., Ca in Ca_2NF) octahedral coordination sphere.

Figure 2 shows an ORTEP-like plot in the same projection as the structure plot in Fig. 1. As mentioned, the displacement parameters listed in Table 2 suggest that there is some disorder in the F positions along the c axis. As seen in Fig. 2, the disorder is apparently due to the sharing of F atoms between square pyramidal sites on either side of the assigned (basically) square planar positions. However, the possibility of partial oxygen substitution on this site as a way to dampen the relatively high-thermal parameter must also be considered. Refinement of the composition Ca_3NOF, or $Ca_2(NOF)_{0.667}$ (i.e., arbitrarily chosen composition), gave slightly higher R values relative to the oxygen-free composition, and again gave relatively high-thermal displacement parameters at the F, O site. Therefore, the observed relatively high-displacement para-

FIG. 2. ORTEP-type plot (100% ellipsoids) for the Ca_2NF structure, with disordering of fluorine positions along the c axis evident.

TABLE 4
Bond Valence Sum Results for Ca_2NF

[a]Bonds	Bond valences		
	Ca	N	F
Ca(1)–N(1) #1	0.495 (×1)	0.495 (×2)	
Ca(1)–N(1) #2	0.419 (×2)	0.419 (×4)	
Ca(1)–F(1) #1	0.187 (×2)		0.187 (×4)
[b]Ca(1)–F(1) #2	0.064 (×1)		0.064 (×2)
$V_{ij} = \Sigma v_{ij}$	1.771	2.666	0.876

[a]See Table 3 for bond lengths.

[b]Weak or nonbonded interaction.

bond length. The sum of bond valences around any central atom of interest in a structure gives an apparent valence, which optimally should match closely with the ideal oxidation state expected for that atom. The R_{ij} values for Ca–N and Ca–F were obtained from the paper by Brese and O'Keeffe (8): for Ca–N, $R_{ij} = 2.14$ and for Ca–F, $R_{ij} = 1.842$. The bond valence sum results for Ca_2NF are summarized in Table 4.

As seen in Table 4, the bond valence sum results indicate that all three atom positions in Ca_2NF are underbonded. For example, the bond valence sum around Ca is calculated to be 1.771, which is lower than the ideally expected value of 2.0 by 11.5%. Such underbonding is not unusual for oxides containing large metal atoms with a metal–oxygen ratio of 1 or greater, where bonds are elongated relative to average lengths due to increased cation–cation interactions (9). In CaO, for example, the bond-valence sum for Ca is 1.835. For the case of Ca_2NF, it is therefore quite feasible that nonbonded interactions have also elongated the bonds to Ca, thus yielding the observed underbonding. This crystal chemical feature is not likely to be accurately reflected in the empirical R_{ij} parameters used in the calculations, since these were derived from many structures (i.e., probably mostly nitrides and fluorides), and represent an "average" case where metal–metal repulsions are not typically as important as they are here.

SUMMARY

The present study found through single-crystal X-ray diffraction that Ca_2NF has a tetragonal structure similar to that of L-Mg_2NF, as opposed to the rocksalt-type CaO structure originally proposed in the literature (2, 3). It is quite possible that Sr_2NF and Ba_2NF are isostructural with L-Mg_2NF as well, and preparation and single-crystal analysis of these compounds will be the focus of future work.

An unusual aspect of this study was the successful single-crystal structure determination and refinement of a sample surrounded by smaller crystallites. The results are an indication of both the significant advantages and dilemmas presented by the more recently developed CCD systems relative to conventional systems. The CCD area detector provided the sensitivity needed to collect data not only for this small sample, but also for the many crystallites. Previously, samples such as this may have been discarded, or in fortunate cases, the twin/crystallites would never have been observed.

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