Preparation and single-crystal structure analysis of Sr$_2$NF

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Abstract

Samples of Sr$_2$NF were prepared and analyzed via single-crystal X-ray diffraction. Two distinct colors (viz. brownish-yellow (BY) and dark red (DR)) of crystalline Sr$_2$NF samples were discovered and found to be isostructural, with slightly different cell dimensions. The structure is essentially that of rocksalt, but with a doubled cubic unit-cell resulting from ordering of N and F atoms. The presence of F interstitials were also detected, and refined as a Frenkel defect. For the BY crystal, the X-ray analysis gave a cell parameter of $a = 10.6920(45)$ Å, and for the DR, $a = 10.7655(20)$ Å. Both crystal types have space group Fd-$3m$ (No. 227), with $Z = 16$. X-ray data were collected on a Bruker SMART APEX 4k CCD Single Crystal Diffractometer. Structure solutions were obtained via direct methods, and X-ray refinements were carried out by full-matrix least squares on F^2 on all data, to give $R_1 = 0.0308$ (all data) and w$R_2 = 0.0665$ for 10 parameters and 96 independent reflections for the BY sample, and $R_1 = 0.0404$ (all data) and w$R_2 = 0.0750$ for 10 parameters and 98 independent reflections for the DR sample. The final position assignments were analyzed via bond valence sum calculations.
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1. Introduction

Studies on the solid-state chemistry of inorganic oxides have traditionally involved investigations of structure and property relationships of classes of compounds as a function of cation composition. Relatively rare are reports of analogous studies in which the cation composition of a model oxide compound is unchanged, while the anion composition is varied, e.g., by substitution of N^{3-} and F$^-$ for two O^{2-} ions. Such compounds were referred to as pseudo-oxides by Andersson [1] in a paper in which structures of three magnesium nitride–fluorides, L-Mg$_2$NF, Mg$_3$NF$_3$, and H-Mg$_2$NF, were investigated via powder X-ray diffraction methods. Whereas L-Mg$_2$NF (i.e., lower temperature, ambient pressure form) reportedly has a tetragonal structure (LiFeO$_2$-antitype) intermediate between the rocksalt and zincblende types, the other two Mg–N–F phases have cubic structures related to rocksalt-type MgO. This was the first report involving quantitative structural studies of pseudo-oxide compounds.

Ehrlich et al. [2] subsequently reported the preparation of powder samples of Ca$_2$NF, Sr$_2$NF and Ba$_2$NF, and based on a qualitative study using the Guinier powder X-ray diffraction method, concluded that all three of these compounds have the rocksalt structure of their analogous oxides. In a previous single-crystal X-ray study [3], however, we prepared a Ca$_2$NF sample and found it to be isostructural with L-Mg$_2$NF; a rocksalt analog was not observed. The present paper is apparently the first quantitative single-crystal structure analysis of Sr$_2$NF to be reported.

2. Experimental

2.1. Sample preparation

Single crystals were prepared by slow cooling from a melt consisting of a 3:1 mole ratio of Sr : SrF$_2$ in an Ni crucible, reacting under a flow of ultra-high-purity N$_2$ gas under conditions identical to those described previously for Ca$_2$NF [3]. Present in abundance in the final product mixture were colorless crystals of SrF_2, and

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brownish-yellow (BY) and dark red (DR) crystals of Sr_2NF. As was the case for Ca_2NF, the Sr_2NF crystals were highly air sensitive. In addition, they were small, and the majority of them were twinned. The BY and DR samples selected for X-ray analysis were both irregular polygonal-shaped crystals, of approximate dimensions $0.08 \times 0.08 \times 0.06$ and $0.10 \times 0.08 \times 0.06$ mm^3, respectively. To protect the crystals from air during data collection, they were each inserted into glass capillary tubes, which were then sealed under inert atmosphere.

2.2. Structure determination

X-ray data were collected on a Bruker SMART APEX 4k CCD Single Crystal Diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (graphite monochromatized Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. The crystal-to-detector distance was 5.985 cm. The diffraction data were obtained by collection of 606 frames at each of three φ settings, $0°$, $120°$, and $240°$, using a scan width of $0.3°$ in ω. At the end of the data collection, 50 initial frames were recollected to monitor crystal decay. The exposure time was 20 s/frame for both collections.

For cell parameter determination for both crystals, reflections were harvested from all 1868 frames of data for a minimum threshold of I/σ of 10, using Bruker's SMART [4] program. The resulting arrays could not be uniformly indexed for either of the crystals, indicating the possible presence of twinning. Bruker's GEMINI [5] program revealed that each of the two samples consisted of a predominant crystallite, with one or more smaller crystallites for which no related orientation matrices could be obtained. Thus, the data analysis proceeded using the matrix of the predominant crystallite in each case, considering that no overlapping reflections were present. Following this analysis, 447 and 335 of the originally harvested 654 and 620 reflections for the BY and DR crystals, respectively, remained in the arrays. The modified arrays were next read into SMART for determination and refinement of the higher symmetry cells from the reduced cell parameters provided by GEMINI. The resulting refined cells for each sample were then used to integrate all the corresponding data in SAINT [4], where global refinement of the unit-cell parameters was also performed to give the final values utilized in the subsequent structural analysis. Prior to structure solution and refinement, an empirical absorption correction was performed on the data files written by SAINT using SADABS [6], which also simultaneously corrected for other effects, such as absorption by the glass capillary.

Space group determinations were performed using Bruker's XPREP [7] program, and the space group *Fd-3m* (#227) was the optimal choice in both cases. The structures were solved via direct methods using the

SHELXS [7] program, and refined via full-matrix least squares on F^2 for all data using SHELXL [7]. The program SHELXP [7] was used to obtain the structure plots which appear in this paper. 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 selected interatomic distances and bond angles are given in Table 3.

3. Results and discussion

3.1. Refinement

Despite the distinctly different colors for the two samples, their structural refinements converged to identical solutions. The structure is related to that of SrO (i.e., rocksalt type), but with a doubled unit-cell parameter. The correct cell was found by harvesting relatively low intensity data (i.e., threshold of $I/\sigma \geqslant 10$) afforded by the CCD detector. Harvesting only higher intensity (i.e., threshold of $I/\sigma \geqslant 40$) data yields the cubic subcell, with Sr atoms in rocksalt-like octahedral positions, and N and F atoms sharing the octahedral anion site. The subcell parameters thus obtained for the isostructural BY and DR phases are 5.3663(72) and 5.3973(92) Å, respectively, and these values are in good agreement with the value of 5.38 Å reported for Sr_2NF by Ehrlich et al. [2]. Assuming that the Guinier powder data Ehrlich et al. collected for their sample did not contain sufficient data to reveal the doubled cell, it is likely that the Sr_2NF samples reported here are isostructural with the earlier reported compound.

The actual doubled cubic cells that emerge when weak reflections (i.e., containing relatively more information from N and F scattering) are harvested and indexed, is elucidated in the structure refinements as resulting from ordering of N and F atoms along all three directions of the unit cells. Following assignment of the octahedral rocksalt-like Sr, N, and F positions (i.e., Sr(1), N(1), and F(1) in Table 2), appreciable residual electron density was still observed in one of the tetrahedral holes. This peak was optimally refined as an interstitial F atom (i.e., F(2) in Table 2), and its site occupancy was constrained to be equal to the number of vacancies in the F(1) site. Thus, a Frenkel defect was modeled. Under this constraint, the F(1) and F(2) occupancies were refined through final convergence. Attempts to refine the occupancies of the other two atoms yielded chemically unreasonable results in both refinements, due to the large correlations of their occupancy factors with the displacement and occupancy factor of the partially occupied, disordered F(1) site. The disorder introduced at the F(1) site by the presence of the F(2) interstitials is evident in the anisotropic displacement parameters,

Table 1
Crystal data summary and refinement results for Sr_2NF samples

	Brownish-yellow (BY) crystal	Dark red (DR) crystal
Structural formula	Sr_2NF	Sr_2NF
Formula weight	208.25	208.25
Crystal size (mm)	$0.08 \times 0.08 \times 0.06$	$0.10 \times 0.08 \times 0.06$
Crystal system	Cubic	Cubic
Space group	Fd-$3m$ (No. 227, origin choice #2)	Fd-$3m$ (No. 227, origin choice #2)
a (Å)	10.692(5)	10.766(2)
V (Å^3)	1222.3(9)	1247.7(4)
Z	16	16
ρ_{calc} (mg/m^3)	4.527	4.435
λ (Mo$K\alpha$) (Å)	0.71073	0.71073
μ (mm^{-1})	34.651	33.946
θ Range for data collection (°)	3.30–28.26	3.28–28.13
Limiting indices	$-14 \leqslant h \leqslant 13$, $-13 \leqslant k \leqslant 14$, $-13 \leqslant l \leqslant 14$	$-14 \leqslant h \leqslant 13$, $-13 \leqslant k \leqslant 13$, $-14 \leqslant l \leqslant 14$
No. of reflections collected	2447	2578
No. of independent reflections	96 ($R_{int} = 0.0432$)	97 ($R_{int} = 0.0627$)
No. of parameters	10	10
Completeness to maximum θ (%)	100.0	99.0
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Final R indices [$I > 2\sigma(I)$]	$R_1(F)^a = 0.0259$, w$R_2(F^2)^b = 0.0604$	$R_1(F)^a = 0.0308$, w$R_2(F^2)^b = 0.0689$
Final R indices (All Data)	$R_1(F)^a = 0.0308$, w$R_2(F^2)^b = 0.0665$	$R_1(F)^a = 0.0404$, w$R_2(F^2)^b = 0.0750$
Goodness-of-fit on F^2	1.161	1.098
Largest diff. peak and Hole (eÅ^{-3})	0.785 and -1.100	1.216 and -0.686

[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 $w^{-1} = \sigma^2(F_o)^2 + (WP)^2 + TP$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$, for the BY crystal, $W = 0.0308$, and $T = 21.44$; for the DR crystal, $W = 0.0236$ and $T = 73.96$.

Table 2
Positional, occupational, and anisotropic[a] and equivalent isotropic[b] displacement parameters (Å$^2 \times 10^4$) for Sr_2NF brownish-yellow (BY) and dark red (DR) crystal refinements

Atom		Fd-$3m$ Site (Origin 2)	site multiplicity[c]	x	y	z	U_{11}	U_{23}	U_{eq}
Sr(1):	BY						5(1)	0(1)	5(1)
		$32e$	1.000	0.0084(1)	0.2416(1)	0.0084(1)			
	DR						11(1)	1(1)	11(1)
N(1):	BY						8(3)	1(2)	8(3)
		$16c$	1.000	0	0	0			
	DR						8(3)	1(3)	8(3)
F(1):	BY		0.8948				52(6)	44(5)	52(6)
		$16d$		0	0.5000	0			
	DR		0.8842				62(8)	54(9)	62(8)
F(2):	BY		0.2104				11(14)	0	11(14)
		$8b$		0.1250	0.6250	0.1250			
	DR		0.2315				1(16)	0	1(16)

[a] The anisotropic thermal parameter is expressed as $\exp[-2\pi^2(h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2hka^*b^* U_{12} + 2hla^*c^* U_{13} + 2klb^*c^* U_{23})]$; $U_{11} = U_{22} = U_{33}$ and $U_{23} = U_{13} = U_{12}$, except $U_{13} = -U_{23}$ for DR crystal, Sr(1) atom.
[b] U_{eq} is defined as one-third of the trace of the U_{ij} orthogonalized tensor.
[c] Occupancy factors were not refined for Sr(1) and N(1) atoms; F(2) interstitial occupancy was constrained to be equal to F(1) vacancies.

which were refined for all atoms. As seen in Table 2, these are fairly typical for Sr(1) and N(1) atoms, but very large for F(1).

3.2. Structure description and analysis

The coordination sphere for Sr(1) in the doubled cubic structure of the BY crystal is shown in Fig. 1,

where atoms are plotted as 50% probability displacement ellipsoids. The severely misshapen F(1) ellipsoids are pointing towards the F(2) interstitial site, and clearly reflect the partial occupancy and disorder of the F(1) site induced by the presence of the nearby interstitial. From Table 2 it is seen that for the case of the DR crystal, the displacement parameters are similar for F(1), and these also are directed toward the F(2) site. The distorted

Table 3
Selected interatomic distances and bond angles for Sr_2NF brownish-yellow (BY) and dark-red (DR) crystal structures

Interatomic distance or bond angle	Distances (Å) or angles (°)	
	BY crystal	DR crystal
Sr(1)–N(1)	2.5867(14)	2.6039(8)
Sr(1)–F(1)	2.7653(13)	2.7849(8)
Sr(1)–F(2)	2.4697(14)	2.4877(12)
Sr(1)–Sr(1)	3.5270(20);	3.5500(19);
	3.7844(16)	3.8105(7)
F(1)–Sr(1)–F(1)	86.24(2)	86.21(3)
N(1)–Sr(1)–F(1)	89.808(2)	89.806(3)
N(1)–Sr(1)–N(1)	93.89(2)	93.92(3)

Fig. 2. Unit-cell structure plot for the final Sr_2NF structure, brownish-yellow (BY) crystal. Ordering of N and F atoms along all three cell axes is evident. Labeled atoms correspond to those shown in Fig. 1; some atoms are omitted for clarity.

Fig. 1. Structure plot for one Sr coordination sphere in the doubled cubic Sr_2NF structure, brownish-yellow (BY) crystal (50% probability displacement ellipsoids). Disordering at the F(1) site due to partial occupancy and the presence of the F(2) interstitial is evident.

nature of the Sr(1) octahedral site indicated by the data in Table 3 is seen to be due to the ordering of N and F atoms, which form two different bond lengths with Sr. As seen in Fig. 2, it is actually this ordering of N and F along each of the cell axes which defines the doubled cell. Thus, the cell edges for the BY and DR crystals are very close to the sum of two Sr–F plus two Sr–N bonds, and would be an exact equality if the bonds angles were 90°.

The slightly different cell parameters (i.e., see Table 1) perceptible in the CCD system for the BY vs DR crystals is most likely due to small differences in their overall unit-cell compositions. While the present experiment did reveal different occupancies of the F(2) interstitial site for the BY vs DR crystals, this difference was probably not significant enough to impact cell
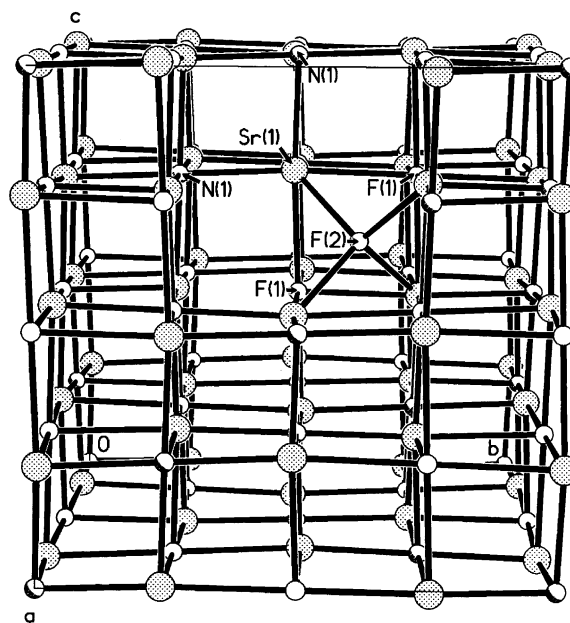
parameters. Specifically, from Table 1, the F(2) interstitial site occupancy is calculated to be 1.68 atoms per unit cell for the BY crystal, and 1.85 atoms per unit cell for the DR crystal. On the other hand, many other compositional variations are possible in nitride–fluoride systems which could subtly affect cell parameters, particularly those involving the large cations. For example, a Sr^{2+} vacancy could be offset by replacing an N^{3-} ion with F^-, which would give a unit-cell formula of $Sr_{31}N_{15}F_{17}$. Refinements of this composition (in which the Frenkel defect was again modeled) were found to be compatible with the X-ray data, as little change in R values relative to the cases using the ideal composition were observed. However, since-crystal compositions could not be determined quantitatively for the present experiment, no conclusion can be made about the exact compositions of the two crystals except that they are close to Sr_2NF.

A curious aspect of this study was the visually distinctive colors of the isostructural Sr_2NF samples. Like many main group metal nitrides (and unlike the corresponding fluorides), the nitride–fluorides are highly colorful, presumably due to the presence of nitrogen-to-metal charge transfer bands within the visible spectrum. By this mechanism, one would expect isostructural samples of like composition to have identical colors. A plausible explanation then for the different colors observed is due to incorporation of color centers in one of the samples. This could occur during crystal growth if isolated strontium metal atoms undergo oxidation to yield the trapped electrons in the lattice.

This phenomenon is well known to occur in nature in halite crystals.

Unlike the case for Ca_2NF [3], no L-Mg_2NF-type phase for Sr_2NF was observed during the course of this study. The metal atoms are essentially 5-coordinated in the tetragonal L-Mg_2NF structure, so it is tempting to state that Sr_2NF preferentially crystallizes in a cubic rocksalt-like cell due to its larger size compared to Mg and Ca. However, as the L-Mg_2NF and rocksalt structures are closely related, L-Sr_2NF bond lengths would not be significantly different than those in the present structure. In the Ca–N–F system, for example, the Ehrlich et al. [2] rocksalt-type Ca_2NF ($a = 4.937$ Å) has Ca–N/F shared bond length, 2.468 Å; in L-Ca_2NF, ($a = 4.902$ Å, $c = 10.516$ Å) the bond lengths are: Ca–N, 2.400 Å ($\times 1$) and Ca–N/F shared, 2.468 Å ($\times 4$), plus there is an additional long Ca–F "bond" with length 2.858 Å. The presence of the short, strong M–N bond compensates for the reduction of metal coordination number in the tetragonal structure, and a bond valence sum analysis of these two structures gives very similar values for the Ca sums. Thus, there appears to be no significant crystal chemical reason why one structure type should be favored over another. From another perspective, the rocksalt subcell, L-Mg_2NF-type, and doubled cubic structures could be considered as manifestations of various N–F ordering scenarios, ranging from no ordering present, to ordering along one cell axis, to ordering along all three axes, respectively. From this perspective, the structure actually prepared depends upon the extent of N–F ordering which has occurred during crystal growth, and it is possible that L-Sr_2NF could be prepared under different growth conditions.

3.3. Bond-valence sum analysis

The program VALENCE [8] was utilized to perform a bond-valence sum analysis for both Sr_2NF crystals. The program computes the bond valence, v_{ij}, between two atoms i and j using the relation:

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

where R_{ij} is a unitless empirical parameter characteristic of the atom pair forming the bond and d_{ij} is the experimental bond length. The default R_{ij} values for Sr–N and Sr–F in VALENCE were 2.249 and 1.996, respectively. 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 bond valence sum results given in Table 4 indicate that this is not the case for Sr(1), N(1), and F(1) atoms in both Sr_2NF crystals, however, which are all significantly underbonded.

As indicated in the previous study on Ca_2NF [3], which had similarly low bond-valence sums, this "underbonding" is not unusual for oxides containing large metal atoms with a metal-to oxygen ratio of one or greater. O'Keeffe [9] has pointed out that in such compounds, bonds are elongated relative to average lengths due to increased cation–cation interactions and thus have lower than "expected" bond valence sums. For example, in SrO ($a = 5.160$ Å), the bond valence sum for Sr is 1.722. It is quite likely that the same phenomenon occurs in M_2NF compounds as well.

Of course, in addition to effects of Sr–Sr cation interactions, the possible presence of undetected Sr^{2+} and N^{3-} vacancies mentioned earlier could also account for some of the observed underbonding character. Finally, note that without the presence of interstitials, the bond valence sums for Sr(1) would be even lower; thus the presence of interstitials helps to "stabilize" the structure.

4. Summary

Single crystals in the Sr–N–F system have been prepared and their structures analyzed quantitatively for the first time. The structure is based on a doubled rocksalt cell, with ideal composition Sr_2NF, and with the doubled unit cell defined by ordering of N and F atoms along all three axes. Residual electron density was refined as a Frenkel defect, with F^- interstitials positioned in tetrahedral sites. Identical structures were refined from two crystals having different colors, which likely have slightly different compositions.

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