

Doubled-cubic Ca₂NF

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Crystals of dicalcium nitride fluoride, Ca₂NF, grown from the melt have been characterized by X-ray diffraction and were found to have a cubic ($Fd\bar{3}m$) structure. Owing to ordering of N and F atoms along all three cell axes, the cell edge is doubled relative to the rocksalt-type structure reported previously. Residual electron density at an interstitial tetrahedral site was refined as a Frenkel defect of F atoms, giving a final composition of Ca₂N(F_{0.913})^{oct}(F_{0.087})^{tet}.

Comment

The compound Ca₂NF belongs to a largely unexplored class of extended inorganic materials first referred to as pseudo-oxides by Andersson (1967), as they have compositions that can be derived from oxides by replacement of O²⁻ with N³⁻ and F⁻ ions. Andersson (1970) published the first quantitative structural study of nitride fluorides, in which three phases in the Mg/N/F system were prepared and characterized by powder X-ray diffraction methods. The three phases, *viz.* L-Mg₂NF, Mg₃NF₃ and H-Mg₂NF, all have structures related to rocksalt to various extents, depending on anion ordering. In the H-Mg₂NF phase, for example, no ordering of N and F atoms occurs and the rocksalt-type structure of MgO is observed. The L-Mg₂NF phase, on the other hand, is tetragonal (*i.e.* anti-LiFeO₂-type structure) due to ordering of N and F atoms along the *c* axis, and has a nearly doubled *c* axis relative to the *a* and *b* axes. Ehrlich *et al.* (1971) subsequently completed a study of M₂NF (*M* = Ca, Sr and Ba), in which they reported the rocksalt structure for all three phases (*i.e.* similar to the analogous oxides) using the Guinier powder diffraction technique. Galy *et al.* (1971) also reported a rocksalt-type structure for Ca₂NF on the basis of powder X-ray diffraction results. We previously reported (Nicklow *et al.*, 2001) the preparation and single-crystal X-ray structure of a Ca₂NF phase with the L-Mg₂NF-type structure. The present study concerns a newly observed phase in the Ca/N/F system, with doubling of the cell axes along all three directions relative to rocksalt-type Ca₂NF. This phase is isostructural with doubled-cubic Sr₂NF reported previously (Wagner, 2002).

Crystals for the present study were grown from the melt of a mixture of Ca metal and CaF₂ reacting in a dynamic flow of N₂

gas. The yellow samples, including that selected for analysis, were typically small and highly air (*i.e.* moisture) sensitive. They were also invariably polycrystalline, usually consisting of a predominant crystallite with one or more other components at symmetrically unrelated orientations. GEMINI (Bruker, 2000) was used to find the orientation matrix of the predominant Ca₂NF crystallite in the selected sample, and the final refined lattice parameter was ultimately determined to be 10.0215 (8) Å. It was immediately recognized that this parameter is approximately double that of the rocksalt-type Ca₂NF reported by Ehrlich *et al.* (1971), with a cell parameter of 4.937 Å. On the basis of the overall analysis of systematic absences, the space group was optimally assigned as $Fd\bar{3}m$ (No. 227). Included in the observed data were 29 low-intensity forbidden reflections, all of type (*0kl*) with *k* + *l* ≠ 4*n*, which are forbidden by the presence of the diamond glide planes. These reflections are accounted for by the refined model described below.

Initial stages of the structure refinement yielded three crystallographically distinct octahedral positions, which were assigned as Ca (32*e*), N (16*d*) and F1 (16*c*), respectively. Following these assignments, appreciable electron density remained at one of the tetrahedral sites (8*a*), and this was optimally refined as an interstitial F atom. The occupancy of this site was constrained to be equal to vacancies at the nearby F1 octahedral position; thus, a Frenkel defect was modeled. Also, the sum of the occupancies of these two partially filled F-atom sites was restrained to keep the total F content fixed at 16 atoms per unit cell. The resulting final empirical composition was Ca₂N(F_{0.913})^{oct}(F_{0.087})^{tet}, corresponding to an average of 1.4 interstitial F atoms per unit cell.

Fig. 1 shows the coordination sphere for one Ca atom, with atoms plotted as 50% probability displacement ellipsoids. The severely misshapen ellipsoids at the octahedral F1 sites reflect the partial occupancy and disorder at this site, as expected from the nearby Frenkel defect. Any one of three adjacent F1 atoms can be positioned 2.170 Å away into the nearby F2 (*i.e.* tetrahedral) site in this Frenkel defect model, with the remaining two F1 atoms expected to relax away from F2. Thus, the ellipsoids are directed away from (and towards) the nearest partially occupied F2 tetrahedral sites, and the 16*c*

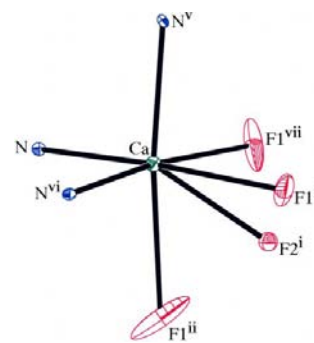


Figure 1

A view of one Ca coordination sphere in the doubled-cubic Ca₂NF structure (50% probability displacement ellipsoids). Elongated ellipsoids at the F1 site are consistent with the modeled Frenkel defect, resulting in partial occupancy of both the F1 site and the F2 interstitial site. Symmetry codes are listed in Table 1.

special position at which the F1 atom is located is really an average position with partial occupancy. Note that attempts to refine a split-atom model for the F1 position failed to yield a stable refinement, as might be expected given that the largest principal axis of the displacement ellipsoid is 0.136 \AA^2 .

Fig. 2 shows the unit-cell plot, and selected bond lengths and angles are given in Table 1. From the figure, ordering of N and F atoms along all three cell axes is clearly seen, accounting for the doubling of the cell edges relative to rocksalt as well as the presence of the diamond glide planes. An interstitial F2 atom is also shown in the figure, with a nearby F1 atom missing, which results in local loss of the diamond glide plane. Therefore, considering the average vacancy of 1.4 F1 sites per unit cell, the model accounts for the presence of the weak reflections in the data mentioned previously that are forbidden for the diamond glide planes. It is also evident in Fig. 1 and from Table 1 that the CaF_3N_3 octahedra are distorted, with $\text{N}-\text{Ca}-\text{N}$ angles greater than 90° and $\text{F1}-\text{Ca}-\text{F1}$ angles smaller. This distortion is merely a consequence of the fact that the Ca atom is closer to the N/N/N face of the octahedron than to the F/F/F face, since the $\text{Ca}-\text{N}$ bonds are shorter than the $\text{Ca}-\text{F1}$ bonds, as also indicated in Table 1. Thus, the Ca atom is positioned off the octahedral center (*i.e.* on a lower-symmetry site) relative to the Ca site in rocksalt-type CaO, whereas the N and F atoms have essentially rocksalt-type positions. In addition, as expected, the $\text{N}-\text{Ca}-\text{N}$ angle is larger than the corresponding angle in doubled-cubic Sr_2NF (93.89° ; Wagner, 2002).

Bond-valence sums were calculated using the empirical parameters of Brese & O'Keeffe (1991), which were reported as 2.14 for $\text{Ca}-\text{N}$ bonds and 1.842 for $\text{Ca}-\text{F}$ bonds. The resulting values are 1.86 for Ca, 2.89 for N, 0.76 for F1 and 1.04 for F2 atoms. These results indicate that the atoms on the doubled-cubic lattice positions are somewhat underbonded. Initially, one might consider that this result can be explained

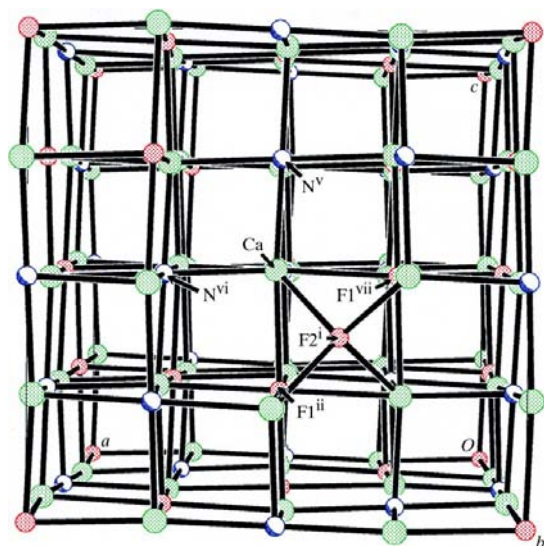


Figure 2
A view of the unit cell for the final Ca_2NF structure. Ordering of N and F atoms along all three cell axes is evident. Some atoms have been omitted for clarity. Symmetry codes are listed in Table 1.

by the relatively expanded lattice caused by the presence of the distorted octahedra. For example, note that doubling of Ehrlich's reported ideal rocksalt-type cell would give a lattice dimension of $4.936 \text{ \AA} \times 2 = 9.872 \text{ \AA}$, which is significantly smaller than the value of $10.0215(8) \text{ \AA}$ for the present structure. However, the bond-valence sums for both the rocksalt-type Ca_2NF phase of Ehrlich *et al.* (1971) and our previously reported L- Ca_2NF phase (Nicklow *et al.*, 2001) indicate underbonding as well (*e.g.* the values for Ca in the two phases are 1.79 and 1.77, respectively). Therefore, further explanation for the underbonding in the present structure must be provided by crystal chemical factors other than lattice expansion. O'Keeffe & Hyde (1984) have noted previously that atoms in oxides with large cation-to-anion ratios (*i.e.* ≥ 1) tend to be underbonded and attribute this observation to bond elongation from relatively strong cation-cation interactions in such compounds. We have consistently observed the same phenomenon in other $M_2\text{NF}$ ($M = \text{Ca}, \text{Sr}$ and Ba) compounds and have discussed it in detail elsewhere (Nicklow *et al.*, 2001; Wagner, 2002; Seibel & Wagner, 2004).

Experimental

Ca metal and CaF_2 (3:1 molar ratio) were mixed in a glove-bag under Ar 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 heated to 1273 K under Ar for 1 h and then cooled to 473 K, at which point the gas flow was switched from Ar to N_2 . The reactants were heated to 1273 K for 12 h, and were subsequently cooled at a rate of 40 K h^{-1} to 473 K and then to room temperature at a non-controlled rate.

Crystal data

Ca_2NF	Mo $K\alpha$ radiation
$M_r = 113.17$	Cell parameters from 2393 reflections
Cube, $Fd\bar{3}m$	$\theta = 3.5\text{--}28.3^\circ$
$a = 10.0215(8) \text{ \AA}$	$\mu = 4.22 \text{ mm}^{-1}$
$V = 1006.46(14) \text{ \AA}^3$	$T = 100(2) \text{ K}$
$Z = 16$	Prism, light yellow
$D_x = 2.987 \text{ Mg m}^{-3}$	$0.11 \times 0.09 \times 0.08 \text{ mm}$

Data collection

Bruker SMART APEX CCD diffractometer	83 independent reflections
ω scans	81 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (SADABS in SAINT-Plus; Bruker, 2003)	$R_{\text{int}} = 0.031$
$T_{\text{min}} = 0.540, T_{\text{max}} = 0.717$	$\theta_{\text{max}} = 28.3^\circ$
2393 measured reflections	$h = -13 \rightarrow 13$
	$k = -13 \rightarrow 13$
	$l = -13 \rightarrow 13$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

$\text{Ca}-\text{F2}^i$	2.3412 (12)	$\text{Ca}-\text{Ca}^{\text{iii}}$	3.263 (2)
$\text{Ca}-\text{N}$	2.4105 (7)	$\text{Ca}-\text{Ca}^{\text{iv}}$	3.5487 (3)
$\text{Ca}-\text{F1}^{\text{ii}}$	2.6081 (8)		
$\text{F2}^i-\text{Ca}-\text{N}^{\text{v}}$	121.94 (2)	$\text{N}^{\text{vi}}-\text{Ca}-\text{F1}^{\text{ii}}$	89.732 (4)
$\text{N}-\text{Ca}-\text{N}^{\text{v}}$	94.61 (3)	$\text{F1}^{\text{ii}}-\text{Ca}-\text{F1}^{\text{vii}}$	85.57 (3)
$\text{N}^{\text{v}}-\text{Ca}-\text{F1}^{\text{ii}}$	173.59 (4)		

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, \frac{3}{4}-y, \frac{3}{4}-z$; (iii) $\frac{5}{4}-x, y, \frac{5}{4}-z$; (iv) $x-\frac{1}{4}, y-\frac{1}{4}, 1-z$; (v) $x, \frac{5}{4}-y, \frac{5}{4}-z$; (vi) $\frac{5}{4}-x, \frac{5}{4}-y, z$; (vii) $\frac{3}{4}-x, \frac{3}{4}-y, z$.

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.064$

$S = 1.39$

83 reflections

10 parameters

$$w = 1/[\sigma^2(F_o^2) + (0.0109P)^2$$

$$+ 23.8669P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$$

Data collection: *SMART* (Bruker, 1997–2002); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* in *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXL97* in *SHELXTL*; molecular graphics: *SHELXP* in *SHELXTL*; software used to prepare material for publication: *SHELXP* in *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1056). Services for accessing these data are described at the back of the journal.

References

- Andersson, S. (1967). *Ark. Kemi.* **26**, 521–538.
- Andersson, S. (1970). *J. Solid State Chem.* **1**, 306–309.
- Brese, N. E. & O’Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.
- Bruker (1997–2002). *SMART* for WNT/2000. Version 5.630. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2000). *GEMINI* (Version 1.02) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2003). *SAINT-Plus*. Version 6.45. Bruker AXS Inc., Madison Wisconsin, USA.
- Ehrlich, P., Linz, W. & Seifert, H. (1971). *Naturwissenschaften*, **58**, 219–220.
- Galy, J., Jaccou, M. & Andersson, S. (1971). *C. R. Acad. Sci.* **272**, 1657–1659.
- Nicklow, R. A., Wagner, T. R. & Raymond, C. C. (2001). *J. Solid State Chem.* **160**, 134–138.
- O’Keeffe, M. & Hyde, B. G. (1984). *Nature (London)*, **309**, 411–414.
- Seibel, H. & Wagner, T. R. (2004). *J. Solid State Chem.* **177**, 2772–2776.
- Wagner, T. R. (2002). *J. Solid State Chem.* **169**, 13–18.