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Magnesium Nitride Fluorides

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Three magnesium nitride fluorides, Mg_3NF_3, L-Mg_2NF and H-Mg_2NF, have been prepared at temperatures between 900–1350°.

Mg_3NF_3 is cubic with $a = 4.216$ Å, space group $Pm3m$, and its structure is related to the structure of both MgO and $MnMg_6O_8$. L-Mg_2NF is tetragonal with $a = 4.186$ Å and $c = 10.042$ Å and the space group is $I4_1/amd$. Its structure is intermediate between the structure types represented by zinc blende and sodium chloride (or MgO). L-Mg_2NF transforms at 20 kb and 1300°C into H-Mg_2NF, which is nearly isostructural with MgO. The anions are ordered in Mg_3NF_3 and L-Mg_2NF, and the X-ray data of H-Mg_2NF indicates also an ordering of the anions for this compound.

L-Mg_2NF and Mg_3NF_3 decompose at 1000–1150°C in an argon atmosphere to Mg-vapour, N_2 and MgF_2.

Introduction

In order to change the composition of a metal oxide, Wadsley successfully used the partial substitution of another metal of higher or lower valency (*1*) and (*2*). Within a narrow region of composition, Wadsley could find a greater number of compounds with complicated but often related structures. The possibility of making pseudo-oxides by the substitution of $N^{3-} + F^-$ for two O^{2-} has recently been discussed (*3*). Metal nitride fluorides is a neglected field in solid state chemistry. The use of them for making compounds of new but wanted structures should be promising. We have chosen to start with magnesium for experimental reasons.

Experimental

Magnesium metal powder and MgF_2, both of high purity, were mixed and heated in an atmosphere of pure nitrogen at temperatures 900–1000°C for several hours. Samples were removed every hour and examined by X-ray powder diffraction. The mixtures were reground in an atmosphere of argon every time. When the ratio $Mg:MgF_2$ was varied, the X-ray analysis showed that two phases had formed, close to the composition ratios 1:1 and 3:1. The same compounds could also be made by mixing Mg_3N_2 and MgF_2 followed by heat treatment at 900–1000°C in dry argon, or at 900–1100°C in sealed nickel capsules. These experiments were carried out in order to obtain crystals; some crystal growth occurred, but the crystals formed were too small to be used for single-crystal X-ray studies.

The magnesium nitride fluorides are not sensitive to moisture in air, but they decompose in acids with the formation of ammonia.

One of the compounds, Mg_3NF_3, was analyzed by its thermal decomposition at 1200°C into magnesium, nitrogen and MgF_2. The observed loss of weight was 33.0%, the calculated is 35.1%, according to the formula:

$$2Mg_3NF_3 = 3MgF_2 + 3Mg + N_2.$$

The remaining product was confirmed to be MgF_2 by X-ray analysis. The formation of magnesium was confirmed by carrying out the decomposition in argon. Beautiful crystals of magnesium were identified downstream in the colder part of the furnace.

The compounds made were studied by X-ray methods. The Hägg-Guinier X-ray powder camera was used for the phase analysis. Intensity data were obtained with a diffractometer, using Cu–Kα radiation, and a proportional counter. The observed intensities were estimated by cutting out and weighing tracings of the diffractometer peaks.

Least-squares crystal-structure refinement was carried out on an IBM 7090 computer, using the *Crystal Structure Calculations System, X-ray* 63 (*4*).

Structural Analysis

The trial compositions Mg_3NF_3 and Mg_2NF were confirmed by density measurements and the structure determinations. The powder pattern of Mg_3NF_3 showed great similarities with that of

MgO, and was also easily indexed with nearly the same cubic unit cell. Mg_3NF_3 is primitive and the density gives one formula per unit cell. Using the space group $Pm3m$ with three Mg in 3 *c*, three F in 3 *d* and one N in 1 *b*, the *R* factor for the first 18 reflections was 2.2% after three least-squares cycles. The atomic form factors used for Mg^{2+}, F^-, and N^{3-} were obtained from the "International Tables for X-ray Crystallography," Vol. III, 1962; the N^{3-} form factors were constructed from the N and N^{1-} curves given. If the anions were assumed to be randomly distributed over 3 *d* and 1 *b*, the *R* factor increased to 6%.

The powder pattern of L-Mg_2NF was indexed in the tetragonal system with $a = 4.186$ Å and $c = 10.042$ Å. The density measurements gave four formula units in the unit cell, which requires one eightfold position for magnesium, and two fourfold positions for nitrogen and fluorine, and these can be provided by the space group $I4_1/amd$. Nitrogen was then placed in 4 *b* and fluorine in 4 *a*. The position 8*e* was chosen for magnesium, and different *z* values tried. With $z = 0.145$ as a start, three least-squares cycles refined this parameter to 0.1595, and *R* factor became 4.4%. With nitrogen and fluorine in 4 *a* and 4 *b*, respectively, and with $z = 0.145$, the *R* factor reached a minimum at 9.5% after several least-squares cycles with the *z* parameter now refined to 0.1597.

The crystallographic constants of the two compounds Mg_3NF_3 and L-Mg_2NF are given in Table I. The indexed Hägg–Guinier powder patterns and a comparison of F_o and F_c are given in Tables II and III. Atomic distances are given in Table IV.

TABLE I

CRYSTALLOGRAPHIC CONSTANTS

Mg_2NF Space group $I4_1/amd$
$a = 4.186$ Å, $c = 10.042$ Å $Dm = 3.05$, $Dx = 3.09$, $Z = 4$ Mg in 8 (*e*) with $z = 0.1595$ N in 4 (b) F in 4 (a)
Mg_3NF_3 Space group $Pm3m$
$a = 4.216$ Å $Dm = 3.16$, $Dx = 3.19$, $Z = 1$ Mg in 3 (c) F in 3 (d) N in 1 (b)

TABLE II

X-RAY POWDER PATTERN OF Mg_2NF. Cu-Kα RADIATION

$\sin^2\theta_{obs}$	*hkl*	$\sin^2\theta$	F_o	F_c
0.03968	101	0.03974	4.2	4.2
0.08688	103	0.08680	19.3	18.0
0.09119	112	0.09125	8.4	7.8
0.09410	004	0.09413	47.4	45.9
0.13552	200	0.13543	51.5	53.1
—	211	—	—	2.4
0.18097	105	0.18093	18.2	17.2
0.22215	213	0.22223	15.2	15.0
0.22948	204	0.22956	32.9	34.0
0.27076	220	0.27086	40.4	41.8
—	116	—	—	6.9
—	301	—	—	2.5
0.31622	215	0.31636	15.0	15.1
0.32206	107	0.32212	19.4	20.1
0.35762	303	0.35766	13.1	12.3
0.36207	312	0.36209	9.4	11.0
0.36486	224	0.36498	26.9	27.5
	008		—	6.6
	321		—	2.5
	305		14.7	13.4
	217		16.4	17.0
	323		11.6	10.3
	109		14.5	13.1
	208		—	5.2
	400		30.8	29.6
	316		—	3.8
	411		—	2.5
	325		11.9	11.9
	307		15.4	14.5
	413		8.8	8.8
	332		—	9.1
	404		20.6	20.1
	219		11.2	11.7
	228		—	4.4
	1110		17.9	18.9
	420		25.6	26.0
	415		11.0	10.8
	327		12.2	12.6
	1011		—	8.2
	424		17.9	17.8
	309		11.4	10.7

Description of the Structures and Discussion

The structure of Mg_3NF_3 is drawn in Fig. 1. Magnesium is octahedrally surrounded by four fluorines and two nitrogens at equal distances of 2.108 Å. Nitrogen is octahedrally surrounded by six cations, as in Ca_2N (*5*) Mg_3N_2 (*6*) and Ca_3N_2 (*7*). Fluorine is surrounded by four cations in a square-planar arrangement.

TABLE III

X-RAY POWDER PATTERN OF Mg_3NF_3. Cu-$K\alpha$ RADIATION

$\sin^2\theta_{obs}$	hkl	$\sin^2\theta_{calc}$	F_o	F_c
0.03344	100	0.03344	8.6	8.5
0.06691	110	0.06688	11.1	10.8
—	111	—	—	0.9
0.13386	200	0.13375	49.0	47.8
0.16716	210	0.16719	6.0	6.1
0.20064	211	0.20063	9.9	9.5
0.26743	220	0.26750	37.4	37.6
0.30092	300 221	0.30096	11.0	11.2
0.33434	310	0.34338	7.6	7.9
0.36780	311	0.36782	6.2	6.2
0.40100	222	0.40126	30.6	31.3
	320		5.3	5.2
	321		6.9	6.7
	400		26.5	26.9
	410 322		9.7	9.5
	411 330		11.9	11.5
	331		5.9	5.9
	420		22.7	23.7
	421		4.6	4.4

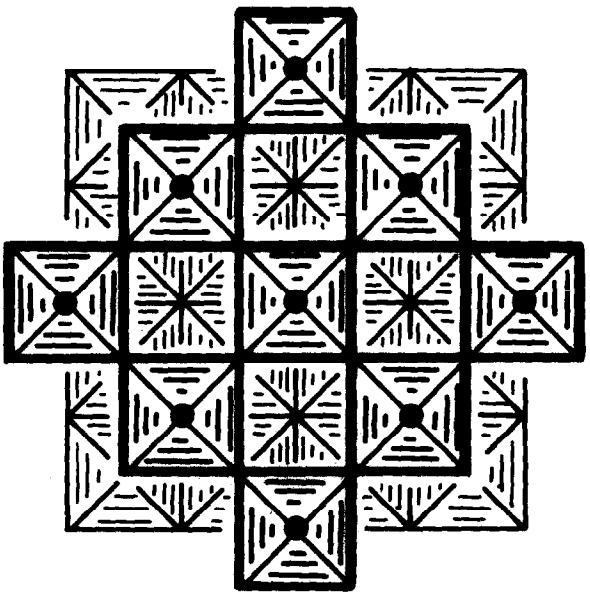

FIG. 1. The structure of Mg_3NF_3. Filled circles represent nitrogen.

TABLE IV

INTERATOMIC DISTANCES IN Mg_2NF AND Mg_3NF_3

Mg_2NF		Mg_3NF_3	
Mg-N	2.159 ± 0.005 Å	4Mg-F	2.108 ± 0.001 Å
2Mg-N	2.123 ± 0.005	2Mg-N	2.108 ± 0.001
2Mg-F	2.123 ± 0.005	N-F	2.980 ± 0.001
N-N	3.268 ± 0.005	F-F	2.980 ± 0.001
N-F	2.960 ± 0.005	N-N	4.216 ± 0.001
F-F	3.268 ± 0.005		
Mg-Mg	2.765 ± 0.010		

The structure of Mg_3NF_3 is very similar to the structure of MgO. The anion arrangement is intact, although the two different anions are ordered. The greatest difference between the two structures, which have nearly the same unit-cell dimensions, is that the position (000) containing Mg in MgO is empty in an ordered way in Mg_3NF_3. In the structure of $MnMg_6O_8$ (8), every second of the empty cation positions in Mg_3NF_3 is filled, which results in a doubling of the cube axis of Mg_3NF_3.

The middle part of Fig. 2 shows the structure of L–Mg_2NF. The structure is related both to the zinc blende and sodium chloride structure types. Compared with MgO, the anion positions are identical, although the ordering of nitrogen and fluorine, as well as the magnesium positions, cause a doubling of one of the dimensions of the MgO structure type, and the new structure is tetragonal. There is also a ~20% expansion in the c direction, if the structure of Mg_2NF is compared with the structure of MgO. The magnesium atom is situated in a square pyramid of three nitrogen and two fluorine atoms. There are two Mg–N and two Mg–F distances of 2.12 Å and one Mg–N distance of 2.16 Å. There is a third Mg–F distance of 2.86 Å; this is the distance to the sixth anion in the octahedron formed by the anions in cubic close packing. The nitrogen atom in Mg_2NF is surrounded by six magnesium atoms, in a somewhat distorted octahedron; the fluorine atom is surrounded by four magnesium atoms as in Mg_3NF_3.

The anion arrangement of the Mg_2NF structure is close to cubic close packing, the deviation is the 20% expansion in the c-axis direction. The upper part of Fig. 2 shows three different polyhedra formed by the anions in Mg_2NF. The octahedron corresponds to the NaCl arrangements, the tetrahedron to the zinc blende structure, and the square pyramid to the Mg_2NF structure type. The transformation

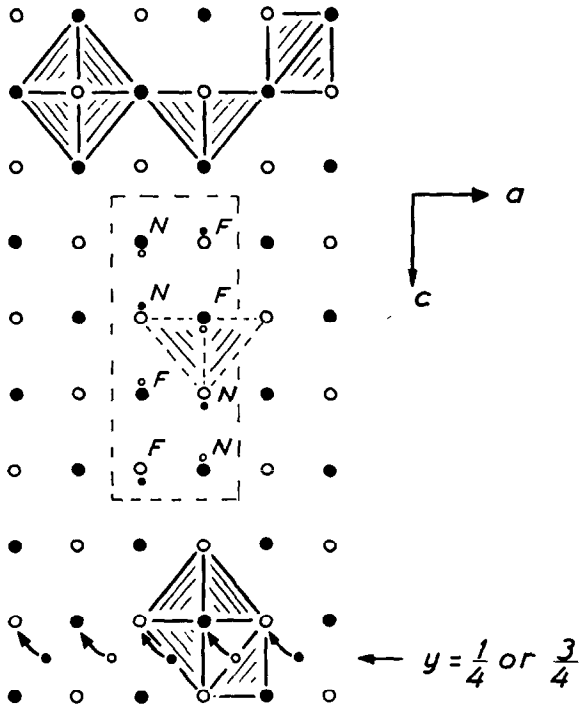

FIG. 2. Large circles are anions, small circles cations. Filled circles on ½, open circles on 0. The anion positions are as in the NaCl structure, except for a 20% verticle expansion. In the top part of the Figure, three different polyhedra types are drawn, from left the octahedron, the square pyramid and the tetrahedron. In the middle part of the Figure is the structure of low-Mg_2NF, where the Mg atoms are in square pyramids. The ordering of nitrogen and fluorine is indicated by letters. In the lowest part of the Figure, the transformation of a tetrahedral structure (zinc blende) to an octahedral (NaCl) is demonstrated. The square pyramid structure (Mg_2NF) can be considered as an intermediate step.

"zinc blende type"→"sodium chloride type" is favoured by high pressure (*9*), the necessary shifts of the cations are shown in the lower part of Fig. 2. The change in coordination goes from four to six. If the cation positions in zinc blende and sodium chloride are compared with the magnesium positions in Mg_2NF, the latter can formally be described as being "on their way," from the positions in zinc blende to the positions in sodium chloride. Thus, L–Mg_2NF is intermediate in its structure, with the five coordination of anions around magnesium in form of a square pyramid.

Mg_2NF is isoelectronic with MgO. In order to make it also isostructural, it is obvious from the discussion above that high pressure is necessary. A series of experiments was carried out with the high

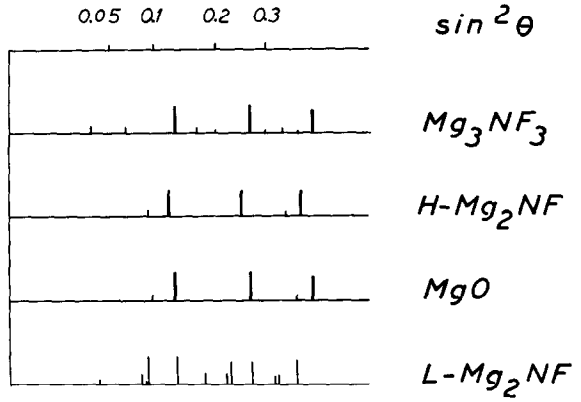

FIG. 3. Guinier powder patterns of Mg_3NF_3, H–Mg_2NF, MgO, and L–Mg_2NF. Cu-$K\alpha$ radiation.

pressure apparatus designed by Wilhelmi (*10*) at temperatures 1100–1350°C and pressures of 25–30 kb. A powder of Mg_2NF transformed into a slightly yellow, crystalline material. The transformation seemed to occur best at 1250–1350°C. X-ray powder pattern showed, in addition to weak lines of L–Mg_2NF, some strong lines of a new phase, which was indexed in a face-centered cubic unit cell of 4.36 Å. Ten minutes heat treatment in argon at 900°C transformed the powder completely to L–Mg_2NF, as found by X-ray analysis. The new phase designated H–Mg_2NF is isostructural with MgO (according to this indexing) (Fig. 3). However, some of the lines were somewhat diffuse, some were sharp. This is probably due to an ordering of nitrogen and fluorine in the lattice, and if so the structure is not cubic. A careful examination is planned. The density was calculated to be 3.27 for H–Mg_2NF, and is the highest of the three magnesium nitride fluorides found.

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