JOURNAL OF SOLID STATE CHEMISTRY **98**, 379–385 (1992)

Crystal Structure and Magnetic Properties of $NaBa_2Mn_3F_{11}$: A New Layer-Type Fluoride Compound

J. DARRIET, M. DUCAU, M. FEIST,* A. TRESSAUD,
AND P. HAGENMULLER

*Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I,
33405 Talence Cedex, France*

Received July 30, 1991

A new $NaBa_2Mn_3F_{11}$ fluoride has been prepared by solid-state reaction. The crystal structure has been determined from X-ray diffraction measurements on a single crystal (R = 0.0317, wR = 0.0295). The crystal symmetry is rhombohedral, space group $R\bar{3}c$ with the unit cell constants of a = 7.003 Å and c = 35.466 Å. The most important feature of the structure is the unusual environment of Mn^{2+}, which is located in a pentagonal bipyramid (CN = 7). To our knowledge this is the second example of such a surrounding for Mn^{2+} in fluoride compounds. These bipyramids are linked by edge sharing and constitute $[Mn_3F_{11}]$ layers which are perpendicular to the c-axis and separated by the Na^+ and Ba^{2+} cations. The surrounding of the Ba^{2+} ions is a tricapped trigonal prism. Along the c-axis these prisms form $[Ba_2F_{15}]$ pairs by edge sharing. The Na atoms exhibit a distorted cubic environment. Above 40 K the magnetic susceptibility follows a Curie–Weiss law with Θ_p = −31.5 K and C = 4.1. The broad maximum observed around T = 15 K can result from the low dimensionality of the magnetic arrangement (2D).

Introduction

The investigation of the ternary system $NaF–BaF_2–FeF_2$ has shown existence of a cubic phase (*1*). The structure corresponds to an ordered perovskite-like arrangement in which the Ba^{2+} and Na^+ cations occupy the A sites of the ideal ABX_3-type perovskite structure. The exact formulation was actually $Na_4Ba_xFe_{4-x}F_{12}$ with x = 0.84(1) (*2*). If one takes into account the cationic repartitions in the structure, the more detailed $Na_3[Ba_xNa_{1-x}](Fe_{4-x}Na_x)F_{12}$ formula with x = 0.84(1) can be proposed.

Isostructural compounds, corresponding to the substitution of Fe^{2+} by Mn^{2+} or Co^{2+} in the B sites, have been prepared and will be published later. In the corresponding copper based system, the new $Na_4BaCu_3F_{12}$ phase had been isolated whose crystal structure derives also from a cubic perovskite but with an ordering for the Na and Cu atoms in the B sites (*3, 4*).

In our investigation of the ternary systems $NaF–BaF_2–MF_2$ (M = Mn, Fe, Co, Ni) evidence was also given in each system of one quaternary phase except for manganese for which a new $NaBa_2Mn_3F_{11}$ compound has been isolated. Its powder XRD pattern led us to think that it should be a new structural type.

---

* Permanent address: Humboldt Universität, Hessische Str., O-1040 Berlin, Germany.

0022-4596/92 $5.00

This paper deals with the determination of the crystal structure and with the magnetic properties of this new phase.

Experimental

Elaboration

$NaBa_2Mn_3F_{11}$ has been synthesized from stoichiometric mixtures of the corresponding binary fluorides, the solid-state reaction being carried out in a platinum tube sealed under dry argon atmosphere. Heating at 600°C for 3 days and then cooling down to room temperature with a 20°C/hr rate led to powder samples for which X-ray diffraction appeared to give a novel diagram. If the compound is heated at higher temperature (t = 700°C), the phase decomposes into two components of a pseudo-binary system, i.e., $NaMnF_3$ and $BaMnF_4$.

Small single crystals were obtained by long annealing at 650°C for 1 week followed by very prolonged cooling (1°C/hr down to 600°C, then 5°C/hr down to room temperature).

TABLE 1

LATTICE CONSTANTS AND CONDITIONS OF DATA COLLECTION AND EVALUATION FOR $NaBa_2Mn_3F_{11}$

Cell dimensions	a = 7.003(1) Å c = 35.466(6) Å V = 1507.0 Å^3 Z = 6
Molar mass	671.5
Obs. specific mass (g cm^{-3})	4.39
Calc. specific mass (g cm^{-3})	4.44
Size of the crystal (mm)	0.15 × 0.07 × 0.03
Measured range (MoK_α)	$2° < \Theta < 40°$
h min/max	−11/11
k	−11/11
l	−25/25
Angle for ω-scan (°)	0.70 + 0.35tgΘ
Number of measured reflections	5066 (twinned crystal)
Independent ($I > 3\sigma I_0$)	316 (single crystal)
Absorption correction (μ = 109.7 cm^{-1})	empirical from psi-scans
Extinction ε refined in $F_c(\text{corr.}) = F_c(1 - \varepsilon F_c^2/\sin\Theta)$	0.21 × 10^{-7}
Goodness of fit S	2.193
$R = (\Sigma D/\Sigma F_0)$	0.0317
$wR = (\Sigma wD^2/\Sigma wF_0^2)^{1/2}$	0.0297

with $D = \Sigma||F_0| - |F_c||$ and weights w proportional to $1/\sigma^2(F_0)$.

X-ray Structure Determination

A single crystal selected from the preparation mentioned above was set up on a four-circle automatic diffractometer CAD4 (Enraf–Nonius). The data were collected using graphite monochromated $MoK\alpha$ radiation.

The conditions are listed in Table I. The scattering factors for neutral atoms, corrected for anomalous dispersion, were applied (*5*, *6*). The structure refinement was performed using SHELX program (*7*). The structure was determined from a Patterson map and the heavy atoms were first located. From successive difference Fourier maps and refinements, the remaining atoms were located and the final R-values decreased down to R = 0.0317 (wR = 0.0295). The final positional and thermal parameters are reported in Table II. A table specifying the calculated and observed structure factors can be obtained on request to the authors (J.D.).

Magnetic Measurements

The magnetic susceptibility of Na $Ba_2Mn_3F_{11}$ has been determined using a SQUID magnetometer (SHE Corp.) in the temperature range 1.8 K < T < 300 K.

Results and Discussion

Preliminary studies on films show that the symmetry is trigonal with the space group $R\bar{3}c$ (n ° 167). The lattice parameters a = 7.003(1) Å and c = 35.466(6) Å (rhombohedral cell: a = 12.495 Å α = 32.56°) were refined from 20 reflections by a double scanning technique. The indexed X-ray powder

TABLE II

FRACTIONAL COORDINATES, DISPLACEMENT PARAMETERS (U_{ij}), AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS B_{eq}(Å^2) IN $NaBa_2Mn_3F_{11}$

Atom	Site	x	y	z	B_{eq}(Å^2)
Na	6b	0	0	0	2.78
Ba	12c	0	0	0.1891(1)	0.74
Mn	18e	0.4459(2)	0	$\frac{1}{4}$	1.55
F_1[a]	36f	0.2665(12)	0.0466(14)	0.7487(5)	1.51
F_1[b]	18e	0.2433(9)	0	$\frac{3}{4}$	4.51
F_2	12c	0	0	0.07343(3)	2.69
F_3	36f	0.0270(6)	0.6286(6)	0.8063(1)	1.57

Atom	Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na	6b	156(19)	U_{11}	743(90)	0	0	$U_{11}/2$
Ba	12c	104(2)	U_{11}	73(7)	0	0	$U_{11}/2$
Mn	18e	363(10)	64(9)	63(13)	27(11)	U23/2	$U_{22}/2$
F_1[a]	36f	149(36)	293(70)	163(56)	151(79)	75(50)	133(42)
F_1[b]	18e	453(29)	1470(89)	131(53)	−31(53)	U23/2	$U_{11}/2$
F_2	12c	383(29)	U_{11}	257(77)	0	0	$U_{11}/2$
F_3	36f	275(23)	210(19)	129(36)	−39(17)	−31(19)	135(19)

[a] This position is half occupied.

[b] Refined parameters when F_I is in the 18e position.

TABLE III

XRD POWDER DIAGRAM OF $NaBa_2Mn_3F_{11}$

d_{obs}(Å)	d_{calc}(Å)	$h\ k\ l$	I(%)	d_{obs}(Å)	d_{calc}(Å)	$h\ k\ l$	I(%)
5.73	5.73	0 1 2	40	2.180	2.180	1 2 5	2
5.01	5.00	1 0 4	5	2.080	2.079	1 0 16	20
3.573	3.575	0 1 8	100	2.036	2.035	1 2 8	55
3.497	3.501	1 1 0	50	2.021	2.021	0 3 0	60
3.360	3.356	1 1 3	30	1.996	1.992	0 3 3	5
3.058	3.058	1 0 10	55	1.969	1.967	0 0 18	20
3.009	3.011	1 1 6	80	1.942	1.942	2 0 14	10
2.987	2.988	2 0 2	80	1.921	1.924	2 1 10	25
2.952	2.951	0 0 12	10	1.870	1.867	1 2 11	2
2.868	2.868	0 2 4	20	1.786	1.787	0 2 16	25
2.618	2.615	1 1 9	5	1.749	1.750	2 2 0	20
2.502	2.501	2 0 8	25	1.676	1.678	2 2 6	10
2.301	2.303	0 2 10	10	1.636	1.636	3 1 5	2
2.287	2.287	2 1 1	20	1.591	1.592	2 1 16	5
2.275	2.273	1 2 2	10	1.570	1.572	3 1 8	5

TABLE IV

INTERATONIC DISTANCES (Å) WITH STANDARD DEVIATIONS FOR THE MAIN DISTANCES AND BOND ANGLES (°) IN $NaBa_2Mn_3F_{11}$

Na	F_3(i)	F_3(ii)	F_3(iii)	F_3(iv)	F_3(v)	F_3(vi)	F_2(vii)	F_2(viii)
F_3(i)	2.519(9)	4.035	4.035	3.017	3.017	5.039	2.852	4.257
F_3(ii)	106.5	2.519(9)	4.035	3.017	5.039	3.017	2.852	4.257
F_3(iii)	106.5	106.5	2.519(9)	5.039	3.017	3.017	2.852	4.257
F_3(iv)	73.6	73.6	180.	2.519(9)	4.035	4.035	4.257	2.853
F_3(v)	73.6	180.	73.6	106.5	2.519(9)	4.035	4.257	2.853
F_3(vi)	180.	73.6	73.6	106.5	106.5	2.519(9)	4.257	2.853
F_2(vii)	67.7	67.7	67.7	112.4	112.4	112.4	2.602(10)	5.209
F_2(viii)	112.4	112.4	112.4	67.7	67.7	67.7	180.	2.602(10)

Ba	F_3	F_3(ix)	F_3(x)	F_3(xi)	F_3(xii)	F_3(xiii)	F_1(xiv)	F_1(xv)	F_1(xvi)
F_3	2.679(4)	3.508	3.508	3.181	3.017	5.099	3.914	5.203	4.873
F_3(ix)	81.8	2.679(4)	3.508	3.017	5.099	3.181	4.873	3.914	5.204
F_3(x)	81.8	81.8	2.679(4)	5.099	3.181	3.017	5.204	4.873	3.914
F_3(xi)	72.4	68.2	142.5	2.705(4)	4.678	4.678	2.781	3.367	4.814
F_3(xii)	68.2	142.5	72.4	119.6	2.705(4)	4.678	3.367	4.814	2.781
F_3(xiii)	142.5	72.4	68.2	119.6	119.6	2.705(4)	4.814	2.781	3.367
F_1(xiv)	92.7	128.5	148.3	61.5	76.5	124.6	2.731(5)	2.991	2.991
F_1(xv)	148.3	92.7	128.5	76.5	124.6	61.5	66.4	2.731(5)	2.991
F_1(xvi)	128.5	148.3	92.7	124.6	61.5	76.5	66.4	66.4	2.731(5)

Mn	F_3(iii)	F_3(x)	F_2(xvii)	F_2(vii)	F_1(xviii)	F_1(xix)	F_1
F_3(iii)	2.050(8)	4.007	3.101	2.853	3.257	2.996	2.781
F_3(x)	155.9	2.050(8)	2.853	3.101	3.340	2.781	2.996
F_2(xvii)	97.1	87.2	2.087(9)	4.105	2.534	4.141	2.534
F_2(vii)	87.2	97.1	159.1	2.087(9)	2.940	2.534	4.141
F_1(xviii)	100.1	103.7	72.5	86.6	2.196(9)	4.505	4.334
F_1(xix)	83.6	76.3	132.9	67.8	154.0	2.427(9)	2.669
F_1	76.3	83.6	67.8	132.9	139.2	66.7	2.427(9)

Note. Symmetry code: (i) $-x, y - x, \frac{3}{2} - z$; (ii) $y, 1 + x, \frac{3}{2} - z$; (iii) $1 - y + x, 1 - y, \frac{3}{2} - z$; (iv) $y - x - \frac{1}{3}, \frac{1}{3} + y, z - \frac{1}{6}$; (v) $\frac{2}{3} - y, \frac{1}{3} - x, z - \frac{1}{6}$; (vi) $\frac{2}{3} + x, \frac{1}{3} - y + x, z - \frac{1}{6}$; (vii) $\frac{1}{3} + x, \frac{2}{3} + y, \frac{2}{3} + z$; (viii) $\frac{1}{3} + x, \frac{2}{3} + y, \frac{2}{3} - z$; (ix) $y - x, 1 - x, z$; (x) $1 - y, 1 - y + x, z$; (xi) $\frac{1}{3} - x, \frac{5}{3} - y, \frac{5}{3} - z$; (xii) $y - \frac{2}{3}, y - x - \frac{1}{3}, \frac{5}{3} - z$; (xiii) $\frac{4}{3} - y + x, \frac{2}{3} + x, \frac{5}{3} - z$; (xiv) $\frac{1}{3} - y + x, \frac{2}{3} + y, \frac{5}{3} - z$; (xv) $\frac{1}{3} + x, \frac{2}{3} + x - y, \frac{5}{3} - z$; (xvi) $\frac{1}{3} - y, \frac{2}{3} - x, \frac{5}{3} - z$; (xvii) $\frac{2}{3} + x, \frac{1}{3} + y, \frac{5}{6} - z$; (xviii) $1 - x + y, 1 - x, z$; (xix) $y, x, \frac{3}{2} - z$.

diagram is given in Table III. In fact all chosen crystals appear to be twinned in the *ab*-plane with a rotation of the axes of 60° around the *c*-axis. The crystal used for the X-ray structural determination corresponded in fact to two single crystals in which the ratio of the intensities of the *h k l* reflections is close to one-third. Only the most intense group of *h k l* reflections has been used to solve the structure.

The barium atoms were first located in the special position (12*c*). A Fourier synthesis then supposed manganese site to be (18*e*) and the residue fell to $R = 0.16$ in the consecutive refinement. The other atoms were then set; at this stage the refinement of all atomic coordinates and isotropic thermal parameters led to $R = 0.0648$ and $wR = 0.0638$. An anisotropic thermal motion of the atoms was now assumed and the resi-

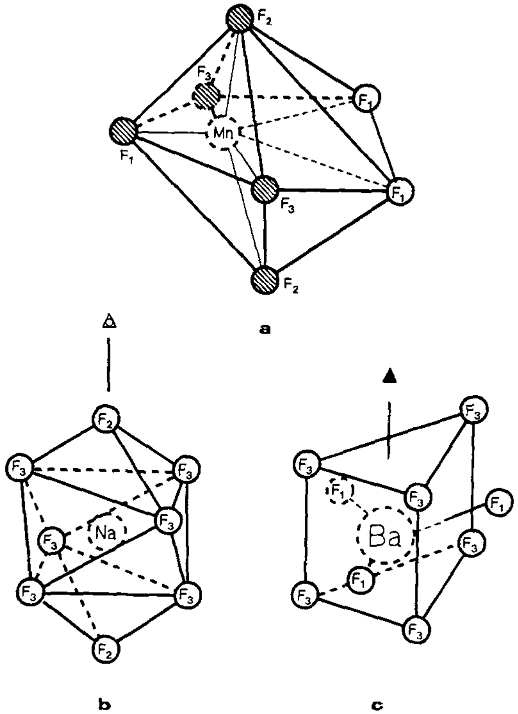

FIG. 1. Representation of the fluorine polyhedra: (a) $[MnF_7]$ bipyramid, (b) $[NaF_8]$, and (c) $[BaF_9]$ tricapped trigonal prism.

dues decreased to $R = 0.0332$ and $wR = 0.0307$. However, as shown by Table II, the thermal motion of the F_1 atom in the special position (18*e*) (point symmetry 2) is too large (B_{eq}(Å^2) = 4.51), especially the component U_{22}. For this reason, the general position (36*f*) was checked with an occupancy rate of one half and it appeared clearly that the F_1 fluorine atom is located in this position: the residue fell down to $R = 0.0317$ and $wR = 0.0295$ and particularly the ellipsoid of the anisotropic thermal motion becomes more coherent (see Table II). The interatomic distances with corresponding standard deviations for the main distances and angles are reported in Table IV.

As can be seen in Table IV, the first coordination sphere of Mn^{2+} seems to be a trigonal bipyramid with the Mn–F distances in the median plane of 2.196 Å for F_1 and 2×2.050 Å for F_3 (Fig. 1a). The axial distances correspond to Mn–F_2 and are equal to 2.087 Å. However, there are also two supplementary F_1 fluorine atoms at a distance of 2.427 Å, which at first sight seemed to be too far from the manganese atom to be connected. In fact a calculation of the bond valence using the concept of electrostatic valence introduced by Pauling (*8*) shows that the influence of these two atoms cannot be neglected. The usefulness of this concept is that the bond valence can be correlated with the bond length (*9–13*). The most commonly used expressions to obtain a relationship between the bond valence (s) and the bond length (d) are those of Zachariasen (*11*) and Brown and co-workers (*12, 13*). Both expressions gave actually similar results and we have chosen the second one: $s = (d/d_0)^{-N}$ as d_0 and N are constants. The values for Mn^{2+} in a fluorine surrounding are $d_0 = 1.72$ and $N = 5.6$ (*10*). The obtained value of the bond valence is $s = 1.97$, if the two extra F_1 atoms are considered to be linked to manganese. They contribute by 15% to the valence bond, which cannot be neglected. The same calculation, F_1 atom being in the special position (18*e*), leads to a bond valence of only $s = 1.85$, which is another proof that this atom is more delocalized in a general position (36*f*). The surrounding of Mn^{2+} in $NaBa_2Mn_3F_{11}$ is therefore a pentagonal bipyramid with coordination number CN = 5 + 2 (Fig. 1a). To our knowledge, this is the second example of this type of environment for manganese in fluoride compounds despite the low covalency of fluorides, the first one being in $MnCrF_5$ (*14*). These pyramids are linked by edge sharing and constitute $[Mn_3F_{11}]_n$ layers (Fig. 2) which are perpendicular to the *c*-axis with a distance between two adjacent layers of 6.03 Å (Fig. 3). These layers are separated by the Na and Ba atoms which are surrounded respectively by eight and nine fluorine atoms (Figs. 1b and 1c).

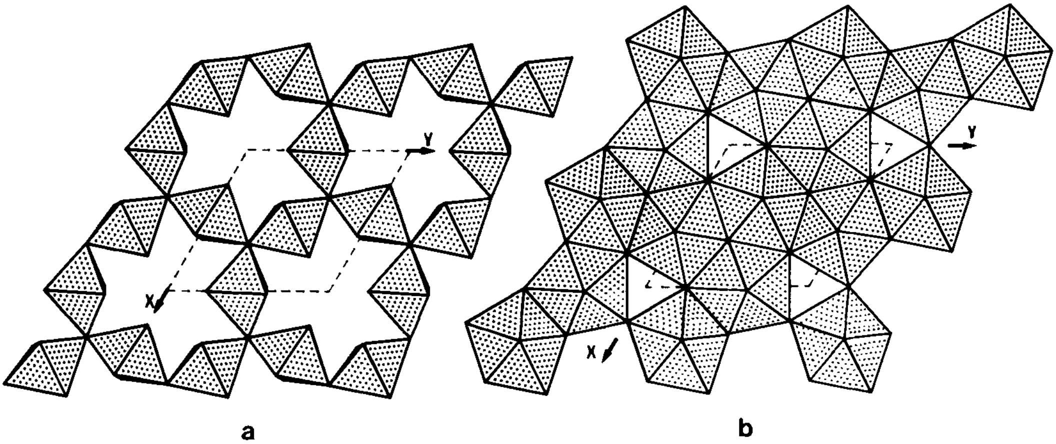

FIG. 2. Representation of a $[Mn_3F_{11}]$ layer at $z \approx 0.75$: (a) network of trigonal bipyramid for Mn^{2+}; (b) network of pentagonal bipyramid for Mn^{2+}.

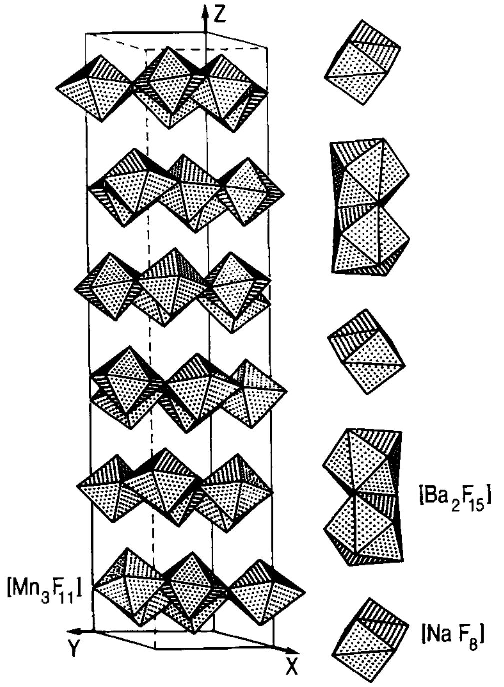

FIG. 3. View of the $[Mn_3F_{11}]$ layers perpendicular to the c-axis. The Na and Ba atoms have been omitted in order to clarify the figure.

The point symmetry $\bar{3}$ of the Na position (6*b*) separates the Na–F distances in two groups: 6 × Na–F_3 and 2 × Na–F_2 (Table IV), the first one constituting an octahedral surrounding. The residual F_2 atoms are located on the ternary axis of the octahedra in such a way that the environment of sodium is a distorted cube (Fig. 1b). A calculation of the bond valence using the tables proposed in Ref. (*15*) gives an s-value of 0.91 confirming the oxidation state of the sodium.

The surrounding of barium, which has point symmetry 3, is a trigonal prism tricapped by the F_1 atoms (Fig. 1c). The bond valence of this cation with such an environment is $s = 2.11$. Along the c-axis, the capped trigonal prisms form pairs $[Ba_2F_{15}]$ by face sharing with the sequence $[NaF_8]$–$[Ba_2F_{15}]$–$[NaF_8]$ along the c-axis (Fig. 3).

The thermal variation of the reciprocal magnetic susceptibility of $NaBa_2Mn_3F_{11}$ is shown in Fig. 4. Above 40 K, the susceptibility follows clearly a Curie–Weiss law with $\Theta_p = -31.5$ K and $C = 4.1$ ($C_{\text{theor.}} = 4.375$ per Mn^{2+}). The rather broad minimum observed around $T = 15$ K can be attributed to antiferromagnetic interactions within the

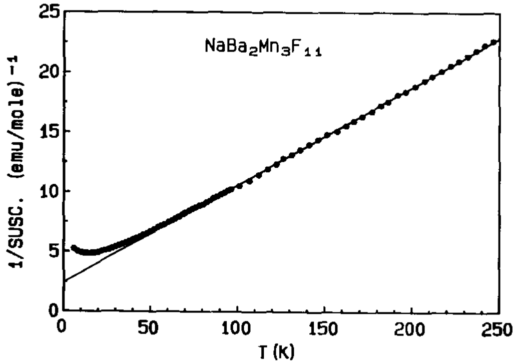

FIG. 4. Variation of reciprocal magnetic susceptibility of $NaBa_2Mn_3F_{11}$.

$[Mn_3F_{11}]_n$ sheets. The interpretation of this behavior in terms of 2D-magnetic systems in which each magnetic center has four nearest neighbors is in progress.

References

1. J. DARRIET, S. G. MAYORGA, AND A. TRESSAUD, *Eur. J. Solid State Inorg. Chem.* **25**, 783 (1990).
2. J. DARRIET, M. DUCAU, AND A. TRESSAUD, *Eur. J. Solid State Inorg. Chem.*, accepted.
3. A. DE KOZAK, M. SAMOUËL, J. RENAUDIN, AND G. FEREY, *Eur. J. Solid State Inorg. Chem.* **25**, 15 (1988).
4. A. DE KOZAK, M. SAMOUËL, J. RENAUDIN, AND G. FEREY, *Eur. J. Solid State Inorg. Chem.* **27**, 771 (1990).
5. D. T. CROMER AND J. D. MANN, *Acta Crystallogr. Sect. A* **24**, 321 (1968).
6. D. T. CROMER, AND D. LIBERMANN, *J. Chem. Phys.* **53**, 1891 (1970).
7. G. M. SHELDRICK, "SHELX 76," Cambridge, United Kingdom (1976).
8. L. PAULING, *J. Am. Chem. Soc.* **51**, 1010 (1929).
9. I. D. BROWN, *Chem. Soc. Rev.* **7**, 353 (1978).
10. I. D. BROWN, *in* "Structure and Bonding in Crystals" (M. O'Keefe and A. Navrotsky, Eds.), Vol. II, pp. 1–29, Academic Press, New York (1981).
11. W. H. ZACHARIASEN, *J. Less-Common Met.* **62**, 1 (1978).
12. I. D. BROWN, AND R. D. SHANNON, *Acta Crystallogr. Sect. A* **29**, 266 (1973).
13. I. D. BROWN, AND K. K. WU, *Acta Crystallogr. Sect. B* **32**, 1957 (1976).
14. G. FEREY, R. DE PAPE, M. POULAIN, D. GRANDJEAN, AND A. HARDY, *Acta Crystallogr. Sect. B* **33**, 1409 (1977).
15. G. FEREY, A. LEBLANC, A. DE KOZAK, AND M. SAMOUËL, *J. Solid State Chem.* **56**, 288 (1985).