The Crystal Structure of Barium Manganese(II) Iron(III) Fluoride BaMnFeF₇

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The crystal structure of the monoclinic compound BaMnFeF₇ has been determined: $a = 553.2(1)$, $b = 1098.0(2)$, $c = 918.3(1)$ pm, $\beta = 94.67(1)°$, $V = 555.9(3) \times 10^{-24}$ cm³, $Z = 4$. All atoms are in general positions of space group $P2_1/c$, weighted $R = 0.031$, using 1771 independent single-crystal reflections with $I > 2\sigma(I)$. The structure consists of edge-sharing dinuclear $Mn_2F_{10}^{6-}$ units (Mn–Mn = 322.2 pm), linked via corners by intermediate FeF₆ octahedra, at which two *cis* ligands remain unbridged. The average distances in the distorted octahedra are Mn–F = 211.6 pm and Fe–F = 192.7 pm. The barium atoms are irregularly 12-coordinated with a mean distance Ba–F = 290.5 pm. The structure is discussed in relation to the trigonal weberite Na₂MnFeF₇ and others.

Introduction

Interested in the network of octahedra formed by transition metal fluorides of general composition $A_nM_2F_7$ (A = alkali or alkaline earth ion), we have recently refined the crystal structures of the compounds K₃Zn₂F₇ (*1*), Na₂NiFeF₇ (*2*), and Na₂MnFeF₇ (*3*). In the two latter sodium compounds—representatives of the orthorhombic and the trigonal weberites, resp. —the nonbridging anions which are required by the stoichiometry M:F = 2:7 occur at the tervalent iron ions only. Pass-

ing to barium compounds Ba$M^{II}M^{III}$F₇ (*4, 5*), another structural way of realizing this stoichiometry might be found. This includes the possibility of fluoride ions outside the octahedral network and coordinated to barium only. Examples for such separate anions are known from the structures of Ba₂MF₆ = (BaF)₂ MF₄ (*6*) and Ba₃(AlF₆)₂ = ½Ba₆F₄(Al₄F₂₀) (*7*).

From some isostructural monoclinic barium compounds Ba$M^{II}M^{III}$F₇ reported recently (*4, 5*), we chose the manganese iron compound BaMnFeF₇ for a complete structure determination (*8*), because we were interested in its structural relations to the corresponding sodium compound Na₂ MnFeF₇ of the trigonal weberite family

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(3). In addition this choice seemed useful to compare the magnetic properties of the isoelectronic d^5 ions Mn^{2+} and Fe^{3+} in both structures, which also may be followed by Mössbauer investigations (8–10).

Experimental

Single crystals of $BaMnFeF_7$ were obtained by heating a dried mixture of stoichiometric amounts of the binary fluorides in sealed platinum tubes for 3 hr at 750°C and very slow cooling to 280°C. Powdered crystals yielded the monoclinic lattice constants given in Table I, in good agreement with those previously reported (5). X-Ray photographs of the single crystals showed the systematic absences of the reflections noted in Table I, which also confirmed the assigned space group $P2_1/c$ (4, 5). The pyk-

nometric density is in agreement with $Z = 4$ formula weights per unit cell.

Some selected single crystals of about 1 mm dimensions, which were translucent and light brown in color, were ground to spheres. One of those spheres was mounted on an automatic four-circle diffractometer Nonius CAD 4 to collect intensity data under the conditions given in Table I. After data reduction (11), correction for absorption (12), and averaging symmetry equivalent measurements, the observed structure factors of 1771 independent reflections were used to solve the structure. All calculations were done at the Telefunkenrechner TR 440 of the Rechenzentrum der Universität Marburg, using the program SHELX 76 (13). Atomic form factors were those of the neutral atoms, as given in parametric form by Cromer and Mann (14).

TABLE I

LATTICE CONSTANTS OF $BaMnFeF_7$ AND CONDITIONS OF INTENSITY DATA COLLECTION

	a (pm)	b (pm)	c (pm)	β (°)	V ($\times 10^{24}$ cm³)
Lattice constants					
This work	553.2(1)	1098.0(2)	918.3(1)	94.67(1)	555.9(3)
Ref. (5)	553.2	1098.5	918.2	94.63	556.2
Density (g cm⁻³)	4.65(4) (measured),		4.649(2) (calculated with $Z = 4$)		
Space group $P2_1/c$ from systematic absences:	$h0l : l \neq 2n$				
	$0k0 : k \neq 2n$				
Single-crystal sphere	Radius: $R = 0.016$ cm				
Absorption (Mo$K\alpha$)	$\mu = 113$ cm⁻¹,		$\mu R = 1.8$		
Range measured (Mo$K\alpha$, graphite monochromated)	$2° \leqq \theta \leqq 32°$				
	$0 \leqq h \leqq 8$				
	$0 \leqq k \leqq 16$				
	$-13 \leqq l \leqq 13$				
Scan conditions	mode : $\omega/2\theta$,	aperture : 0.8° + 0.35tgθ,		$t_{max} = 180$ sec	
Reflections measured					
total			2121		
symmetry independent			1952		
independent and $I > 2\sigma$ (I)			1771		

TABLE II

Positional and Thermal Parameters^a of the Atoms in BaMnFeF$_7$, All in General Position 4e of Space Group $P2_1/c$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Ba	0.2290(1)	0.1688(<1)	0.0417(<1)	1.04(1)	0.84(1)	0.74(6)	0.06(1)	−0.15(1)	0.03(1)
Fe	0.6941(1)	0.1214(1)	0.7657(1)	0.58(2)	0.77(2)	0.58(2)	0.00(2)	−0.11(2)	0.02(2)
Mn	0.8111(2)	0.0638(1)	0.3808(1)	0.69(2)	0.84(2)	0.68(2)	−0.02(2)	−0.14(2)	−0.02(2)
F1	0.4088(7)	0.2852(4)	0.2848(4)	1.14(13)	1.62(13)	0.92(11)	−0.21(10)	0.06(9)	−0.68(11)
F2	0.4943(7)	0.0275(3)	0.2509(4)	1.14(13)	1.18(12)	1.35(12)	0.17(10)	−0.48(10)	−0.36(10)
F3	0.1394(7)	0.3993(3)	0.0091(4)	1.18(13)	0.96(12)	1.48(12)	−0.24(9)	−0.48(10)	0.38(10)
F4	0.9822(7)	0.4821(3)	0.2812(4)	0.97(13)	1.43(13)	1.23(12)	−0.09(10)	0.03(10)	−0.41(10)
F5	0.1003(7)	0.7365(3)	0.2136(4)	1.07(13)	0.99(12)	1.88(13)	−0.31(10)	−0.02(11)	−0.19(10)
F6	0.3446(7)	0.6457(3)	0.9403(4)	1.68(14)	1.65(13)	0.63(10)	−0.01(9)	0.04(10)	−0.30(11)
F7	0.7158(7)	0.4032(4)	0.4747(4)	1.64(14)	1.86(14)	0.68(11)	−0.06(10)	−0.03(10)	−0.28(12)

^{a} Anisotropic temperature factors correspond to B in $\exp(-B \sin^2 \theta/\lambda^2)$ with B_{ij} given in 10^{-20} m^2. The extinction parameter in F_c(corr.) $= F_c(1 - \epsilon Fc/\sin \theta)$ refined to $\epsilon = 5.73 \times 10^{-7}$ and the proportionality factor for the weights $w = k/\sigma^2(F_0)$ to $k = 0.594$.

Structure Determination

In space group $P2_1/c$, No. 14 of International Tables (15), which is the only one in accordance with the systematic absences observed, the general position is fourfold:

$$4e \pm (x, y, z; \bar{x}, \tfrac{1}{2} + y, \tfrac{1}{2} - z).$$

All additional four special positions are twofold and have all their coordinates fixed. A three-dimensional Patterson synthesis indicated, that none of these special positions could be occupied. Therefore all atoms of BaMnFeF$_7$—10 in the asymmetric unit—were to be localized in the general position mentioned.

The evaluation of the Patterson in a first step led to the localization of all three cations. A difference Fourier synthesis following the least-squares refinement of these cation positions indicated three out of seven anion sites. Final steps of trial and error, in which octahedral coordination of the transition metal atoms was assumed, revealed the positions of the remaining four fluorine atoms. The refinement at this stage, with isotropic temperature factors and with iron in the smaller octahedral holes, yielded $R = \Sigma | |F_0| - |F_c| |/\Sigma|F_0| = $

0.068. Anisotropic refinement improved the result to $R = 0.052$. As an inspection of the corresponding F_0, F_c list now showed some F_0 values of strong reflections lying considerably lower than their calculated F_c counterparts, an extinction correction (16), simplified to F_c(corr) $= F_c(1 - \epsilon F_c^2/\sin \theta)$, seemed useful. Including refinement of the extinction parameter ϵ (13) and introducing weights $w = $ prop. $1/\sigma^2(F_0)$ the final residuals were $R = 0.033$ resp. $R_w = \Sigma w^{1/2}(| |F_0| - |F_c| |)/\Sigma w^{1/2}|F_0| = 0.031$ for 1771 independent reflections. The resulting atomic parameters are given in Table II and the structure factors listed elsewhere.[1]

Results and Discussion

Figure 1 shows the BaMnFeF$_7$ structure in a stereoscopic drawing. The details, how

[1] See NAPS document No. 03872 for 10 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance in U.S. funds only for each NAPS Accession Number. Institutions may use purchase orders when ordering; however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are $7.75. Microfiche are $4.00. Outside of the U.S. and Canada, postage is $3.00 for a photocopy or $1.50 for a fiche.

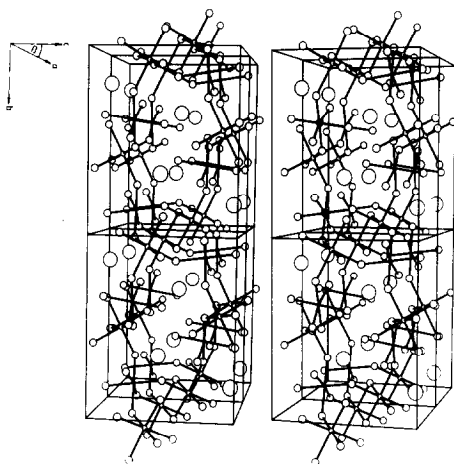FIG. 1. Stereoscopic view of the BaMnFeF$_7$ structure. To show the network of octahedra four unit cells are drawn.

the octahedra are linked to form the three-dimensional network shown, may be seen from Figs. 2 and 3. The interatomic distances and angles are given in Table III.

All anions in the BaMnFeF$_7$ structure are part of the coordination sphere of the transition metal ions, just as is the case in the weberites Na$_2$$M^{II}$$M^{III}F_7$. There are also two

FIG. 2. FeF$_6$ octahedron in the BaMnFeF$_7$ structure, linked to three binuclear Mn$_2$F$_{10}$ groups only.
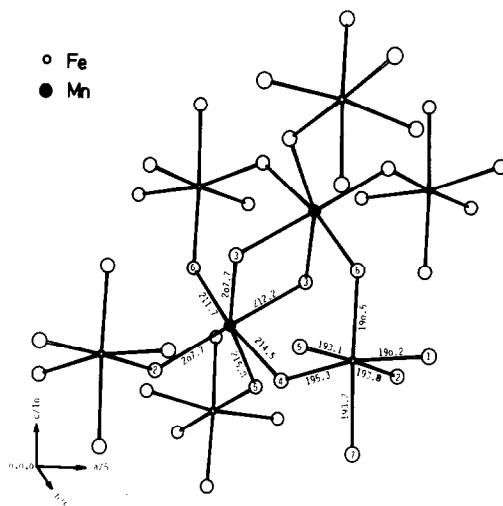

FIG. 3. Binuclear Mn$_2$F$_{10}$ group, linked to six FeF$_6$ octahedra in the structure of BaMnFeF$_7$.

terminal ligands in *cis* position of the FeF$_6$ octahedron, as found for one of the two iron sites in the Na$_2$MnFeF$_7$ structure (*3*). But contrary to the infinite chains of *trans* corner-sharing M^{II}F$_6$ octahedra in the weberites the MnF$_6$ octahedra in BaMnFeF$_7$ form separated dinuclear units Mn$_2$F$_{10}$ by edge-sharing.

As demonstrated in Fig. 2, the FeF$_6$ octahedra are isolated from each other, but each is connected via corners to three of these binuclear groups Mn$_2$F$_{10}$. One of these groups is linked by two fluorine atoms, F4 and F6, in *cis* position of the FeF$_6$ octahedron. The opposite *cis* ligands F1 and F7 of this octahedron are those, which do not participate in linking.

The Mn$_2$F$_{10}$ units are also isolated from each other. In Fig. 3 it is shown, how they are connected via all their free corners to six FeF$_6$ octahedra, two of which are linked twice in such a way, that they additionally bridge the binuclear Mn$_2$F$_{10}$ groups by the *cis* bonds mentioned. This kind of arrangement is also found in the rutile structure, from which this detail of the BaMnFeF$_7$ structure is a section. The Mn–Mn distance of 322.2 pm in the edge-sharing unit, how-
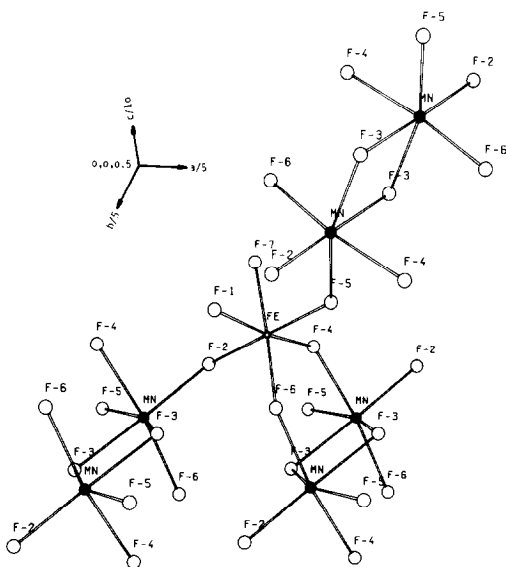
TABLE III

INTERAMTOMIC DISTANCES AND ANGLES IN THE BaMnFeF$_7$ STRUCTURE

				Angle at Fe
Fe–F1 (term.)	190.2(4) pm	F4–F7	255.1(6) pm	82.1(2)°
Fe–F6	190.5(4)	F2–F7	266.7(5)	87.1(2)
Fe–F5	193.1(4)	F1–F7	266.8(5)	88.2(2)
Fe–F7 (term.)	193.2(4)	F2–F4	267.5(5)	86.9(2)
Fe–F2	193.8(4)	F1–F6	267.7(6)	89.4(2)
Fe–F4	195.3(4)	F5–F6	271.6(5)	90.1(2)
Fe–F (aver.)	192.7	F1–F2	273.9(6)	91.0(2)
		F4–F5	273.6(5)	89.6(2)
F1– Fe–F4	170.1(2)°	F2–F6	275.0(5)	91.4(2)
F2– Fe–F5	176.3(2)	F5–F1	276.6(6)	92.4(2)
F6– Fe–F7	177.1(2)	F5–F7	276.8(6)	91.5(2)
Fe– F5–Mn	126.8(2)	F4–F6	296.2(5)	100.3(2)
Fe– F2–Mn	129.1(2)	F–F (av.)	272.3	
Fe– F4–Mn	132.1(2)			
Fe– F6–Mn	133.7(2)			Angle at Mn
Mn–F2	207.7(4) pm	F3–F3′	269.3(5) pm	79.8(1)°
Mn–F3	207.7(4)	F3′–F5	277.9(5)	81.0(1)
Mn–F6	211.7(4)	F3′–F6	279.8(6)	82.6(2)
Mn–F3′	212.2(4)	F3–F4	286.0(5)	85.3(2)
Mn–F4	214.5(4)	F4–F5	294.6(5)	86.4(1)
Mn–F5	215.8(4)	F2–F4	297.6(6)	89.6(2)
Mn–F (aver.)	211.6	F3′–F4	299.4(5)	89.1(2)
		F3–F6	302.0(5)	92.1(1)
Mn–Mn	322.2(1) pm	F5–F6	311.1(5)	93.4(1)
Mn– F3–Mn	100.2(2)°	F2–F6	318.0(5)	98.6(2)
F3–Mn–F5	159.1(2)°	F2–F3	319.6(5)	100.6(2)
F4–Mn–F6	171.7(2)	F2–F5	320.6(5)	98.4(2)
F2–Mn–F3′	178.7(2)	F–F (av.)	298.0	
Ba–F3	259.1(3) pm	Ba–F7	291.9/293.7/296.3(4) pm	
Ba–F1	268.2/269.2(4)	Ba–F5	303.3/309.6(4)	
Ba–F2	279.1(4)	Ba–F6	311.0(4)	
Ba–F4	291.9/313.0(4)	Ba–F (av.)	290.5 (C.N. 12)	

ever, is considerably smaller here than that of 330.9 pm in the rutile structure of MnF$_2$ (*17*). This shortening against electrostatic repulsion is caused by the bridging FeF$_6$ octahedra being much smaller than the MnF$_6$ octahedra, which they clamp together.

The mean distances Fe–F in B́aMnFeF$_7$ are about the same as in the corresponding octahedron of Na$_2$MnFeF$_7$ (in parentheses): 191.8 (191.8) pm for the *cis* terminal bonds and 193.2 (193.9) pm for the

bridging ones. The overall average distance Fe–F = 192.7 (193.2) pm also agrees very well with the distances reported for quite different structures such as 192.8 pm for CsFeF$_4$ (*18*), K$_2$FeF$_5$ (*19*) and Rb$_2$LiFeF$_6$ (*20*), or 192.9 pm for SrFeF$_5$ (*21*).

The mean distance Mn–F = 211.6 pm in BaMnFeF$_7$ is very close to the value of 212.2 pm given for the rutile MnF$_2$ (*17*), but significantly longer than in Na$_2$MnFeF$_7$ and Na$_2$MnVF$_7$ (*3*) (208.0 and 207.4 pm, resp.). The difference may be caused by an overall

expanding effect of edge-sharing, which does not occur in the weberites.

As may be seen from Table III, a distortion of the octahedra in $BaMnFeF_7$ is reflected even more than in the range of M—F distances, in deviations of the angles F–M–F from 90 and $180°$ resp., up to about 10%. The fluorine bridging angles, important with respect to magnetic superexchange interactions in the antiferromagnetic compound (8, 9), are also remarkably low. The Mn–F–Mn angle of $100.2°$ in $BaMnFeF_7$ compared to $128.8°$ in Na_2MnFeF_7 is, of course, a consequence of the edge-sharing in the barium compound. But also the Mn–F–Fe bridges in it, which range from 126.8 to $133.7°$ (average $130.4°$), are significantly more bent than in the sodium compound (135.3 to $144.8°$, average $138.5°$). This difference may account for the lower temperature of magnetic order, $T_N = 85(2)$ K in $BaMnFeF_7$, compared to 94(1) K in Na_2MnFeF_7 (8, 9).

The barium ions in the $BaMnFeF_7$ structure have an irregular 12-coordination with a mean distance Ba–F = 290.5 pm. In the distorted cuboctahedron of $BaGaF_5$ a value of 288.2 pm has been found (22), similar to 289.0 pm in the distorted icosahedral coordination of barium in the $BaLiCrF_6$ structure (23).

Acknowledgments

References

1. E. HERDTWECK AND D. BABEL, Z. Kristallogr. 153, 189 (1980).

2. R. HAEGELE, W. VERSCHAREN, D. BABEL, J.-M. DANCE, AND A. TRESSAUD, J. Solid State Chem. 24, 77 (1978).

3. W. VERSCHAREN AND D. BABEL, J. Solid State Chem. 24, 405 (1978).

4. J. RAVEZ, R. DE PAPE, AND P. HAGENMULLER, Bull. Soc. Chim. Fr. 4375 (1967).

5. A. DE KOZAK AND M. SAMOUËL, Rev. Chim. Miner. 15, 268 and 406 (1978).

6. H. G. VON SCHNERING, Z. Anorg. Allg. Chem. 353, 13 (1967).

7. R. DOMESLE AND R. HOPPE, Angew. Chem. (Internat. Ed.) 19, 489 (1980).

8. H. HOLLER, Diplomarbeit, University of Marburg (1980).

9. D. BABEL, H. HOLLER, A. DE KOZAK, AND M. SAMOUËL, Paper presented at the 7th European Symposium on Flourine Chemistry, September 15–19, Venice (1980).

10. J. PEBLER, K. SCHMIDT, D. BABEL, AND W. VERSCHAREN, Z. Naturforsch. B 32, 369 (1977).

11. U. MÜLLER, W. MASSA, AND R. SCHMIDT, STRUX, Program system for handling diffractometer data, Marburg, (1979).

12. R. SCHMIDT, ABSCOR, Program for generating absorption corrected data, Marburg (1979).

13. G. M. SHELDRICK, SHELX - 76, Program for crystal structure determination, Cambridge (1976).

14. D. T. CROMER AND J. B. MANN, Acta Crystallogr. A 24, 321 (1968).

15. "International Tables for X-Ray Crystallography," Vol. I. Kynoch Press, Birmingham (1969).

16. W. H. ZACHARIASEN, Acta Crystallogr. 16, 1139 (1963).

17. W. H. BAUR, Acta Crystallogr. 11, 488 (1958).

18. D. BABEL, F. WALL, AND G. HEGER, Z. Naturforsch. B 29, 139 (1974).

19. M. VLASSE, G. MATEJKA, A. TRESSAUD, AND B. M. WANKLYN, Acta Crystallogr. B 33, 3377 (1977).

20. W. MASSA AND D. BABEL, Z. Anorg. Allg. Chem. 469, 75 (1980).

21. R. VON DER MÜHLL, F. DAUTH, AND J. RAVEZ, J. Solid State Chem. 8, 206 (1973).

22. R. DOMESLE AND R. HOPPE, Rev. Chim. Miner. 15, 439 (1978).

23. D. BABEL, Z. Anorg. Allg. Chem. 406, 23 (1974).