

## Structure Determination of NaPbFe<sub>2</sub>F<sub>9</sub> by X-Ray Powder Diffraction

A. LE BAIL

*Laboratoire des Fluorures, UA CNRS 449, Faculté des Sciences,  
Université du Maine, 72017 Le Mans Cedex, France*

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The crystal structure of NaPbFe<sub>2</sub>F<sub>9</sub>, prepared by recrystallization of a glass was solved using X-ray powder diffraction data. The cell is monoclinic (space group *C2/c*, *Z* = 4) with *a* = 7.308(3), *b* = 12.559(5), *c* = 7.640(3) Å, and  $\beta = 93.06(2)^\circ$ . Initial positional parameters for Pb and Fe were obtained from direct methods applied to 445 reflections which were derived using the pattern decomposition method. The structure was refined using the Rietveld method. The final reliability factors (%) are  $R_1 = 5.1$ ,  $R_p = 8.2$ , and  $R_{wp} = 9.2$ . The structure is compared with Fe<sub>3</sub>F<sub>8</sub>·2H<sub>2</sub>O presenting shifted hexagonal tungsten bronze layers. © 1989 Academic Press, Inc.

### Introduction

In the course of the study of recrystallization processes of glasses in the NaF–PbF<sub>2</sub>–FeF<sub>3</sub> system (1), an unknown phase was isolated with the formulation NaPbFe<sub>2</sub>F<sub>9</sub>. Structural determinations were recently performed on numerous ennefluorides possessing the same general formula A<sub>2</sub>M<sub>2</sub>F<sub>9</sub>, that is to say: Ba<sub>2</sub>M<sup>II</sup>M<sup>III</sup>F<sub>9</sub> (*M*<sup>II</sup> = Fe, Co, Ni, Zn and *M*<sup>III</sup> = V, Cr, Fe) (2, 3); KPbCr<sub>2</sub>F<sub>9</sub> (4), A<sup>I</sup>BaM<sup>III</sup><sub>2</sub>F<sub>9</sub> (*A*<sup>I</sup> = Na, K and *M*<sup>III</sup> = V, Fe, Ga, Cr) (5, 6); and Ba<sub>2</sub>ZnAlF<sub>9</sub> (7). As in K<sub>2</sub>Ta<sub>2</sub>O<sub>3</sub>F<sub>6</sub> (8, 9), their structure is built from isolated double *cis* chains of octahedra but major differences concerning the arrangement of the mono- and divalent cations inserted between the chains were observed and discussed in (6). When such double chains encounter couples of inserted cations like KBa, KPb, and NaBa, the structure of NaPbFe<sub>2</sub>F<sub>9</sub> becomes interesting because it presents the association of those possessing the smallest radii. In fact,

it was rapidly clear that this new phase was not related to the other ennefluorides. Due to the lack of single crystals, the structure was entirely determined from the X-ray powder pattern.

### Experimental

The glass was obtained by heating the anhydrous fluoride mixture in the stoichiometric ratios NaF : PbF<sub>2</sub> : 2FeF<sub>3</sub> at 700°C in a dry box in an inert atmosphere. The melt, in a covered platinum crucible, was cast and rolled in a bronze mold heated at 200°C. Glass transition at  $T_g = 252 \pm 5^\circ\text{C}$ , crystallization at  $T_c = 307 \pm 5^\circ\text{C}$ , and melting at  $T_m = 563 \pm 5^\circ\text{C}$  were determined by DTA measurements. The NaPbFe<sub>2</sub>F<sub>9</sub> crystallized phase is obtained when the glass is heated between  $T_c$  and 450°C (10°C/min) and then quenched in air. The rapidity of the preparation seems to prevent the formation of high proportions of other phases which are always present when direct syn-

theses are attempted:  $\text{Na}_5\text{Fe}_3\text{F}_{14}$  (10),  $\text{Pb}_5\text{Fe}_3\text{F}_{19}$  (11), and another phase which was indexed in the monoclinic system with  $a = 16.389(3)$ ,  $b = 11.184(2)$ ,  $c = 7.583(1)$ ,  $\beta = 102.07(9)$  (spacegroup  $C2/m$ ) which could be isotypic with  $\text{Ba}_7\text{CuFe}_6\text{F}_{34}$  (12).

It was not possible to obtain single crystals; the X-ray powder diffractogram used for the structure determination was recorded on a Siemens diffractometer (back-monochromatized  $\text{CuK}\alpha$ ). The sample retained for analysis was recrystallized from the glass at  $450^\circ\text{C}$ . Preparations obtained at lower temperatures showed reflections with significantly larger linewidths. Impurities remaining in the sample (principally  $\text{Na}_5\text{Fe}_3\text{F}_{14}$ ) were estimated to be less than 3%.

### Data Analysis

Indexing of the powder pattern was obtained using the program DICVOL (13, 14). A probable solution was proposed in the monoclinic system; the systematic extinctions are consistent with space groups  $C2/c$  and  $Cc$ . The lattice parameters are  $a = 7.308(3)$ ,  $b = 12.559(5)$ ,  $c = 7.640(3)$  Å, and  $\beta = 93.06(2)^\circ$ . The calculated density for  $Z = 4$  is  $4.866 \text{ g cm}^{-3}$ .

Individual intensities were then extracted from the powder pattern by a profile fitting procedure which does not require a structural model but constrains the angular position of the reflections to be consistent with the cell parameters (15). Conventional Rietveld profile reliability factors were  $R_p = 5.6$  (%) and  $R_{wp} = 6.5$  (%) for 445 reflections up to  $110^\circ 2\theta$ .

Intensities were converted into structure factors and used as input data for the program SHELX (16). Lead and iron atoms were localized by using the direct methods (option TANG of SHELX) and Fourier synthesis. Scattering factors for  $\text{Pb}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Na}^+$ , and  $\text{F}^-$  were taken from the "International Tables of Crystallography" (17). Refinement of the metal coordinates led to an

agreement factor  $R = 0.26$ . Fluorine and sodium were then located on a difference Fourier map. The  $R$  factor dropped to 0.10 after refinement of all atomic coordinates and isotropic thermal parameters (with the constraint that all  $\text{F}^-$  would have the same  $B$  value). The Fourier difference map revealed a large positive peak on the sodium site.

At this stage, we went back to the Rietveld method applied with this structural model. This was necessary because some of the intensities previously obtained were dubious as a consequence of very near overlapping with others. Conventional Rietveld reliability factors were  $R_1 = 9.2$  (%),  $R_p = 13.4$  (%), and  $R_{wp} = 14.7$  (%); the Fourier difference map confirmed the large positive peak on the sodium site, isotropic thermal agitations were found to be abnormally large for  $\text{Pb}^{2+}$  and negative for  $\text{Na}^+$ . This suggested that there was some degree of mixing of sodium and lead atoms in the

TABLE I  
STRUCTURE AND PROFILE PARAMETERS FOR  
 $\text{NaPbFe}_2\text{F}_9$  (SD IN PARENTHESES)

Atom	Site	x	y	z	$B(\text{Å}^2)$
$\text{Na}_{0.9}\text{Pb}_{0.1}$	4c	$\frac{1}{4}$	$\frac{1}{4}$	0	5.4(3)
$\text{Pb}_{0.9}\text{Na}_{0.1}$	4e	0	0.0275(1)	$\frac{1}{4}$	1.3(1)
Fe(1)	4d	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	1.0(1)
Fe(2)	4b	0	$\frac{1}{2}$	0	1.6(1)
F(1)	8f	0.256(1)	0.0409(9)	0.976(1)	2.2(1)
F(2)	8f	0.207(2)	0.1937(7)	0.280(1)	2.2(1)
F(3)	8f	0.082(1)	0.1527(8)	0.578(1)	2.2(1)
F(4)	8f	0.039(1)	0.3453(8)	0.463(1)	2.2(1)
F(5)	4e	0	0.527(1)	$\frac{1}{4}$	2.2(1)

Cell parameters (Å):  $a = 7.308(3)$ ,  $b = 12.559(5)$ ,  
 $c = 7.640(3)$ ,  $\beta = 93.06(2)$

Volume (Å<sup>3</sup>): 700.21

$2\theta$  range ( $^\circ$ ): 10–110

Step scan ( $^\circ 2\theta$ ): 0.04

No. of reflections: 445

No. of structural parameters: 20

No. of profile parameters: 14

Zero point ( $^\circ 2\theta$ ): 0.097(5)

Profile parameters (See Ref. (15)):  $U1 = 0.88(6)$ ,

$V1 = -0.66(5)$ ,  $W1 = 0.23(1)$ ,  $U2 = -1.1(1)$ ,

$V2 = 1.1(1)$ ,  $W2 = 1.09(3)$ ,  $C = -0.089(3)$ ,  $D = -0.27(1)$

Reliability factors (%):  $R_1 = 5.1$ ,  $R_p = 8.2$ ,  $R_{wp} = 9.2$ ,

$R_e = 2.4$

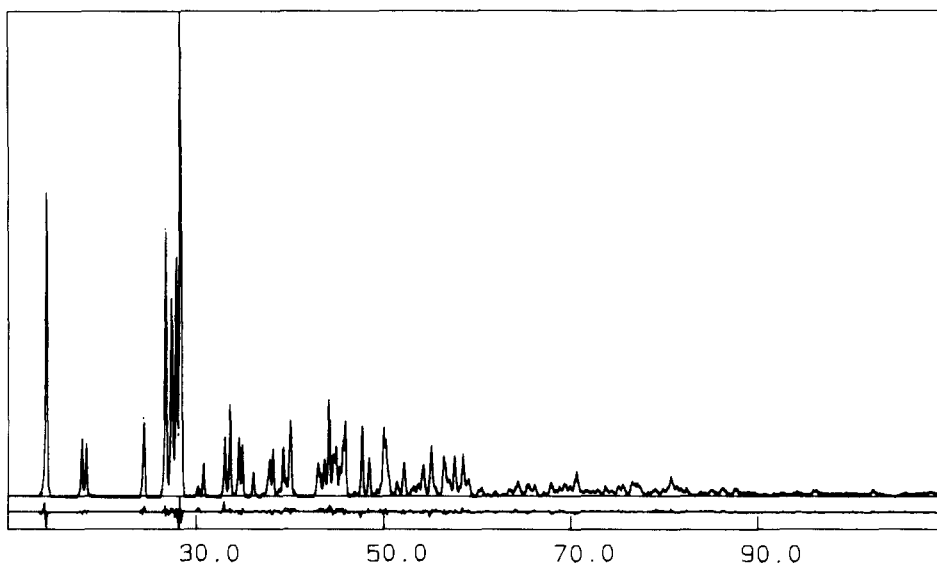


FIG. 1. Observed (···) and calculated (—) X-ray powder pattern. The difference pattern appears below at the same scale.

two sites. Further refinement in this sense led to a significant drop in the agreement factors:  $R_1 = 5.1(\%)$ ,  $R_p = 8.2(\%)$ , and  $R_{wp} = 9.2(\%)$ , the degree of disorder being  $10.1(1)\%$ . Trying in the  $Cc$  space group did not improve these results. The final positional and thermal parameters are given in Table I. Bond distances are reported in Table II and the observed and calculated patterns are represented on Fig. 1.

### Description of the Structure and Discussion

A (001) projection of the structure of NaPbFe<sub>2</sub>F<sub>9</sub> is shown in Fig. 2. The framework structure is formed by 3D corner sharing of octahedra. Infinite chains run parallel to the  $c$  axis (Fe(2) only) and along the  $[110]$  and  $[\bar{1}\bar{1}0]$  directions (alternating Fe(1) and Fe(2)). Bridging fluorines are always in *trans* position. The octahedra exhibit strong distortions in angles and distances, one having two and the other four terminal ligands (respectively Fe(1) and Fe(2)); such

a situation is encountered in Na<sub>5</sub>Fe<sub>3</sub>F<sub>14</sub> (10)). The fluorine atoms surrounding Na lie at the corners of a distorted flattened hexagonal bipyramid where the apical distances are 2.29 Å and the remaining ones are longer than 2.45 Å; such a polyhedron is encountered for one of the two independent Na atoms in the orthorhombic weberite

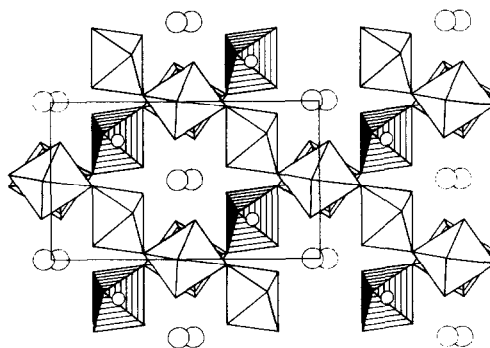


FIG. 2. (001) projection of the structure of NaPbFe<sub>2</sub>F<sub>9</sub>. Octahedra at  $z = 0$  are hatched, those at  $z = \frac{1}{2}$  are not. Na<sup>+</sup> and Pb<sup>2+</sup> ions are represented respectively by small and large circles.

TABLE II  
DISTANCES (Å) AND ANGLES (°) IN NaPbFe<sub>2</sub>F<sub>9</sub> (SD IN PARENTHESES, \* INDICATES  
TERMINAL FLUORINE)

Fe(1) octahedral environment		
2 Fe(1)–F(2)*1.84(1)	F(3)–F(2) 2.67(1)	F(3)–Fe(1)–F(2) 92.5(7)
2 Fe(1)–F(3)*1.86(1)	–F(2) 2.55(1)	F(3)–Fe(1)–F(4) 94.7(9)
2 Fe(1)–F(4) 1.96(1)	–F(4) 2.81(1)	F(2)–Fe(1)–F(4) 90.6(7)
	–F(4) 2.59(1)	
	F(2)–F(4) 2.67(1)	
	–F(4) 2.70(1)	Fe(1)–F(4)–Fe(2) 134(1)
⟨Fe(1)–F⟩ 1.89	⟨F–F⟩ 2.65	
Fe(2) octahedral environment		
2 Fe(2)–F(1)*1.85(1)	F(1)–F(5) 2.68(1)	F(1)–Fe(2)–F(5) 90.1(6)
2 Fe(2)–F(5) 1.94(1)	–F(5) 2.69(1)	F(1)–Fe(2)–F(4) 98.1(8)
2 Fe(2)–F(4) 1.99(1)	–F(4) 2.52(1)	F(5)–Fe(2)–F(4) 91.6(7)
	–F(4) 2.90(1)	
	F(5)–F(4) 2.74(1)	
	–F(4) 2.82(1)	Fe(2)–F(5)–Fe(2) 159(1)
⟨Fe(2)–F⟩ 1.93	⟨F–F⟩ 2.73	
Na environment		Pb environment
2 Na–F(2) 2.29(1)		2 Pb–F(2) 2.58(1)
2 Na–F(4) 2.46(1)		2 Pb–F(1) 2.62(1)
2 Na–F(1) 2.63(1)		2 Pb–F(3) 2.70(1)
2 Na–F(3) 2.75(1)		2 Pb–F(1) 2.89(1)
		2 Pb–F(3) 2.99(1)
⟨Na–F⟩ 2.53		⟨Pb–F⟩ 2.76

structure (18) and also for three-fourths of the Na atoms in the trigonal weberites (19, 20). As for NaPbFe<sub>2</sub>F<sub>9</sub>, the Na atoms in the weberites show abnormally high tempera-

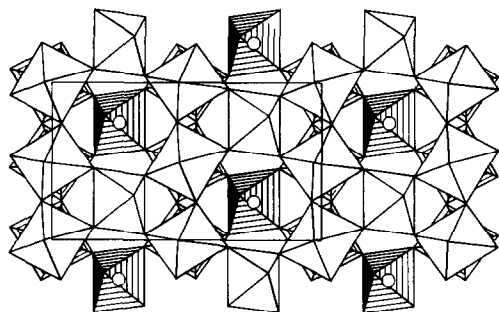


FIG. 3. The effect of replacing Pb<sup>2+</sup> by F<sup>-</sup> creates new octahedral sites (compare with Fig. 2); then the relation with hexagonal tungsten bronze layers become obvious.

ture factors. The coordination number of Pb<sup>2+</sup> may be considered as being 10, forming nearly a bicapped square antiprism. It may be remarked that F<sup>-</sup> and Pb<sup>2+</sup> reproduce the anionic packing observed in WO<sub>3</sub>,  $\frac{1}{3}$ H<sub>2</sub>O (21), or Fe<sub>3</sub>F<sub>8</sub>(H<sub>2</sub>O)<sub>2</sub> (22, 23) which may be described in terms of hexagonal tungsten bronze (HTB) layers alternatively shifted. Figure 3 illustrates this comparison, Pb<sup>2+</sup> has been replaced by F<sup>-</sup>, creating a new octahedral site; this hypothetical compound would have the formulation NaFe<sub>3</sub>F<sub>10</sub>.

A question arises about the possibility of statistical substitution between Na<sup>+</sup> and Pb<sup>2+</sup> ions, whose radii are rather different (1.18 and 1.29 Å, respectively, for eightfold coordination; Shannon values (24)). Structurally, the accommodation of lead in the so-

dium site appears possible by a simple rotation of the Fe(1)F<sub>6</sub> octahedra around the axis joining its two bridging fluorines F(4). Consequently, the F(2) fluorines corresponding to the two shortest Na–F bonds can substantially move more far from the sodium atoms; then the site becomes credible for the occupation by lead.

In order to obtain a better understanding of this new structure type, a magnetic characterization of NaPbFe<sub>2</sub>F<sub>9</sub> is intended. The two sites of iron offer opportunities to obtain isolated magnetic chains of corner linked octahedra, if ordered substitutions are possible with gallium or indium. Investigations are in progress.

## References

1. J. P. MIRANDAY, C. JACOBONI, AND R. DE PAPE, *Rev. Chem. Miner.* **16**, 277 (1979).
2. A. DE KOZAK AND M. SAMOUEL, *Rev. Chim. Miner.* **15**, 406 (1978).
3. A. DE KOZAK, M. LEBMANC, M. SAMOUEL, G. FERÉY, AND R. DE PAPE, *Rev. Chim. Miner.* **18**, 659 (1981).
4. M. VLASSE, J. P. CHAMINADE, J. M. DANCE, M. SAUX, AND P. HAGENMULLER, *J. Solid State Chem.* **41**, 272 (1982).
5. A. DE KOZAK, M. SAMOUEL, M. LEBLANC, AND G. FERÉY, *Rev. Chim. Miner.* **19**, 668 (1982).
6. G. FERÉY, M. LEBLANC, A. DE KOZAK, M. SAMOUEL, AND J. PANNETIER, *J. Solid State Chem.* **56**, 288 (1985).
7. T. FLEISCHER AND R. HOPPE, *Z. Anorg. Allg. Chem.* **492**, 83 (1982).
8. J. P. CHAMINADE, M. VLASSE, M. POUCHARD, AND P. HAGENMULLER, *Bull. Soc. Chem.* **9–10**, 1791 (1974).
9. M. VLASSE, J. P. CHAMINADE, AND M. POUCHARD, *Bull. Soc. Fr. Mineral. Cristallogr.* **99**, 3 (1976).
10. M. VLASSE, F. MENIL, C. MORILIERE, J. M. DANCE, A. TRESAUD, AND J. PORTIER, *J. Solid State Chem.* **17**, 291 (1976).
11. C. JACOBONI, A. LE BAIL, R. DE PAPE, AND J. P. RENARD, *Stud. Inorg. Chem.* **3**, 687 (1983).
12. J. RENAUDIN, G. FERÉY, A. DE KOZAK, AND M. SAMOUEL, *Rev. Chim. Miner.* **24**, 295 (1987).
13. D. LOUËR AND M. LOUËR, *J. Appl. Cryst.* **5**, 271 (1972).
14. D. LOUËR AND R. VARGAS, *J. Appl. Crystallogr.* **15**, 542 (1982).
15. A. LE BAIL, H. DUROY, AND J. L. FOURQUET, *Mat. Res. Bull.* **23**, 447 (1988).
16. G. M. SHELDRICK, "SHELX 76 Program for Crystal Structure Determination," University of Cambridge, England (1976).
17. "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham (Present distributor: Reidel, Dordrecht) (1974).
18. G. GIUSEPETTE AND C. TADINI, *Tschermarks Min. Petr. Mitt.* **25**, 57 (1978).
19. W. VERSCHAREN AND D. BABEL, *J. Solid State Chem.* **24**, 405 (1978).
20. G. COURBION, G. FERÉY, H. HOLLER, AND D. BABEL, *Eur. J. Solid State Inorg. Chem.* **25**, 435 (1988).
21. B. GERAND, G. NOWOGROCKI, AND M. FIGLARZ, *J. Solid State Chem.* **38**, 312 (1981).
22. E. HERDTWECK, *Z. Anorg. Allg. Chem.* **501**(6), 131 (1983).
23. M. LEBLANC, G. FERÉY, Y. CALAGE, AND R. DE PAPE, *J. Solid State Chem.* **53**, 360 (1984).
24. R. D. SHANNON, *Acta Crystallogr. A* **32**, 751 (1976).