Complex Copper(II) Fluorides

III. Crystal Structure of $Ba_2CuV_2F_{12}$: A New Bidimensional MX_4 Network[1]

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$Ba_2CuV_2F_{12}$ is triclinic (S.G.: $P\bar{1}$): $a = 5.365(1)$ Å, $b = 6.950(1)$ Å, $c = 7.433(1)$ Å, $\alpha = 65.05(1)°$, $\beta = 70.26(2)°$, $\gamma = 73.19(2)°$, $Z = 1$. The structure is refined from 1623 independent reflections using the SHELX program to $R = 0.0327$ ($R_w = 0.0331$). The network is built from layers of edge-sharing bioctahedral units $[CuVF_{10}]$ linked by single VF_6 octahedra. Cu and V are randomly distributed within the bioctahedral units. The Ba^{2+} ions are inserted between these layers and adopt a 12-fold coordination. © 1986 Academic Press, Inc.

Introduction

We recently described the crystal structure of $BaCuFeF_7$ (2) which is one of the very rare $3d$ transition metals fluorides whose structure is built from edge-sharing octahedra. The other compounds which exhibit this peculiarity are $Ba_6Zn_7F_{26}$ (3), $Ba_2Ni_3F_{10}$ (4), $BaMnFeF_7$ (5), H.T. BaZnFe F_7 (6), and $AM^{II}M^{III}F_6$ with A = Li, Na, NH_4^+; M = $3d$ metal (7–9). Some of these compounds are interesting from a magnetic point of view since they allow one to understand the mechanism of superexchange which arises when the M–F–M angles are close to 90°. Among all the possibilities of 90° magnetic coupling between M^{2+} and M^{3+} ions, the couple d^2–d^9 (V^{3+}–Cu^{2+}) is particularly interesting and we tried to syn-

thetize $BaCuVF_7$. Despite several trials under various conditions, we could not isolate such a composition. The systematic study of the ternary diagram BaF_2–CuF_2–VF_3 (10) shows the absence of $BaCuVF_7$ but indicates the existence of $Ba_2CuV_2F_{12}$. We report here its crystal structure which corresponds to a new structural type built from a MX_4 skeleton. We also synthetized the isostructural compounds $Ba_2CuAl_2F_{12}$ ($a = 5.137(2)$ Å, $b = 6.817(2)$ Å, $c = 7.363(3)$ Å, $\alpha = 64.64(3)°$, $\beta = 70.84(3)°$, $\gamma = 72.89(3)°$) and $Ba_2CuGa_2F_{12}$ ($a = 5.285(2)$ Å, $b = 6.867(2)$ Å, $c = 7.393(2)$ Å, $\alpha = 64.79(2)°$, $\beta = 70.51(2)°$, $\gamma = 73.23(2)°$).

Experimental

Pale green shapeless crystals of $Ba_2 CuV_2F_{12}$ were obtained in platinum tubes sealed under argon from a mixture $2CuF_2$–

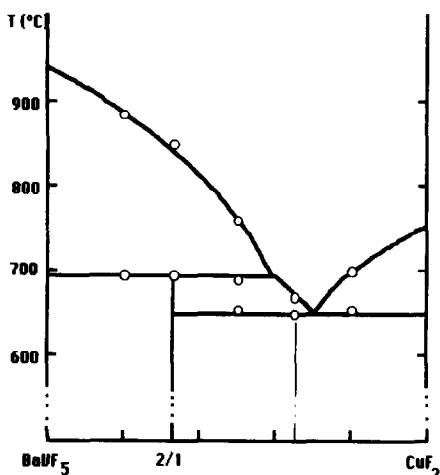[1] For parts I and II, see Refs. (1, 2).

FIG. 1. Pseudobinary phase diagram BaVF$_5$–CuF$_2$.

1BaF$_2$–1VF$_3$ melted at 655°C and cooled at 120°C/hr. This starting mixture was chosen after considering the pseudobinary phase diagram which appear in Fig. 1. Laue and precession photographs show that the symmetry is triclinic. The intensity data were collected on a CAD4 Nonius diffractometer. The experimental conditions and crystallographic characteristics are summarized in Table I.

Corrections for Lorentz and polarization effects were applied using the SHELX program (11) without any correction for absorption, owing to the small dimensions of the crystal. Atomic scattering factors were taken from the "International Tables for X-Ray Crystallography" (12) for Ba^{2+}, Cu^{2+}, V^{3+}, and F$^-$ ions. Anomal dispersion corrections were applied.

Structure Determination

The structure was solved from a Patterson map calculated in the $P1$ space group according to Abrahams' method (13). Two barium ions were located and their atomic coordinates were refined to a reliability factor: $R = 0.55$. A Fourier map then revealed the positions of the $3d$ cations which

showed a symmetry center. After applying the corresponding translation, the coordinates of the cations were refined to $R = 0.41$ in the $P\bar{1}$ group. At this stage of the refinement, it was impossible to identify the chemical nature of the two different metallic sites ($1h$) and ($2i$). The F$^-$ ions were then located from a new Fourier synthesis. The refinement of all the atomic parameters and isotropic temperature factors easily converged to $R = 0.085$ ($R_w = 0.094$). The residual falls to $R = 0.0327$ ($R_w = 0.0331$) by applying anisotropic thermal motion and a secondary extinction factor of 2.04 × 10^{-7} if V^{3+} is placed in $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The location of Cu^{2+} at these coordinates leads to $R = 0.060$ ($R_w = 0.069$). This implies that the general position ($2i$) for $3d$ metallic ions is occupied by 1Cu^{2+} + 1V^{3+}. A strict cationic order in the

TABLE I

EXPERIMENTAL DATA FOR A Ba$_2$CuV$_2$F$_{12}$ CRYSTAL

Symmetry: triclinic ($P\bar{1}$)
Cell parameters:

$a = 5.365(1)$ Å; $b = 6.950(1)$ Å; $c = 7.433(1)$ Å;
$\alpha = 65.05(1)°$; $\beta = 70.26(2)°$; $\gamma = 73.19(2)°$
$V = 233.02$Å^3 – $Z = 1$ – $M = 668.1$ g mole^{-1}
$D_{exp} = 4.65(7)$ g cm^{-3} – $D_{calc} = 4.76$ g cm^{-3}

Crystal dimensions: shapeless (mean length:
   0.045 mm)
Operating features:
   Radiation: Mo ($\lambda = 0.71069$)
   Monochromator: graphite
   Scan mode: ω Sweep: 0.9 + 0.4 tg(2θ)°
   Scanning speed: (20.1166/NV)° mn^{-1} with NV
      integer
Linear absorption coefficient: 126 cm^{-1} (MoK_α)
Range measured: 1.5° < θ < 35°

   $-8 \le h \le 8$; $-11 \le k \le 11$; $0 \le l \le 12$

Number of reflections:

   total = 1726
   independent = 1623

Number of refined parameters: 80
Secondary extinction: 2.04(8) × 10^{-7}
Residual peak height in the final difference F map:

   max = 4.1 e · Å^{-3}
   min = −2.8 e · Å^{-3}

TABLE II

ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS[a]

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq} (Å²)
Ba	0.7075(1)	0.7968(1)	0.7641(1)	170(1)	141(1)	164(1)	−87(1)	−20(1)	−24(1)	0.98
V	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	96(3)	84(3)	113(3)	−46(3)	−28(3)	−6(2)	0.61
Cu/V	0.0522(1)	0.7753(1)	0.1679(1)	116(2)	89(2)	101(2)	−43(2)	−27(2)	3(2)	0.67
F 1	0.1730(6)	0.6542(4)	0.9626(4)	289(14)	197(11)	170(11)	−109(10)	−52(10)	−39(10)	1.33
F 2	0.4649(5)	0.7813(4)	0.4946(4)	222(12)	91(9)	213(12)	−63(9)	−88(10)	2(8)	1.09
F 3	0.1236(5)	0.4870(4)	0.6513(4)	147(10)	175(11)	183(12)	−61(9)	−29(9)	−13(9)	1.12
F 4	0.0224(5)	0.0950(4)	0.6419(4)	199(11)	172(10)	121(10)	−81(8)	1(8)	−46(9)	1.05
F 5	0.2517(6)	0.0363(5)	0.9542(5)	162(11)	404(17)	248(14)	−200(13)	−79(10)	38(10)	1.61
F 6	0.6039(5)	0.3894(5)	0.7616(4)	159(10)	202(11)	134(10)	−69(9)	−45(8)	47(9)	1.14

[a] The vibrational coefficients are relative to the expression: $T = \exp(-2\pi^2(h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2klb^* c^* U_{23} + 2hla^* c^* U_{13} + 2hka^* b^* U_{12}))$ with standard deviations in parentheses and U_{ij} values $\times 10^4$.

structure would require a splitting of the (2i) position in two distinct sites, i.e., the use of the noncentric space group: $P1$. Several attempts to refine the structure in this

TABLE III

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN $Ba_2CuV_2F_{12}$

Barium polyhedron

Ba–F 4: 2.716(3)	Ba–F 4: 2.745(3)	
Ba–F 2: 2.783(3)	Ba–F 3: 2.793(3)	
Ba–F 2: 2.833(3)	Ba–F 5: 2.836(4)	
Ba–F 5: 2.878(4)	Ba–F 1: 2.951(3)	
Ba–F 1: 2.989(3)	Ba–F 1: 3.037(3)	
Ba–F 6: 3.048(3)	Ba–F 6: 3.212(3)	
⟨Ba–F⟩ 2.90(14)		

Single V octahedron

		Angle at V
V–F2$_t$: 2 × 1.894(2)	F2–F6: 2 × 2.679(3)	87.6(1)
V–F3$_b$: 2 × 1.959(3)	F2–F3: 2 × 2.690(3)	88.5(1)
V–F6$_b$: 2 × 1.976(3)	F2–F3: 2 × 2.759(4)	91.4(1)
	F3–F6: 2 × 2.779(4)	89.8(1)
⟨V – F⟩ 1.943(35)	F3–F6: 2 × 2.787(4)	90.1(1)
	F2–F6: 2 × 2.794(3)	92.4(1)

Bioctahedral CuV unit

		Angle at M
M–F4$_t$: 1.859(3)	F1–F6: 2.579(4)	83.7(1)
M–F1$_t$: 1.886(3)	F1–F3: 2.678(4)	86.4(1)
M–F6$_b$: 1.978(3)	F5–F5: 2.696(6)	81.9(2)
M–F5$_b$: 1.990(4)	F4–F5: 2.737(7)	93.8(3)
M–F3$_b$: 2.022(3)	F1–F5: 2.745(4)	87.6(2)
M–F5$_b$: 2.122(4)	F4–F6: 2.747(4)	91.4(1)
	F1–F5: 2.779(5)	90.1(2)
⟨M–F⟩ 1.976(87)	F4–F5: 2.812(6)	86.6(2)
	F3–F6: 2.826(5)	89.9(1)
F1–M–F4: 172.4(3)°	F5–F6: 2.885(9)	89.3(2)
F3–M–F5: 174.0(5)°	F3–F4: 2.960(8)	99.3(2)
F5–M–F6: 169.5(5)°	F3–F5: 3.034(9)	98.3(3)
M–F5–M: 98.1(3)°		

Intermetallic distances

V–M: 3.590(1)
M–M: 3.107(1)

group lead to slightly better reliability factors ($R = 0.029$, $R_w = 0.030$) which are the same for the two cationic distributions (Cu: positive coordinates and V: negative coordinates or vice versa); however, in each case, some thermal ellipsoids are nonpositive definite. Therefore the crystal structure will be described in the $P\bar{1}$ centrosymmetric space group. It is noteworthy that the residual peaks in the final Fourier difference map are all close to the barium ions and are negligible around Cu and V positions. Table II presents the final results for the nine independent positions and the interatomic distances are listed in Table III. The indexed X-ray powder spectrum is reported in Table IV. The list of structure factors may be obtained on request to one of the authors (G.F.).

Discussion of the Structure

$Ba_2CuV_2F_{12}$ adopts an original layered structure. The layers lying in the (101) planes, can be described by a new arrangement of octahedra in the crystal chemistry of fluorides: edge-sharing bioctahedral $CuVF_{10}$ units appear inside which Cu^{2+} and V^{3+} ions are randomly distributed (Fig. 2). VF_6 single octahedra share their equatorial
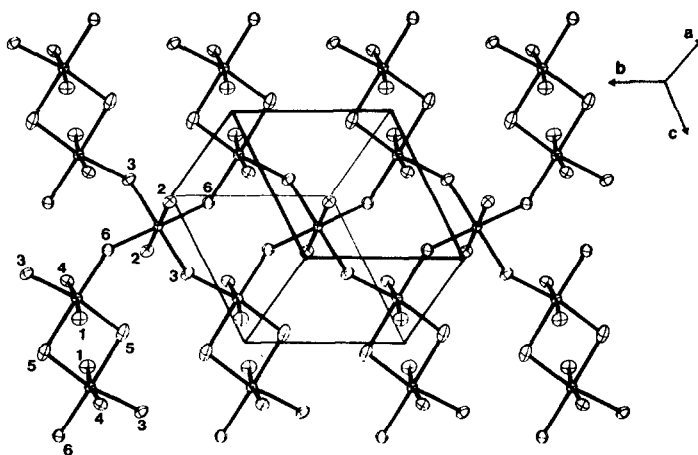
FIG. 2. Perspective view of the structure of $Ba_2CuV_2F_{12}$ showing one MX_4 layer. The numbers indicate the type of fluorine (see Table II).

fluorine with four bioctahedra and form a plane with the composition M_3F_{12} (or MF_4); this geometry was hitherto unknown for such a composition in fluorides of low dimensionality. The previously described octahedral networks were either built from perovskite-like planes like in K_2NiF_4 (*14*) or $AFeF_4$ with A = K (*15*), Rb (*16*), Cs (*17*), NH_4 (*18*); corrugated planes of corner-sharing octahedra as in $NaFeF_4$ (*19*) and $NaCrF_4$ (*20*) or in $BaMF_4$ with M = Mn (*21*), Cu (*22*); tetragonal bronze layers like in β-$RbAlF_4$ (*23*); or columns of triangular cycles of octahedra like in $KCrF_4$ (*24*) and $CsMF_4$ with M = Cr (*25*), Al (*26, 27*).

This new geometry is intermediate between that of perovskite-like planes and of planes built exclusively from bioctahedral units like in H.T. $BaZnFeF_7$ (*6*) or BaCu FeF_7 (*2*). Therefore it can be ideally described as resulting from a periodic $\frac{1}{2}$ $\vec{n}_{[110]}$ crystallographic shear along ($\bar{1}10$) planes of the ReO_3 structure (Fig. 3). The layers are stacked as indicated in the Fig. 4. This implies that each octahedron has four bridging

(a)   (b)

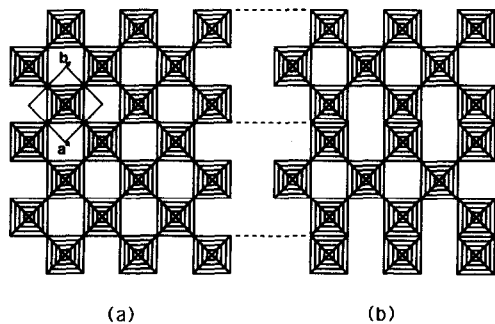FIG. 3. A layer of the ReO_3 structure before (a) and after (b) the crystallographic shear which describes the structure of $Ba_2CuV_2F_{12}$.
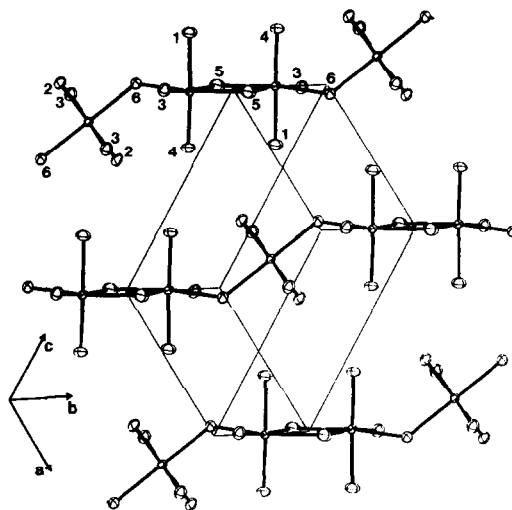

FIG. 4. Stacking of three consecutive MX_4 layers in $Ba_2CuV_2F_{12}$; barium ions inserted between the planes are not indicated.

TABLE IV

INDEXATION OF THE X-RAY POWDER PATTERN (CuK_α)

| h	k	l	θ	D_{calc}	D_{obs}	I_{calc}
0	0	1	6.77	6.5366	a	1
0	1	0	7.13	6.2076	a	2
0	1	1	7.87	5.6234	5.625	2
1	1	1	9.47	4.6825	a	3
1	0	1	9.77	4.5396	4.545	28
1	1	0	10.43	4.2553	4.255	12
0	1	-1	11.51	3.8608	3.860	28
1	-1	0	12.38	3.5922	3.590	36
1	0	-1	12.51	3.5555	3.551	100
1	1	2	12.81	3.4753		81
0	1	2	12.91	3.4482	3.460	2
0	2	1	13.49	3.3015	3.300	26
0	0	2	13.63	3.2683	3.267	27
1	2	1	13.70	3.2514	3.251	41
1	-1	-1	13.99	3.1869	3.183	15
1	-1	1	14.34	3.1107		42
1	0	2	14.34	3.1091	3.108	7
0	2	0	14.37	3.1038		27
1	1	-1	14.92	2.9927	2.990	6
1	2	2	15.08	2.9611	2.963	11
1	2	0	15.60	2.8636	2.864	22
0	2	2	15.90	2.8117	2.812	29
2	1	1	16.78	2.6687	2.666	49
0	1	-2	17.66	2.5397	2.536	3
2	0	0	18.04	2.4873	a	1
2	1	0	18.25	2.4594		2
1	-1	-2	18.30	2.4527	2.455	6
1	-2	0	18.32	2.4508		7
1	-2	-1	18.50	2.4274	2.428	5
1	-1	2	18.85	2.3837	2.382	17
2	2	1	18.98	2.3685	a	1
1	2	3	19.09	2.3549	a	2
2	2	2	19.21	2.3413	2.340	23
0	1	3	19.26	2.3351		11
2	0	2	19.84	2.2698	a	3
1	2	-1	19.94	2.2582		54
1	3	2	20.00	2.2518	2.253	3
0	3	1	20.35	2.2153	a	14
1	0	3	20.42	2.2077	2.206	30
0	2	3	20.57	2.1924	2.192	36
2	-1	0	20.66	2.1829		13
1	-2	1	20.67	2.1818	2.180	3
0	0	3	20.70	2.1789		4
1	1	-2	20.92	2.1572		5
2	0	-1	20.96	2.1535	2.155	15
1	-2	-2	21.17	2.1332		5
2	-1	1	21.20	2.1300		32
0	3	2	21.22	2.1282	2.130	2
2	2	0	21.23	2.1276		7
2	1	3	21.73	2.0805	2.080	9
0	3	0	21.86	2.0692	2.069	13
2	1	-1	22.03	2.0539	2.052	6
1	3	0	22.20	2.0388	2.038	3
1	3	3	22.45	2.0173		9
2	-1	-1	22.47	2.0157	2.016	9
2	3	2	22.86	1.9824	a	4

^{a} Unobserved reflections.
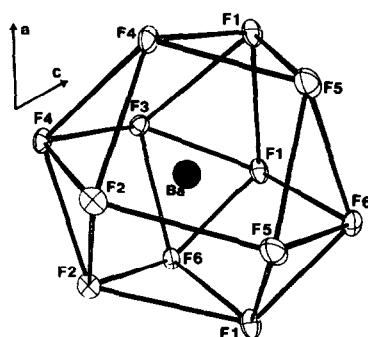
FIG. 5. (010) projection showing the hexagonal close packing of fluorine atoms around barium ions.

(F_b) and two terminal (F_t) fluorine atoms. As previously noticed (28), M–F_t distances are smaller than M–F_b ones (Table III). In the VF_6 octahedron, the mean distance is close to the sum of the ionic radii (29). The random distribution of Cu and V inside the bioctahedral units prevents from drawing any conclusion about distances.

Barium ions are inserted between the layers. They are 12-coordinated, their coordination polyhedron being of the hexagonal close-packed type (Fig. 5). The average value of Ba–F distances (2.902 Å) is very close to the sum of the ionic radii of $^{XII}Ba^{2+}$ (1.61 Å) and $^{II}F^-$ (1.285 Å). Using these values, the packing fraction is 0.608. The antiferromagnetic behavior of this compound ($T_N \approx 12$ K) is presently under investigation.

Acknowledgments

References

1. M. SAMOUËL, A. DE KOZAK, J. RENAUDIN, M. LEBLANC, AND G. FEREY, Rev. Chim. Min. 22, 64 (1985).

2. J. RENAUDIN, Y. CALAGE, M. SAMOUËL, A. DE KOZAK, M. LEBLANC, AND G. FEREY, *Rev. Chim. Min.* **22**, 74 (1985).

3. J. RENAUDIN, M. SAMOUËL, M. LEBLANC, A. DE KOZAK, AND G. FEREY, *J. Solid State Chem.* **59**, 103 (1985).

4. M. LEBLANC, G. FEREY, AND R. DE PAPE, *J. Solid State Chem.* **33**, 317 (1980).

5. H. HOLLER, D. BABEL, M. SAMOUËL, AND A. DE KOZAK, *J. Solid State Chem.* **39**, 345 (1981).

6. H. HOLLER AND D. BABEL, *Z. Anorg. Allgem. Chem.* **491**, 137 (1982).

7. G. COURBION, C. JACOBONI, AND R. DE PAPE, *J. Solid State Chem.* **45**, 127 (1982).

8. M. LEBLANC, G. FEREY, Y. CALAGE, AND R. DE PAPE, *J. Solid State Chem.* **47**, 24 (1983).

9. N. N. GREENWOOD, A. T. HOWE, AND F. MENIL, *J. Chem. Soc. A* 2218 (1971).

10. M. SAMOUËL AND A. DE KOZAK, *Rev. Chim. Min.,* in press.

11. G. M. SHELDRICK, "SHELX: A Program for Crystal Structure Determination," Cambridge (1976).

12. "International Tables for X-Ray Crystallography," Vol. IV, Birmingham (1974).

13. S. C. ABRAHAMS, *J. Chem. Phys.* **46**(6), 2052 (1967).

14. D. BALZ AND K. PLEITH, *Z. Electrochem.* **59**, 545 (1955).

15. G. HEGER, R. GELLER, AND D. BABEL, *Solid State Commun.* **9**, 335 (1971).

16. A. TRESSAUD, J. GALY, AND J. PORTIER, *Bull. Soc. Fr. Minér. Cristall.* **92**, 335 (1969).

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

18. M. LEBLANC, G. FEREY, AND R. DE PAPE, *Acta Crystallogr. C* **41**, 657 (1985).

19. J. M. DANCE, A. TRESSAUD, W. MASSA, AND D. BABEL, *J. Chem. Research S,* 202 (1981).

20. G. KNOKE, W. VERSCHAEREN, AND D. BABEL, *J. Chem. Research S* **213**, 2579 (1979).

21. E. T. KEVE, S. C. ABRAHAMS, AND J. L. BERNSTEIN, *J. Chem. Phys.* **51**, 4928 (1969).

22. H. G. VON SCHNERING, B. KOLLOCH, AND A. KOLODZIEJCZYK, *Angew. Chem.* **12**, 440 (1971).

23. J. L. FOURQUET, F. PLET, AND R. DE PAPE, *Acta Crystallogr. B* **36**, 1997 (1980).

24. J. C. DEWAN AND A. J. EDWARDS, *J. Chem. Soc. Chem. Commun.* **15**, 533 (1977).

25. D. BABEL AND G. KNOKE, *Z. Anorg. Allg. Chem.* **442**, 151 (1978).

26. R. LOSCH AND C. H. HEBECKER, *Z. Naturforsch. B* **34**, 131 (1979).

27. J. L. FOURQUET, F. PLET, G. COURBION, A. BULOU AND R. DE PAPE, *Rev. Chim. Min.* **16**, 490 (1979).

28. G. FEREY, M. LEBLANC, A. DE KOZAK, M. SAMOUËL, J. PANNETIER, *J. Solid State Chem.* **56**, 288 (1985).

29. R. D. SHANNON, *Acta Crystallogr. A* **32**, 751 (1976).