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Crystal Chemistry of Anion-excess ReO_3-Related Phases: Crystal Structure of β-$PrZr_3F_{15}$

J. P. LAVAL* AND A. ABAOUZ

URA CNRS no. 320, Céramiques Nouvelles, Université de Limoges,
123 Avenue A Thomas, 87060 Limoges Cedex, France

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β-$PrZr_3F_{15}$, a new low temperature (<800°C) variety in the MZr_3F_{15} series, crystallizes in the rhombohedral, noncentrosymmetrical $R3m$ space group, with the hexagonal parameters a = 12.316(8), c = 6.115(4) Å (Z = 3). The crystal structure was solved on the basis of single crystal data (R = 0.033). It is derived from the ReO_3 type by a structural mechanism, thoroughly described, involving full cationic ordering and ordered insertion of excess anions, transforming the MX_6 octahedra respectively into corner-shared $[ZrF_7]^{3-}$ pentagonal bipyramids and $[PrF_9]^{6-}$ tricapped trigonal prisms. β-$PrZr_3F_{15}$ can thus be considered as a new member of the structural family of anion-excess ReO_3-related phases such as $SmZrF_7$, $Zr(O,F)_{3+x}$, β-$BaZr_2F_{10}$, $Bi(Y)Zr_3F_{15}$, and cubic $(Zr,M)F_{3+x}$ phases.

Introduction

Among the various MF_3–$M'F_4$ systems, namely LnF_3–ZrF_4 (*1–3*), LnF_3–HfF_4 (*3*), LnF_3–TbF_4 (*4*), MF_3–ZrF_4 (M = Ti,In (*5*), U^{III} (*6*), Bi (*7*)), UF_3–UF_4 (*8*) and InF_3–UF_4 (*9*), some have been thoroughly investigated. However, only few structure types are described: monoclinic $SmZrF_7$ (*10*), rhombohedral $BiZr_3F_{15}$ (*7*) and YZr_3F_{15} (*11*) compounds, and cubic ReO_3-type and trigonal tysonite-type solid solutions.

The present article deals with the description of a new structure type: β-$PrZr_3F_{15}$, a low temperature MZr_3F_{15} polymorph, previously unknown and isolated also for M = Nd.

Experimental

In the PrF_3–ZrF_4 system, at temperatures higher than 800°C, a nonstoichiometric phase of structure related to that of $BiZr_3F_{15}$ and YZr_3F_{15} has been prepared and characterized (*11*) as the α-$PrZr_3F_{15}$ phase. At 800°C, a new stoichiometric phase, called β-$PrZr_3F_{15}$, is obtained pure by heating a mixture of praseodymium and zirconium fluorides in $\frac{1}{3}$ proportion for 2 days in a Pt sealed tube.

Single crystals of good quality were grown in a two-phase mixture of composition PrF_3–$5ZrF_4$ heated at 800°C for 2 days in a Pt sealed tube and then water-quenched. The crystallographic characteristics of β-$PrZr_3F_{15}$ and of isomorphous β-$NdZr_3F_{15}$ are reported in Table I.

A single crystal of light green color and

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* To whom correspondence should be addressed.

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TABLE I

REFINED CELL PARAMETERS FOR β-MZr_3F_{15} COMPOUNDS

Ln	a (Å)	b (Å)	d_{exp}	d_{calc}	Z
Pr	12.316(8)	6.115(4)	4.36	4.34	3
Nd	12.284(8)	6.098(4)	4.44	4.39	3

regular shape was isolated for structure investigation. It was assimilated to a sphere of 0.17 mm diameter and its X-ray diffraction intensities were recorded on a NONIUS-C.A.D. 4 automatic diffractometer under the conditions reported in Table II. Due to the low μR coefficient (≈ 0.6), no absorption correction was performed.

Structure Determination

Structure refinement was carried out with the program SHELX-76 (*12*), utilizing the scattering factors and the anomalous dispersion factors taken from the International Tables for X-Ray Crystallography (*13*).

By analysis of the Patterson function, the cationic positions were determined in the noncentrosymmetrical $R3m$ (no. 160) space group (hexagonal multiple cell), with an ordered distribution of Pr^{3+} ($3a$: 0, 0, z) and Zr^{4+} ($9b$: x, $-x$, z) atoms. After several cycles of refinement, the R-factor converged to 11.2%. Then, a Fourier-difference synthesis revealed four anionic sites. Refinement of all atomic positions and isotropic thermal factors led to $R = 4.7\%$ and after introduction of anisotropic temperature factors for all atoms, the R-factor converged to $R = 3.3\%$ with reasonable values for all parameters. No improvement resulted either from the introduction of a weighting scheme or of a secondary extinction correction.

TABLE II

DATA COLLECTION PARAMETERS

Symmetry: rhombohedral (space group: $R3m$; no. 160)
Crystal radius: 0.08 mm
$\mu R = 0.6$
Radiation: Mo$K\alpha$
Scan: ω-2θ
Scan width: $(1. + 0.35\mathrm{tg}\theta)°$
Aperture: $(3. + 1.\mathrm{tg}\theta)$ mm.
Recording range:
$0 \leq h \leq +22$
$0 \leq k \leq +22$
$-11 \leq l \leq +11$
Number of measured reflections: 564
Number of weak reflections: 72
Number of observed reflections with $I/\sigma(I) > 0.5$: 445[a]
Number of refined variables: 36
No weighting scheme.
No absorption correction.
$R = 0.033$; $R_w = 0.033$

[a] This low value of $I/\sigma(I)$ was selected because of unusually high $\sigma(I)$ coefficients resulting from a slight instability of the X-ray generator during data collection, but without high loss of accuracy, as attested by structure refinement.

The structural parameters are reported in Table III and the main interatomic distances in Table IV.

Structure Description

The projection of the structure of β-$PrZr_3F_{15}$ onto the hexagonal *xoy* plane is represented in Fig. 1.

(*a*) *Anionic Polyhedra*

Two kinds of anionic polyhedra are shown in Fig. 2.

Pentagonal bipyramid $[ZrF_7]^{3-}$. Its pentagonal basis is made up of four F_4 (d_{Zr-F} = 2.123(6) and 2.167(6) Å) and one F_3 (d_{Zr-F} = 2.023(9) Å) anions. Both F_2 and F_1 apical anions are closer to the Zr cation (respectively 1.957(9) and 1.967(8) Å).

Tricapped trigonal prism $[PrF_9]^{6-}$. Three F_2 and three F_3 anions respectively form the two opposite triangular faces of the trigonal prism, with the shortest Pr–F bonds Pr–F_2 = 2.360(9) Å and Pr–F_3 = 2.331(9) Å. Three F_1 anions cap the lateral faces with longer Pr–F distances (2.438(9) Å).

(*b*) *Structure Organization*

Each $[ZrF_7]^{3-}$ pentagonal bipyramid (P.B.) is corner-shared to four identical ones

TABLE III

ATOMIC PARAMETERS AND ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$) FOR β-$PrZr_3F_{15}$

At site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
Pr 3a	3333	6667	1717(2)	34(3)	34	32(3)	17(1)	0	0	0.26(2)
Zr 9b	4771(1)	5229	6667[a]	46(3)	46	40(3)	30(4)	−2(1)	2	0.35(2)
F_1 9b	2191(4)	7809	1854(15)	202(33)	202	163(32)	186(38)	−19(12)	19	1.5(3)
F_2 9b	4074(5)	5926	4585(15)	208(33)	208	155(40)	113(37)	−56(19)	56	1.5(3)
F_3 9b	4121(7)	5879	9076(24)	256(37)	256	472(60)	81(43)	−186(28)	186	2.6(4)
F_4 18c	6283(6)	5860(6)	4422(9)	107(25)	160(27)	106(18)	69(22)	35(18)	9(18)	1.0(2)

[a] Constrained parameter.

and three $[PrF_9]^{6-}$ tricapped trigonal prisms (T.T.P.). Likewise, each $[PrF_9]^{6-}$ polyhedron is corner-shared to nine P.B. Therefore, Pr and Zr cations only connected through F corners are rather distant from one another (Zr–Zr = 4.185 Å, Zr–Pr = 4.178, 4.353, and 4.309 Å). Two Pr and six Zr cations constitute a rather distorted P cubic subunit, Pr atoms occupying two opposite corners, along a parallel to the [001] axis of the hexagonal multiple cell (e.g., in Fig. 1: Pr (0.33, 0.67, 0.17 and 0.33, 0.67, 1.17), associated with the six nearest Zr cations with z = 0.67 and z = 1.00).

A close structural relationship between β-$PrZr_3F_{15}$ and the ReO_3 type is clearly evident in Fig. 3 which shows a perspective drawing of (a) ReO_3 structure; (b) the distorted P cubic subunit of β-$PrZr_3F_{15}$ considering only the eight cations of the subcell and the F anions linking these cations; (c) the same subunit with all the anions which build the P.B. and the T.T.P. These $[PrF_9]^{6-}$ and $[ZrF_7]^{3-}$ polyhedra, sharing F_1, F_2, or

TABLE IV

MAIN INTERATOMIC DISTANCES

M–M (Fig. 5)	Zr–F (Fig. 2)	Pr–F (Fig. 2)	F–F (Fig. 2)
			about Pr:
Zr–Zr = 4.185 Å	Zr–F_1 = 1.967(8) Å	Pr–F_1 = 2.438(9) Å	F_2–F_1 = 2.715(9) Å
Pr–Zr = 4.178	–F_2 = 1.957(9)	–F_2 = 2.360(9)	F_3–F_1 = 2.748(12)
= 4.309	–F_3 = 2.023(9)	–F_3 = 2.331(9)	F_2–F_3 = 3.369(20)
= 4.353	–F_4 = 2.123(6)		F_2–F_2 = 2.737(20)
	–F_4' = 2.167(6)		F_3–F_3 = 2.910(25)
			about Zr:
	⟨Zr–F⟩ = 2.076 Å	⟨Pr–F⟩ = 2.376 Å	F_3–F_2 = 2.748(17)
			F_4–F_2 = 2.764(13)
			F_4'–F_3 = 2.407(9)
			F_4–F_4 = 2.639(13)
			F_4'–F_4 = 2.525(7)
			F_4'–F_1 = 2.873(10)
			F_4–F_1 = 2.910(10)
			F_4'–F_2 = 3.019(15)
			F_3–F_1 = 3.013(17)

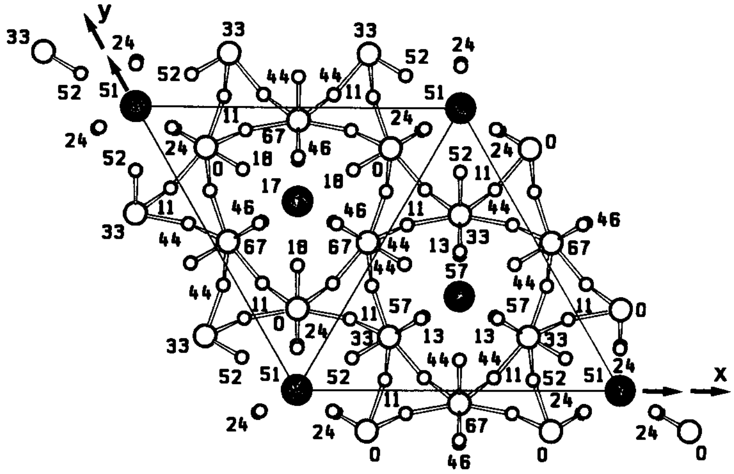

FIG. 1. (001) projection of β-$PrZr_3F_{15}$ (hexagonal cell). Numbers indicate z coordinate of atoms (*100). For drawing clearness, only $0 \leq z \leq 0.67$ coordinates and only Zr–F chemical bonds are represented. Pr, dark large spheres; Zr, light large spheres; F, small spheres.

F_4 corners, constitute a "$PrZr_3F_{12}$" unit with a ReO_3-like structure. The F_3 anions are excess ones, directly connecting one Pr and one Zr cation situated in the opposite corners of a side of the ReO_3-like subcell. Therefore, this almost square face is transformed into two triangular ones via shortening of Pr–Zr distance from $\approx 4.2\sqrt{2}$ Å to 4.353 Å. Each Pr^{3+} polyhedron (Fig. 3b) shares three F_3 anions with three Zr^{4+} polyhedra of the three adjacent square faces of a same subcell, about a three-fold axis. This bridging results in a shift of Pr cations along the Oz hexagonal axis and thus is the main cause of the distortion of the P cubic subcell.

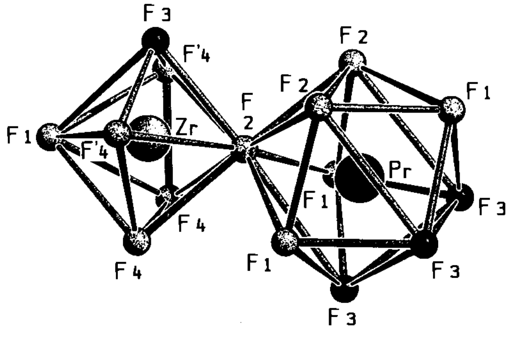

FIG. 2. Perspective drawing of corner-shared $[ZrF_7]^{3-}$ pentagonal bipyramid and $[PrF_9]^{6-}$ tricapped trigonal prism. Darker small spheres (F_3 anions) refer to the structural mechanism of Figs. 3 and 6.

Like the ReO_3 one, the three-dimensional structure of β-$PrZr_3F_{15}$ results from the stacking of identical layers of corner-shared anionic polyhedra. Figure 4 represents such a basic layer: the bridging of Pr and Zr cations, transforming one square face into two triangular ones, is clearly evident. The cationic plane net (Fig. 5c) in this basic layer (called $[3.4^3][3^2.4^3]^2$ with Schlaffli notation) is very close to a $3^2.4.3.4.$ one (Fig. 5b), an important semiregular net in the classification of O'Keeffe and Hyde (*14*), present in many alloy structures (Pb_3Ge, $CuAl_2$, Ir_3Si, . . .) and transitional between regular 3^6 (triangular) and 4^4 (square) nets. The transformation of a 4^4 square net, like the ReO_3 cationic one, into a $3^2.4.3.4.$ net can be described as resulting either from a $\pi/12$ rotation of square groups of atoms about a four-fold axis or from the direct conversion of

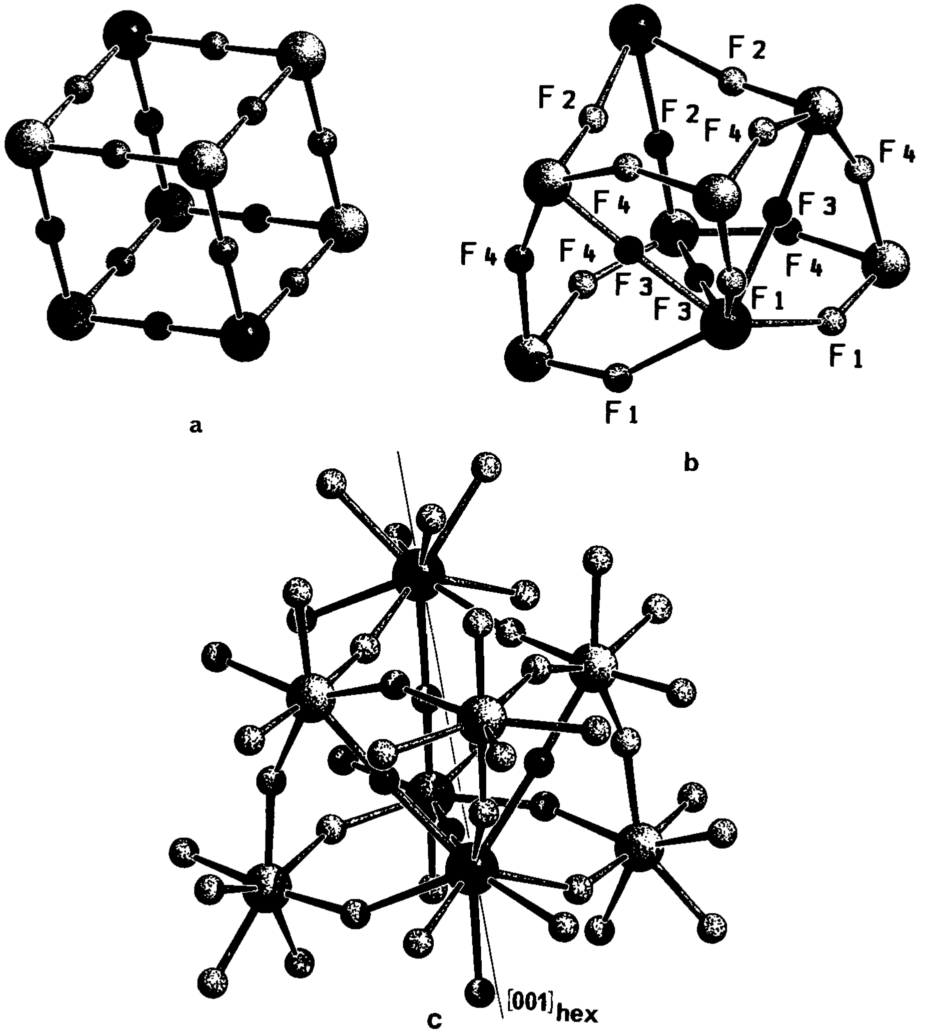

FIG. 3. Comparison of the structures of: (a), ReO_3; (b), β-$PrZr_3F_{15}$ with a perspective view of a ReO_3-like network, including only anions directly connecting Pr and Zr cations; (c), β-$PrZr_3F_{15}$ with the same perspective view showing the ReO_3-like association of two $[PrF_9]^{6-}$ and six $[ZrF_7]^{3-}$ polyhedra enclosing an empty cavity. Pr, darker large spheres; Zr, lighter large spheres; F, small spheres; F_3, darker small spheres ("excess" anions).

half square faces into 60° rhombuses (as shown by arrows in Fig. 5a). In the β-$PrZr_3F_{15}$ plane net, such a conversion is obviously related to F_3 bridging between Pr and Zr cations. However, this bridging affects only a quarter of square faces in the $[3.4^3][3^2.4^3]^2$ plane net and not a half as in a $3^2.4.3.4.$ one. This distribution of triangular and square faces cannot give a regular plane net. Therefore, small shifts of Pr and Zr cations occur, distorting the square faces and twisting the plane net in such a way that its projection appears like a true $3^2.4.3.4.$ one (Figs. 5b and 5c).

Considering the structural relationship between β-$PrZr_3F_{15}$ and ReO_3, $[ZrF_7]^{3-}$ and $[PrF_9]^{6-}$ polyhedra directly derive from MF_6 octahedra by adding the F_3 excess anions

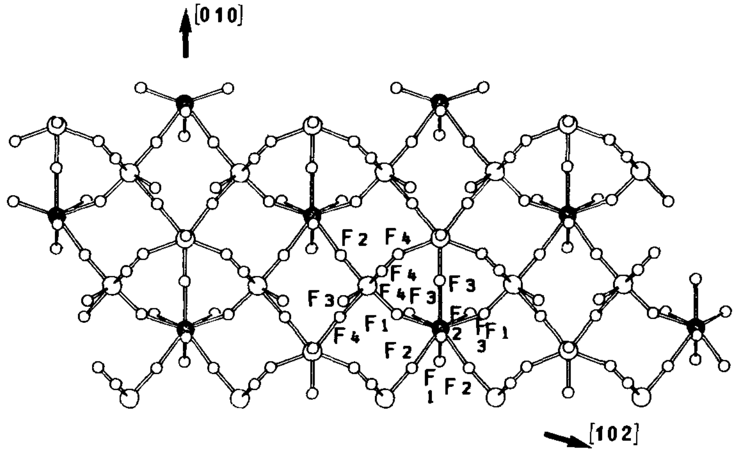

FIG. 4. ReO$_3$-like plane net resulting from the association of adjacent sides of the ReO$_3$-related network of β-PrZr$_3$F$_{15}$ structure represented on Fig. 3c: the structure can be entirely described by a stacking of corner-shared identical layers (Fig. 3c showing the connection between two successive sheets). The symbols are the same as on Fig. 1.

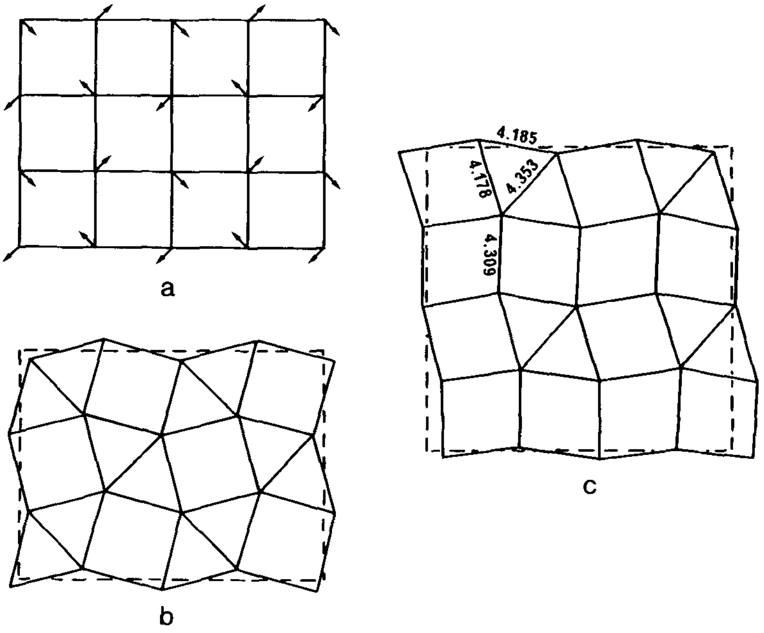

FIG. 5. Structural relation between (a) a 4^4 cationic plane net of ReO$_3$; (b) a $3^2.4.3.4.$ plane net; and (c) a $[3.4^3][3^2.4^3]^2$ cationic plane net of β-PrZr$_3$F$_{15}$ (as on Fig. 4 but rotated by 45° in the figure plane). The arrows in (a) represent the direction of rotation of square groups of atoms in the ReO$_3$ cationic plane net (or of direct conversion of square faces into triangular ones), transforming this plane net into a $3^2.4.3.4.$ one.

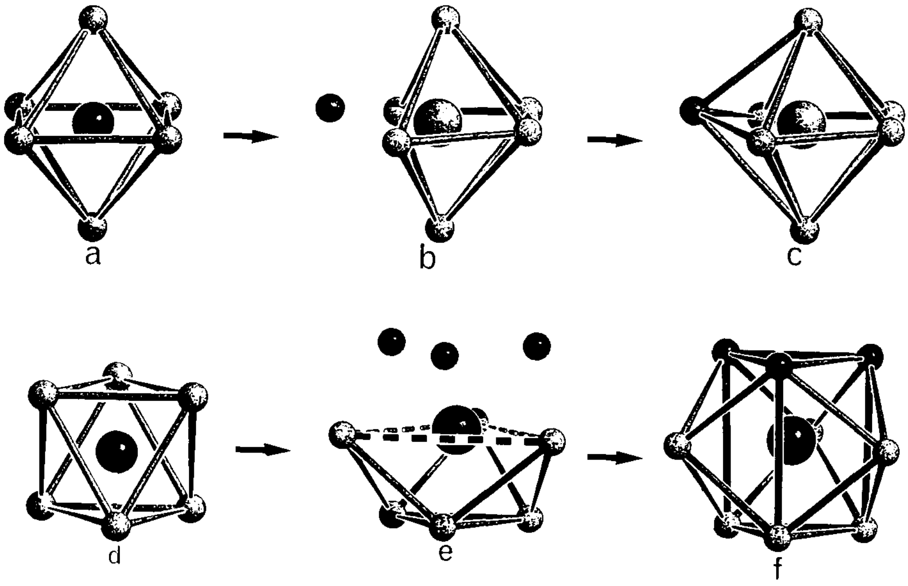

FIG. 6. Transformation of a ReO_3-type octahedron, seen along a fourfold axis (a) and along a threefold one (d), respectively into a pentagonal bipyramid (c) by adding one F_3 excess anion (b), and into a tricapped trigonal prism (f) by adding three F_3 excess anions (e).

according to the mechanism schematized in Fig. 6; it implies:

for the Zr^{4+} polyhedron, the transformation of a basis square face F_4–F_4–F_4–F_4 (Fig. 6a,b) into a pentagonal F_4–F_4–F_4–F_4–F_3 one (Fig. 6c);

for the Pr^{3+} polyhedron, the addition of an excess triangular F_3–F_3–F_3 face and, as above described, a correlative shifting of Pr^{3+} along the Oz axis (Fig. 6d,e) from $z = 0$ to $z = 0.1717$ (1.05 Å) to the center of the T.T.P. so created (Fig. 6f).

Thus, Pr^{3+} shifting, particularly evident on Figs. 3a and 3b, is the result of two closely related structural mechanisms:

shortening of Zr–Pr distance by bridging through F_3 anions; and

regularization of the T.T.P. formed by the addition of three bridging F_3 anions about each Pr cation.

Such a tendency for cations to shift from the ideal ReO_3 cationic site toward excess anions is a general feature of structures deriving from the ReO_3 type by anion excess and has been previously discussed (*15*, *16*). The cationic shift increases when an X corner of a MX_6 octahedron is respectively replaced by an X–X edge (0.2 Å in $Zr(F, O)_{3.33}$), by a triangular face (0.7 Å for Sm in $SmZrF_7$), and by a square face (1.54 Å for Ba in β-$BaZr_2F_{10}$). The direct insertion of a triangular face, transforming an octahedron into a T.T.P., constitutes a new way to introduce an excess of anions into a ReO_3-type structure.

A close structural relationship between $PrZr_3F_{15}$ polymorphs has been demonstrated, but this point will be developed in a forthcoming publication.

Conclusions

Several structures of fluorozirconates of composition lying between MF_3 and MF_4 can be derived from the ReO_3 type through a mechanism involving cationic ordering (full or partial) and increasing cationic coordination, in order to accommodate excess anions. β-$PrZr_3F_{15}$ is a new original example of this structural family, called anion-excess ReO_3 phases, whose well defined members are mainly $SmZrF_7$, $Zr(O, F)_{3+x}$, $Bi(Y)Zr_3F_{15}$, β-$BaZr_2F_{10}$, and cubic $(Zr, M)F_{3+x}$ phases.

Because of the extreme adaptability of this structure type, numerous phases of various compositions can be related more or less directly to it and will be the subject of further investigation.

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References

1. M. Poulain, M. Poulain, and J. Lucas, *Mater. Res. Bull.* **7,** 319 (1972).
2. M. Poulain, M. Poulain, and J. Lucas, *Rev. Chim. Miner.* **12,** 9 (1975).
3. Yu. M. Korenev, P. I. Antipov, and N. V. Novoselova, *Zh. Neorg. Khim.* **25,** 1255 (1980).
4. M. N. Brechovski, A. I. Popov, Yu. M. Kiselev, A. L. Plinskii, and V. A. Fedorov, *Zh. Neorg. Khim.* **34**(4), 1021 (1989).
5. J. C. Champarnaud-Mesjard, J. P. Laval, and B. Gaudreau, *Rev. Chim. Miner.* **11,** 735 (1974).
6. G. Fonteneau and J. Lucas, *J. Inorg. Nucl. Chem.* **36,** 1515 (1974).
7. E. Caignol, J. Metin, R. Chevalier, J. C. Cousseins, and D. Avignant, *Eur. J. Solid State Inorg. Chem.* **25,** 399 (1988).
8. R. E. Thoma, H. Insley, and G. D. Brunton, *J. Inorg. Nuc. Chem.* **36,** 1095 (1974).
9. J. C. Champarnaud-Mesjard and B. Gaudreau, *C.R. Acad. Sci. Paris, Ser. C* **282,** 745 (1976).
10. M. Poulain, M. Poulain, and J. Lucas, *J. Solid State Chem.* **8,** 132 (1973).
11. J. P. Laval and A. Abaouz, submitted for publication.
12. G. M. Sheldrick, "SHELX76, Program for crystal structure determination," Cambridge Univ. (1976).
13. "International Tables for X-ray crystallography," Kynoch Press, Birmingham (1968).
14. M. O'Keeffe and B. G. Hyde, *Philos. Trans. R. Soc. London, Ser. A* **295,** 553 (1980).
15. J. P. Laval, B. Frit, and J. Lucas, *Mater. Sci. Forum* **6,** 457 (1985).
16. J. P. Laval, B. Frit, and J. Lucas, *J. Solid State Chem.* **72,** 181 (1988).