# New Heptafluorozirconates and -hafnates $A^{I}B^{II}Zr(Hf)F_{7}$ ( $A^{I} = Rb$ , Tl; $B^{II} = Ca$ , Cd) – Synthesis, Structures, and Structural Relationships

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**Abstract.** Four new ABZrF<sub>7</sub> heptafluorozirconates (A = Rb, Tl; B = Ca, Cd) and their homologous heptafluorohafnates, all colorless, orthorhombic Cmcm (n°63), Z = 4, have been synthesized by heating stoichiometric mixtures of RbF or TlF, CaF<sub>2</sub> or CdF<sub>2</sub> and ZrF<sub>4</sub> (HfF<sub>4</sub>) in sealed platinum tubes at temperature ranging from 550 °C (Tl) to 600 °C (Rb). The crystal structures of both RbCdZrF<sub>7</sub> and TlCdZrF<sub>7</sub> have been solved from single-crystal X-rays diffraction data. Rietveld refinements were performed from X-rays powder patterns for RbCaZrF<sub>7</sub> and TlCaZrF<sub>7</sub>. In this series of heptafluorides, both B<sup>2+</sup> and Zr<sup>4+</sup> cations exhibit a pentagonal bipyramidal 7-coordination. Their structural relationships with other heptafluorozirconates  $A^{I}B^{II}ZrF_7$  as well as  $\beta$ -KYb<sub>2</sub>F<sub>7</sub> are discussed. RbCaZrF<sub>7</sub>: a = 6.863(1) Å, b = 11.130(1) Å, c = 8.485(1) Å; TlCaZrF<sub>7</sub>: a = 6.868(1) Å, b = 11.165(1) Å, c = 8.486(1) Å; RbCdZrF<sub>7</sub>: a = 6.780(1) Å, b = 11.054(4) Å, c = 8.420(4) Å; TlCdZrF<sub>7</sub>: a = 6.784(3) Å, b = 11.099(2) Å, c = 8.424(9) Å.

Keywords: Zirconium fluoride; Hafnium fluoride; Heptafluorozirconates; Crystal structure

#### Introduction

Due to their low phonon energies and high optical transparency from mid – UV to mid – IR, fluorohafnates and fluorozirconates in particular are well known as being good candidates for manufacturing optical fibres with ultra low losses for telecommunications, optical waveguides and infrared optoelectronic devices [1–3]. They may also enter into glassy compositions of interest since they are doped or codoped with rare earths for optical applications such as optical amplifiers [4–6] or upconverted luminescence of the  $Er^{3+}$  ion [7–14]. Fluorohafnates also are promising materials for dense scintillating glasses the applications of which are manifold such as high energy physics [15], long-wavelength luminescence [16] or in X–CT for industrial and medical applications [17].

Most of the above evoked optical properties or applications depend on the host matrices structures, even for glassy materials where the structural approach requires a good knowledge of the structures of the crystalline phases of  $ZrF_4$  and  $HfF_4$  containing corresponding systems. With the aim to found new host matrices suitable for potential optical applications a study of the phases relationship in the  $MF-M'F_2-ZrF_4$  (M = Rb, Tl; M' = Ca, Cd) systems has been carried out using X-ray diffraction. During this investigation new phases with formula  $M^IM'^{II}ZrF_7$  have been evidenced and the Cd ones could have easily been ob-

Laboratoire des Matériaux Inorganiques, UMR CNRS 6002 Université Blaise Pascal tained with a lot of single-crystals extracted from the batches. This paper deals with the crystal structures determination and refinements from single-crystal and powder X-rays diffraction data for Cd and Ca compounds, respectively. Then, as zirconium and hafnium are chemically very similar, their crystal chemical properties are considered as being identical and it is therefore easy to transpose results obtained with the less expansive zirconium tetrafluoride to the hafnium ones. The crystal chemical characteristics of the homologous fluorohafnates have been determined and are given in the present report.

### **Experimental Details**

#### Synthesis of the samples

All the samples were synthesized in the solid state from stoichiometric mixtures of MF (M = Rb, Tl), M'F<sub>2</sub> (M' = Ca, Cd) and ZrF<sub>4</sub> (HfF<sub>4</sub>) heated at 550 °C (Tl) or 600 °C (Rb) for three days in sealed platinum tubes.

The rubidium fluoride was a commercial reagent grade fluoride (Merck Selectipur) heated at 400 °C under vacuum prior to use in order to remove any possible trace of water. The thallous fluoride was a home made product prepared according to a process previously described [18]. Both CaF<sub>2</sub> and CdF<sub>2</sub> difluorides were commercial reagent grade products (Merck (Ca), Serlabo (Cd)). The zirconium tetrafluoride has been prepared from zirconium oxide (Aldrich < 5 microns) by attack by a boiling solution of hydrofluoric acid at 40 %, followed by a slow evaporation on a sand bath yielding ZrF<sub>4</sub>, H<sub>2</sub>O as dry residue. Then this dry residue has been heated 12 h at 500 °C under a pure fluorine gas flow, resulting in a well crystallized monoclinic zirconium tetrafluoride  $\beta$ -ZrF<sub>4</sub>. The same process has been applied to prepare HfF<sub>4</sub> from HfO<sub>2</sub> (Strem chemicals).



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Table 1	Details of d	ata collections,	data	processing	and	refinements	for	TlCdZrF <sub>7</sub>	and	RbCdZrF7	<sup>a)</sup> .
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Formula	RbCdZrF <sub>7</sub>	TlCdZrF <sub>7</sub>
$\overline{M_w/g \cdot mol^{-1}}$	422.08	486.68
Symmetry, space group	orthorhombic, Cmcm (nº63)	orthorhombic, Cmcm (n°63)
Unit cell parameters /Å	6.780(1)	6.784(3)
	11.054(4)	11.099(2)
	8.420(4)	8.424(9)
$V/Å^3$	631.1(6)	634.3(8)
Z	4	4
Calculated density $/g \cdot cm^{-3}$	4.442	5.665
Temperature /K	294	294
Radiation	$MoK_{\alpha}$ ( $\lambda = 0.71073$ Å)	$MoK_{\alpha}$ ( $\lambda = 0.71073$ Å)
Absorption coefficient $\mu$ /mm <sup>-1</sup>	12.746	30.339
Absorption correction	-	γ-scan
		$(T_{min} = 0.6115, T_{max} = 0.9935)$
Scan mode	ω-2θ	ω-2θ
Scan width	$0.80 + 0.35 \tan\theta$	$0.80 + 0.35 \tan\theta$
Scan aperture /mm	$2.70 + 0.40 \tan\theta$	$2.70 + 0.40 \tan\theta$
Angular domain	$1 \le \theta \le 40$	$1 \le \theta \le 40$
	$0 \le h \le 12$	$0 \le h \le 12$
	$0 \le k \le 19$	$0 \le k \le 20$
	$0 \le 1 \le 15$	$0 \le 1 \le 15$
Intensity control	3600s, $\sigma = 0.02$	3600s, $\sigma = 0.02$
Number of measured reflections	2254	1133
Number of unique reflections with $I > 4\sigma(I)$	528	610
R <sub>int</sub> (I/F <sub>O</sub> ) (Friedel pairs merged)	0.027/0.022	_
Number of refined parameters	36	36
Weighting scheme	$\omega = 1 / [\sigma^2 F_0^2 + (0.017 \text{ x P})^2]$	$\omega = 1 / [\sigma^2 F_0^2 + (0.0485 \text{ x P})^2]$
	$P = Max (F_0^2, 0) + 2 x F_c^2) / 3$	$P = Max (F_0^2, 0) + 2 x F_c^2) / 3$
R <sub>1</sub>	0.0268	0.0341
wR <sub>2</sub>	0.0598	0.0956
Goodness of fit	0.940	1.003
$\Delta \rho max.,min. /(e / Å^3)$	1.30, -1.44 close to F(4)	3.74, -2.29 close to Tl

<sup>a)</sup> Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-xxxx, CSD-xxxx or on request from the authors.

Atoms	Sites	x	У	Z		$U_{eq.}/\AA^2$
Rb	4b	0.5	0.0	0.0		0.029(1)
Cd	4c	0.0	0.1905(1)	0.25		0.010(1)
Zr	4c	0.5	0.3087(1)	0.25		0.007(1)
F(1)	4c	0.5	0.4904(8)	0.25		0.063(2)
F(2)	8g	0.3213(8)	0.1518(3)	0.25		0.025(1)
F(3)	8g	0.2037(7)	0.3586(3)	0.25		0.023(1)
F(4)	8f	0.5	0.2961(4)	0.0143	(7)	0.038(1)
Atoms	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Rb	0.0511(4)	0.0181(3)	0.0177(3)	0.0	0.0	-0.0018(8)
Cd	0.0082(5)	0.0108(4)	0.0105(5)	0.0	0.0	0.0
Zr	0.0066(6)	0.0089(6)	0.0064(6)	0.0	0.0	0.0
F(1)	0.020(2)	0.010(3)	0.160(7)	0.0	0.0	0.0
F(2)	0.013(2)	0.010(2)	0.051(3)	0.003(1)	0.0	0.0
F(3)	0.011(2)	0.020(2)	0.038(2)	0.004(2)	0.0	0.0
F(4)	0.038(2)	0.071(3)	0.005(2)	0.0	0.0	0.003(2)

Table 2 Atomic coordinates and anisotropic displacement parameters for RbCdZrF7.

Table 3	Atomic	coordinates	and	anisotropic	displacement	para-
meters fo	r TlCdZ	rF <sub>7</sub> .				

Atoms	Sites	х	у	Z		$U_{eq}$ /Å <sup>2</sup>
Tl	4b	0.5	0.0	0.0		0.033(1)
Cd	4c	0.0	0.1905(1)	0.25		0.010(1)
Zr	4c	0.5	0.3094(1)	0.25		0.007(1)
F(1)	4c	0.5	0.4910(6)	0.25		0.050(1)
F(2)	8g	0.3213(7)	0.1542(4)	0.25		0.027(1)
F(3)	8g	0.2037(6)	0.3589(4)	0.25		0.024(1)
F(4)	8f	0.5	0.2991(8)	0.0137	7(5)	0.039(2)
Atoms	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Tl	0.0530(3)	0.0189(2)	0.0269(2)	0.0	0.0	-0.0019(3)
Cd	0.0070(3)	0.0111(4)	0.0104(3)	0.0	0.0	0.0
Zr	0.0076(4)	0.0076(5)	0.0069(4)	0.0	0.0	0.0
F(1)	0.021(3)	0.017(4)	0.111(9)	0.0	0.0	0.0
F(2)	0.012(2)	0.013(2)	0.054(3)	-0.001(1)	0.0	0.0
F(3)	0.013(2)	0.016(2)	0.044(3)	0.004(1)	0.0	0.0
F(4)	0.039(3)	0.072(5)	0.006(2)	0.0	0.0	0.003(2)

The form of the anisotropic displacement parameters is:  $exp[-2\pi^2 \{U_{11}(ha^*)^2 + U_{22}(kb^*)^2 + U_{33}(lc^*)^2 + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*\}].$ 

Colorless translucent single-crystals of TlCdZrF7 and RbCdZrF7 were extracted from the batches and were subsequently used for the crystal structures determination.

## X-rays diffraction

Single-crystals data for RbCdZrF7 and TlCdZrF7 were recorded at room temperature with an Enraf Nonius CAD4 diffractometer. For The form of the anisotropic displacement parameters is:

 $exp[-2\pi^{2}\{U_{11}(ha^{*})^{2} + \hat{U}_{22}(kb^{*})^{2} + U_{33}(lc^{*})^{2} + 2U_{12}hka^{*}b^{*} + 2U_{13}hla^{*}c^{*} + 2U_{23}klb^{*}c^{*}\}].$ 

the first one Friedel's pairs were collected and no absorption correction was made, whereas for the latter only an asymmetrical unit has been recorded to save time as the structure was found to be centric and an empirical absorption correction based on y-scans was applied. Data reduction were performed with the SDP package [19] and refined with SHELXL-97 software [20] implemented in the program package WinGX [21]. Details of the single-crystal data collections, data processing and refinements are given in table 1. The atomic coordinates and the anisotropic displacement param-

Zr <sup>IV</sup> polyhedror	n [CN7]		Cd <sup>II</sup> polyhedron [C]	N7]	Rb <sup>I</sup> polyhedron [C	CN8 + 2]
$ \begin{array}{c} Zr - F(4)^{i,iii} \\ Zr - F(1)^{I} \\ Zr - F(3)^{i,vi} \\ Zr - F(2)^{i,vi} \end{array} $	x 2 x 2 x 2 x 2	1.989(6) 2.009(9) 2.084(5) 2.115(5)	$\begin{array}{rl} Cd &- \ F(1)^{i} \\ Cd &- \ F(2)^{i,vi} & x \\ Cd &- \ F(4)^{ii,iv} & x \\ Cd &- \ F(3)^{i,vi} & x \end{array}$	$\begin{array}{c} 2.212(8) \\ 2 & 2.220(1) \\ 2 & 2.230(6) \\ 2 & 2.316(4) \end{array}$	$\begin{array}{l} Rb -F(2)^{i,ii,v,vi}\\ Rb -F(3)^{i,ii,v,v}\\ Rb -F(4)^{i,ii} \end{array}$	x 4 2.952(3) x 4 2.963(3) x 2 3.276(5)
$d < Zr - F > = d_{Shannon} = 2.11$	2.055 Å Å		d < Cd – F> = 2.2 d <sub>Shannon</sub> = 2.36 Å	49 Å	d < Rb - F > = 2 $d_{Shannon} = 2.99$	3.021 Å Å

 Table 4
 Main interatomic distances in RbCdZrF7

Symmetry code: (i) x, y, z; (ii) x, -y, -z; (iii) x, y,  $\frac{1}{2}$ -z; (iv) x, -y,  $\frac{1}{2}$ +z; (v) -x, -y-z; (vi) -x, y, z; (vii) -x, -y,  $\frac{1}{2}$ +z; (viii) -x, y,  $\frac{1}{2}$ -z.

Table 5	Main	interatomic	c distances	in	TlCdZrF <sub>7</sub> .
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Zr <sup>IV</sup> Polyhedron [CN7]	Cd <sup>II</sup> Polyhedron [CN7]	Tl <sup>I</sup> Polyhedron[CN8 + 2]
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rcl} Tl & - \ F(3)^{i,ii,v,vi} & x \ 4 & 2.966(3) \\ Tl & - \ F(3)^{i,ii,v,v} & x \ 4 & 2.972(3) \\ Tl & - \ F(4)^{i,ii} & x \ 2 & 3.322(9) \end{array}$
d < Zr - F > = 2.055  Å $d_{Shannon} = 2.11 \text{ Å}$	d < Cd - F> = 2.250 Å d <sub>Shannon</sub> = 2.36 Å	d < Tl - F > = 3.040  Å

Symmetry code: (i) x, y, z; (ii) x, -y, -z; (iii) x, y, 1/2-z; (iv) x, -y, 1/2+z; (v) -x, -y-z; (vi) -x, y, z; (vii) -x, -y, 1/2+z; (viii) -x, y, 1/2-z.

Table 6 Details of data collections and Rietveld refinements of  $TlCaZrF_7$  and  $RbCaZrF_7$ .

Chemical formula	RbCaZrF <sub>7</sub>	TlCaZrF <sub>7</sub>
$M_w/g \cdot mol^{-1}$	349.77	468.68
Symmetry	orthorhombic	orthorhombic
Space group	Cmcm (nº63)	Cmcm (nº63)
Unit cell parameters /Å	· /	
a	6.863(1)	6.868(1)
b	11.130(1)	11.165(1)
с	8.485(1)	8.486(1)
V (Å <sup>3</sup> )	648.10(1)	650.69(1)
Z	4	4
Calculated density /g·cm <sup>-3</sup>	3.585	4.784
Wavelength incident		
radiation /Å	1.54056	1.54056
Profile function	Pseudo-Voigt	Pseudo-Voigt
	Thompson-Cox Hastings	Thompson-Cox Hastings
R factors (%)	$R_{\rm P} = 9.67, R_{\rm wp} = 11.6$	$R_{\rm P} = 15.0, R_{\rm wp} = 17.1$
	$R_{exp} = 2.89$	$R_{exp} = 3.12$
	$R_{\rm F}^{-1}$ = 5.12, $R_{\rm B}$ = 5.56	$R_F^{n_F} = 6.16, R_B = 7.19$

Table 7Atomic coordinates and isotropic displacement parameters for  $RbCaZrF_{7}$ .

Atoms	Sites	х	У	Z	$B_{iso.}$ /Å <sup>2</sup>
Rb	4 b	0.5	0.0	0.0	3.48(4)
Ca	4 c	0	0.1898(3)	0.25	1.95(8)
Zr	4 c	0.5	0.3062(1)	0.25	1.82(3)
F(1)	4 c	0.5	0.4989(9)	0.25	5.2(2)
F(2)	8 g	0.3226(7)	0.1514(4)	0.25	3.02(2)
F(3)	8 g	0.2085(7)	0.3563(4)	0.25	2.82(1)
F(4)	8 f	0.5	0.3005(4)	0.0144(6)	4.91(1)

eters are gathered in tables 2 and 3. The main interatomic distances are given in tables 4 and 5.

X-rays powder diffraction patterns for TlCaZrF<sub>7</sub> and RbCaZrF<sub>7</sub> were recorded with a Siemens D501 powder diffractometer using the Cu  $K_{\alpha 1,2}$  radiation.

 Table 8
 Atomic coordinates and isotropic displacement parameters for TlCaZrF<sub>7</sub>.

Atoms	Sites	Х	У	Z	B <sub>iso.</sub> /Å <sup>2</sup>
Tl	4 b	0.5	0.0	0.0	3.5(1)
Ca	4 c	0	0.1908(9)	0.25	0.8(2)
Zr	4 c	0.5	0.3076(4)	0.25	1.3(1)
F(1)	4 c	0.5	0.492(1)	0.25	1.8(3)
F(2)	8 g	0.3229(15)	0.1511(12)	0.25	1.4(3)
F(3)	8 g	0.221(2)	0.3598(15)	0.25	5.0(5)
F(4)	8 f	0.5	0.3001(8)	0.0092(16)	3.4(3)

Rietveld refinements were performed using the program FULLP-ROF [22]. Details of the data collections and refinements are given in table 6. Figure 1 displays the final fit between calculated and observed X-ray diffraction patterns of the TlCaZrF<sub>7</sub> fluoride. The atomic coordinates and isotropic displacement parameters of RbCaZrF<sub>7</sub> and TlCaZrF<sub>7</sub> are gathered in tables 7 and 8 respectively. The main interatomic distances are given in tables 9 and 10.

The homologous heptafluorohafnates have been synthesized and their crystal chemical characteristics are gathered in table 11.

#### Structures Description and Discussion

In all of these heptafluorozirconates  $ABZrF_7$  (A = Rb, Tl; B = Ca, Cd) there are nearly regular pentagonal bipyramidal 7-coordination of B<sup>2+</sup> and Zr<sup>4+</sup> cations and all the bond distances in all of these 7-coordination polyhedra (tables 4, 5, 9 and 10) are shorter than the Shannon's distances i.e. the sum of the Shannon ionic radii [23], apart the Zr-F(2) distance which is equal within the e. s. d. to the Shannon ones. However these distances are in good agreement with equivalent distances reported in the literature [24-26].

Zr <sup>IV</sup> polyhedron [CN7]	Ca <sup>II</sup> polyhedron [CN7]	Rb <sup>I</sup> polyhedron [CN8 + 2]
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{cccc} Ca & - & F(1)^i & 2.236(11) \\ Ca & - & F(4)^{i,vi} & x & 2 & 2.246(5) \\ Ca & - & F(2)^{ii,iv} & x & 2 & 2.255(5) \\ Ca & - & F(3)^{i,vi} & x & 2 & 2.341(5) \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$
d < Zr-F> = 2.058  Å $d_{Shannon} = 2.11 \text{ Å}$	d < Ca-F> = 2.274  Å $d_{Shannon} = 2.40 \text{ Å}$	d < Rb-F > = 3.064  Å $d_{\text{Shannon}} = 2.99 \text{ Å}$

 Table 9
 Main interatomic distances in RbCaZrF<sub>7</sub>

Symmetry code: (i) x, y, z; (ii) x, -y, -z; (iii) x, y, 1/2-z; (iv) x, -y, 1/2+z; (v) -x, -y-z; (vi) -x, y, z; (vii) -x, -y, 1/2+z; (viii) -x, y, 1/2-z.

 Table 10
 Main interatomic distances in TlCaZrF<sub>7</sub>.

Zr <sup>IV</sup> polyhedron [CN7]			Ca <sup>II</sup> polyhedron	Ca <sup>II</sup> polyhedron [CN7]			Tl <sup>1</sup> polyhedron[CN8 + 2]		
$ \begin{array}{l} Zr  -  F(3)^{i,vi} \\ Zr  -  F(4)^{i,iii} \\ Zr  -  F(1)^i \\ Zr  -  F(2)^{i,vi} \end{array} $	x 2 x 2 x 2	2.003(14) 2.045(14) 2.060(1) 2.129(13)	$\begin{array}{l} Ca - F(4)^{ii,iv} \\ Ca - F(1)^i \\ Ca - F(2)^{i,vi} \\ Ca - F(3)^{i,vi} \end{array}$	x 2 x 2 x 2 x 2	2.202(14) 2.220(1) 2.261(11) 2.422(17)	$\begin{array}{l} Tl - F(2)^{i,ii,v,vi}\\ Tl - F(3)^{i,ii,v,v}\\ Tl - F(4)^{i,ii} \end{array}$	x 4 x 4 x 2	2.971(9) 3.042 (11) 3.352 (9)	
d < Zr-F > = 2.059  Å $d_{Shannon} = 2.11 \text{ Å}$			d < Ca-F> = 2 $d_{Shannon} = 2.40$	d < Ca-F > = 2.284  Å $d_{\text{Shannon}} = 2.40 \text{ Å}$			d < Tl-F> = 3.076 Å		

Symmetry code: (i) x, y, z; (ii) x, -y, -z; (iii) x, y,  $\frac{1}{2}$ -z; (iv) x, -y,  $\frac{1}{2}$ +z; (v) -x, -y-z; (vi) -x, y, z; (vii) -x, -y,  $\frac{1}{2}$ +z; (viii) -x, y,  $\frac{1}{2}$ -z.

 Table 11
 Crystal chemical characteristics of heptafluorohafnates

 ABHfF<sub>7</sub>

Compounds	a /Å	b /Å	c /Å	V /Å <sup>3</sup>	$D_{cal.}/g \cdot cm^{-3}$
RbCaHfF <sub>7</sub>	6.850(1)	11.111(1)	8.472(1)	644.81(2)	4.504
TlCaHfF <sub>7</sub>	6.855(1)	11.148(1)	8.472(1)	647.44(2)	5.706
RbCdHfF <sub>7</sub>	6.757(1)	11.058(1)	8.404(1)	627.89(1)	5.562
TlCdHfF <sub>7</sub>	6.780(1)	11.092(1)	8.427(1)	633.68(2)	6.588



Figure 1 Final Rietveld plot of  $TICaZrF_7$  from X-ray powder diffraction data: observed (full circles) and calculated (solid line) patterns, difference (observed minus calculated, lower solid line) and Bragg reflections (vertical markers).

Each pentagonal bipyramid, either  $(ZrF_7)^{3-}$  or  $(BF_7)^{5-}$ , shares two edges involving F(2) and F(3) fluorine atoms

with two adjacent(BF<sub>7</sub>)<sup>5</sup> or  $(ZrF_7)^{3-}$  pentagonal bipyramids and three corners with three other  $(BF_7)^5$  or  $(ZrF_7)^{3-}$ pentagonal bipyramids involving one equatorial F(1) and two apical F(4) fluorine atoms (figure 2).



**Figure 2** View of the crystal structure of ABZrF<sub>7</sub> heptafluorozirconates projected along [0 0 1].

Thus, by sharing F(2)-F(3) edges, alternating  $(ZrF_7)^{3-}$ and  $(BF_7)^{5-}$  pentagonal bipyramids form infinite zigzag chains running along the *a* direction. These chains are further linked together by sharing F(1) corners alternatively from side to side to form  $BZrF_{11}$  ( $M_2X_{11}$ ) layers. These layers are perfectly plane insofar as all atoms Zr, B = Ca, Cd, F(1), F(2) and F(3) lie in the z =  ${}^{1}/_{4}$  mirror plane. Further corner-sharing between these layers involving only F(4) fluorine atoms gives the 3D framework of the structure.

This 3D polyhedral string delimits pseudo hexagonal channels running along the *c* direction and accommodating the  $Rb^+$  or  $Tl^+$  ions (figure 2). These last ones are located at half distance between the  $M_2X_{11}$  layers, in the average plane of the F(4) fluorine atoms.

A similar polyhedral linking has been found in the high temperature form  $\beta$  of KYb<sub>2</sub>F<sub>7</sub> [27] and in the heptafluoroindate KIn<sub>2</sub>F<sub>7</sub> [28]. This suggests that two Yb<sup>3+</sup> ions might easily be substituted for the couple B<sup>2+</sup>-Zr<sup>4+</sup> (B = Ca, Cd) without any charge compensation. This may be envisaged in three different ways:

i) The two Yb<sup>3+</sup> ions may be substituted for the couple  $B^{2+}$ -Zr<sup>4+</sup> in the dimeric structural unit  $[BZrF_{12}]^{6-}$  built of edge sharing between  $(ZrF_7)^{3-}$  and  $(BF_7)^{5-}$  pentagonal bipyramids (figure 3a).

ii) The two Yb<sup>3+</sup> ions may be substituted for the couple  $B^{2+}$ -Zr<sup>4+</sup> in the  $[BZrF_{13}]^{7-}$  structural entity built of corner sharing between  $(ZrF_7)^{3-}$  and  $(BF_7)^{5-}$  involving the equatorial F(1) corner (figure 3b).

iii) This substitution may take place in the  $[BZrF_{13}]^{7-}$  structural entity resulting of the corner-sharing between both  $(ZrF_7)^{3-}$  and  $(BF_7)^{5-}$  involving the F(4) apical corner (figure 3c).

A number of fluorozirconates with the  $A^{I}B^{II}ZrF_{7}$  general formula have been reported for different combinations of the  $B^{II}$  and  $Zr^{IV}$  cations, namely  $AMnZrF_{7}$  (A = Rb, Tl) [29], KPdZrF<sub>7</sub> [30], KCuZrF<sub>7</sub> [31], KVZrF<sub>7</sub> [32], KSnZrF<sub>7</sub> [33] (see also figure 4). Apart for this last one which is a special case with a very distorted coordination polyhedron of the Sn<sup>2+</sup> ion, all the other fluorozirconates afore-mentioned exhibit a 3D framework built of lavers further linked together by corner-sharing only and characterized by the presence of pseudo-hexagonal channels. They can be divided in three different structural types (since KVZrF<sub>7</sub> is isotypic with KPdZrF<sub>7</sub>), the characteristic building layers of which, although being quite different, have the same formula. The main differences arise from the respective coordinations of the  $B^{2+}$  and  $Zr^{4+}$  cations and therefore from the polyhedra connection modes within the layers. For example, in the AMnZrF<sub>7</sub> fluorides as well as in the title compounds. both  $B^{2+}$  and  $Zr^{4+}$  cations are 7-coordinated by the fluoride ions whereas in KPdZrF7 the Pd2+ cations have an octahedral coordination and the  $Zr^{4+}$  ones a 7-coordination. However, in KPd(Hf)ZrF7 (figure 4c) we can still distinguish infinite zigzag chains built of trans corner-sharing binuclear  $(PdZrF_{11})^{5-}$  structural units, running along the [1 0 1] and  $\begin{bmatrix} 1 & 0 & \overline{1} \end{bmatrix}$  directions and joined together by cornersharing alternatively from side to side. Contrary to the title compounds where each  $(ZrF_7)^{3-}$  pentagonal bipyramid is linked to three  $(BF_7)^{5-}$  pentagonal bipyramids by sharing two edges and one equatorial corner, in KPd(Hf)ZrF7 each  $(ZrF_7)^{3-}$  pentagonal bipyramid is linked to three octahedra  $(PtF_6)^{4-}$  by sharing two equatorial corner and one edge also delimited by two other equatorial corners. Thus, to compensate for the loss of one fluoride ion due to the change of the coordination of the B cations from pentagonal bipyramidal to octahedral a corner is substituted for one shared edge out of two within the zigzag chains. In the KCuZr(Hf)F<sub>7</sub> (figure 2b) fluoride the coordination numbers of the  $Cu^{2+}$  (B cation) and  $Zr^{4+}$  cations are 6 and 8, respectively. But contrary to the title compounds where the  $B^{2+}$  and  $Zr^{4+}$  cations regularly alternate, these cations are now gathered together in pairs. This comes down to substitute in the title compounds polyhedral string (figure 4a) a new structural unit  $(BZrF_{11})_2^{10-}$  built of edge sharing between an octahedron  $(BF_6)^{2-}$ , two square antiprisms



Figure 3 Different ways to conceive the selection of the pair  $B^{2+}$ -Zr(Hf)<sup>4+</sup> for the substitution of 2 Ln<sup>3+</sup> for this pair.



Figure 4 Structural relationships between the  $A^{I}B^{II}ZrF_{7}$  heptafluorozirconates (a)  $A^{I}B^{II}ZrF_{7}$  ( $A^{I} = Rb$ , Tl;  $B^{II} = Ca$ , Cd), (b) KCuZrF<sub>7</sub> and (c) KPd(V)ZrF<sub>7</sub>.

 $(ZrF_8)^{4-}$  and another octahedron for two  $(BZrF_{12})^{6-}$  structural units (figure 4c) within the zigzag chains. This lead to the doubling of the unit cell parameter in the *b* direction along which the zigzag chains are running. These chains are linked together by corner-sharing between the  $(CuF_6)^{2-}$  octahedra and by edge-sharing between  $(ZrF_8)^{4-}$  square antiprisms. It is also worth noting that in this KCuZr(Hf)F<sub>7</sub> structural type the octahedra  $(CuF_6)^{2-}$  share only corners between themselves whereas the  $(ZrF_8)^{4-}$  square antiprisms only share edges between themselves. These ABZrF<sub>7</sub> compounds thus illustrate three ways of attaining both F: B and F: Zr ratios of 7: 1 with coordination numbers of 6 and 7 for the B atoms and 7 and 8 for the Zr ones.

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