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Crystal Structures of The Fluorite-Related Phases $CaHf_4O_9$ and $Ca_6Hf_{19}O_{44}$

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Crystal structures for the fluorite-related phases $CaHf_4O_9$ (ϕ_1) and $Ca_6Hf_{19}O_{44}$ (ϕ_2) have been determined from X-ray powder diffraction data. ϕ_1 is monoclinic, $C2/c$, with $a = 17.698$ Å, $b = 14.500$ Å, $c = 12.021$ Å, $\beta = 119.47°$ and $Z = 16$. ϕ_2 is rhombohedral, $R\bar{3}c$, with $a = 12.058$ Å, $\alpha = 98.31°$ and $Z = 2$.

Both phases are superstructures derived from the defect fluorite structure by ordering of the cations and of the anion vacancies. The ordering is such that the calcium ions are always 8-coordinated by oxygen ions, while the hafnium ions may be 6-, 7-, or 8-coordinated. The closest approach of anion vacancies is a $\frac{1}{2}\langle 111 \rangle$ fluorite subcell vector, and in each structure vacancies with this separation form strings.

1. Introduction

The existence of three ordered fluorite-related phases in the system HfO_2–CaO was reported originally by Delamarre and Perez y Jorba (*1–3*). These phases, which were all assumed to have the composition $CaHf_4O_9$, were denoted ϕ, ϕ_1 and ϕ_2, and unit cells for ϕ and ϕ_2 were derived from X-ray powder data. Subsequently, Michel (*4*) reported the preparation of phases analogous to ϕ_1 and ϕ_2 in the system ZrO_2–CaO, and showed from single crystal data that ϕ_2 was rhombohedral.

We have prepared ϕ, ϕ_1 and ϕ_2 by methods similar to those of Delamarre (*3*). The use of electron diffraction from single crystal fragments of these phases, together with X-ray powder data, enabled us to determine their unit cells, their relationships to the fluorite-type subcell and their diffraction symbols unambiguously and precisely (*5*); these data for ϕ_1 and ϕ_2 are given in Table I. If it is assumed that the ϕ phases are derived from the fluorite structure type by ordering of the cations or anions, the size and symmetry of the unit cell places restrictions on their compositions. On this basis we derived the following formulae

$$\phi: Ca_2Hf_7O_{16}, \quad \phi_1: CaHf_4O_9, \quad \phi_2: Ca_6Hf_{19}O_{44},$$

and these were confirmed by the preparation of single phases at these compositions.

This paper describes the determination of the structures of ϕ_1 and ϕ_2 from X-ray powder intensity data. Because of extensive overlap of non-equivalent reflexions, Patterson methods could not be used, and trial structures were therefore derived from the known relationships to the fluorite-type subcell. This approach was successful in the case of ϕ (*6*) which is a relatively simple structure with few variable parameters. In the present case, the structures are considerably more complex, nevertheless the results are meaningful in terms of cation ordering and the probable location of vacant anion sites.

2. Experimental

X-ray reflexion intensities for nickel-filtered CuKα radiation were recorded on chart using

TABLE I

CRYSTALLOGRAPHIC DATA FOR $CaHf_4O_9$ AND $Ca_6Hf_{19}O_{44}$

Phase	$CaHf_4O_9$ (ϕ_1)	$Ca_6Hf_{19}O_{44}$ (ϕ_2) $R\bar{3}c$	
Space group	$C2/c$ Monoclinic	Rhombohedral	Hexagonal
Unit cell dimensions	$a = 17.698(2)$ Å	$a = 12.0585$ Å	$a = 18.2435(8)$ Å
	$b = 14.500(1)$		
	$c = 12.021(1)$		$c = 17.6125(16)$
	$\beta = 119.468(6)°$	$\alpha = 98.305°$	
	$V = 2685.8$ Å^3	$V = 1692.2$ Å^3	$V = 5076.6$ Å^3
	$Z = 16$	$Z = 2$	$Z = 6$
Relationship to subcell	$a = [222]_f$	$u = \frac{1}{2}[\bar{2}33]_f$	$a_1 = \frac{1}{2}[\bar{5}50]_f$
	$b = [\bar{2}20]_f$	$v = \frac{1}{2}[3\bar{2}3]_f$	$a_2 = \frac{1}{2}[0\bar{5}5]_f$
	$c = \frac{1}{2}[\bar{3}\bar{3}2]_f$	$w = \frac{1}{2}[33\bar{2}]_f$	$c = [222]_f$

a powder diffractometer with a scintillation counter at a scan speed of 1/16° min^{-1} in 2 Θ. The peak areas were measured with a planimeter and assigned to the appropriate reflexions or groups of reflexions: in the case of partially resolved peaks subjective judgement was involved in this assignment. No attempt was made to prevent preferred orientation in the samples as this was not expected to be a problem with these pseudo-cubic materials.

3. Refinement

The data were refined using our program POWDER which treats coincident or unresolved reflexions as single observations (*6*). The function minimized was

$$\Delta^2 = \sum w_i[I_t(\text{obs}) - I_t(\text{calc})]^2,$$

and the residual quoted throughout is

$$R = \tfrac{1}{2}\Delta[\sum w_i I_t(\text{obs})^2]^{-1/2}$$

which is almost equivalent numerically to the widely used weighted residual based on *F*. The multiplicities and *LP* factors were included in the calculated intensities. The weight allotted to each observation was the product of a subjective term which reflected uncertainty in assigning areas to incompletely resolved peaks, and a statistical term of the form

$$(I(\text{obs}) + I_0)^{-1}$$

where I_0 is set equal to about twice the smallest measured intensity (i.e., peak area). The exact value of I_0 is not critical.

Reflexions which lay in regions of the pattern for which no significant intensity above background was recorded were given intensities of half the minimum measurable, and included in the refinement. It is important to include these non-observed reflexions, as they constitute a significant fraction of the data, and a structure which fails to predict low intensities for these reflexions is clearly wrong. A relevant point here is that overlapping non-observed reflexions may be treated as independent and need not be grouped.

Scattering factors for neutral atoms (*7*) corrected for anomalous dispersion (*8*) were used; the factors for hafnium were also corrected for the zirconia content of about 8 mole% in the hafnia used to prepare the samples. Temperature factors were not included in the refinement of the structure of ϕ_2. In the case of ϕ_1 the different ions were assigned arbitrary factors $B_{Hf} = 0.0$, $B_{Ca} = 1.0$ and $B_O = 3.0$ Å^2. Replacement of these values by zero at the completion of the structure analysis did not alter the calculated intensities significantly; it was therefore concluded that meaningful factors could not be derived from the data.

The structure determinations were carried out by a sequence of steps as follows:

(a) The possible arrangements of a fluorite-type structure which were consistent with the diffraction symmetry of the supercell were determined. The different arrangements are related by translations which are simple fractions of lattice vectors.

(b) Fully ordered arrangements of cations consistent with the models derived in (a) were investigated as possible trial structures by calculating the residuals after refining the scale factor. Ideal fluorite coordinates and a complete anion lattice were assumed at this stage. Noncentrosymmetric structures were not considered initially in the case of ϕ_1. Only a few of the many possibilities had residuals which were low enough to justify further consideration.

(c) All the general cation coordinates were refined. Initially these were refined in small groups to avoid difficulties arising from degeneracy or high correlations between coordinates. Finally, all the coordinates were refined simultaneously and their values were found to be independent of the sequence of previous coordinate refinements. At this stage one model of each structure had a significantly lower residual than the others.

(d) It has been assumed so far that the fluorite anion lattice is complete, whereas in fact, in both structures, there is insufficient oxygen to satisfy the fluorite composition MX_2. Density measurements (*5*) indicated that this discrepancy is associated with the absence of oxygen from some of the anion sites. Because of the small contribution from oxygen to the total scattering, efforts to locate these vacancies by refining the occupancies of the anion sites were unsuccessful. An alternative method, based on the sizes of the cation tetrahedra surrounding each anion site, was used. The probable electrostatic effect of an anion vacancy would be to dilate the surrounding tetrahedron of cations. The most convincing evidence for this dilation is found in the C-rare earth structure type, which is derived from the fluorite structure by the ordered omission of one quarter of the anions, and the slight relaxation of the remaining ions. In the resulting structure, the cation tetrahedra which surround vacant anion sites have six long edges, while those which surround occupied sites have four short and two long edges (the latter arise from adjacent vacancies). For example, in the accurately known structure of *C*-type In_2O_3 (*9*), the distances are 3.83 Å and 3.35 Å, giving average edge lengths of 3.83 Å and 3.52 Å for tetrahedra surrounding vacant and occupied anion sites respectively. Similar differences have been found in other fluorite-related anion-deficient structures such as $Ca_2Hf_7O_{16}$ (*6*), $Zr_5Sc_2O_{13}$ (*10*) and $Zr_3Yb_4O_{12}$ (*11*).

The cation–cation distances were therefore calculated from the cation coordinates derived in step (c), and those anion sites which were surrounded by the largest tetrahedra of cations were taken to be vacant.

(e) Oxygen was removed from the sites which were determined as vacant, and these final models, which then had the correct compositions, were given several further cycles of coordinate refinements.

4. The Structure of ϕ_2–$Ca_6Hf_{19}O_{44}$

4.1. *Analysis*

Reflexion intensities from ϕ_2, which were recorded for $2\ \Theta \leqslant 90°$, included 443 nonequivalent reflexions, but coincidence and overlap reduced the number of distinct observations to 106.

The rhombohedral unit cell of ϕ_2 contains 12 calcium ions, 38 hafnium ions, 88 oxygen ions and 12 formal anion vacancies. In the noncentrosymmetric space group $R3c$, this implies that hafnium occupies one $2(a)$ site and six $6(b)$ sites, and calcium occupies two $6(b)$ sites (the nomenclature is that used in the International Tables for X-ray Crystallography). There are twelve distinct cation arrangements possible, of which six are also the possible arrangements in the centrosymmetric space group $R\bar{3}c$. The residual was calculated for each of these configurations, and values ranging from 0.23 to 0.33 were obtained. A centrosymmetric structure containing one hafnium in the $2(a)$ site of $R\bar{3}c$ (point symmetry 32) gave the lowest residual. When the cation coordinates for this configuration were refined in $R\bar{3}c$, the residual fell from 0.23 to 0.12.

Two noncentrosymmetric arrangements had initial residuals less than 0.25, but refining the cation coordinates did not reduce them below 0.18, despite the greater number of parameters to be varied. The best initial centrosymmetric structure with hafnium in the 2(*b*) site (point symmetry $\bar{3}$) was also refined without success. We therefore concluded that ϕ_2 is centrosymmetric, space group $R\bar{3}c$, and all further refinement was carried out on the model in which hafnium occupies the 2(*a*) site is this space group.

The sizes of the cation tetrahedra surrounding each anion site were then determined. Most of the tetrahedra had mean edge lengths which were quite close to the overall mean of 3.64 Å; one tetrahedron was exceptional with a mean edge length of 3.88 Å and this was taken as defining the vacant anion site.

The appropriate oxygen was removed from the model, leaving one 4(*c*) and seven 12(*f*) anion sites occupied, in accord with the overall stoichiometry. All 32 variable atomic coordinates were then refined. The final residual was 0.076, and the ionic coordinates, together with their standard deviations, are listed in Table II, together with the ideal fluorite-derived coordinates which served as a starting point for the refinement. The observed and calculated intensities are listed in Table III. The data in Tables II and III refer to the hexagonal representation of the unit cell. An attempt to refine an overall temperature factor yielded a small negative value with a large standard deviation; for this reason, a temperature factor was not included in the structure determination. Apparent negative temperature factors may arise in powder work from surface roughness if the sample is highly absorbing (*12*).

4.2. *Description*

The structure of ϕ_2 is most readily described by using the hexagonal representation, and referring to an idealized model in which the ions retain the fluorite-derived coordinates given in Table II. The unit cell contains six identical layers of cations parallel to the (0001) plane: these correspond to $(111)_f$ layers in the fluorite structure.[1] Each cation layer is

TABLE II

IONIC COORDINATES IN ϕ_2–$Ca_6Hf_{19}O_{44}$[a, b]

Atom	Site	x_f	x	y_f	y	z_f	z
Hf1	2(*a*)	0.0	0.000	0.0	0.000	0.25	0.250
Hf2	6(*e*)	0.4	0.388(2)	0.0	0.000	0.25	0.250
Hf3	6(*e*)	0.8	0.811(2)	0.0	0.000	0.25	0.250
Hf4	12(*f*)	0.4	0.388(1)	0.2	0.204(2)	0.25	0.258(2)
Hf5	12(f)	0.6	0.617(2)	0.2	0.205(1)	0.25	0.256(1)
Ca1	6(*e*)	0.2	0.212(9)	0.0	0.000	0.25	0.250
Ca2	6(*e*)	0.6	0.599(12)	0.0	0.000	0.25	0.250
O1	4(*c*)	0.0	0.000	0.0	0.000	0.0	0.053(21)
O2	12(f)	0.4	0.351(15)	0.0	−0.006(16)	0.125	0.128(15)
O3	12(*f*)	0.4	0.411(13)	0.2	0.193(19)	0.125	0.133(13)
O4	12(*f*)	0.4	0.404(13)	0.2	0.215(18)	0.375	0.376(14)
O5	12(*f*)	0.6	0.574(18)	0.2	0.163(12)	0.125	0.137(14)
O6	12(*f*)	0.6	0.599(19)	0.2	0.181(12)	0.375	0.379(14)
O7	12(*f*)	0.2	0.215(17)	0.0	−0.015(14)	0.125	0.111(14)
O8	12(*f*)	0.6	0.594(20)	0.0	−0.015(18)	0.125	0.115(15)
V	12(*f*)	0.8		0.0		0.375	

[a] Fractional coordinates referred to the hexagonal cell.

[b] The subscript *f* indicates ideal fluorite coordinates. The vacant anion site is labelled *V*.

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[1] It is convenient to refer to certain directions and planes in terms of the fluorite subcell, both to emphasize similarities between the structures described, and to avoid the unwieldy numbers that would arise if supercell indices were used: such indices are denoted by the subscript *f*. This can lead to confusion when general forms are mentioned so we have used a notation whereby an asterisk appended to a subcell form, e.g. $\langle 110\rangle_f^*$, implies the form generated by the symmetry elements of the supercell.

TABLE III

OBSERVED AND CALCULATED INTENSITIES FOR ϕ_2–$Ca_6Hf_{19}O_{44}$

h	k	l	i_c	I_c	I_o
1	1	0	3.41	3.41	.80
0	1	2	7.55	7.55	10.00
2	0	2	2.66	2.66	3.50
2	1	1	13.68	13.68	14.90
0	3	0	.24	.24	1.80
1	2	2	1.72		
1	1	3	.02	1.74	.40
2	2	0	2.53	2.53	2.50
1	3	1	1.63		
1	0	4	2.09	3.73	3.20
3	1	2	1.20	1.20	.05
0	2	4	2.15	2.15	2.40
0	4	2	3.10		
2	2	3	41.44	44.54	49.00
3	2	1	.30		
2	1	4	1.40	1.70	.20
4	1	0	4.67	4.67	7.60
2	3	2	.73	.73	1.80
1	3	4	1.11	1.11	.50
3	3	0	1.42		
1	2	5	4.82	6.24	11.30
5	0	2	210.96		
4	1	3	.05		
1	4	3	.16	211.17	215.00
2	4	1	.10		
4	0	4	3.18		
0	0	6	76.96	80.24	82.00
4	2	2	1.41	1.41	.40
5	1	1	.18		
3	2	4	.19		
1	1	6	.92	1.28	.75
3	1	5	.81	.81	.20
1	5	2	1.73		
3	3	3	.43	2.16	1.70
6	0	0	1.68	1.68	.10
4	3	1	12.81		
0	5	4	96.50		
0	3	6	.51		
3	0	6	.02	109.85	105.60
2	5	0	1.76		
2	3	5	.01	1.77	.80
3	4	2	2.17	2.17	1.10
2	4	4	.68		
2	2	6	1.25	1.93	1.20
1	6	1	.16		
5	1	4	.17	.33	.50
6	1	2	.14		
5	2	3	.14		
2	5	3	.02		
2	1	7	1.16	1.46	.70
4	4	0	.68		
4	2	5	.00	.69	.10
3	5	1	.44		
4	3	4	1.35		
4	1	6	.22		
1	4	6	3.46	5.47	5.20
1	5	5	.03	.03	.05
0	7	2	2.11		
5	3	2	.14		
1	3	7	.38		
0	1	8	3.00		
6	2	1	2.09	7.73	8.80
2	6	2	.02		
4	4	3	1.75		
2	0	8	.00	1.77	1.90
1	6	4	1.91		
3	3	6	.08	1.99	1.10
7	1	0	.88		
3	4	5	10.52	11.40	10.20
3	2	7	.20		
1	2	8	.26	.46	.10
5	4	1	.34		
7	0	4	.53		
3	5	4	.19	1.06	.60
3	6	0	1.04		
6	1	5	.14	1.18	.40
4	5	2	3.76		
7	1	3	5.04		
1	7	3	1.48		
3	1	8	.24		
6	2	4	.23		
0	6	6	.34		
6	0	6	1.59	12.68	15.90
8	0	2	.22		
2	4	7	.09		
0	4	8	.03		
2	7	1	16.25		
5	2	6	1.35		
2	5	6	.10		
1	1	9	.13	18.17	17.60
5	3	5	.29	.29	.10
7	2	2	.55		
6	3	3	.38		
3	6	3	.67		
5	1	7	.02		
2	3	8	.78	2.38	2.10
2	6	5	.13	.13	.60
8	1	1	.62		
5	4	4	.47	1.09	2.80
5	5	0	52.84	52.84	58.40
1	8	2	.28		
4	3	7	4.13		
5	0	8	62.72		
4	6	1	.05		
0	8	4	.54		
4	4	6	.18		
2	2	9	6.55	74.45	80.00
6	4	2	.40		
4	2	8	.27		
7	3	1	.00		
2	7	4	1.02	1.69	1.10
0	9	0	.43		
4	5	5	.02		
1	0	10	.88	1.33	1.20
3	7	2	.23		
5	5	3	01		
1	6	7	.13		
1	5	8	1.48	1.84	1.80
8	2	0	.00		
0	2	10	.48	.48	.80
8	1	4	.01		
1	7	6	.19		
7	1	6	.57		
4	1	9	.21		
1	4	9	.00	.97	.60
7	2	5	9.02		
2	1	10	.43	9.44	9.80
3	5	7	.09		
3	4	8	.31		
4	6	4	.06	.46	.30
8	2	3	.12		
2	8	3	.01		
6	2	7	.69		
6	5	1	.02		
1	9	1	.07		
7	3	4	.01		
3	6	6	.05		
6	3	6	.46		
3	3	9	.31	1.72	1.50
4	7	0	.00		
1	8	5	.95		
1	3	10	.61	1.56	.70
9	1	2	.77		
5	6	2	1.16		
6	1	8	.00	1.93	2.30
6	4	5	.00		
4	0	10	2.17	2.17	3.00
3	8	1	4.15	4.15	5.50
3	7	5	.08	.08	.05
3	2	10	.10	.10	.05
8	3	2	.20		
7	4	3	.02		
4	7	3	.04		
5	4	7	.08		
0	7	8	.96		
5	3	8	.19	1.49	1.90
0	10	2	20.65		
2	6	8	.11		
9	2	1	.00		
6	5	4	3.23		
1	9	4	1.45		
5	5	6	48.21		
5	2	9	.24		
2	5	9	.00		
1	2	11	.61		
0	5	10	26.60		
2	9	2	.05		
2	7	7	8.26	109.42	110.70
6	6	0	.01		
2	4	10	.04	.04	.20
5	7	1	.15		
3	8	4	.78		
0	9	6	.01		
9	0	6	1.08		
3	1	11	.18	2.20	2.90
10	1	0	.46		
5	6	5	.01		
9	1	5	.03		
5	1	10	.35	.86	1.90
7	5	2	.31		
8	1	7	.07		
4	5	8	3.58		
8	4	1	3.75		
10	0	4	15.22		
8	2	6	.34		
2	8	6	.00		
4	4	9	.11	23.40	24.90
4	8	2	.38		
6	6	3	.20		
4	6	7	.01		
8	0	8	.05		
9	2	4	.53		
0	0	12	5.80	6.98	7.80
2	3	11	.08		
9	3	0	.62		
8	3	5	2.44		
4	3	10	.11	3.26	4.60
1	10	3	.02		
10	1	3	.07		
7	3	7	.03		
7	2	8	.09		
1	1	12	.21	.43	.50
5	7	4	1.02		
7	4	6	.01		
4	7	6	.28		
7	1	9	1.51		
1	7	9	.03	2.85	3.60
2	9	5	.09		
1	6	10	.39	.48	.90
11	0	2	2.01		
9	3	3	3.95		
3	9	3	6.31		
1	8	8	.25		
2	10	1	.05		
8	4	4	.84		
0	3	12	.17		
3	0	12	.06		
4	2	11	.00	13.65	12.30
10	2	2	.39		
6	4	8	.80		
7	6	1	.00		
2	2	12	.11		
6	3	9	.04		
3	6	9	.18		
1	5	11	.03	1.55	1.90
8	5	0	.44		
7	5	5	.01		
7	0	10	.01		
3	5	10	.01		
6	7	2	.04		
1	9	7	.04		
6	5	7	.03		
3	7	8	.00	.59	.10
4	8	5	2.13		
6	2	10	.01	2.14	2.40
11	1	1	.26		
4	9	1	.06		
0	11	4	1.26		
3	4	11	4.03	5.61	6.00
9	4	2	00		
1	11	2	.08		
8	5	3	.15		
5	8	3	.19		
3	8	7	2.51		
2	10	4	.05		
1	4	12	1.23		
4	1	12	.44		
6	6	6	.03	4.68	5.50
10	3	1	.36		
7	6	4	.08		
1	10	6	.70		
10	1	6	.11		
5	5	9	.00		
6	1	11	.00	1.26	.40
5	4	10	.02	.02	.05
3	10	2	.26		
9	2	7	.04		
5	6	8	.18		
9	1	8	.04		
3	3	12	.15		
2	1	13	.50	1.18	.30
0	12	0	.09		
10	2	5	.09		
0	8	10	.17	.35	.10
11	1	4	.05		
4	9	4	.00		
9	3	6	.18		
3	9	6	.41		
5	3	11	.13		
11	2	0	.00		
7	7	0	.07		
6	7	5	.00		
2	7	10	.25	1.09	.80
5	7	7	.08		
8	3	8	.00		
6	8	1	.10		
1	3	13	.07		
2	8	9	.01		
8	2	9	.29		
2	6	11	.07	.62	1.20
8	6	2	.02		
8	4	7	2.37		
0	10	8	11.69		
9	5	1	.04		
10	3	4	.43		
6	0	12	.84		
0	6	12	.00	15.39	14.70
1	11	5	.20		
9	4	5	.18		
8	1	10	.01	.39	1.00
5	9	2	.27		
7	7	3	5.09		
11	2	3	1.43		
2	11	3	.60		
2	9	8	.01		
2	5	12	.01		
5	2	12	.40		
3	2	13	.11	7.90	6.60
4	10	0	.77		
4	6	10	.35	1.12	.80
1	12	1	.25		
5	8	6	.69		
8	5	6	.29		
7	4	9	.00		
4	7	9	.17		
4	5	11	.00		
0	1	14	.40		
3	10	5	.10		
7	3	10	.08	1.99	1.50
12	1	2	.24	.24	.05
7	5	8	.00	.00	.05
6	8	4	.07	.07	.05
2	0	14	.07	.07	.05
10	4	3	.20		
4	10	3	.06		
2	10	7	.00		
4	8	8	.10		
3	11	1	.08		
9	5	4	.90		
4	4	12	.01		
2	4	13	.03		
7	2	11	2.55		
1	2	14	.00	3.94	3.40
11	3	2	12	.12	.05
7	6	7	.01	.01	.05
5	1	13	.03	.03	.05
8	6	5	.07	.07	.20
8	7	1	.07		
1	12	4	.14		
1	8	11	.18		
3	1	14	.01		
9	6	0	.15		
5	9	5	.03		
1	9	10	1.40		
6	5	10	2.28		
0	13	2	.15		
7	8	2	.04		
11	1	7	.05		
4	9	7	.08		
11	0	8	1.07		
12	2	1	3.99		
1	7	12	.01		
7	1	12	.25		
0	12	6	.30		
12	0	6	.11		
4	3	13	.78		
6	6	9	.06		
6	4	11	.05		
0	4	14	.29	11.49	8.60
2	12	2	.13		
10	2	8	.51		
5	10	1	.00		
3	11	4	.01		
7	7	6	.06		
11	2	6	.08		
2	11	6	.01		
10	1	9	.17		
1	10	9	.00		
3	7	11	.10		
2	3	14	.08		
12	1	5	.84		
3	8	10	.00		
10	5	2	11.49		
9	6	3	06		
6	9	3	.00		
10	3	7	.37		
6	7	8	.01		
3	6	12	.02		
6	3	12	.20		
1	6	13	.03	14.19	11.30
10	0	10	7.83	7.83	7.60
11	4	1	.05		
8	7	4	.08		
13	0	4	.23		
9	3	9	1.30		
3	9	9	4.35		
5	0	14	10.09		
1	13	0	.03		
11	3	5	.11		
9	2	10	.47		
1	1	15	.01		
4	11	2	.03		
1	11	8	.01		
9	4	8	.00		
12	2	4	.06		
10	4	6	.21		
4	10	6	.92		
3	5	13	.00		
4	2	14	.23	18.17	16.80
6	8	7	.17		
5	10	4	9.67		
6	2	13	.14		
9	1	11	.08		
5	6	11	.05		
1	5	14	.95		
3	12	0	.02		
7	8	5	.02		
5	7	10	.70		
1	13	3	.12		
13	1	3	.19		
9	5	7	.04		
3	10	8	.08		
5	5	12	12.85		
8	8	0	.04		
2	12	5	3.95		
8	4	10	.40		
2	2	15	1.21		
7	9	1	.11		
11	4	4	.00		
5	8	9	.06		
8	5	9	.05		
8	3	11	.99		
3	4	14	.14		
10	5	5	.00	32.03	27.80
9	7	2	.05		
3	12	3	.00		
12	3	3	.09		
1	12	7	.11		
10	6	1	.16		
0	9	12	.02		
9	0	12	.79		
5	4	13	.01	1.23	1.10
14	0	2	.10		
6	10	2	1.34		
8	8	3	3.26		
8	6	8	.00		
2	13	1	.34		
2	8	12	.02		
8	2	12	.18		
6	9	6	.41		
9	6	6	.07		
2	9	11	.05		
6	1	14	.01		
11	5	0	1.65		
4	11	5	.01		
0	11	10	.27		
1	4	15	.00		
4	1	15	.02		
13	2	2	.04		
3	11	7	.06		
5	9	8	.00		
2	7	13	2.73	10.56	10.00
2	10	10	.00	00	.20

associated with anion layers at $z = \pm 1/24$ relative to the cations. It must be stressed that this is merely a convenient way of describing the structure; it does not imply that ϕ_2 is in any sense a layer structure. The (0001) layer stacking is such that the structure contains discrete $\{11\bar{2}0\}$ (or $\{1\bar{1}0\}_f^*$) sheets of composition HfO_2, which do not contain either calcium ions or anion vacancies; i.e. apart from small displacements, these sheets retain a perfect fluorite structure. They divide the structure into triangular prisms parallel to [0001], within which all the departures from the fluorite structure and composition occur.

One of the (0001) layers of cations in ϕ_2 is illustrated in Fig. 1(a). The broken lines represent the intersections of the sheets of perfect fluorite composition with this plane. The full lines represent the intersections of the triangular prisms, which contain all the calcium ions and vacancies. The structure within a triangular prism is shown in Fig. 1(b). The calcium ions form helical chains which extend along the hexagonal c axis, successive ions being related by $\frac{1}{2}\langle 110\rangle_f^*$ vectors. The formal anion vacancies also form helical chains in which vacancies and hafnium ions alternate. Successive vacancies within a chain are related by $\frac{1}{4}\langle 111\rangle_f$ vectors.

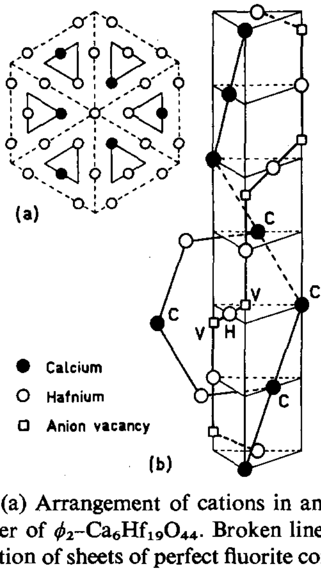

FIG. 1. (a) Arrangement of cations in an idealized (0001) layer of ϕ_2–$Ca_6Hf_{19}O_{44}$. Broken lines indicate the projection of sheets of perfect fluorite composition (HfO_2), and full lines outline the prisms containing the calcium ions and anion vacancies. (b) Ionic arrangement within a prism, showing helical chains of calcium ions and of vacancies. A "kite" configuration of calcium ions (marked C) is also shown.

In the lower half of Fig. 1(b) some additional cations are included to illustrate the cation arrangement in the $\{1\bar{1}1\}_f^*$ layers. The hafnium ion H, which is associated with two vacancies V along $\langle 1\bar{1}1\rangle_f^*$, lies at the centre of a hexagon of cations containing four calcium ions C in a "kite" configuration.

The arrangement of vacancies in ϕ_2 is such that all the calcium ions (the larger cations) have the eightfold coordination of the ideal fluorite structure, while hafnium ions are either six-, seven- or eightfold coordinated. Also, no two vacancies are closer than the $\frac{1}{4}\langle 111\rangle_f$ distance noted above.

5. The Structure of ϕ_1–$CaHf_4O_9$

5.1. *Analysis*

For this phase the diffractometer scan was restricted to 2Θ angles less than about 50°, the 220 fluorite being the highest angle reflexion recorded. This region contained 201 nonequivalent reflexions, reduced by overlap to 116 observations. Higher angle data was not collected as the nonfluorite peaks were all small and compounded of very many reflexions, and were therefore unlikely to contain appreciable information.

For trial structures in ϕ_1 the space group initially was assumed to be centrosymmetric, $C2/c$. As will be discussed later, attempts to find an alternative noncentrosymmetric trial trial structure supported the choice of the centrosymmetric space group. Two distinct fluorite-related arrangements are allowed by the space group; in one case the 80 cations (64 Hf, 16 Ca) occupy four $4(e)$ sites with diad symmetry and eight $8(f)$ general positions, in the other case ten $8(f)$ sites are occupied and there are no cations in special positions. The first case allows a greater number of possible ordered arrangements than the second, but for a particular ordered arrangement there will be fewer parameters to vary if it is of the first type.

For the case with all the cations in general positions, every distinct ordered arrangement was used as a trial structure with atoms initially in ideal fluorite positions. Only one of these arrangements (denoted I), which gave a residual of 0.154 was regarded as a possible starting point; the residuals for the other configurations ranged from 0.188 to 0.366 and were significantly worse than the residuals for some models discussed in the next paragraph.

A slightly different approach was adopted for the trial structures with some cations in special positions. The possibility that all 16 calcium ions occupy the four 4(*e*) sites was eliminated by direct trial; the residual was about 0.50. Thus calcium must occupy at least one 8(*f*) site. Each distinct 8(*f*) site was tested in turn, leaving the remaining cation sites occupied by hafnium. Two possibilities only (denoted II and III) yielded low residuals ($R = 0.162$ and 0.170, respectively) and for each of these the occupancies of the remaining cation sites were refined. A sequential method was used in which any site occupancies which increased to values beyond that appropriate for hafnium were reset to the hafnium value and thereafter excluded from the refinement. In each case a few cycles were sufficient to locate the remaining calcium ions, which were on 4(*e*) sites. The residuals for II and III at this stage were 0.135 and 0.146 with all ions in ideal fluorite positions. The two models were very similar, one being derived from the other by exchanging the (010) layers at $y = 1/16$ and $y = 5/16$.

The differences between the residuals for models I, II and III were not statistically significant (the variance ratio did not reach the 5% significance level for any pair) so that all were retained as trial structures. When the cation coordinates were refined the residuals fell to 0.098, 0.072 and 0.098, respectively. At this stage II was significantly better than either I or III.

An attempt was made to determine whether any ordered noncentrosymmetric structure (in *Cc*) might have been a better trial structure than the centrosymmetric structures investigated. For ordered structures in *Cc*, calcium ions must occupy four of the twenty nonequivalent cation sites so that, even allowing that many arrangements are equivalent, the number of possibilities is too large for each to be examined. Our procedure was to assume an ideal fluorite structure of hafnium ions only, ignoring the anions, and to introduce the calcium ions one by one by replacement of hafnium. At each stage all the symmetrically distinct positions for the calcium ion being introduced were considered, and the configuration with the lowest residual was used as the basis for the next stage. (Refining the occupancies of the remaining cations after two calcium ions had been introduced failed, probably because the structure was degenerate.) The cation ordering found in this way was identical to that in the centrosymmetric model II. This is persuasive, if not conclusive, evidence that the centrosymmetric model II for ϕ_1 is basically correct. The possibility of noncentrosymmetric displacements of the cations from their ideal positions was not investigated as the refinement in *C*2/*c* was satisfactory, and in *Cc* the ratio of observations to parameters would have been too low to allow any meaningful conclusions to be drawn.

The composition of ϕ_1 ($CaHf_4O_9$) is such that two of the twenty fluorite-derived 8(*f*) anion sites must be vacant. The location of one of these sites followed the lines already described. The largest cation tetrahedron in model II had a mean edge length of 3.77 Å, and this was taken to define one of the vacant anion sites. The mean edge length of four other tetrahedra ranged from 3.71 Å to 3.73 Å, and the remaining tetrahedra were appreciably smaller.

Two crystal chemical arguments were used in an attempt to decide which of these four larger tetrahedra defined the most likely location of the second vacant anion site:

(a) The ionic radius of calcium is about 40% higher than that of hafnium (*13*); calcium should therefore tend to have a higher coordination. In both $Ca_2Hf_7O_{16}$ (*6*) and $Ca_6Hf_{19}O_{44}$ the calcium ions retain the eightfold coordination of the fluorite structure, so that this feature might be expected to appear in $CaHf_4O_9$ also. One of the four larger tetrahedra of cations included a calcium ion, and was therefore excluded.

(b) None of the known anion-deficient fluorite-related structures (including the pyrochlore and C–rare earth oxide structures) contain vacancies which approach one another closer than $\langle 110\rangle_f$. The most common separation between pairs of vacancies is $\frac{1}{2}\langle 111\rangle_f$, the $\frac{1}{2}\langle 110\rangle_f$ separation occurs only in the C–rare earth oxide structure, and separations of $\frac{1}{2}\langle 100\rangle_f$ have not been reported. Two of the remaining tetrahedra defined sites which were related to the site already selected as vacant by $\frac{1}{2}\langle 100\rangle_f$ vectors, and were therefore rejected. The third, which is related to the vacant site by $\frac{1}{2}\langle 111\rangle_f$, was selected as the site of the remaining vacancies.

When the oxygen ions were removed from these sites and the cation coordinates refined, the residual fell from 0.072 to 0.068. This change is not statistically significant, but at least it is in the right direction.

In the final stage of refinement corrections for anomalous dispersion were introduced. This led to a further small reduction to 0.062 in the residual, but the changes in cation coordinates were trivial compared with their standard deviations. Because of the unfavourable data:parameter ratio, no attempt was made to vary the 54 positional coordinates of the anions. The refined cation coordinates are listed in Table IV, together with the ideal fluorite coordinates which provided the starting point for this analysis. Observed and calculated intensities are listed in Table V.

Because the structural models I and III gave relatively low residuals after the initial refinement of cation positions, they were given further consideration along with II. Model I was rejected on the crystal chemical grounds discussed earlier. No two anion sites satisfied the criteria that calcium should remain in eightfold coordination and that vacancies should not be separated by $\frac{1}{2}\langle 100\rangle_f$ vectors. Model III contained one possible pair of sites which were separated by $\frac{1}{2}\langle 110\rangle_f$, and which left the calcium coordination at eight. With these sites vacant, this model when refined gave a residual of 0.077, but the standard deviations of all the position parameters were about 50% worse than those obtained for model II. In addition, while vacancy pairs separated by $\frac{1}{2}\langle 110\rangle_f$ do occur in the C–rare earth structure, they have never been reported in structures where the vacancy concentration is less than 25%; hence they would not be expected in ϕ_1, where the vacancy concentration is 10%. These arguments support the

TABLE IV

IONIC COORDINATES IN ϕ_1-$CaHf_4O_9$[a]

Atom	Site	x_f	x	y_f	y	z_f	z
Hf1	4(*e*)	0.0	0.000	0.1875	0.190(4)	0.25	0.250
Hf2	4(*e*)	0.5	0.500	0.1875	0.183(4)	0.25	0.250
Hf3	8(*f*)	0.4	0.395(3)	0.1875	0.179(3)	0.45	0.457(3)
Hf4	8(*f*)	0.9	0.891(3)	0.1875	0.178(3)	0.45	0.456(3)
Hf5	8(*f*)	0.8	0.804(3)	0.1875	0.194(3)	0.65	0.669(3)
Hf6	8(*f*)	0.6	0.595(2)	0.0625	0.077(3)	0.55	0.546(3)
Hf7	8(*f*)	0.1	0.105(3)	0.0625	0.057(3)	0.55	0.552(3)
Hf8	8(*f*)	0.7	0.697(3)	0.0625	0.052(2)	0.35	0.363(3)
Hf9	8(*f*)	0.2	0.187(3)	0.0625	0.064(2)	0.35	0.338(4)
Ca1	4(*e*)	0.0	0.000	0.0625	0.053(14)	0.75	0.750
Ca2	4(*e*)	0.5	0.500	0.0625	0.060(14)	0.75	0.750
Ca3	8(*f*)	0.3	0.310(10)	0.1875	0.182(9)	0.65	0.643(12)
*V*1	8(*f*)	0.025		0.1875		0.45	
*V*2	8(*f*)	0.325		0.0625		0.35	
			$B_{Hf} = 0.0$	$B_{Ca} = 1.0$	$B_O = 3.0$		

[a] The twenty 8(*f*) anion sites have coordinates $(x_f \pm \frac{1}{8}, y_f, z_f)$, where (x_f, y_f, z_f) are the ideal fluorite coordinates of the cations. Eighteen of these sites are occupied by oxygen and two, *V*1 and *V*2 above, are vacant. (For cations in the 4(*e*) sites, the two associated anion sites are symmetrically equivalent.)

TABLE V

Observed and Calculated Intensities for ϕ_1–$CaHf_4O_9$

h	k	l	i_o	I_o	I_o	h	k	l	i_o	I_o	I_o	h	k	l	i_o	I_o	I_o	h	k	l	i_o	I_o	I_o
1	1	0	.08	.08	.11	1	5	-1	.00	.00	.02	6	4	-3	.04			5	1	-6	.08	.08	.09
1	1	-1	1.38	1.38	1.00	5	3	-1	.00	.00	.02	2	6	-2	.01			2	4	-5	.06		
2	0	0	.05	.05	.02	4	4	-1	.01	.01	.02	6	4	-1	.00			6	0	-6	.05		
0	2	0	.03	.03	.05	1	1	-4	.14	.14	.05	7	3	-2	.01	.20	.19	6	0	2	.01		
1	1	1	.17	.17	.15	4	4	-2	.11	.11	.02	5	5	-1	.00			3	1	-6	.01		
0	2	1	1.17	1.17	1.10	2	2	-4	.01	.01	.02	2	2	-5	.01			1	7	-2	.18		
2	0	-2	.19	.19	.20	6	2	-2	.01	.01	.05	7	3	-3	.04	.06	.16	3	7	-1	.35		
2	2	-1	.24	.24	.20	5	1	-4	.01	.01	.05	6	2	1	.01	.01	.02	3	1	4	.00	.66	.80
1	1	-2	.01	.01	.10	4	2	-4	.03	.03	.05	1	1	-5	.00	.00	.02	7	1	1	.06		
3	1	-1	.29	.29	.30	1	5	1	.00	.00	.02	5	1	2	.03			5	5	1	.06		
2	2	0	.61	.61	.74	2	4	-3	.05	.05	.02	0	6	2	.01	.04	.05	9	1	-3	.07		
0	0	2	.51	.51	.45	5	3	-3	.02	.02	.05	8	0	-2	.01			7	3	-5	.02	.21	.40
3	1	-2	.06			6	2	-3	.02			2	6	1	.02	.03	.05	1	1	5	.03		
3	1	0	.52	.58	.42	6	2	-1	.60	.61	.69	7	1	0	.06			4	2	-6	.00	.03	.05
1	3	0	.07	.07	.05	1	5	-2	.00			2	4	3	.02			8	0	0	.00		
2	2	-2	.06	.06	.02	1	3	3	.11			2	0	4	.25	.32	.44	3	7	-2	.04		
1	3	-1	.09	.09	.02	3	5	-1	.06	.16	.11	5	5	-3	.01	.01	.02	3	7	0	.10		
4	0	-2	.01	.01	.05	5	3	0	.34	.34	.22	7	3	-1	.00	.00	.02	4	6	1	.09		
0	2	2	.34	.34	.35	4	4	-3	11.44			6	2	-5	.02	.02	.02	2	0	-6	.10		
2	2	1	.03	.03	.05	4	0	2	6.01	17.45	18.00	3	3	-5	.00			9	1	-4	.00		
1	1	2	.13	.13	.20	3	5	-2	.07	.07	.02	1	3	4	.07			9	1	-2	.06		
1	3	1	.03	.03	.02	3	5	0	.04	.04	.02	3	3	3	.05	.11	.08	8	2	-5	.45		
4	0	0	1.17	1.17	1.25	0	4	3	.25	.25	.02	8	0	-4	.02	.02	.05	6	4	-5	.00		
3	1	-3	.30			7	1	-2	.02	.02	.05	0	4	4	.05	.05	.10	6	4	1	.42	1.26	1.54
3	1	1	.07	.37	.37	0	2	4	.37			4	6	-1	.01			7	5	-2	.02	.02	.04
4	2	-1	.04			7	1	-3	.02	.39	.29	1	5	3	.05			7	5	-3	.01		
1	3	-2	1.05			1	3	-4	.00	.00	.02	5	3	-5	.11			6	2	-6	.35		
3	3	-1	.41	1.50	1.44	6	2	-4	.14			5	5	0	.00			6	2	2	.07	.43	.32
1	1	-3	.20	.20	.18	6	2	0	.03			8	2	-3	.06			8	4	-3	.46	.46	.54
4	2	-2	1.40	1.40	1.56	0	6	0	.03			7	3	-4	.24	.46	.55	7	1	-6	.10		
0	4	0	.03	.03	.02	4	2	2	.00			7	1	-5	.10			5	1	3	.00	.10	.26
2	0	2	.03	.03	.02	1	5	2	.02			4	6	-2	.42	.51	.28	8	4	-2	.02		
3	3	-2	.20			5	3	-4	.03	.26	.19	6	4	-4	.07			2	6	-4	.02		
3	3	0	.23	.44	.10	4	4	1	.00			8	2	-2	.00			1	7	2	.00	.04	.07
2	2	-3	1.38	1.38	1.30	7	1	-1	.02	.02	.08	6	4	0	.07	.14	.14	6	6	-2	.02	.02	.02
0	4	1	.03			3	1	-5	.02			4	4	2	.02	.02	.05	4	6	-4	.01	.01	.02
5	1	-2	.11	.14	.13	1	1	4	.16			3	5	-4	.01			2	4	4	.04	.04	.02
4	2	0	.08	.08	.02	3	1	3	.04			3	5	2	.05			8	2	0	.18	.18	.08
5	1	-1	.29	.28	.10	0	6	1	.10	.31	.32	2	2	4	.01	.06	.08	2	2	-6	.07	.07	.02
2	4	-1	1.00	1.00	.80	3	5	-3	.08			2	6	-3	.27	.27	.20	7	5	-1	.01	.01	.02
4	2	-3	.00			3	5	1	.03			1	7	0	.01	.01	.02	3	5	-5	.00		
1	3	2	.11	.11	.05	2	6	-1	.09			4	6	0	.00	.00	.02	1	5	4	.03		
2	2	2	.45	.45	.20	5	1	-5	.03	.22	.19	8	2	-4	.01	.01	.04	5	3	-6	.04		
5	1	-3	.01	.01	.02	5	3	1	.16			1	7	-1	.05			3	5	3	.04	.11	.04
0	2	3	.05	.05	.02	2	6	0	.09	.26	.18	4	2	3	.17			6	6	-3	.01		
2	0	-4	14.15			2	4	-4	.02	.02	.02	1	3	-5	.07			6	6	-1	.12	.13	.08
2	4	1	28.19			6	4	-2	.02	.02	.02	1	5	-4	.13			0	4	5	8.65		
6	0	-2	13.92	56.26	59.20	4	4	-4	.02	.02	.02	5	3	2	.00	.43	.60	0	8	0	4.15		
4	2	1	.20	.20	.05	4	2	-5	.04	.04	.05	1	7	1	.03	.03	.02	8	0	-6	4.12		
1	5	0	.09			5	5	-2	.13			0	6	3	.01	.01	.02	8	4	-1	8.47	25.39	24.30
5	3	-2	.00	.09	.08																		

selection of model II as the most probable structure for ϕ_1.

5.2. Description

The structure of ϕ_1 is more complex than that of ϕ_2, but certain features can be distinguished and compared with similar features in ϕ_2. In the first instance, the distribution of calcium ions and vacancies is much more homogeneous than in ϕ_2; there are no obvious planes or layers of perfect fluorite composition. The calcium ions occur in chains, with neighbours separated by $\frac{1}{2}\langle 110\rangle_f$, but the chains have a much more irregular structure than those in ϕ_2 in that they change direction more frequently and tend to "wander" through the structure. The vacancies occur in groups of four, separated by three different $\frac{1}{2}\langle 111\rangle_f$ vectors, and do not form infinite chains as in ϕ_2. Nevertheless, within the chains in ϕ_2, the same arrangement of four vacancies can be distinguished; an example can be seen in Fig. 1(b), beginning with the vacancies V–V and including the next two vacancies higher up the figure.

Another feature of the structure of ϕ_1 which it shares with ϕ_2 is the occurrence of calcium ions in the "kite" configuration illustrated (for ϕ_2) in the lower part of Fig. 1(b); in ϕ_1 these kites lie on $(\bar{1}\bar{1}1)_f$ planes.

6. Discussion

The two structures described here, together with that of $Ca_2Hf_7O_{16}$ (ϕ) described previously (*6*), form a group of fluorite-related phases which, despite quite dissimilar unit cells, have a number of common features which relate to the arrangement of the formal anion vacancies. These vacancies are distributed so that the larger of the two cations, calcium, retains the full eightfold coordination of the ideal fluorite structure, while the smaller hafnium ions may be six-, seven- or eightfold coordinated. The fundamental vacancy group appears to be a $\frac{1}{2}\langle 111\rangle_f$ pair, with a cation in the middle. These pairs may be isolated as in $Zr_5Sc_2O_{13}$ (*10*), and $Zr_3M_4O_{12}$ (M = Sc, Yb) (*11*), and ϕ; alternatively they may coalesce to form finite groups as in ϕ_1, or extended chains as in ϕ_2 and the pyrochlore and C–rare earth structures.

It is surprising that the relatively complicated structures described here can be tackled with any success by powder methods. We believe that this can be attributed chiefly to two factors: firstly the structures are closely related to the simple fluorite structure which provided a starting point for refinements, and secondly electron diffraction data provided an unambiguous unit cell, its relationship to the subcell and also some space group data. The method of refinement, which avoids the problem of assigning individual structure factors to coincident or overlapping reflexions, may also have contributed.

Finally it must be pointed out that the structure determinations described here are not complete. The cation ordering and positions have been established with reasonable certainty. The anion distribution is less certain: in ϕ_2 the distribution of anion vacancies is probably correct, but the refined anion coordinates have large standard deviations, so that no attempt was made to derive bond lengths from these coordinates. In the case of ϕ_1, even the location of the vacancies is a little uncertain: the proposed arrangement is satisfactory on general crystal chemical grounds and is consistent with the X-ray data, but is not necessarily the only possibility. Resolution of these problems must await single crystal data, or perhaps powder data on corresponding phases on the ZrO_2–CaO system where scattering from the anions is relatively more important.

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