JOURNAL OF SOLID STATE CHEMISTRY **13**, 345–350 (1975)

The Structure of the Fluorite-Related Phase $Ca_2Hf_7O_{16}$

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Received April 8, 1974; revised August 5, 1974

The atomic arrangement in the fluorite-related phase, $Ca_2Hf_7O_{16}$, has been determined by powder X-ray diffraction. The unit cell is rhombohedral, $R\bar{3}$, with $a = 9.5273$ Å, $\alpha = 38.801°$, and $Z = 1$, and its volume is $2\frac{1}{4}$ times that of the fluorite subcell from which it is derived. The cations are ordered on the cation sites of the fluorite structure with the calcium ions segregated into discrete layers parallel to the (111) fluorite plane: there is some evidence that the formal anion vacancies are also ordered.

Introduction

Many pseudo binary oxide systems containing hafnia or zirconia have large regions of solid solution in which the crystal structure is an anion deficient "defect fluorite" type. At certain compositions vacancy or cation ordering may occur giving rise to new structures which contain prominent fluorite sub cells. The preparation of the fluorite related phase $Ca_2Hf_7O_{16}$ in the $CaO:HfO_2$ system by coprecipitation of the hydroxides followed by heat treatment is described in another paper (*1*). In that paper we also discuss the determination of the unit cell and its relationship to the fluorite sub cell, together with the density of the material; this information is summarized in Table I.

This paper describes the determination of the atomic arrangement, i.e., the ordering, in $Ca_2Hf_7O_{16}$ by powder X-ray diffraction.

Experimental

X-Ray reflexion intensities were measured on a powder diffractometer using Ni-filtered Cu$K\alpha$ radiation and a scintillation counter. The peaks were recorded on a chart using the continuous scan mode at a scan rate of 1/16° $\min^{-1}$ in 2θ, and the peak areas were subsequently measured with a planimeter. This procedure was preferred to step scanning, as it simplified the handling of incompletely resolved peaks. Preferred orientation was not expected to be a problem in this pseudocubic material, and electron diffraction patterns from numerous fragments deposited on carbon films showed no evidence of the effect.

Refinement

Powder data have the disadvantage of both fortuitously overlapping reflexions and, for

TABLE I

UNIT CELL DATA FOR $Ca_2Hf_7O_{16}$

Rhombohedral, $R\bar{3}$ (?$R3$)	Hexagonal representation
$a = 9.5273$ Å	$a = 6.3294 \pm 3$ Å
$\alpha = 38.801°$	$c = 26.396 \pm 2$ Å
$V = 305.26$ Å^3	
$Z = 1$	
$D_m = 8.346 \pm 7$ g cm^{-3}	
$D_c = 8.354$ (~8*m/o* ZrO_2 in HfO_2)	

(Standard deviations refer to the last place quoted)

Relationship of rhombohedral axes to subcell axes

$$\begin{pmatrix} \mathbf{u} \\ \mathbf{v} \\ \mathbf{w} \end{pmatrix} = \begin{pmatrix} 1/2 & 1 & 3/2 \\ 3/2 & 1/2 & 1 \\ 1 & 3/2 & 1/2 \end{pmatrix} \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{pmatrix}$$

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many space groups, coincidence of nonequivalent reflexions so that the number of reflexions that can be measured unambiguously may be much smaller than the number of measurable peaks. Rietveld (*2*) showed that this difficulty could largely be overcome by refining directly in terms of intensities, and applied the technique successfully to both X-ray and neutron diffraction powder data. Similar techniques have been used by a number of other workers (*3–5*). Following these lines we have written a full-matrix least-squares program, POWDER, based extensively on ORFLS (*6*) which treats groups of overlapping or coincident reflexions as single observations. The Lorentz-polarization and multiplicity factors were included in the calculated intensities, for comparison with the measured values which were used without any adjustments.

The function minimized was $\sum_i w_i[I_i(\text{obsd}) - I_i(\text{calcd})]^2$ and the residual quoted is

$$R = \tfrac{1}{2}\{\sum_i w_i[I_i(\text{obsd}) - I_i(\text{calcd})]^2 / \sum_i w_i I_i(\text{obsd})^2\}^{1/2}.$$

The factor $\frac{1}{2}$ may appear arbitrary but it is shown in the appendix that for statistically equivalent weighting schemes with nonoverlapping reflexions R is effectively equal to the widely used weighted residual based on F, denoted by Hamilton as R'' (*7*). This residual is therefore comparable numerically with the conventional and weighted residuals based on F quoted in the great majority of structure determinations.

The weight assigned to each observation was the product of two terms, an observational term which indicated uncertainty in the measured peak area arising from partial overlap or local background instability and which was unity for most observations, and a statistical term of the form $1/(I(\text{obsd}) + I_0)$. This form, which is simply derived from counting statistics, is appropriate when intensities measured with a counter are used directly in the refinement (*2*). If all observations are given equal statistical weight undue emphasis is placed on the strongest reflexions. While this can markedly decrease the value of R it may also increase the estimated standard deviations of the atomic parameters. I_0 was set at about twice the weakest intensity measured, but could be varied by an order of magnitude without significantly affecting the refined parameters.

The principal merit in refining in terms of intensities is that the additive property enables overlapping and ambiguously indexed reflexions to be used and this is almost essential with most powder data. There may also be some merit in an approach which seeks to fit the model to the actual observations rather than to derived quantities such as $|F|$ or F^2. This second factor is minor, however, and in most cases is more than offset by the fact that intensity data as such is not useful for Patterson or Fourier syntheses.

Another advantage of intensity refinement (which it shares with refinement in F^2) over that in |F| is that degeneracy in the trial structure is readily detected. If an ideal subcell is used as the basis for a trial structure for a supercell the calculated intensities are zero for all the superstructure reflexions and the refinement may fail. The physical explanation is that for these reflexions both positive and negative changes to any coordinate produce the same intensity change and the refinement is unable to decide between them. In practice an attempt to refine a degenerate parameter on the basis of intensities results in unreasonably large shifts in that parameter. A solution to the problem is to perturb sufficient of the parameters to remove the degeneracy, ensuring that all the possibilities are considered. The same method would work for refinement based on $|F|$, but there is now the likelihood that possible initial perturbations may be overlooked, or that the degeneracy may not be detected at all. Because of the algebraic details of $|F|$ refinement very small unintentional perturbations, e.g., a coordinate represented by 0.3333 instead of 1/3, may remove the degeneracy and allow the refinement to proceed normally. Since alternative initial perturbations of the degenerate parameters may then not be tested as possible trial structures there is no certainty that the refined structure is the correct one.

Structure Determination

The data set used in the structure determination comprised all those reflexions with Bragg angles less than 45°: this included 169 symmetrically independent reflexions, but overlap and coincidence reduced the number of independent observations to 88.

Unobserved reflexions were divided into two groups. A few, which lay in the tails of strong partially resolved peaks and could not be assigned to any one peak, were ignored in the refinement. Non observed reflexions which did not coincide with other peaks were given intensities equal to about half the weakest measured intensity, and unit observational weight. In the final stage of the refinement the weight of these reflexions for which I(calcd) was less than I (obsd) was reduced to 0.1.

Scattering factors for neutral atoms (*8*) were used with corrections for anomalous dispersion (*9*). The factors for hafnium were adjusted to take account of the fact that the hafnium oxychloride from which the sample was prepared contained about 8 mole% of zirconium oxychloride.

The X-ray and electron diffraction data reported previously (*1*) showed all the reflexions characteristic of a rhombohedral cell so that the space group was $R3$ or $R\bar{3}$, since $R32$, $R3m$ and $R\bar{3}m$ are not consistent with the relationship between the unit cell and the fluorite subcell. Refinement was carried out initially in the centrosymmetric space group $R\bar{3}$.

The triply primitive hexagonal cell used for convenience contains three formula units of $Ca_2Hf_7O_{16}$, and comparison with the fluorite structure suggests that the cations should occupy 18(f) sites, 6(c) sites and 3(a) sites. Initially, no assumptions were made as to either cation or anion ordering and the atoms were distributed randomly over their ideal fluorite sites. This model could not be refined as it is degenerate with respect to all the atomic parameters.

To eliminate the degeneracy one coordinate of the cations occupying the (f) sites was perturbed in both positive and negative senses. Cation positions were refined for each perturbation and in both cases an R of about 17% was obtained. Cation occupancies were then varied. One perturbation indicated that calcium was located predominantly on the 6(c) sites and R fell to about 9%. This arrangement is in fact the only one possible if the cations are to be fully ordered, regardless of whether the space group is $R\bar{3}$ or the noncentrosymmetric $R3$. The second perturbation gave an unacceptable set of occupancies and a much larger R and therefore was rejected.

With the ordering and the positions of the cations approximately determined an attempt was made to locate the anions. There are 48 oxygen atoms distributed amongst two groups of 18(f) sites and three groups of 6(c) sites: refinement of the occupancies of these sites using the ideal fluorite positions was not completely conclusive, though the (c) site at 0,0,1/12 had much the lowest occupancy. The dimensions of the cation tetrahedra surrounding each of the five independent oxygen sites were examined and it was found that the average metal–metal distance in the tetrahedron surrounding the 0,0,1/12 position was 3.86 Å, compared with 3.55–3.66 Å in the other tetrahedra. Since it is known that in related structures the cation polyhedra enclosing an anion vacancy are dilated (*10*) this confirms the (c) site at 0,0,1/12 as the most probable location of the oxygen vacancy.

The cation coordinates were now refined assuming both cation and anion ordering and the residual was reduced to 7.88%. To avoid oscillation of some of the parameters it was necessary to multiply the shifts calculated in each refinement cycle by about 0.7 before adjusting the parameters. Finally, all the coordinates were refined together and the residual was further reduced to 7.03%: in the final cycle the parameter changes were less than one tenth of the estimated standard deviations.[1] The observed and calculated intensities at this stage are shown in Table II. The refined atomic coordinates and their estimated standard deviations are given in Table III which also indicates the site of the

[1] When this final refinement was performed with all the observations given equal statistical weight R was reduced to 2.18%. However, the estimated standard deviations of the parameters were increased by about 50%.

TABLE II

Observed and Calculated Intensities for $Ca_2Hf_7O_{16}$

h	k	l	i_c	I_c	I_o
0	0	3	39.46	39.46	33.10
1	0	1	0.01	0.01	0.52
1	0	-2	3.53	3.53	3.60
0	0	6	2.88	2.88	2.58
1	0	4	15.28	15.28	18.50
1	0	-5	14.35	14.35	14.70
1	1	0	10.93	10.93	11.92
1	0	7	2.03	2.03	0.50
1	1	3	5.02		
1	1	-3	216.33	221.35	219.80
0	0	9	67.61	67.61	67.70
1	0	-8	1.11	1.11	2.10
2	0	-1	8.22	8.22	8.00
2	0	2	1.47	1.47	1.72
1	1	6	85.57		
1	1	-6	4.94	90.51	98.70
2	0	-4	0.52	0.52	1.46
2	0	5	0.00	0.00	0.20
1	0	10	0.11	0.11	0.20
2	0	-7	1.74	1.74	1.28
0	0	12	4.65		
1	0	-11	0.34	4.98	7.20
1	1	9	6.48		
1	1	-9	0.81	7.29	5.20
2	0	8	5.33	5.33	4.40
2	1	1	4.89		
1	2	-1	0.57	5.45	7.25
2	1	-2	1.12		
1	2	2	6.93	8.05	10.87
2	1	4	1.01		
1	2	-4	0.25	1.26	1.44
2	1	-5	2.28		
1	2	5	0.13	2.41	3.28
1	0	13	2.03		
2	0	-10	3.18	5.20	2.16
3	0	0	67.79	67.79	64.20
2	1	7	0.16		
1	2	-7	3.99	4.15	**
1	1	12	0.11		
1	1	-12	69.13		
2	0	11	0.45	69.70	74.70
3	0	3	1.48		
3	0	-3	1.49	2.97	4.45
1	0	-14	1.04	1.04	0.50
0	0	15	0.02		
2	1	-8	3.11		
1	2	8	0.01	3.14	1.58
3	0	6	0.48		
3	0	-6	0.47	0.95	0.58
2	0	-13	0.48		
2	1	10	2.33		
1	2	-10	0.12	2.93	2.10
2	2	0	0.74	0.74	0.20
1	0	16	0.09	0.09	0.20
2	1	-11	0.67		
1	2	11	3.04	3.71	2.86
2	2	3	26.50		
2	2	-3	0.70	27.21	25.30
2	0	14	0.21	0.21	**
3	0	9	25.86		
3	0	-9	25.88	51.74	54.80
1	1	15	30.13		
1	1	-15	3.08	33.20	35.90
3	1	-1	0.49		
1	3	1	2.30	2.79	3.92
3	1	2	1.28		
1	3	-2	3.20	4.48	6.50
1	0	-17	0.16	0.16	0.50
2	2	6	0.83		
2	2	-6	15.24	16.07	17.10
3	1	-4	2.94		
1	3	4	1.57	4.50	6.70
0	0	18	6.00	6.00	8.57
3	1	5	3.71		
1	3	-5	0.85	4.56	5.01
2	1	13	0.21		
1	2	-13	0.11	0.32	0.20
2	0	-16	0.68	0.68	0.50
3	1	-7	0.52		
1	3	7	1.81	2.33	3.42
3	0	12	2.23		
3	0	-12	2.25	4.48	5.34
2	1	-14	0.69		
1	2	14	0.05	0.75	0.50
2	2	9	0.05		
2	2	-9	1.11	1.16	0.50
3	1	8	0.40		
1	3	-8	0.61	1.00	0.70
4	0	1	0.21	0.21	0.20
4	0	-2	0.04	0.04	0.20
2	0	17	1.51	1.51	0.50
1	0	19	0.03	0.03	0.50
4	0	4	2.07	2.07	1.88
1	1	18	1.35		
1	1	-18	0.02	1.38	2.00
4	0	-5	1.92	1.92	1.00
3	1	-10	0.37		
1	3	10	1.05	1.42	0.50
2	1	16	0.07		
1	2	-16	1.15		
4	0	7	0.04	1.26	1.62
2	2	12	17.75		
2	2	-12	0.03		
3	1	11	0.87		
1	3	-11	2.01		
1	0	-20	0.34	20.99	17.08
3	0	15	0.01		
3	0	-15	0.01	0.02	0.30
4	0	-8	0.04	0.04	0.30
0	0	21	0.74		
3	2	1	0.64		
2	3	-1	2.61	4.00	5.06
3	2	-2	0.95		
2	3	2	0.00	0.95	0.70
2	1	-17	0.74		
1	2	17	0.07	0.81	0.20
2	0	-19	0.47	0.47	0.20
3	2	4	0.48		
2	3	-4	0.28	0.76	0.50
3	2	-5	0.28		
2	3	5	0.06	0.33	0.20
3	1	-13	1.62		
1	3	13	1.16		
4	0	10	0.06	2.84	1.00
4	1	0	0.24		
1	4	0	0.26		
3	2	7	0.96		
2	3	-7	0.05		
4	0	-11	0.03		
2	0	20	0.28	1.82	2.16
4	1	-3	9.26		
1	4	3	0.12		
1	4	-3	9.31		
4	1	3	0.13	18.82	18.20
3	1	14	2.20		
1	3	-14	0.14	2.33	**
2	2	15	0.92		
2	2	-15	10.82	11.75	14.30
3	2	-8	0.84		
2	3	8	2.11	2.95	**
1	0	22	0.38	0.38	**
1	1	21	0.00		
1	1	-21	10.46	10.47	11.10
4	1	6	5.95		
1	4	6	5.94		
4	1	-6	0.21		
1	4	-6	0.20	12.30	11.50
2	1	19	0.61		
1	2	-19	0.04	0.65	**
3	0	18	7.27		
3	0	-18	7.27	14.54	15.25
4	0	13	1.48		
3	2	10	0.44		
2	3	-10	1.87	3.79	2.40
1	0	-23	0.30	0.30	0.20
3	1	-16	0.49		
1	3	16	0.51	1.00	0.20
3	2	-11	0.64		
2	3	11	0.01	0.65	0.20
2	1	-20	0.02		
1	2	20	1.20	1.22	0.20
4	0	-14	1.00	1.00	0.20
4	1	9	0.49		
4	1	-9	0.01		
1	4	9	0.51		
1	4	-9	0.02	1.03	0.40
0	0	24	0.03	0.03	0.20
2	0	-22	0.11	0.11	0.20
5	0	-1	2.17	2.17	2.54

TABLE III

FRACTIONAL ATOMIC COORDINATES (HEXAGONAL) WITH ESTIMATED S D IN PARENTHESES

Atom	x	y	z
Hf(1)	0.000	0.000	0.0000
Hf(2)	−0.001 (2)	0.361 (2)	0.1133 (4)
Ca	0.000	0.000	0.3348 (25)
O (1)	0.000	0.000	0.2465 (56)
O (2)	0.000	0.000	0.4068 (53)
O (3)	−0.006 (18)	0.340 (18)	0.0335 (27)
O (4)	−0.003 (19)	0.374 (16)	0.1976 (29)
Vacancy	*0.000*[a]	*0.000*[a]	*0.0833*[a]

[a] Figures in italics correspond to coordinates derived by comparison with the ideal fluorite structure.

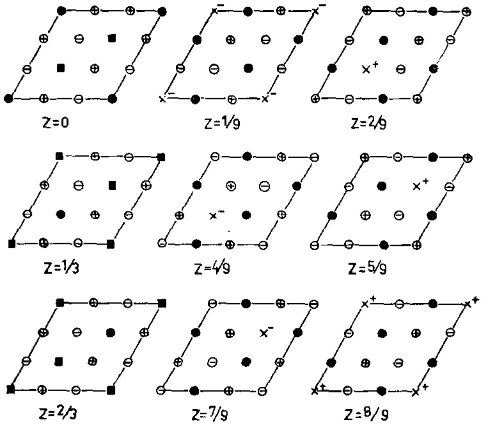

FIG. 1. Sections parallel to (001) of the idealized hexagonal unit cell of $Ca_2Hf_7O_{16}$. ● Hf; ■ Ca; ⊕ O at $Z + 1/36$; ⊖ O at $Z - 1/36$; × vacant anion site.

formal anion vacancy; it will be seen that the anion coordinates are of low accuracy.

The residual was further reduced by including an overall isotropic temperature factor, but its refined value was slightly negative, and therefore physically unacceptable; it did not differ significantly from zero. A similar effect was noticed by Longo and Sleight (*3*) who suggested that it could arise from surface roughness if the sample was highly absorbing. Since the temperature factor is unimportant for low angle reflexions from heavy atoms it was assumed to be equal to zero here. The residual was also reduced slightly by allowing some cation disorder, and the lowest value was obtained when about 12% of the calcium sites were occupied by hafnium. This disorder is quite feasible, but statistically did not represent a significant improvement on the fully ordered model.

An attempt to further refine the structure in the noncentrosymmetric space group $R3$ did not result in any noticeable improvement in the residual despite the greater number of parameters. Also the parameters in the noncentrosymmetric case did not differ significantly from those in the centrosymmetric model. We therefore conclude that within the limits imposed by the data the space group may be taken as $R\bar{3}$.

Discussion

The idealized hexagonal unit cell of $Ca_2Hf_7O_{16}$ is illustrated in Fig. 1, which shows the nine layers of cations with their immediately adjacent anions that comprise the structure. This structure is derived from the fluorite type by the segregation of the calcium atoms on to certain planes parallel to (111) of the cubic subcell. In the hexagonal representation these planes are parallel to (001). Those at $z = 0$, $\pm 1/3$ contain two calcium and one hafnium atoms per unit cell while the planes at $z = \pm 1/9$, $\pm 2/9$, $\pm 4/9$ contain hafnium atoms only. In the real structure some of the cation coordinates depart appreciably from their ideal fluorite-derived values, and this may be attributed to the repulsive effect of the anion vacancies. Table IV gives the dimensions of the cation tetrahedra enclosing each of the five nonequivalent anion sites. An idea of the distortion of the fluorite structure due to the ordering may be obtained by noting that in the fluorite structure with the same subcell volume the distances between all nearest neighbour cations would be 3.63 Å, compared with 3.47 to 3.97 Å in the ordered structure.

The calculated anion–cation distances range from 2.03 to 2.42 Å, except for one very short oxygen–calcium distance of 1.90 Å. However, in view of the large standard deviations in these distances (from 0.10 to 0.15 Å) no real significance can be attached to them so that they are not presented individually.

TABLE IV

INTERATOMIC DISTANCES IN NEAREST-NEIGHBOUR CATION TETRAHEDRA

Central anion	Cations	Interatomic distance (Å)[a]
O (1)	Hf:Hf	3 × 3.50
	Hf:Ca	3 × 3.64
O (2)	Hf:Hf	3 × 3.52
	Hf:Ca	3 × 3.58
O (3)	Hf:Hf	3.77
	Hf:Ca	3.58, 3.64, 2 × 3.66
	Ca:Ca	3.66
O (4)	Hf:Hf	2 × 3.47, 3.50, 3.52, 3.64, 3.97
Vacancy	Hf:Hf	3 × 3.77, 3 × 3.97

[a] Multipliers indicate the number of symmetrically equivalent distances within each tetrahedron.

The anion vacancies are so ordered that the hafnium atoms in (*a*) sites are sixfold coordinated by oxygen while those in (*f*) sites are sevenfold coordinated; the calcium atoms retain the full eightfold coordination of the fluorite structure. This is consistent with the general rule that the larger ions tend to occupy the sites with the higher coordination; the ionic radius of Ca^{2+} in eightfold coordination is 1.26 Å, and that of Hf^{4+} is 0.97 Å (*11*).

Alternatively, the structure can be described in terms of the *I* and *F* units of Thornber, Bevan, and Graham (*10*). In these terms the rhombohedral unit cell is composed of one *I* unit of composition M_7O_{12} (or M_7O_{36} considered in isolation) in which all the cations are hafnium, and two *F* units with the composition MO_2 (MO_8 in isolation) containing the calcium. Thus the structure described here fits into the general framework of fluorite-related M_nO_{2n-2} phases postulated by Thornber, Bevan, and Graham.

Appendix

Relationship between Weighted Residuals based on I *and on F*

$$R = \tfrac{1}{2}\Big\{ \sum_i w_i^I \, [I_i(\text{obsd}) - I_i\,(\text{calcd})]^2 \Big/ \sum_i w_i^I I_i\,(\text{obsd})^2\Big\}^{1/2}$$

where $w_i^I = 1/\text{var}I_i$ for the statistically best weighting. Now $I_i = k_i F_i^2$ so that var $I_i = 4k_i^2F_i^2$ var F_i, where k_i includes *Lp*, multiplicity factors, etc.

Substituting for *I* and *w* in the expression for *R*, and noting that for a refined structure *F*(obsd) and *F*(calcd) need only be distinguished in difference terms, yields

$$R = \Big\{ \sum_i w_i^F [|F_i(\text{obsd})| - |F_i(\text{calcd})|]^2 \Big/ \sum_i w_i^F F_i(\text{obsd})^2\Big\}^{1/2} = R'',$$

where $w_i^F = 1/\text{var}\ F_i$.

Acknowledgment

The authors would like to thank Mr. J. G. Alipress for collecting the diffractometer data, and for helpful discussions on this work.

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