JOURNAL OF SOLID STATE CHEMISTRY **19**, 103–111 (1976)

Crystal Structures of Some Fluorite-Related M_7O_{12} Compounds

H. J. ROSSELL

CSIRO Division of Tribophysics, P.O. Box 4331, Melbourne 3001, Australia

Received April 26, 1976

Powder X-ray diffraction techniques have been used to determine the crystal structures of $Ti_3Sc_4O_{12}$, $Nb_{1.5}Sc_{5.5}O_{12}$, $NbSc_6O_{11}F$, $NbSc_5HfO_{12}$, $Zr_3Er_4O_{12}$, and $Hf_3Sc_4O_{12}$ and to reexamine the structures of $Zr_3Sc_4O_{12}$ and $Zr_3Yb_4O_{12}$. All the compounds have the same fluorite-related superstructure as reported previously for Pr_7O_{12}, UY_6O_{12}, $Zr_3Sc_4O_{12}$, and $Zr_3Yb_4O_{12}$. Most of the compounds exhibit cation ordering, a situation observed previously only in UY_6O_{12}. One-seventh of the cations occupy a set of special sites of symmetry $\bar{3}$ and are octahedrally coordinated by oxygen. These cations are of the type that has the smallest available ionic radius. The remaining cations occupy a set of general sites randomly with respect to atom type and are sevenfold coordinated by oxygen. In $Hf_3Sc_4O_{12}$, only partial ordering of this nature occurs, while it is confirmed that no cation ordering occurs in $Zr_3Sc_4O_{12}$. Some aspects of the cation order–disorder situation are discussed.

Introduction

Compounds of the general formula M_7O_{12} which possess a common fluorite-related superstructure have been reported for various systems, e.g., Ce_7O_{12} (*1*), Pr_7O_{12} (*2*), Tb_7O_{12} (*3*), $Zr_7O_8N_4$ (*4*), $Zr_3Sc_4O_{12}$, $Zr_3Tm_4O_{12}$, $Zr_3Er_4O_{12}$, $Zr_3Yb_4O_{12}$ (*5–7*), $Ti_3Sc_4O_{12}$(*8*), WY_6O_{12} (*9*), WTb_6O_{12}, WLu_6O_{12} (*10*), UY_6O_{12}, and ULu_6O_{12} (*11*). Crystal structures have been determined for Pr_7O_{12}(*12*), UY_6O_{12} (*11*), $Zr_3Sc_4O_{12}$ (*6*), and $Zr_3Yb_4O_{12}$ (*13*). The space group is $R\bar{3}$, No. 148 (or $R3$, No. 146). One-seventh of the cations are located at the special site 1(*a*), (0,0,0), and the remainder in the general 6(*f*) positions. The formally vacant anion sites, relative to the M_7O_{14} fluorite parent, are at the 2(*c*) positions $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ on the triad axis; there is some relaxation of ions from their fluorite positions around these vacant sites.

For the compound UY_6O_{12}, the U cation occupies the special origin site, but for the other three compounds, the situation is not clear. Thus, for Pr_7O_{12}, it was deduced that Pr^{4+} occupied the special site, while no cation ordering was found in $Zr_3Sc_4O_{12}$ and only a tendency for Zr to occupy the special site in $Zr_3Yb_4O_{12}$, suggesting that in the latter two cases the difference between the ordered structures and the disordered fluorite substructure lies chiefly in the arrangement of formal anion vacancies. This seems unlikely, since oxides of anion-deficient fluorite-type possess high anion mobility in the temperature range (1300–1600°C) at which the compounds were formed (*14*), so that if ordering of vacant sites were the only requirement for compound formation this should be fast and should occur at relatively low temperatures, whereas most of these ternary compounds form slowly at high temperatures. If the cations were ordered, as they are in UY_6O_{12}, then the slow formation could be accounted for by the known very low cation mobilities.

Structural studies in this laboratory (*15, 16*) have shown that complete cation ordering occurs in other fluorite related compounds, and so it was of interest to examine some of the M_7O_{12} compounds to determine whether or not they exhibit cation ordering also. The compounds studied were $Zr_3Er_4O_{12}$, $Zr_3Yb_4O_{12}$, $Zr_3Sc_4O_{12}$, $Hf_3Sc_4O_{12}$, $Ti_3Sc_4O_{12}$,

Printed in Great Britain

$Nb_{1.5}Sc_{5.5}O_{12}$, $NbSc_6O_{11}F$, and $NbSc_5HfO_{12}$; the last three have not been reported previously. The structure determinations of $Zr_3Sc_4O_{12}$ and $Zr_3Yb_4O_{12}$ were repeated because it was felt that the earlier studies contained unsatisfactory features, particularly in the choice of weighting scheme.

Experimental

1. *Materials*

Zirconium carbonate paste from Magnesium Elektron Ltd., containing some 2 wt% HfO_2, was dissolved in analytical grade nitric acid to form a stock solution.

Pure $HfCl_4$ from Wah Chang was hydrolyzed and dissolved in dilute HCl.

Sc_2O_3 (99.5%) from Amdel, and Er_2O_3 and Yb_2O_3 from Atomergic Chemetals, although stated to be free from other rare earths, nevertheless contained some unknown material that prevented the preparation of pure compounds. The oxides were purified by dissolution in nitric acid, followed by precipitation with oxalic acid in acid solution. The oxalates were calcined to decompose them to oxides, and the process was repeated.

Nb_2O_5 (99.5%) from Koch–Light Ltd. was calcined at 1000°C for 16 hr and used without further treatment.

2. *Compounds*

$Zr_3Sc_4O_{12}$, $Hf_3Sc_4O_{12}$, $Zr_3Er_4O_{12}$, and $Zr_3Yb_4O_{12}$ were prepared by coprecipitation as hydrated oxides from acid solution with ammonia. Precipitates were washed, calcined at 1000°C, and pelleted. The compounds $Zr_3Er_4O_{12}$ and $Zr_3Yb_4O_{12}$ were formed by heating at 1400°C for 3–4 days, and $Hf_3Sc_4O_{12}$ was formed by heating at 1200°C for several weeks.

In the case of $Zr_3Sc_4O_{12}$, different specimens were heated for periods up to many months at temperature of 850, 1000, 1200, and 1350°C. The compound formed very quickly, e.g., 5 min at 1200°C, and was the same no matter what heat treatment was used.

$NbSc_5HfO_{12}$. A coprecipitate of hydrated oxides containing 1Hf:5Sc was prepared as above, ignited at 800°C, ground under acetone with the required amount of Nb_2O_5, pelleted, and heated at 1400°C for 1 week.

$NbSc_6O_{11}F$. The compound NbO_2F was prepared by evaporating to dryness a solution of Nb_2O_5 in 40% HF and heating the residue at 270°C for 5 hr (*17*). An X-ray powder pattern showed lines of the required product only. Weighed quantities of Sc_2O_3 and NbO_2F were ground together and loaded into a gold tube, which was welded shut under vacuum and heated at 1000°C for 2 weeks.

$Nb_{1.5}Sc_{5.5}O_{12}$. Weighed amounts of constituent oxides were ground together under acetone, pelleted, and heated at 1280°C for 10 days.

$Ti_3Sc_4O_{12}$. A coprecipitate of hydrated oxides was prepared using ammonia and an acid solution of Sc^{3+} and Ti^{3+} (from $TiCl_3$). It was fired at 1280°C for 1 week.

The course of superstructure formation could be followed by examination of Guinier photographs (see below): For all compounds except $Zr_3Sc_4O_{12}$ and $Hf_3Sc_4O_{12}$ the fluorite subcell lines were sufficiently widely split to allow detection of any disordered fluorite material remaining in the specimen.

3. *Diffraction Studies*

X-ray powder photographs of all compounds were taken with a Hägg–Guinier focusing camera of diameter 100 mm, using copper $K\alpha_1$ radiation and thoria ($a_0 = 5.5972$ Å) as internal standard. Unit cell dimensions were evaluated from about 20 lines by a least-squares procedure.

In all cases, the symmetry, $R\bar{3}$ or $R3$, was checked by examination of electron diffraction patterns of a single crystal fragment. These patterns were obtained using a JEM 200 electron microscope fitted with a tilting stage and operated at 200 kV.

Intensity data for copper $K\alpha$ radiation were obtained on a recorder chart using a powder diffractometer fitted with a scintillation counter and a graphite monochromator, and scanned at $\frac{1}{4}$°/min in 2θ. Preferred orientation effects were not expected with these pseudocubic materials and were shown in fact to be negligible in the case of $Nb_{1.5}Sc_{5.5}O_{12}$ and $NbSc_6O_{11}F$ by the procedure of dilution with the organic glass poly(ethylenephthalate).

Partially overlapping peaks on the recorder chart were separated where practicable, and the peak areas were measured with a planimeter.

Structure Refinement

Structure refinement was carried out using the least-squares program POWDER, developed in this laboratory, which treats overlapping or coincident reflexions as single observations, and which refines in terms of intensity. The quantity minimized is $\sum w(I_{obs}-I_{calc})^2$, where $w = K/(I_{min} + I_{obs})$, I_{min} is an intensity about equal to the smallest observable, and K is a multiplier reflecting a subjective assessment of the relative accuracy of any particular intensity measurement.

The residual R used here is $\frac{1}{2}[\sum w(I_{obs}-I_{calc})^2/\sum w\ I_{obs}^2]^{\frac{1}{2}}$ which is comparable numerically to the weighted residual R'' commonly used in single-crystal structure refinements based on F (*16*). It was found that for a well-refined structure, the standard deviations of refined parameters were at a shallow minimum for some reasonable value of I_{min}, and these are the parameters reported here. The value of R was not the lowest obtainable: A lower value could be obtained by changing the weighting scheme, e.g., to unit weights, but then the estimated standard deviations of refined parameters increased markedly.

Scattering factors for neutral atoms (*18*) were used, together with corrections for anomalous dispersion (*19*); the latter are particularly important in the case of rare-earth atoms and copper radiation. A weighted mean of scattering factors was used in those cases where more than one atom type occupied a site.

An overall isotropic temperature factor of zero was used in all cases. It was found that isotropic temperature factors of individual atoms, when refined, were all about that value with large standard deviations. The value is not unreasonable, considering the refractory nature of the materials, the low-angle data used, and the consequences of surface roughness in the specimens.

In the triply primitive hexagonal representation of the space group $R\bar{3}$, a fluorite-related structure with cell contents $M_{21}O_{36}V_6$ (V = anion vacancy) has three cations located at the equipoints 3(*a*) (0,0,0) and the remainder at a general 18(*f*) set of positions, anions at two sets of 18(*f*) positions, and anion vacancies at the 6(*c*) set of positions.

Some difficulty was experienced in finding a suitable trial structure. A model with atoms in ideal fluorite positions cannot be used because of degeneracy (all structure factors are extrema or zero), while simple perturbations did not allow refinement to proceed satisfactorily. Finally, a model was used for which (i) cations were ordered in the sense that one atom type occupied the special 3(*a*) site, and the others occupied the general 18(*f*) site randomly (or in two groups on 9(*b*) sites in the noncentrosymmetric space group $R3$); (ii) anion vacancies were located on triad axis at $(0,0,\frac{1}{4})$; (iii) anions adjacent to the vacant sites had relaxed toward it by 0.25 Å, a condition found in other fluorite-related structures (*15*, *16*) so as to form the vertices of a regular octahedron centered on the 3(*a*) cation; and (iv) cations adjacent to the anion vacancy had moved away from it by 0.2 Å, as also found in other structures.

Refinement of this model resulted in low R values and acceptably small estimated standard deviations of refined parameters. Further, in contrast to earlier attempts mentioned above, a real minimum had been reached in that perturbation of any parameters, followed by refinement, returned to the original results. The various ordered arrangements of cations were tried in the model. Variation of cation occupancies during refinement also indicated the cation arrangement in most cases, and as well, the refined value for the occupancy of an oxygen atom on the nominally vacant site was close to zero. Thus it was felt that a correct structure had been arrived at.

Results and Discussion

Lattice parameters for the various compounds are shown in Table I. The values agree with those previously published, where available, but it may be noted that effectively

TABLE I

UNIT CELL DATA

	Rhombohedral		Hexagonal		
	a (Å)	α (°)	a (Å)	c (Å)	V (Å^3)
$Ti_3Sc_4O_{12}$	5.9701(6)	99.13(2)	9.0880(7)	8.5443(11)	611.1(2)
$Nb_{1.5}Sc_{5.5}O_{12}$	6.0830(9)	99.12(4)	9.2590(13)	8.7083(18)	646.5(2)
$NbSc_6O_{11}F$	6.0931(7)	99.12(4)	9.2746(11)	8.7224(9)	649.8(2)
$NbSc_5HfO_{12}$	6.1036(7)	99.20(4)	9.2964(10)	8.7185(12)	652.5(2)
$Hf_3Sc_4O_{12}$	6.1395(6)	99.29(1)	9.3710(7)	8.7060(8)	662.1(1)
$Zr_3Sc_4O_{12}$	6.1544(8)	99.52(3)	9.3960(10)	8.7200(20)	666.7(2)
$Zr_3Yb_4O_{12}$	6.3351(7)	99.32(2)	9.6570(8)	9.0235(10)	728.8(2)
$Zr_3Er_4O_{12}$	6.3711(7)	99.29(2)	9.7102(8)	9.0804(11)	741.5(2)
	For cubic, $\alpha = 99.59°$				

Relationship to cubic subcell:

$$\begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix} = \begin{pmatrix} 1 & \frac{1}{2} & -\frac{1}{2} \\ -\frac{1}{2} & 1 & \frac{1}{2} \\ -\frac{1}{2} & -\frac{1}{2} & -1 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} \qquad \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & 1 & -\frac{3}{2} \\ -\frac{3}{2} & \frac{1}{2} & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}$$

doubled c parameters have been listed for a number of M_7O_{12} compounds, including some of those discussed here (*8*, *24*). No evidence is given for this: Indeed, indexed powder patterns of $Zr_3Yb_4O_{12}$ (*8*) and $Hf_3Sc_4O_{12}$ (*20*) show all hkl to have l even. The single-crystal electron diffraction patterns obtained in the present study confirm the unit cell to be as tabulated above.

The results of the structure determinations (hexagonal axes) are shown in Tables II and III. Atomic coordinates agree in general with those of published structures of this type, e.g., Pr_7O_{12} (*12*) and $Zr_3Yb_4O_{12}$ (*13*), although the x and y coordinates in the latter publication must be interchanged in order to agree with the data presented there and with the results obtained here.

For all compounds except $Zr_3Sc_4O_{12}$ and $Hf_3Sc_4O_{12}$, the cations exhibit a form of ordering related to that observed in UY_6O_{12} (*11*), viz., one atom type, $M1$, occupies the set of special sites $3(a)$, while the remainder occupy a set of general $18(f)$ sites randomly, so that they behave in diffraction as a single atom type, $M2$. In the particular case of $NbSc_6O_{11}F$, cation ordering is complete and is the same as in UY_6O_{12}.

The essentially equal scattering factors of Ti and Sc precluded direct demonstration of cation ordering in $Ti_3Sc_4O_{12}$, but it was judged to be present because (a) the distortion of the cubic subcell is of similar magnitude to that observed in those compounds where cation ordering does occur, and (b) calculated interatomic spacings are much closer to the values expected from tabulated ionic radii (*21*) if ordering is assumed.

The result for $Zr_3Yb_4O_{12}$ differs from the earlier report of only partial cation order in this compound. It is possible that the discrepancy is due to the particular specimens studied: As will be discussed below, the state of cation order for this material can depend on the conditions of preparation.

Partially ordered cations were found for $Hf_3Sc_4O_{12}$. The distribution was obtained by refinement of the cation occupancies, with subsequent adjustments to the scattering factors. Calculated intensities of low-angle reflections were quite sensitive to small variations in cation occupancy, so the cation

TABLE II

ATOMIC COORDINATES[a]

	$Ti_3Sc_4O_{12}$	$Nb_{1.5}Sc_{5.5}O_{12}$	$NbSc_6O_{11}F$[b]	$NbSc_5HfO_{12}$	$Hf_3Sc_4O_{12}$	$Zr_3Sc_4O_{12}$	$Zr_3Yb_4O_{12}$	$Zr_3Er_4O_{12}$
*M*1 at (0,0,0)	Ti	Nb	Nb	Nb	0.39(4)Sc +0.61(6)Hf	(3Zr + 4Sc)/7	Zr	Zr
*M*2	(Ti + 2Sc)/3	(Nb + 11Sc)/12	Sc	(5Sc + Hf)/6	0.56(6)Sc +0.44(4)Hf	(3Zr + 4Sc)/7	(Zr + 2Yb)/3	(Zr + 2Er)/3
x	0.2949(15)	0.2989(9)	0.2962(11)	0.2966(8)	0.2891(10)	0.2906(12)	0.2887(9)	0.2887(8)
y	0.4126(11)	0.4147(8)	0.4147(10)	0.4130(7)	0.4089(7)	0.4100(10)	0.4118(8)	0.4122(6)
z	0.0188(13)	0.0242(7)	0.0225(10)	0.0214(7)	0.0186(7)	0.0162(9)	0.0180(6)	0.0153(6)
OI *x*	0.320(5)	0.305(3)	0.307(3)	0.299(4)	0.301(7)	0.293(6)	0.292(8)	0.302(7)
y	0.481(4)	0.474(3)	0.469(3)	0.461(3)	0.467(5)	0.453(5)	0.463(7)	0.471(5)
z	−0.210(6)	−0.215(2)	−0.215(3)	−0.220(3)	−0.222(6)	−0.225(6)	−0.234(6)	−0.216(4)
OII *x*	0.301(5)	0.301(3)	0.298(3)	0.301(4)	0.306(6)	0.304(5)	0.303(8)	0.300(7)
y	0.447(4)	0.449(3)	0.451(3)	0.453(3)	0.446(6)	0.453(5)	0.440(8)	0.444(5)
z	0.266(5)	0.272(2)	0.272(3)	0.276(3)	0.277(6)	0.281(6)	0.291(6)	0.263(5)
R	0.0491	0.0433	0.0516	0.0446	0.0315	0.0457	0.0422	0.0404
Number of observations	42	57	56	55	44	43	57	53

[a] Numbers in parentheses are estimated standard deviations, which apply to the last quoted places. The formally vacant anion site is at (0,0,¼).

[b] O and F occupy anion sites randomly.

TABLE III

SOME INTERATOMIC DISTANCES AND ANGLES

	$Ti_3Sc_4O_{12}$	$Nb_{1.5}Sc_{5.5}O_{12}$	$NbSc_6O_{11}F$	$NbSc_5HfO_{12}$	$Hf_3Sc_4O_{12}$	$Zr_3Sc_4O_{12}$	$Zr_3Yb_4O_{12}$	$Zr_3Er_4O_{12}$
Hexagonal cell volume	611.1	646.5	649.8	652.5	662.1	666.7	728.8	741.5
Octahedron about *M*1								
*M*1–OIa (Å)	1.94	1.96	2.01	2.03	1.98	2.08	2.01	2.06
OIa–*M*1–OIc (°)	93.4	95.2	95.8	98.4	98.4	101.0	101.8	95.8
OIa–*M*1–OIb (°)	86.6	84.8	84.2	81.6	81.6	79.0	78.2	84.2
OIa–OIc (Å)	2.83	2.89	2.98	3.08	2.99	3.20	3.12	3.07
OIa–OIb (Å)	2.66	2.64	2.69	2.66	2.58	2.64	2.54	2.77
Polyhedron about *M*2								
*M*2–OI (Å)	2.03	2.15	2.12	2.15	2.16	2.14	2.33	2.16
OIa	2.09	2.17	2.14	2.12	2.15	2.12	2.24	2.30
OIb	2.65	2.62	2.61	2.52	2.49	2.40	2.46	2.62
OII	2.13	2.18	2.20	2.25	2.27	2.34	2.48	2.27
OIIa	2.06	2.10	2.10	2.09	2.05	2.06	2.11	2.17
OIIb	2.06	2.10	2.14	2.13	2.09	2.14	2.10	2.23
OII*c*	2.07	2.05	2.04	2.06	2.22	2.16	2.27	2.27
M tetrahedron about *V*								
M–*V* (Å): 1 of	2.13	2.18	2.18	2.18	2.18	2.18	2.26	2.27
3 of	2.33	2.38	2.37	2.39	2.41	2.40	2.45	2.46
O octahedron about V								
O–V (Å): 3 of	1.96	2.03	2.07	2.13	2.12	2.23	2.26	2.14
3 of	2.27	2.26	2.24	2.22	2.30	2.23	2.35	2.46
Fluorite spacings								
M–O	2.11	2.15	2.16	2.16	2.18	2.18	2.24	2.26
O–O	2.44	2.49	2.49	2.50	2.51	2.51	2.59	2.60

NOTES. (1) Estimated standard deviations for interatomic distances and angles vary according to the particular compound; most lie in the ranges:

M–O 0.05–0.08 Å, O–O 0.08–0.13 Å, angles 1.5–2.5°.

(2) Fluorite spacings have been calculated for a cubic subcell that has 4/21 the volume of the appropriate hexagonal supercell.

distribution could be defined reasonably closely. The variations in cation occupancy noted in Table II represent limits beyond which standard deviations of atomic parameters began to be appreciably larger. In particular, those distributions representing either complete cation disorder or such cation order as found in $Zr_3Er_4O_{12}$ were readily rejected. The cation distribution could be accounted for if it were assumed that the sample consisted of cation-ordered $Hf_3Sc_4O_{12}$ mixed with disordered fluorite material, but this model also could be rejected on the basis of refinement results.

Specimens of $Hf_3Sc_4O_{12}$ that had been annealed at 1100, 1150, 1200, or 1250°C for 1 month showed no differences in lattice parameters or in diffraction intensities, indicating that no variation in cation distribution occurred under these conditions.

No cation ordering was found in $Zr_3Sc_4O_{12}$, thus confirming the results of the previous structure determination. As in the case of $Hf_3Sc_4O_{12}$, the cation distribution could be readily decided from the behavior of calculated intensities of low-angle reflections. A number of specimens were given differing heat treatments in an attempt to produce a cation-ordered form, but without success: All specimens were the same as judged from lattice parameters and diffraction intensities.

In all the compounds, the formal anion vacancies are located on the triad axis at $(0,0,\frac{1}{4})$, and as they appear in pairs, one on each side of $M1$, the coordination of this cation is reduced from eight, as in the ideal fluorite structure, to six. The anions adjacent to the vacant site relax toward it by about 0.3 Å, a value in agreement with that found in other fluorite-related ordered oxides (*15*, 16), and this results in a coordination octahedron of oxygen around $M1$ that is compressed along the triad axis compared to a regular octahedron. The octahedron around the smallest cation (assumed to be Ti^{4+}) is the more nearly regular, with O–$M1$–O angles closest to 90°, but the values cannot depend simply on the cation radius as seen from the compounds with $M1 = Zr$ (Table III).

The $M2$ cations have moved by up to 0.2 Å from their ideal fluorite positions in directions away from the vacant anion site, resulting in a marked dilation of the tetrahedron of four cations surrounding this site, which again is characteristic of structures such as these. Each $M2$ cation is surrounded by seven oxygen atoms which form the vertices of a distorted cube with one corner removed (the vacant anion site).

The octahedrally coordinated $M1$ cation, which may be regarded as a complex consisting of a pair of anion vacancies separated by a $\frac{1}{2}\langle 111 \rangle$ (fluorite) vector with the cation in between, is a basic feature of fluorite-related oxides studied so far. It appears in structures of relatively high vacancy concentration, as in the compounds described here and in pyrochlore (*23*) as well as those of lower vacancy concentration such as $CaHf_4O_9$(*15*) and $Zr_5Sc_2O_{13}$ (*6*), and in the grossly nonstoichiometric fluorite phase of at least one system (*25*). The various fluorite-related structures display different packings of the complex, such as the isolated units in the structure discussed here, or associated groups as in $Ca_6Hf_{19}O_{44}$ (*15*). Thus there is evidence that the vacancy-pair complex has marked stability, i.e., an anion-deficient fluorite-related system can achieve a lower free energy by adoption of this vacancy arrangement.

For those systems where there are several cation types, it would be natural for the smallest available cation to adopt the smallest, i.e., octahedral coordination, and this implies cation ordering in a structure with ordered pairs of anion vacancies. This situation has been observed in the CaO–HfO_2 fluorite-related structures as well as in most of the examples studied here. It was to confirm this point that the compounds $NbSc_6O_{11}F$ and $NbSc_5HfO_{12}$ were prepared: Nb^{5+} is sufficiently small to be octahedrally coordinated in most of its relevant compounds (*23*).

Cation ordering will occur when a sufficient lowering of the free energy can be achieved in a system despite the countering effect of configurational entropy associated with such ordering. This would appear to be the case when the cations are sufficiently different in size to give variation in metal–oxygen bond strengths. However, depending on the values of enthalpy and entropy involved, it could well be that no effective net free energy lowering would occur through cation ordering, so that an equilibrium phase could exhibit partial or total cation disorder, yet still have ordered anion vacancies. The compounds $Zr_3Sc_4O_{12}$ and $Hf_3Sc_4O_{12}$ may be of this type: The ionic radii for octahedral coordination are similar, viz., Zr^{4+} 0.72 Å, Hf^{4+} 0.71 Å, and Sc^{3+} 0.745 Å (*21*).

At low temperatures, an increase in the driving force for cation ordering is likely because of the decrease in the effect of entropy, but kinetic factors may be of importance. It has been observed that order–disorder processes in $Zr_3Er_4O_{12}$ and $Zr_3Yb_4O_{12}$ are slow at 1600°C (see below). Similar processes would be even slower if $Hf_3Sc_4O_{12}$ and $Zr_3Sc_4O_{12}$; the former could be prepared only below 1280°C, and by comparison with other corresponding HfO_2- and ZrO_2-based systems, cation ordering in the latter would be expected to occur at about 1000°C. However, no evidence has been obtained here, or presented in the literature, to show that at relatively low temperatures cation ordering occurs or is enhanced in these two compounds.

The compound $Zr_3Yb_4O_{12}$ also has been prepared as a cation-disordered superstructure (*13*); here the octahedral cationic radii are more disparate (0.72 and 0.87 Å). During the present study, this particular form of $Zr_3Yb_4O_{12}$ was confirmed by following the stated method, viz., rapid cooling of a melt formed in an argon arc, with a subsequent short (half-hour) anneal at 1000°C to restore the correct oxygen content. The structure was not investigated in detail, but it was noted that Guinier patterns of this material and of $Zr_3Sc_4O_{12}$ showed marked similarity in intensity relations of the lines and in the evidence for very small subcell distortion. Conversion to the cation-ordered form occurred on annealing at 1400°C for 7 days.

Cation-ordered $Zr_3Yb_4O_{12}$ from coprecipitated material, when heated above 1600°C and quenched, gave Guinier patterns at room temperature that showed only the lines expected for the fluorite structure. The effect of subsequent anneals at 1000–1400°C was to restore the cation-ordered form in the upper half of the temperature range. The order–disorder process was slow; conversion to the fluorite phase took 1 to 2 days at 1600°C, while the reverse transition required about 4 days at 1400°C.

Parallel experiments with $Zr_3Er_4O_{12}$ produced no evidence for a cation-disordered superstructure, but a sluggish transition from superstructure to fluorite-type phase occurred at 1500°C. The octahedral radius for Er^{3+} is 0.89 Å compared to 0.87 Å for Yb^{3+}, so that if cation size is important for the formation of the cation-disordered superstructure, a well-defined limit can be assigned.

The evidence above shows that the cation-disordered superstructure in $Zr_3Yb_4O_{12}$ is metastable, and the equilibrium phases have the cation-ordered superstructure below 1600°C and the fluorite structure above this temperature. Its formation during rapid cooling of the fluorite phase is a consequence of the stability of the vacancy-pair complex allied with favorable cationic radii, high anion mobilities, and low cation mobilities.

The effect of annealing this phase at or below 1600°C would be to allow cation ordering to proceed, and it would seem likely that the structure with partially ordered cations observed previously represents an intermediate state in this process. The crystal used in that study was prepared by annealing arc-melted material. It has been observed frequently in this laboratory at least, that the rate of ordering processes in fluorite-related systems can be severely retarded in specimens which have been melted, as compared to specimens prepared from coprecipitates or from reaction of mixed powders: Grain size and the nature of grain boundaries presumably influences the rate at which the distortions accompanying the ordering process can be accommodated. For example, formation of ordered $Zr_3Er_4O_{12}$ at 1400°C took about 4 days for coprecipitated material, but several months in the case of arc-melted specimens. The effect was not so marked in $Zr_3Yb_4O_{12}$; nevertheless, it could be a factor influencing the formation of the structure under consideration.

A detailed study of the order–disorder transition of these compounds, involving such techniques as high temperature diffraction and conductivity measurements, would be of some interest. There is the possibility that the transition from ordered structure to the fluorite phase may involve separate transition points for anions and cations, but perhaps more importantly, information could be provided on the conditions of stability of the ordered phases and on the structure of the grossly nonstoichiometric fluorite phase.

Acknowledgments

The author wishes to thank Mr. N. Buckley, of the Division of Mineral Chemistry, this Organization, for the use of the diffractometer, Mr. J. G. Allpress, of this Division, for the sample of $Nb_{1.5}Sc_{5.5}O_{12}$ and for preparing electron diffraction patterns of some of the samples, Professor Y. Tretyakov, Moscow State University for the sample of $Ti_3Sc_4O_{12}$, and Dr. H. G. Scott of this Division, for helpful discussion.

References

1. D. J. M. Bevan, *J. Inorg. Nucl. Chem.* **1**, 49 (1955).
2. R. E. Ferguson, E. D. Guth, and L. Eyring, *J. Amer. Chem. Soc.* **76**, 3890 (1954).
3. N. C. Baenziger, H. A. Eick, H. S. Schuldt, and L. Eyring, *J. Amer. Chem. Soc.* **83**, 2219 (1961).
4. J.-C. Gilles, *Corrosion et Anticorrosion* **12**, 15 (1964).
5. R. Collongues, F. Queyroux, M. Perez y Jorba, and J.-C. Gilles, *Bull. Soc. Chim. Fr.* 1141 (1965).
6. M. R. Thornber, D. J. M. Bevan, and J. Graham, *Acta Crystallogr.* **B24**, 1183 (1968).
7. M. R. Thornber, D. J. M. Bevan, and E. Summerville, *J. Solid State Chem.* **1**, 545 (1970).
8. L. N. Komissarova, B. I. Pokrovskii, and V. V. Nechaeva, *Dok. Akad. Nauk. SSSR* **168**, 1076 (1966).
9. H. J. Borchardt, *Inorg. Chem.* **2**, 170 (1963)
10. G. J. McCarthy, R. D. Fischer, G. G. Johnson Jr., and C. E. Gooden, N.B.S. Special Publ. 364, Solid State Chem., p. 397 (1972).
11. S. F. Bartram, *Inorg. Chem.* **5**, 749 (1966).
12. R. B. von Dreele, L. Eyring, A. L. Bowman, and J. L. Yarnell, *Acta Crystallogr.* **B31**, 971 (1975).
13. M. R. Thornber and D. J. M. Bevan, *J. Solid State Chem.* **1**, 536 (1970).
14. T. H. Etsell and S. N. Flengas, *Chem. Rev.* **70**, 339 (1970).
15. J. G. Allpress, H. J. Rossell, and H. G. Scott, *J. Solid State Chem.* **14**, 264 (1975).
16. H. J. Rossell and H. G. Scott, *J. Solid State Chem.* **13**, 345 (1975).
17. L. K. Frevel and H. W. Rinn, *Acta Crystallogr.* **9**, 626 (1956).
18. D. T. Cromer and J. T. Waber, *Acta Crystallogr.* **18**, 104 (1965).
19. D. T. Cromer and D. Liberman, *J. Chem. Phys.* **53**, 1891 (1970).
20. L. N. Komissarova and F. M. Spiridonov, *Dok. Chem. USSR* **182**, 864 (1968).
21. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.* **B25**, 925 (1969); **B26**, 1046 (1970).
22. D. K. Smith and H. W. Newkirk, *Acta Crystallogr.* **18**, 983 (1965).
23. G. M. Clark, "The Structures of Non-molecular Solids," p. 156, Applied Science Publ. Ltd., London (1972).
24. M. Perez y Jorba, *Ann. Chim.* **7**, 479 (1962).
25. J. G. Allpress and H. J. Rossell, *J. Solid State Chem.* **15**, 68 (1975).