41. *The Thorium Dioxide–Thorium Tetrafluoride System.*

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The thorium dioxide–thorium tetrafluoride system has been studied by *X*-ray diffraction. Thorium tetrafluoride dissolves in thoria to the extent of about 25 moles %, the cell constant *a* increasing from 5·586 to 5·663 *kX*. The arrangement of the anions in these mixed crystals is discussed. No solid solubility of thoria in thorium tetrafluoride was observed. Thorium oxyfluoride, $ThOF_2$, was formed by the reaction of equimolar mixtures of thoria and the tetrafluoride at 900° in an inert atmosphere. Diffraction photographs showed that the true unit cell of the oxyfluoride is orthorhombic and not hexagonal as previously suggested. The deviation from hexagonal symmetry is probably due to the oxygen and fluorine atoms' segregating into distinct sets of lattice sites. Attempts to prepare disordered thorium oxyfluoride with a random anion distribution were unsuccessful.

X-Ray powder diffraction and density studies of anomalous mixed-crystal systems such as CaF_2–YF_3,[1,2,3] CaF_2–ThF_4,[3] BaF_2–UF_3,[4] and BaF_2–UF_4 [5] have shown that, in the fluorite mixed-crystal phase, the cations are randomly distributed over the normal cation sites of the fluorite-type lattice (the positions 000 etc.), and the extra anions needed for electric neutrality occupy, presumably statistically, the largest " holes " in the lattice (the positions $\frac{1}{2}00$ etc.). Alberman and Anderson,[6] in discussing the effect of interstitial anions on a fluorite-type lattice, suggest that the net effect on the cell dimensions is determined by the interplay of the size and charge of the substituting cation with the distortion caused by the interstitial anion. Thus, if the radii of the cations are similar, the lattice-distortion effect will probably predominate, causing the cell to expand as the anion–cation ratio increases. This is true for the systems CaF_2–YF_3,[3] SrF_2–LaF_3,[3,7] and CaF_2–ThF_4.[3] If, however, the substituting cation is smaller as well as more highly charged, these effects may outweigh the distortion effect of the interstitial anions so that the cell contracts as the anion–cation ratio increases, as in the systems BaF_2–UF_3,[4] SrF_2–UF_3, and BaF_2–UF_4.[5]

These considerations also apply to certain oxide systems [8,9,10] and, as now shown, oxide–fluoride systems having the fluorite-type structure.

Zachariasen [11] found that in the La_2O_3–LaF_3 system lanthanum oxyfluoride, LaOF, can exist in two forms; when the composition corresponds exactly to LaOF the structure is rhombohedral, and when there is an excess of lanthanum trifluoride the structure is tetragonal. Both structures are based on a fluorite-type lattice. The deviation from cubic symmetry is due to the segregation of oxygen and fluorine atoms into distinct sets of lattice sites.

The present work gives evidence for the existence of a fluorite-type mixed crystal containing randomly distributed oxygen and fluorine atoms. In these mixed crystals there are two possible anionic arrangements: (i) the normal anion positions $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, etc., in the unit cell are all occupied and the interstitial positions $\frac{1}{2}00$, etc., are statistically filled or (ii) both sets of lattice sites are statistically occupied. However, the difference in the calculated intensities is so small that it is not possible to distinguish between them.

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[1] Vogt, *Neues Jahrb. Mineral.*, 1914, **2**, 9.
[2] Goldschmidt, *Geochem. Verteilungsgesetze*, 1926, **7**, 88.
[3] Zintl and Udgård, *Z. anorg. Chem.*, 1939, **240**, 150.
[4] D'Eye and Martin, *J.*, 1957, 1847.
[5] D'Eye and Ferguson, unpublished work.
[6] Alberman and Anderson, *J.*, 1949, S305.
[7] Ketelaar and Willems, *Rec. Trav. chim.*, 1937, **56**, 29.
[8] Hering and Perio, *Bull. Soc. chim. France*, 1952, **19**, 351.
[9] Rundle, Baenziger, and Wilson, 1947, MDDC-1608 (American Atomic Energy Report).
[10] Gronvold, *J. Inorg. Nuclear Chem.*, 1955, **1**, 257.
[11] Zachariasen, *Acta Cryst.*, 1951, **4**, 231.

Solid Solubility Limits.—The results of previous[1,2] work on systems such as CaF_2–ThF_4[3] and BaF_2–UF_3[4] show that at the limit of solid solubility there are two interstitial anions per unit cell. Thus, in the present system, the solid solubility limit of thorium tetrafluoride in thoria should be 25 moles %. We have been unable to confirm this figure owing to the difficulty of preparing homogeneous mixed-crystals phases. We found no solid solubility of thoria in thorium tetrafluoride.

Thorium Oxyfluoride.—Zachariasen[12] found from *X*-ray powder data that thorium oxyfluoride had a bimolecular hexagonal unit cell with $a = 4{\cdot}039 \pm 0{\cdot}002$ *kX* and $c = 7{\cdot}290 \pm 0{\cdot}004$ *kX*. As the structure was supposed to be of the LaF_3-type an alternative hexagonal unit cell was suggested[13] which contained six molecular units of $ThOF_2$ and had the dimensions $a = 4{\cdot}039\sqrt{3}$ and $c = 7{\cdot}290$ *kX*. Both structures require a random distribution of the oxygen and fluorine atoms over the anion positions in the lattice.

We now find that thorium oxyfluoride has an orthorhombic unit cell, the dimensions being closely related to those of the bimolecular hexagonal cell by the expressions $a_O \sim 2\sqrt{3}a_H$, $b_O \sim a_H$, $c_O \sim c_H$, where the subscripts O and H denote orthorhombic and hexagonal symmetry respectively. We suggest that the deviation from hexagonal symmetry is due to the ordering of the oxygen and fluorine atoms. All our attempts to prepare disordered thorium oxyfluoride, which would give diffraction photographs with no superlattice lines, were unsuccessful.

EXPERIMENTAL

Thorium Dioxide.—Thoria of small particle size was prepared by thermal decomposition of thorium oxalate[14] at 450° in air.

Thorium Tetrafluoride.—Thorium tetrafluoride of small particle size was prepared by the thermal degradation of the hydrate, ThF_4,yH_2O,[15,16,17] at 400° *in vacuo* or in an inert atmosphere.

Mixed Crystals.—Most samples were prepared by heating intimate mixtures of the tetrafluoride and thoria, in the requisite quantities, either (i) in platinum boats in argon which was purified by passage through traps cooled in liquid oxygen and then over heated copper turnings or (ii) *in vacuo* in sealed platinum bombs. In the latter method the sample was placed in a 4 mm. diameter platinum tube, sealed at one end. The open end was connected through glass tubing to a vacuum system. The apparatus was evacuated and the sample outgassed at 200°. When cool, the platinum tube was crimped about 1 in. above the level of the sample and an oxy–coal gas flame was played across the crimped portion. The platinum bomb was then sealed inside an evacuated quartz bomb.

Samples were generally heated at about 1000° for 6 hr. The thoria-rich mixed crystals could not be melted owing to their high m. p. (m. p. of thoria is *ca.* 3000°). These preparations were therefore never homogeneous.

Zachariasen[11] prepared samples in the range MF_3—M_2O_3, where M is lanthanum or yttrium, by heating the trifluoride at 900° in an atmosphere of low humidity. Hydrolysis proceeds until the fluoride is completely converted into oxide. We similarly prepared samples by heating thorium tetrafluoride in air at 440° in open platinum dishes; this temperature gave a convenient rate of hydrolysis. However, at the thoria-rich end of the system the samples were again never homogeneous.

Chemical Analysis.—The fluorine in the sample was estimated by the pyrohydrolytic method.[18] Steam was passed over the sample in a platinum boat, which was heated to 900—1000°. The resulting hydrofluoric acid–water mixture was condensed and titrated with

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[12] Zachariasen, *Acta Cryst.*, 1949, **2**, 388.
[13] Oftedal, *Z. phys. Chem.*, 1931, *B*, **13**, 190.
[14] D'Eye and Sellman, *J. Inorg. Nuclear Chem.*, 1955, **1**, 143.
[15] D'Eye and Booth, *J. Inorg. Nuclear Chem.*, 1955, **1**, 326.
[16] D'Eye, Booth, and Harper, U.K.A.E.A. Report A.E.R.E. C/R 1735 (1955).
[17] D'Eye and Booth, *J. Inorg. Nuclear Chem.*, 1957, **4**, 13.
[18] Gillies, Keen, Lister, and Rees, U.K.A.E.A. Report A.E.R.E. C/M 225 (1954).

standard alkali. The steam jet was then removed and the residual oxide ignited in air and weighed as thorium dioxide.

X-*Ray Diffraction.*—For the *X*-ray examination of the mixed crystals we used a Guinier-type focusing camera [19] and monochromatised Cu-K_α radiation from a bent quartz plate. To avoid shrinkage errors in the measurement of the Bragg angle θ, a 0·1 mm. scale was photographed on the film before processing.

RESULTS AND DISCUSSION

Samples of 0—20 moles % of thorium tetrafluoride consisted, after heating, of two fluorite-type phases. As the diffraction photographs of these phases show no splitting of the cubic lines or any weak lines which could be attributed to a superlattice it seems that the oxygen and fluorine atoms in these mixed crystals are not ordered. The cell constant for these cubic phases was in the region from 5·586 ± 0·005 *kX*, the value for pure thoria, to 5·663 ± 0·005 *kX*. Therefore as thorium tetrafluoride is incorporated into the thoria lattice, the lattice expands.

Neither the solid solubility limit nor the mode of incorporation of the tetrafluoride in the thoria lattice could be determined experimentally as, even after long annealing, the mixed crystal phases were not homogeneous. However, by analogy with other systems, it would be expected that the extra anions ($2F^-$ replacing O^{2-}) needed for electric neutrality occupy interstitial positions in the lattice and that the cation lattice is intact. Similarly the limit of solid solubility of thorium tetrafluoride in thoria should be 25 moles %. The phase with a cell parameter of 5·663 is probably that at the limit of solid solubility.

Samples of 20—50 moles % of thorium tetrafluoride were again at least two-phase—thorium oxyfluoride and either one or two cubic phases with cell constants in the range given above. If only one cubic phase occurred with the oxyfluoride then the cell constant of this phase was 5·663. This supports the suggestion that the phase at the limit of solid solubility has a cell parameter of 5·663 *kX*.

TABLE 1. *Diffraction data for thorium oxyfluoride.*

Intensity	*hkl*	$\sin^2\theta$ (obs.)	$\sin^2\theta$ (calc.)
vw	200	0·0119	0·0120
w−	101	0·0142	0·0142
w	201	0·0232	0·0232
vvw	010	0·0369	0·0363
vvw	301	0·0381	0·0381
s	002	0·0450	0·0450
m	011	0·0477	0·0475
	400		0·0478
m+	102	0·0481	0·0480
	210		0·0482
vvw	111	0·0503	0·0504
w−	202	0·0569	0·0569
s	401	0·0590	0·0590
s	211	0·0593	0·0594
vvw	302	0·0717	0·0719
vvw	311	0·0739	0·0743
w	410	0·0840	0·0840
	112		0·0842
vvw	501	0·0860	0·0859
w+	402	0·0926	0·0928
m	212	0·0930	0·0932
w+	411	0·0952	0·0953
w	103	0·1040	0·1043
w	600	0·1074	0·1076
vw	203	0·1128	0·1132
vvw	502	0·1197	0·1197
vw	303	0·1279	0·1282
vw	412	0·1288	0·1290
vvw	113	0·1402	0·1405
s	610	0·1438	0·1438
m	020	0·1450	0·1450
m−	403	0·1488	0·1491
s−	213	0·1491	0·1495
w	602	0·1523	0·1526
vvw	512	0·1562	0·1559
	021		0·1562
vvw	121	0·1594	0·1592
vvw	313	0·1638	0·1644
vvw	221	0·1680	0·1682
vvw	503	0·1758	0·1760
w+	004	0·1796	0·1800
vw	413	0·1852	0·1853
s	612	0·1886	0·1888
m	022	0·1898	0·1900
w−	420	0·1925	0·1928
	122		0·1930
w	222	0·2025	0·2020
	801		0·2025
m+	421	0·2039	0·2040
w	721	0·2276	0·2276
	810		0·2275
	404		0·2278
w−	422	0·2380	0·2378

Samples of 50—100 moles % of tetrafluoride were two-phase, the oxyfluoride and tetrafluoride. No solid solubility of thoria in thorium tetrafluoride was observed.

Thorium Oxyfluoride.—The reflections with high intensity on the *X*-ray powder diffraction pattern of thorium oxyfluoride can be indexed in terms of the bimolecular

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[19] D'Eye, U.K.A.E.A. Report A.E.R.E. C/R 1524 (1954); *Nature*, 1955, **175**, 623.

hexagonal cell suggested by Zachariasen. However there were many weak lines which could not be so accounted for and the reflections with indices *hk*0 and *hkl* are split. As the positions and intensities of the extra reflections and the line splitting are independent of the method of preparation of the sample these effects are not likely to be due to traces of impurity or to a solid solubility range. Indeed the *X*-ray photograph was successfully indexed on the basis of an orthorhombic unit cell with $a = 14{\cdot}07 \pm 0{\cdot}01$ *kX*, $b = 4{\cdot}041 \pm 0{\cdot}005$ *kX*, and $c = 7{\cdot}253 \pm 0{\cdot}005$ *kX*. The agreement between the calculated and observed values of $\sin^2 \theta$ is good (Table 1). The observed indices of the reflections show that the *hk*0 planes are absent when $h = 2n + 1$. The volume of the unit cell is four times that of the bimolecular hexagonal cell and contains eight molecular units of $ThOF_2$. The pseudo-hexagonal indices which correspond to the orthorhombic indices of the reflections are given in Table 2.

The deviation from hexagonal symmetry can be accounted for by an ordering of the oxygen and fluorine atoms. The probable atomic arrangement in the ordered orthorhombic lattice can be derived by considering the atomic arrangement of the atoms in the larger of the two hexagonal cells. The atoms in the latter structure occupy the following special positions of space group D_{6h}^3—$P6_3/mcm$.; thorium on 6(*g*) and the anions on 2(*a*), 4(*c*), and 12(*k*). This structure can be considered to be made up of layers of cations and anions with each cation surrounded by three anions and each anion by three cations. The anions in these layers occupy the positions 2(*a*) and 4(*c*) in the unit cell. Above and below each cation there is a further anion. These anions, which sit between the layers, occupy the position 12(*k*) and are not structurally equivalent to those in the layers. If the six oxygen atoms occupy the positions in the layers and the twelve fluorine atoms the positions between the layers, instead of both atoms being statistically distributed over all the eighteen anion sites, then the resultant lattice distortion will probably account for the deviation from hexagonal symmetry.

TABLE 2. *Corresponding reflections.*

Orthorhombic	Pseudo-hexagonal	Orthorhombic	Pseudo-hexagonal
002	002	403	103
011, 400	100	213	
102, 210		004	004
401	101	612	112
211		022	
402	102	420	200
212		122	
610	110	222, 801	201
020		421	

We could not prepare hexagonal thorium oxyfluoride which would have no ordering of the anions.

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