686. *The Barium Fluoride–Uranium Tetrafluoride and the Strontium Fluoride–Thorium Tetrafluoride System.*

By R. W. M. D'Eye and I. F. Ferguson.

The BaF_2–UF_4 and the SrF_2–ThF_4 system have been examined by *X*-ray diffraction and density measurements. The tetrafluoride dissolves in the difluoride to the extent of about 25 moles %, the unit-cell constant decreasing in the former and increasing in the latter system. Barium and strontium fluorides dissolve in barium uranium hexafluoride and strontium thorium hexafluoride respectively to the extent of about 20 moles % with the creation of anion vacancies. At 60 moles % of uranium tetrafluoride a previously unidentified compound is formed. Below this exists a two-phase region down to UF_4. An analogous compound is not found in the SrF_2–ThF_4 system, so that, between 50 and 100 moles % of thorium tetrafluoride, only strontium thorium hexafluoride and thorium tetrafluoride are found.

From *X*-ray 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 ThO_2–ThF_4,[5] it has been concluded that the fluorite mixed-crystal phase contains interstitial anions and that, at the solid-solubility limit, the fluorite unit cell contains two additional fluorine atoms. Further, the unit cell contracts when the substituting cation is smaller and has a higher charge and expands when it is of similar size. These conclusions are substantiated by the present work.

Barium uranium hexafluoride, strontium thorium hexafluoride, and thorium oxide difluoride are reported [6] to have the LaF_3-type hexagonal structure with a random distribution of cations in the first two and of anions in the last compound. Although later work showed that the true symmetry of thorium oxide fluoride was lower than this, presumably because of the distortion brought about by an ordering of the anions,[5] no similar evidence is found in the present work to suggest a lower symmetry, and hence an ordering of the cations, for the two hexafluorides.

Barium and strontium fluoride dissolve in barium uranium hexafluoride and strontium thorium hexafluoride respectively with the formation of anion vacancies rather than interstitial cations. In both instances the solid solubility limit is about 20 moles %. Thus the mode of incorporation of the difluoride into the lattice is strictly analogous to that of barium fluoride into uranium trifluoride.[4]

EXPERIMENTAL

Materials.—" AnalaR " strontium fluoride was used. Barium fluoride was precipitated by ammonium fluoride from a barium nitrate solution. Uranium tetrafluoride was prepared by hydrofluorination of uranium dioxide, and thorium tetrafluoride by dehydration of a hydrate, ThF_4,yH_2O.[7]

Mixed Crystals.—The requisite amounts of the constituents were intimately mixed and heated for about 30 min. in graphite crucibles in an atmosphere of argon. This was first purified by passing it through traps cooled with liquid oxygen and then over heated, freshly reduced, copper turnings. Samples rich in barium fluoride and uranium tetrafluoride were heated at 1200° c and 900° c respectively, and those rich in strontium fluoride and thorium tetrafluoride were heated at 1350° and 1000° respectively. To ensure that the mixed crystals were homogeneous they were ground and re-heated. Mixtures of approximately equimolar proportions were cooled slowly, by gradually lowering the temperature of the furnace, and quickly, by

---

[1] Vogt, *Neues Jahrb. Min.*, 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, *J.*, 1958, 196.

[6] Zachariasen, *Acta Cryst.*, 1949, **2**, 388.

[7] D'Eye and Booth, *J. Inorg. Nuclear Chem.*, 1955, **1**, 326; 1957, **4**, 13; D'Eye, Booth, and Harper, U.K.A.E.A. Report A.E.R.E. C/R 1735 (1955).

immediate removal from the furnace. Although graphite crucibles were used no evidence of carbide formation was observed.

X-*Ray Diffraction Analysis.*—Photographs were obtained with a Guinier-type focusing camera,[8] monochromatised and focused Cu-K_α radiation from a bent quartz plate being used. A 0·1 mm. scale was photographed on the film before processing, to avoid shrinkage errors in the measurement of the Bragg angle.

Pyknometric Density.—Densities were calculated from the difference in weight of the material in air and in toluene. Low values, caused by incomplete filling of the microcapillaries in the surface structure of the crystals, were avoided by adding the pyknometric liquid to the solid under a vacuum. Both the solid and the toluene were outgassed before use.

Chemical Analysis.—The fluorine in the sample was estimated by the pyrohydrolytic method.[9] 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 standard alkali. The steam-jet was then removed, and the residual oxide ignited in air and weighed.

RESULTS AND DISCUSSION

The cell constant of the BaF_2–UF_4 fluorite mixed-crystal phase decreases approximately linearly with increasing uranium tetrafluoride content down to the solid solubility limit of about 25 moles % (Table 1). From the cell constant the density was calculated on the basis of: (i) interstitial anions with a complete cation lattice, and (ii) a complete anion lattice with a defective cation lattice. The measured density corresponds closely to that calculated on the former assumption (Table 1).

TABLE 1.

BaF_2–UF_4 *anomalous mixed crystals*

UF_4 (moles %)	$a \pm 0·005$ (Å)	*d*, calc. on interstitial anions (g./c.c.)	*d*, calc. on vacant cations (g./c.c.)	*d*, measured (g./c.c.)
0	6·198	4·88		4·85
10	6·152	5·41	4·91	5·31
15	6·144	—	—	—
20	6·122	5·87	4·89	5·81
25	6·097	—	—	—
30	6·098		plus hexagonal phase.	

SrF_2–ThF_4 *anomalous mixed crystals*

ThF_4 (moles %)	$a \pm 0·005$ (Å)	
0	5·808	
10	5·817	
20	5·837	
26	5·839	
28	5·848	plus hexagonal phase
32	5·851	plus hexagonal phase

At the limit of solid solubility of uranium trifluoride in barium fluoride, 50 moles %, the unit cell has a parameter of 6·046 Å and contains ten F^-, two U^{3+}, and two Ba^{2+} ions, the cations being randomly distributed over the normal cation positions.[4] In the present system at the solid solubility limit the unit cell has a parameter of 6·097 Å, again contains ten F^- ions, but now the cation lattice comprises a random distribution of one U^{4+} and three Ba^{2+} ions. The cell parameter, as might be expected, is greater in this instance because only one Ba^{2+} ion has been replaced by a smaller, more highly charged ion.

The cell constant of the SrF_2–ThF_4 mixed crystals increases, in contrast to the previous system, with increasing tetrafluoride content up to the solid solubility limit at about 25 moles % (Table 1). The difference between the ionic radii of Sr^{2+} (1·13 Å) and Th^{4+}

---

[8] D'Eye, U.K.A.E.A. Report A.E.R.E. C/R 1524 (1954).

[9] Gillies, Keen, Lister, and Rees, U.K.A.E.A. Report A.E.R.E. C/M 225 (1954).

(0·95 Å) is less than that between Ba^{2+} (1·35 Å) and U^{4+} (0·89 Å) and is apparently insufficient to compensate for the distortion effect of the interstitial anions. Thus the lattice expands with increasing interstitial content.

Between about 75 and 56 moles % of difluoride, the diffraction photographs show that two phases are present: a fluorite phase representing the limit of solid solubility of the tetrafluoride in the difluoride, and a hexagonal phase representing the limit of solid solubility of the difluoride in the MXF_6 (M = Ba, Sr; X = U, Th) compound.

The incorporation of the difluoride into the compound MXF_6 must lead to either vacant anion sites or interstitial cations. A comparison between the densities calculated on these two assumptions with that observed shows the former to be correct (Table 2).

TABLE 2.

$BaUF_6$–BaF_2 *anomalous mixed crystals*

BaF_2 (moles %)	$a \pm 0·005$ (Å)	$c \pm 0·005$ (Å)	*d*, calc. on vacant anions (g./c.c.)	*d*, calc. on interstitial cations (g./c.c.)	*d*, measured (g./c.c.)
0	4·279	7·481	6·85		6·76
11	4·286	7·493	6·70	6·85	6·67
15	4·283	7·492	6·67	6·86	6·64
21	4·281	7·504	6·59	6·87	6·56
28	4·282	7·506	plus cubic phase		

$SrThF_6$–SrF_2 *anomalous mixed crystals*

SrF_2 (moles %)	$a \pm 0·005$ (Å)	$c \pm 0·005$ (Å)
0	4·132	7·341
8	4·136	7·365
15	4·138	7·368

When barium fluoride dissolves in uranium trifluoride,[4] which is isostructural with $BaUF_6$ and $SrThF_6$, both the *a* and the *c* axis expand. However, in the present work it can be seen from Table 2 that only the *c* axis expands appreciably. This still does not allow a prediction to be made whether the anion vacancies are randomly distributed or concentrated in one or other of the two structurally different sets of anion positions.[4,5]

The observed and calculated values of $\sin^2 \theta$ for barium uranium hexafluoride, indexed on the basis of a hexagonal LaF_3-type structure, are given in Table 3. The diffraction patterns of this salt and of strontium thorium hexafluoride were the same irrespective of the rate at which the materials were cooled. It was therefore impossible to prepare these compounds with an ordered arrangement of the cations.

TABLE 3. *Diffraction data for* $BaUF_6$.

I *	$\sin^2 \theta$ (obs.)	$\sin^2 \theta$ (calc.)	*hkl*	*I* *	$\sin^2 \theta$ (obs.)	$\sin^2 \theta$ (calc.)	*hkl*	*I* *	$\sin^2 \theta$ (obs.)	$\sin^2 \theta$ (calc.)	*hkl*
w	0·0424	0·0424	002	m−	0·1722	0·1721	112	vvw	0·3071	0·3075	105
w+	0·0431	0·0432	100	w+	0·1837	0·1835	201	w	0·3132	0·3132	211
s	0·0538	0·0538	101	vvw	0·2118	0·2127	104	vvw	0·3455	0·3449	212
w	0·0856	0·0856	102	w−	0·2684	0·2681	203	vw	0·3888	0·3891	300
m	0·1298	0·1297	110	w−	0·2990	0·2988	114	vw	0·3973	0·3977	213
m	0·1385	0·1385	103	vvw	0·3027	0·3026	210	vw	0·4314	0·4314	302
vvw	0·1694	0·1694	004								

* *I* = intensity.

In the BaF_2–UF_4 system a new phase appears at approximately 60 moles % of uranium tetrafluoride. The *X*-ray diffraction pattern of this has so far not been indexed. The $\sin^2 \theta$ and intensity values are listed in Table 4. Thus between 50 and 60 moles % of uranium tetrafluoride the diffraction photographs show two phases, the new phase and

TABLE 4. *Compound formed at* 60 *moles* % *of* UF_4 *in the system* BaF_2–UF_4.

I *	$\sin^2 \theta$	*I* *	$\sin^2 \theta$	*I* *	$\sin^2 \theta$	*I* *	$\sin^2 \theta$
w+	0·0116	m−	0·0368	vw	0·0513	w+	0·0719
vvw	0·0172	m−	0·0396	w+	0·0527	vvw	0·0794
w+	0·0214	m+	0·0425	m+	0·0540	m−	0·0824
vw	0·0317	m−	0·0444	m+	0·0562	vw	0·0892
m−	0·0353	m−	0·0503	vw	0·0688	w−	0·1100

* *I* = intensity.

barium uranium hexafluoride. Again, the region from 60 to 100 moles % of uranium tetrafluoride is two-phase, the new phase and uranium tetrafluoride.

No similar phase appears in the SrF_2–ThF_4 system: between 50 and 100 moles % of thorium tetrafluoride the diffraction photographs show only two phases, strontium thorium hexafluoride and thorium tetrafluoride.

No evidence of solid solubility of the new compound in uranium tetrafluoride or of strontium thorium hexafluoride in thorium tetrafluoride is found.

The authors thank Mrs. G. W. Stuart for taking the *X*-ray photographs and for help in the experimental work.

ATOMIC ENERGY RESEARCH ESTABLISHMENT,
HARWELL, BERKSHIRE.

[*Received, May* 4*th,* 1959.]