349. *The Barium Fluoride–Uranium Trifluoride System.*

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The system UF_3–BaF_2 has been examined by *X*-ray and density measurements and by thermal analysis. Uranium trifluoride dissolves in solid barium fluoride to the extent of about 50 mole %, the cell constant *a* decreasing from 6·189 to 6·034 kX; barium fluoride dissolves in uranium fluoride to the extent of about 20 mole %. These two conjugate solid solutions exist between definite concentration limits. It is also shown that uranium trifluoride may form a solid solution in strontium fluoride.

The melting point of uranium trifluoride is found to be about 1495°; its addition to barium fluoride increases the melting point of the latter, and it is suggested that the system has a peritectic point at about 1400°.

Vogt's [1] thermal analytical work indicated that 45 mole % of yttrium trifluoride could be dissolved in calcium fluoride. This was substantiated by Goldschmidt's [2] *X*-ray diffraction study of the mineral fluorite (Ca, Y)F_3. Goldschmidt suggested that in these mixed crystals the calcium and yttrium ions were randomly distributed over the normal cation sites of the fluorite-type lattice, *i.e.*, the positions 000, etc., in the unit cell, and that the extra fluoride ions needed for electric neutrality occupied, presumably statistically, the

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[1] Vogt, *Neues Jahrb. Mineral.*, 1914, **2**, 9.

[2] Goldschmidt, *Geochem. Verteilungsgesetze*, 1926, **7**, 88.

largest " holes " in the lattice, *i.e.*, the positions ½00, etc. The composition of the mixed crystals could also be accounted for if the cation lattice were incomplete, $2Y^{3+}$ replacing $3Ca^{2+}$, with the anion lattice intact. However, density and *X*-ray diffraction studies of the systems CaF_2–YF_3 ($Ca^{2+} = 0{\cdot}99$, $Y^{3+} = 0{\cdot}93$ kX), SrF_2–LaF_3 ($Sr^{2+} = 1{\cdot}13$, $La^{3+} = 1{\cdot}15$ kX), and CaF_2–ThF_4 ($Ca^{2+} = 0{\cdot}99$, $Th^{4+} = 1{\cdot}02$ kX) by Zintl and Udgård,[3] and of SrF_2–LaF_3 by Ketelaar and Willems,[4] proved that Goldschmidt's concept of interstitial anions and an intact cation lattice was correct. Results of our present study of the BaF_2–UF_3 system also agree with the interstitial anion theory.

For mixed-crystal formation Zintl *et al.*[3] considered that the cations in the component fluorides should have similar ionic radii. This is not necessarily the case. For example, our investigation of the BaF_2–UF_3 system ($Ba^{2+} = 1{\cdot}35$, $U^{3+} = 1{\cdot}04$ kX) shows that uranium trifluoride has an appreciable solid solubility in barium fluoride, mixed crystals with the fluorite-type structure being formed. We also have a single measurement which shows that uranium trifluoride and strontium fluoride ($Sr^{2+} = 1{\cdot}13$ kX) form mixed crystals.

Alberman and Anderson,[5] in their discussion of the effect of incorporating interstitial anions into 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, SrF_2–LaF_3, and CaF_2–ThF_4. If, however, the substituting cation is smaller, as well as carrying a higher charge, these effects may outweigh the distortion effect of the interstitial anions and result in contraction of the cell as the anion : cation ratio increases. We find this is the case for the BaF_2–UF_3 system where the cell constant contracts from $a = 6{\cdot}189 \pm 0{\cdot}005$ kX for barium fluoride to $6{\cdot}034 \pm 0{\cdot}005$ kX for a mixed crystal containing 50 mole % of uranium trifluoride.

The incorporation of interstitial atoms into the positions ½00, etc., in a unit cell with the fluorite-type structure should enhance the intensity of diffraction planes with all indices even. However, these intensity changes should only be discerned when the scattering power of the cations and anions is comparable. Thus as expected, intensity changes were found in the CaF_2–YF_3 but not in the BaF_2–UF_3 system.

Solid Solubility Limits.—For the systems CaF_2–YF_3 and SrF_2–YF_3, mixtures containing more than 33·3 moles % of the trifluoride consisted of the cubic solid-solution phase and the hexagonal trifluoride.[3] However, no mention has been made of the possibility of solid solution of the difluoride in the trifluoride. With the CaF_2–ThF_4 system an unidentified phase plus the solid-solution cubic phase was found in mixtures containing between 27·3 and 50 moles % of thorium tetrafluoride. We suggest that this unidentified phase was $CaThF_6$ (cf. ref. 6).

We find that the solid solubility limit of uranium trifluoride in barium fluoride is roughly 50 moles %, corresponding to two interstitial anions per unit cell. Two phases were present in samples with a higher uranium trifluoride content; the cubic solid-solution phase and an hexagonal phase with cell dimensions only slightly larger than those for pure uranium trifluoride. The cell dimensions of the hexagonal phase decreased with increasing trifluoride content, suggesting a solid solution range of barium fluoride in uranium trifluoride.

The incorporation of barium fluoride into the uranium trifluoride lattice could be explained either if the cation lattice remained intact with, to preserve electric neutrality, a deficient anion lattice, or if the anion lattice remained intact with interstitial cations, $3Ba^{2+}$ replacing $2U^{3+}$. The latter possibility is unlikely in a close packed structure such

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[3] Zintl and Udgård, *Z. anorg. Chem.*, 1939, **240**, 150.
[4] Ketelaar and Willems, *Rec. Trav. chim.*, 1937, **56**, 29.
[5] Alberman and Anderson, *J.*, 1949, S 305.

as uranium trifluoride.[6,7] In fact, calculations of packing and interatomic distance seem to preclude the idea of interstitial cations. Our density and *X*-ray diffraction data confirm this prediction.

EXPERIMENTAL

Uranium Trifluoride.—This was prepared by a method similar to that described by Warf [8] in which finely divided uranium powder is heated with the stoicheiometric quantity of uranium tetrafluoride in an inert atmosphere. *X*-Ray analysis showed that some products contained traces ($<2\%$) of uranium dioxide.

Mixed Crystals.—These were prepared by heating intimate mixtures of barium fluoride and uranium trifluoride, in the requisite quantities, in graphite crucibles in an atmosphere of argon which was purified by passage through traps cooled with liquid oxygen and then over heated uranium turnings. The mixtures for *X*-ray analysis were heated for about 30 min. at 1300° and cooled fairly rapidly by removal from the furnace. Although graphite crucibles were used no evidence of carbide formation was found. Some melts had a thin skin of carbon which was readily scraped away. The mixed crystals rich in uranium trifluoride were deep purple-black, and those rich in barium fluoride were pinkish-brown.

Thermal Analysis.—Cooling curves were obtained on some of the samples by means of a Pt–13% Rh/Pt thermocouple inserted into a well in the base of the crucible. The samples were cooled at the rate of about 1° per min. by means of a motorised Variac transformer delivering power to a molybdenum resistance-wound heater. The graphite crucibles were thoroughly outgassed before use for an hour *in vacuo* at 1400—1500°.

X-*Ray Diffraction.*—For the *X*-ray examination of the mixed crystals we used a Guinier-type focusing camera [9] and monochromatised and focused 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.

Pyknometric Density.—Densities were calculated from the difference in weight of the mixed crystal in air and in toluene. To avoid low density values, through incomplete filling of the microcapillaries in the surface structure of the crystals, the pyknometric liquid was added to the solid under a vacuum. Both the solid and the toluene were thoroughly outgassed *in vacuo* before use.

RESULTS AND DISCUSSION

X-*Ray and Density.*—The values of the cell constant, *a*, for various mixed crystal compositions are shown in the Table. The cell constant decreases approximately linearly with increasing uranium trifluoride content down to the solid solubility limit of 50 moles %.

From these cell constants densities were calculated on the assumption of (i) interstitial anions with a complete cation lattice and (ii) a complete anion lattice with a defective cation lattice (see Table). The measured density corresponds closely to that calculated on the former basis.

At a composition of 66·66 moles % of uranium trifluoride the diffraction photograph shows that two phases were present; a fluorite phase with a cell parameter corresponding to that for the limit of solid solubility of uranium trifluoride in barium fluoride and a hexagonal phase with cell constants slightly larger than those for pure uranium trifluoride. This hexagonal phase is a solid solution of barium fluoride in uranium trifluoride, and its composition must correspond to the limit of solid solubility of the barium fluoride, about 20 moles %, in the trifluoride.

The mode of incorporation of the barium fluoride into the uranium fluoride has been determined from *X*-ray-diffraction and density measurements. For example, the density was calculated for a composition of 90 moles % of uranium fluoride both on the assumption

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

[7] Staritzky and Douglas, *Analyt. Chem.*, 1956, **28**, 1056.

[8] Warf, A.E.C.D. 2413 (1948).

[9] D'Eye, A.E.R.E. C-R 1524 (1954); *Nature*, 1955, **175**, 623.

(i) that the uranium and barium ions were randomly distributed over the normal cation sites, *i.e.*, the positions 6(*g*) $x0\frac{1}{4}$, etc. (space group $P6_3$ mcm),[7] in the unit cell, with the anion lattice incomplete, and (ii) that the anion lattice is complete, *i.e.*, the positions 2(*a*) $00\frac{1}{4}$, etc., 4(*c*) $\frac{1}{3}\frac{2}{3}\frac{1}{4}$, etc., 12(*k*) $x0z$, etc., in the unit cell, with interstitial cations to preserve the charge balance. The calculated densities for these two possibilities are respectively 8·52 and 8·81 g./c.c. The measured density is 8·50 g./c.c., in good agreement with the density calculated on the assumption (i) above of vacant anion sites. Further weight to this anion-vacancy mechanism is given by considerations of interatomic distances which show that the lattice is unlikely to accommodate interstitial cations.

BaF_2–UF_3 *anomalous mixed crystals.*

BaF_2 (moles %)	*a* (± 0·005) (kX)	*d*, calc. on interstitial anions (g./c.c.)	*d*, calc. on vacant cations (g./c.c.)	Measured density (g./c.c.)	Remarks
100	6·189	—	—	4·85	
93·8	6·169	5·14	4·99	5·07	
87·06	6·139	5·45	5·11	5·45	
80·00	6·137	5·69	5·17	5·74	
75·00	6·110	5·94	5·28	5·87	
66·66	6·079	—	—	—	
50·00	6·034	—	—	—	
33·33	6·035	—	—	—	Minor phase, cubic; major phase, hexagonal; *a* = 4·197; *c* = 7·359
10	—	—	—	—	Single hexagonal phase; *a* = 4·153; *c* = 7·329
0	—	—	—	—	Hexagonal UF_3; *a* = 4·131; *c* = 7·335

A sample of composition 33·3 moles % of UF_3 in SrF_2 had $a = 5{\cdot}821 \pm 0{\cdot}005$ kX.

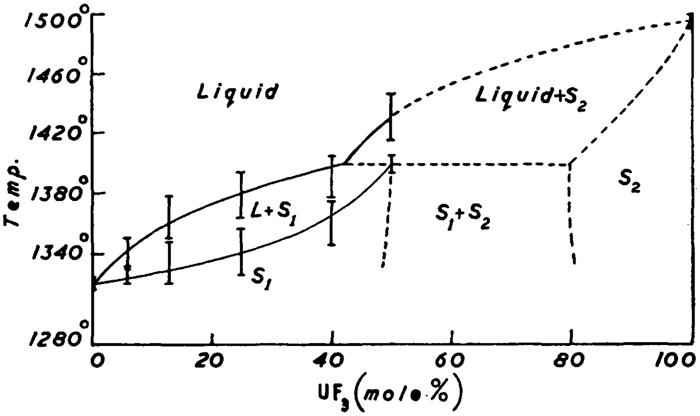
If the variable parameter for the cation positions is exactly $x = \frac{1}{3}$, the structure can be considered to be made up of layers of uranium and fluorine ions with each uranium surrounded by three equidistant fluoride ions and each fluorine ion surrounded by three equidistant uranium ions. These fluoride ions occupy the positions 2(*a*) and (4(*c*) in the unit cell. Above and below each uranium there is a further fluoride ion. These fluoride ions, which sit between the layers, occupy the positions 12(*k*) in the unit cell. The fluoride ions in the layers have three nearest uranium neighbours whereas those between the layers only have one nearest uranium neighbour. Thus the fluoride ions in the layers are not structurally equivalent to those between the layers.

Therefore it is possible that the anion vacancies generated to accommodate the barium fluoride in the uranium trifluoride lattice are not statistically distributed over all the anion sites but are concentrated in either the positions 2(*a*) and 4(*c*), *i.e.*, the positions in the layers, or 12(*k*), *i.e.*, the positions between the layers.

Cooling Curve Results.—Most of the cooling curves had the expected feature of a change of slope bounded by two points of inflection corresponding to liquidus and solidus points. In one case (50 moles % of UF_3), the second point of inflection (solidus) was followed by a horizontal section on the curve; this denoted the presence of an invariant system at this point. The reproducibility of the points was not very good; *X*-ray analysis of those samples which had been held at 1400—1500° for an extended period (as in cooling at 1° per min.) showed the presence of $BaUF_6$. This must have been formed by way of disproportionation of UF_3, *i.e.*, $4UF_3 \longrightarrow 3UF_4 + U$, and its presence would account for the rather indistinct points of inflection in the cooling curves. Disproportionation in the mixtures was not serious at about 1300°; for pure uranium trifluoride it was minimised by rapid heating to about 1480°, and the heating and cooling curves being then observed over the range 1480—1510°. At about 1500° approximately 20% of the trifluoride disproportionated in 1 hr.

The points of inflection are shown in the Figure. The *X*-ray diffraction results have shown that there is no compound formation in the BaF_2–UF_3 system and that two conjugate solid solutions may exist between certain concentration limits. It is therefore possible to have three phases present (two solid and one liquid), the system having in consequence an invariant point. The thermal data for the equimolar UF_3–BaF_2 mixture suggest that this point is about 1400°. In view of this we suggest that the system is of the peritectic type and we propose the phase diagram shown in the Figure.

Proposed UF_3—BaF_2 *phase diagram.*



S_1 = *Solid solution of* UF_3 *in* BaF_2. S_2 = *Solid solution of* BaF_2 *in* UF_3.

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