[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Structures of Complex Fluorides.[1] Barium Fluosilicate and Barium Fluogermanate

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The isomorphous compounds barium fluosilicate and barium fluogermanate are interesting examples of complex fluorides which are sparingly soluble in water. The X-ray data to be presented in this paper lead to a determination of the atomic arrangement which exists within crystals of these substances. They are found to crystallize in a new but quite simple and compact structural type of evidently very large crystal energy, in qualitative agreement with the observation of near insolubility in water.

Small, needle-like crystals of barium fluosilicate were obtained by the slow evaporation of dilute hydrochloric acid solutions. In agreement with Groth,[2] these needles were found to be hexagonal prisms with rhombohedral ends. Both X-ray and microscopic data confirm this assignment to the hexagonal system.

Using filtered CuKα radiation complete sets of oscillation photographs were prepared from single crystals of barium fluosilicate. Needles of 0.1 mm. or smaller diameter were employed for photographs with [00·1] as the axis of oscillation, while sections about 0.1 mm. long cut from similar needles were used for photographs with [10·0] and [11·0] as axes of oscillation. The symmetry of the patterns obtained is that of $D_3^d - \bar{3}m$. This was confirmed also by a carefully oriented Laue photograph. The hexagonal axes have a = 7.17 Å., c = 6.99 Å. An approximate determination of the density by the pycnometer method gave 4.29 g./cc.; the calculated value for three stoichiometric molecules within the unit cell is 4.41 g./cc.

It was observed, however, that only reflections with $(h - k + l)/3$ integral appear. The fundamental lattice is then rhombohedral, the hexagonal unit having lattice points at 000; $^1/_3$, $^2/_3$, $^1/_3$; $^2/_3$, $^1/_3$, $^2/_3$. The rhombohedral unit, containing one stoichiometric molecule, has a = 4.75 Å., α = 97° 58′.

All classes of reflections consistent with the rhombohedral unit are observed. The possible space-groups[3] are, therefore, D_{3d}^5, D_3^7 and C_{3v}^5. A reasonable structure which accounts for all of the diffraction data can be developed from $D_{3d}^5 - R\bar{3}m$, the space-group of highest symmetry. The atomic positions within the rhombohedral unit are: Si at 000; Ba at $^1/_2$, $^1/_2$, $^1/_2$; 6F at x, x, z; x, z, x; z, x, x; $\bar{x}, \bar{x}, \bar{z}$; $\bar{x}, \bar{z}, \bar{x}$; $\bar{z}, \bar{x}, \bar{x}$. With appropriate values of x and z, each silicon will be surrounded by six fluorine atoms at the corners of an octahedron of symmetry D_3^d. For $x = -0.254$, $z = 0.085$, this SiF_6 group becomes a regular octahedron with Si–F = 1.71 Å., an average value calculated from a number of previously studied fluosilicates having the ammonium chloroplatinate type of structure.[4] A comparison of observed structure amplitudes with those calculated on the basis of this structure (Table I) furnishes convincing evidence that it is essentially correct.

The structure factor characterizing this atomic arrangement for the plane (hkl) is

$$S = f_{Si} + f_{Ba}\cos\pi(h + k + l) + 2f_F\{\cos 2\pi(hx + kx + lz) + \cos 2\pi(hx + kz + lx) + \cos 2\pi(hz + kx + lx)\}$$

The atomic form factors of Pauling and Sherman[5] are used throughout our calculations.

The observed intensities were estimated by visual comparison with an intensity scale prepared for this purpose. After division by the Lorentz and polarization factor, $(1 + \cos^2 2\Theta)/2 \sin 2\Theta$ they were corrected approximately for absorption[6] in the crystal specimen, and, where necessary, for their positions in the layer lines.[7] The observed reflection amplitudes of Table I are proportional to the square roots of the corrected intensities thus obtained.

The agreement between the calculated and observed reflection amplitudes of Table I is remarkably good, in part because both barium and silicon

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(1) For earlier papers in this series see (a) THIS JOURNAL, **61**, 1252 (1939); (b) **61**, 2849 (1939).

(2) P. Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1906, Erster Teil, p. 548.

(3) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder Borntraeger, Berlin, 1935, Erster Band, Gruppentheoretische Tafeln, p. 262.

(4) "Strukturberichte," *Z. Krist. Ergänzungsband*, 1933–1935, p. 480.

(5) L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

(6) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder Borntraeger, Berlin, 1935, Zweiter Band, mathematische und physikalische Tafeln, p. 583.

(7) H. Ott, Wien-Harms, "Handbuch der Experimental-physik," Akad. Verlagsgesellschaft m. b. H., Leipzig, 1928, Band VII, 2, Teil, p. 160.

occupy positions which are completely determined by symmetry requirements. Since no temperature factor is included in the calculated amplitudes, they are not expected to decrease as rapidly with increasing sin Θ/λ as are the observed values.

Only powder photographs were prepared of barium fluogermanate, but the data lead to the conclusion that this substance is completely isomorphous with the fluosilicate. As an aid in indexing the reflections and determining the lattice constants for barium fluogermanate, powder photographs were taken for both compounds, using both Cu$K\alpha$ and Cr$K\alpha$ radiation. The lattice constants for barium fluogermanate are $a = 7.29$ Å., $c = 7.10$ Å. for the hexagonal unit, and $a = 4.83$ Å., $\alpha = 98°1'$ for the rhombohedral cell. In this case, also, the MF_6 group was assumed to be a regular octahedron, the Ge–F separation of 1.77 Å. being taken from our previous work[1b] on the isomorphous compounds ammonium and potassium fluogermanate. The

TABLE I

COMPARISON OF CALCULATED[a] AND OBSERVED REFLECTION AMPLITUDES IN BARIUM FLUOSILICATE

(*hkl*)	*F* Calcd.	*F* Obsd.	(*hkl*)	*F* Calcd.	*F* Obsd.
100	−23	24	$3\bar{1}3$	−27	19
$1\bar{1}0$	54	65	$4\bar{2}\bar{2}$	26	23
110	53	60	411	42	29
$11\bar{1}$	−20	25	330	17	15
111	−70	73	$4\bar{3}0$	−18	19
200	27	29	$4\bar{1}\bar{3}$	33	30
$20\bar{1}$	−56	55	322	−12	11
$2\bar{1}\bar{1}$	28	28	$41\bar{3}$	34	26
201	−31	24	402	33	23
$21\bar{1}$	67	51	331	−25	18
$2\bar{2}0$	44	47	$5\bar{1}\bar{1}$	− 8	10
211	29	28	$33\bar{3}$	−20	16
$2\bar{2}1$	−18	22	$4\bar{3}\bar{2}$	−29	24
300	−26	25	500	−26	20
$22\bar{1}$	1	0	$4\bar{3}2$	−20	16
$30\bar{1}$	29	25	$5\bar{1}\bar{2}$	37	27
220	29	29	$4\bar{4}0$	30	28
$3\bar{1}\bar{1}$	−43	35	$5\bar{2}\bar{2}$	−12	16
$3\bar{1}1$	−27	20	$4\bar{4}1$	−16	17
$22\bar{2}$	54	36	332	37	20
$30\bar{2}$	−17	24	$5\bar{3}0$	23	20
221	−32	28	$4\bar{3}\bar{3}$	25	15
$2\bar{3}1$	40	34	$5\bar{3}\bar{1}$	−28	19
311	−10	10	422	22	16
$2\bar{3}2$	−38	27	511	−24	15
$3\bar{3}0$	60	47	$5\bar{3}1$	−18	9
$3\bar{2}2$	−23	19	$4\bar{4}2$	27	19
$4\bar{1}\bar{1}$	50	34	$3\bar{1}2$	37	18
222	49	33	$5\bar{2}\bar{3}$	31	24
400	48	28	$6\bar{1}\bar{1}$	28	13
$3\bar{3}1$	−19	22	$5\bar{4}0$	−26	13
$4\bar{2}0$	36	29	$5\bar{4}\bar{2}$	23	13
312	36	28	$44\bar{1}$	−23	8
$4\bar{2}\bar{1}$	−17	19	333	−20	8
401	−39	26	$44\bar{2}$	34	17
$3\bar{3}2$	26	23	600	17	12

[a] Temperature factor not included.

TABLE II

INTENSITIES OF POWDER REFLECTIONS FOR BARIUM FLUOGERMANATE[a]

{*hkl*}	Intensity Calcd.	Intensity Obsd.
100	7	10
$1\bar{1}0$	490	>200
110	350	>200
$11\bar{1}$	<1	0
111 200	70	80
$2\bar{1}0$	120	80
$2\bar{1}\bar{1}$	57	50
210 $21\bar{1}$	380	>200
$2\bar{2}0$	92	50
211 $2\bar{1}\bar{2}$	40	30
$22\bar{1}$ 300 $30\bar{1}$	60	40
220 $3\bar{1}\bar{1}$	54	30
$31\bar{1}$ $3\bar{2}\bar{2}$	58	40
310 $30\bar{2}$	110	80
221 $3\bar{1}\bar{2}$	60	40
$31\bar{2}$	51	30
311	<1	0
$32\bar{1}$ $3\bar{2}\bar{2}$	50	30
320 $3\bar{3}0$	46	30
$32\bar{2}$ $40\bar{1}$ $4\bar{1}\bar{1}$ 222	50	30
400 $3\bar{1}\bar{3}$	27	20
$40\bar{2}$ $41\bar{1}$ 321 $4\bar{1}\bar{2}$	80	60
410	<1	0
$41\bar{2}$ $32\bar{3}$	31	30
$33\bar{1}$ $4\bar{2}\bar{2}$	11	10
303 411 $33\bar{2}$ $40\bar{3}$	46	30
$42\bar{1}$ $4\bar{1}\bar{3}$ 322	27	20
$41\bar{3}$ 420 $42\bar{2}$	71	50
331	<1	0
$33\bar{3}$ $5\bar{1}\bar{1}$	<1	0
$50\bar{1}$ $4\bar{2}\bar{3}$	29	20
500	3	0
421	4	0
$42\bar{3}$ $50\bar{2}$ $3\bar{1}\bar{2}$	34	20
$51\bar{1}$ $4\bar{4}0$	11	10
$43\bar{1}$ 510	21	10
$51\bar{2}$ $44\bar{1}$	20	10
$43\bar{2}$	2	0
332 430	19	10
$50\bar{3}$ $5\bar{1}\bar{3}$	25	10
422 511	9	2

[a] Temperature factor not included.

corresponding values of the parameters are $x = -0.259$, $z = 0.086$.

Table II contains a comparison of calculated with observed intensities of reflection for powder data from barium fluogermanate, CuKα being the radiation employed. Theoretical relative intensities were calculated from the expression,[8]

$$I = \text{Constant}\left(\frac{1 + \cos^2 2\Theta}{2 \sin 2\Theta \sin \Theta}\right) jS^2$$

The visually estimated intensities were corrected approximately for absorption[6] in the specimen. Although the structure is extremely simple, the values of the lattice constants are such as to result in many cases of near superposition of two or more reflections. Even though the powder specimen used was only about 0.1 mm. in diameter, most of the apparent lines appearing at the larger values of sin Θ are actually composite. Such groups of reflections are bracketed in Table II, the calculated intensities being, of course, the arithmetical sum of the individual intensities. Because of the greater resolution the lattice constants were determined from photographs taken with CrKα radiation.

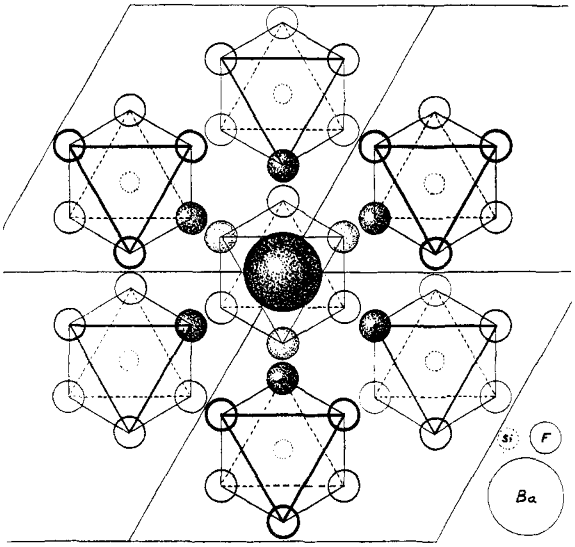

Fig. 1.—Diagrammatic projection on (111) of the rhombohedral unit of structure of barium fluosilicate.

A diagram of the derived structure is shown in Fig. 1. It may be considered as a cesium chloride-like arrangement of Ba^{++} and $MF_6^=$ ions with a rhombohedral angle of about 98° instead of 90°. The coördination number of barium toward fluorine is twelve. Each barium ion in barium fluosilicate has six fluorine atoms as neighbors at a distance of 2.88 Å. (three above and three below), and six others at 2.75 Å. (arranged in a staggered ring about the central cation). The difference of about 0.13 Å. between these two types of Ba–F separations may be attributed in large part to variations in the coulombic repulsions exerted between barium ions and the partially ionic silicon atoms at the centers of the neighboring complexes. Thus the distance from a barium ion to the silicon atoms above and below is only 3.495 Å., whereas the distance from barium to the silicon atoms associated with the fluorine atoms forming the girdle is 4.30 Å.

In barium fluogermanate the Ba–Si separation along the unique axis is 3.55 Å., the corresponding Ba–F distance 2.92 Å.; the second type of Ba–Si separation is 4.37 Å., and the corresponding Ba–F distance 2.77 Å. The average Ba–F separation in barium fluogermanate is thus indicated as being about 0.03 Å. larger than in the fluosilicate. This effect may not be real, since an error of 0.01–0.02 Å. in our assumed values for the Si–F and Ge–F values would vitiate the result. Nevertheless, the reasonable assumption of a somewhat larger effective charge associated with germanium than with silicon would result in the kind of phenomenon noted.

The only close approach of fluorine atoms of adjacent complexes is in the girdle of six around each barium ion. In barium fluosilicate this distance is 2.77 Å., while in barium fluogermanate it is 2.79 Å. These values are about 0.1 Å. larger than twice the ionic radius of fluoride ion.

It is probable that the complex anions, $SiF_6^=$ and $GeF_6^=$, are not exactly regular octahedra, but are slightly stretched along the three-fold axis (retaining, however, the symmetry, D_3^d). Such a departure from regularity would tend to stabilize the BaF_{12} coördination group, the most important result being to decrease the characteristic repulsive forces arising from the interpenetrations of the closed shells of adjacent atoms or ions. Since, however, it is even more necessary to keep the characteristic repulsive potential energy of the MF_6 group close to the minimum value corresponding to complete regularity, we can be sure that any distortion of the complex anion will be very slight.

The substitution of a much smaller cation, such as Mg^{++}, for Ba^{++} in the structural type under discussion would result in a marked increase in the

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[8] R. W. G. Wyckoff, "The Structure of Crystals," Chemical Catalog Company, New York, N. Y., 2nd ed., 1931, p. 165.

anion–anion repulsions in the girdle around the cation and a consequent destabilization of the structure. For compounds of formula RMX_6, we can predict that the barium fluosilicate type of structure will be stable if the radius ratio of R to X is about equal to or is greater than unity. Thus, such compounds as $RTaF_6$, in which R stands for K^+, Rb^+, Cs^+, Tl^+ might well assume this structure. Cesium hexafluotantalate is described[9] as rhombohedral with $\alpha = 95°40'$, and very probably belongs to this structural type.

It is of interest to compare the structure described in this paper with the quite stable structures of potassium fluosilicate and potassium fluogermanate. In potassium fluogermanate[1b] the potassium and fluorine atoms are approximately in hexagonal closest-packing. In cubic potassium fluosilicate[4] these atoms are approximately in cubic closest-packing. (The hexagonal modification of potassium fluosilicate, stable just below room temperature, has not been investigated in detail.) Since Ba^{++} and K^+ are assigned nearly identical ionic radii (1.33–1.35 Å. for coördination number six), reasonable structures for the barium compounds might be obtained by substituting barium for half the potassium ions in the structures of the potassium salts. It is clear from Fig. 1, however, that the actual structure of the barium compounds is not based on closest-packing of barium and fluorine atoms. Actually the molecular volumes of barium fluosilicate and barium fluogermanate are, respectively, 23.8% and 14.3% less than those of the corresponding potassium salts. The crystal energies are evidently much larger for the barium than for the potassium salts. Although the magnitude of the crystal energy is only one of the factors which determine solubility, the fact that, depending on the temperature, the solubility of barium fluosilicate is only $^1/_5$ to $^1/_{10}$ that of the sparingly soluble potassium salt seems reasonable in view of the foregoing comparisons.

The X-ray powder diffraction data given by Hanawalt, Rinn, and Frevel[10] for barium fluotitanate and barium fluosilicate indicate that $BaTiF_6$ also possesses the structure derived in this paper. Taken with MoKα radiation, only about half a dozen of the lines listed by these authors arise from single reflections, and it is difficult, therefore, to give accurate values of the lattice constants. Approximate values for the three-molecule hexagonal unit are a = 7.36 Å., c = 7.25 Å., and for the one-molecule rhombohedral unit a = 4.89 Å., $\alpha = 97°40'$. The intensities given are qualitatively at least in line with those expected for the type of structure discussed in this paper. The TiF_6 group is without doubt somewhat larger than either SiF_6 or GeF_6; the Ti–F separation may be estimated as 1.82 ± 0.02 Å.

Summary

It is shown from X-ray data that crystals of the isomorphous compounds barium fluosilicate and barium fluogermanate possess one-molecule rhombohedral units of structure with a = 4.75 Å., $\alpha = 97°58'$ and a = 4.83 Å., $\alpha = 98°1'$, respectively, space-group $D^5_{3d} - R\,3m$. The structure can be described formally as a cesium chloride-like arrangement of bivalent cations (Ba^{++}) and nearly regular octahedral anions (SiF_6^{-4}, GeF_6^{-4}, TiF_6^{-4}), but having a rhombohedral angle of about 98° instead of 90°. Actually, however, each barium ion is nearly equidistant from twelve fluorine atoms of eight neighboring anions to give a BaF_{12} coördination group. This structural type may be expected for compounds of formula RMX_6 for which the radius ratio of R to X is about equal to or is greater than unity.

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[9] Reference 2, p. 580.

[10] Hanawalt, Rinn and Frevel, *Ind. Eng. Chem., Anal. Ed.*, **10**, 457 (1938).