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The Crystal Structure of $KBrF_4$*

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$KBrF_4$ is tetragonal, with $a = 6{\cdot}162 \pm 0{\cdot}002$, $c = 11{\cdot}081 \pm 0{\cdot}002$ kX. The observed density leads to 4 molecules in the cell, with a calculated density $\varrho = 3{\cdot}06$ g.cm.$^{-3}$. The space group is D_{4h}^{18}–$I4/mcm$. The fluorine atoms are distributed in tetrahedral configurations about each bromine atom, with Br–F = 1·81 Å. The F–F distances within the BrF_4 group are 2·81 and 3·03 Å. Each potassium is bonded to 8 fluorines, with K–8F = 2·84 Å.

Introduction

Samples of $KBrF_4$ were prepared by the reaction of KF with BrF_3. A form suitable for powder photographs was obtained by removing the excess BrF_3 under vacuum at 130° C., leaving the residue as a granular material which was ground and mounted in Kel–F or quartz capillary tubes. Since $KBrF_4$ will react with traces of moisture, the capillary tubes were filled under dry conditions.

The reaction of $KBrF_4$ with moisture results in the formation of decomposition products of unknown composition. Even under favorable conditions of preparation, weak lines of the decomposed material always appeared on the powder photographs. Despite the presence of these spurious maxima, a tetragonal cell was chosen with

$$a = 6{\cdot}162 \pm 0{\cdot}002,\quad c = 11{\cdot}081 \pm 0{\cdot}002 \text{ kX.},$$

and this was subsequently verified by single-crystal observations. (Cell dimensions are based on Cu $K\alpha_1\alpha_2 = 1{\cdot}5387$ kX.)

Single crystals were prepared and mounted in Kel–F capillary tubes. The decomposition products produced a sufficient number of interfering powder lines which made the single-crystal patterns useless for intensity purposes. It was not possible to obtain more than one 180° oscillation photograph about the c axis and one zero-level Weissenberg pattern before decomposition became complete. Consequently, it was necessary to use powder patterns in the structure determination.

Determination of the structure

In order to improve resolution, a narrow quartz capillary, less than 0·01 cm. in diameter, was used for the final powder pattern. This was required in order to separate impurity maxima from the $KBrF_4$ pattern and also to resolve a number of interfering $KBrF_4$ lines.

For the powder pattern, the following reflections were observed: hkl with $h+k+l = 2n$, $0kl$ with $k, l, = 2n$, or possibly, $k+l = 2n$, $hk0$ with $h+k = 2n$, hhl with $l = 2n$, $h00$ with $h = 2n$, $00l$ with $l = 2n$.

A number of reflections hkl with l odd were observed on the powder pattern. On the other hand, only a few such reflections were observed on the oscillation pattern, in particular, 211, 213, and 215. However, these maxima fall on, or are nearly coincident with, impurity powder lines. For the zero-level Weissenberg pattern, reflections $hk0$ occurred with $h+k = 2n$.

The lack of definite information on the $0kl$ reflections, and the presence of only a limited number of reflections with l odd made the space-group assignment uncertain. Consequently the structure was determined by trial from intensity considerations.

Flotation experiments indicated a density value between 2·8 and 3·1 g.cm.$^{-3}$. This led to 4 molecules in the unit cell and a calculated X-ray density of 3·06 g.cm.$^{-3}$. Thus, 4 K, 4 Br, and 16 F atoms must be placed in the cell.

Although the 16 F atoms can produce a sizeable effect on the line intensities, one may expect the major scattering to arise from the 4 K and 4 Br atoms. Examination of the intensities of Table 1 indicates that the probable positions for these atoms are:

$$4\text{ Br in } 0, 0, 0;\ 0, 0, \tfrac{1}{2};\ \tfrac{1}{2}, \tfrac{1}{2}, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}.$$
$$4\text{ K in } \tfrac{1}{2}, 0, \tfrac{1}{4};\ \tfrac{1}{2}, 0, \tfrac{3}{4};\ 0, \tfrac{1}{2}, \tfrac{1}{4};\ 0, \tfrac{1}{2}, \tfrac{3}{4}.$$

In locating the F positions, it was assumed that the fluorine atoms would be distributed in some characteristic configuration about each bromine and that the Br–F bond lengths would approximate the value of 1·78 Å found in BrF_3 (Rogers, Wahrhaftig & Schomaker, 1947).

A study of the $hh0$ reflections led readily to possible x and y coordinates for the fluorine atoms. For the 220 reflection, the potassium and bromine atoms account practically for the observed intensity. However, for the 110 and 330 reflections, the contributions of these atoms are too small to explain the observed intensities, indicating that there must be a large fluorine contribution. For the 330 reflection, the fluorine scattering must be near its maximum value. This requires

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Table 1. *Crystallographic data*

hkl	$(\sin^2\theta)_o$	$(\sin^2\theta)_c$	$I_o^{\frac{1}{2}}$	$I_c^{\frac{1}{2}}$
002	0·01938	0·01938	65	94
110	0·03110	0·03121	97	111
112	0·05053	0·05056	203	219
200	0·06243	0·06241	93	91
004	0·07735	0·07735	32	34
202 }*	0·08284	0·08273	35	35 }
211 }		0·08283	70	58 }
114	0·1082	0·1085	22	22
213*	0·1214	0·1214	51	61
220*	0·1248	0·1248	73	77
204	0·1393	0·1396	110	110
222	0·1436	0·1441	34	33
310	—	0·1559	0	4
006 }	0·1735	0·1735	~ 0	3 }
312 }	0·1752	0·1752	90	91 }
215*	0·1981	0·1986	<33	3
224 }	0·2019	0·2019	58	58 }
116 }	0·2047	0·2047	57	54 }
321	—	0·2075	0	3
314 }*	0·2333	0·2331	39	27 }
206 }	0·2359	0·2360	26	35 }
323	—	0·2461	0	4
400	0·2494	0·2494	23	23
402 }	0·2689	0·2687	24	12 }
411 }		0·2699		9 }
330	0·2807	0·2806	27	27
332 }	0·3007	0·2999	43	45 }
226 }		0·3004	19	35 }
413 }	0·3078	0·3085	23	20 }
008 }	~0·3093	0·3085	27	23 }
420 }	0·3118	0·3118	43	43 }
217 }	~0·3158	0·3142	19	20 }
325	—	0·3231	0	2
404 }	0·3261	0·3265	45	45 }
316 }	0·3298	0·3294	50	60 }
422 }	~0·3318	0·3310	19	20 }
118	0·3389	0·3397	18	14
334	—	0·3577	0	2
208	0·3702	0·3709	28	28
415	~0·384	0·3855	18	12
424	0·3894	0·3889	35	37
510	0·4056	0·4053	18	13
406 }	0·4246	0·4230	18	16 }
512 }		0·4246	37	39 }
228	0·4337	0·4333	27	27
327	—	0·4389	0	2
336 }	0·4541	0·4539	20	17 }
521 }		0·4568		12 }
318 }	~0·465	0·4644	12	9 }
219 }		0·4684		5 }
0,0,10 }	0·4829	0·4821	17	10 }
514 }		0·4825		10 }
426	~0·486	0·4853	13	9
523	0·4954	0·4954	~18	11
440 }	0·4987	0·4987	23	19 }
417 }	—	0·5012	—	9 }
1,1,10	0·5133	0·5131	25	25
442	~0·5189	0·5181	~12	9
530	~0·5310	0·5300	~ 0	5
2,0,10	—	0·5444	0	4
532	0·5494	0·5492	22	28
408	0·5585	0·5579	18	17

that x and y be approximately $\pm\frac{1}{6}$ relative to each bromine at $0, 0, 0$ and $0, 0, \frac{1}{2}$, and $\frac{1}{2}\pm\frac{1}{6}$ relative to the bromines at $\frac{1}{2}, \frac{1}{2}, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The coordinates so chosen lead to reasonably good agreement between calculated and observed intensities for the $h00$ and $hk0$ reflections. However, x and y were varied independently about the value $\frac{1}{6}$ in order to determine if x and y were equivalent. Final trial calculations on all $h00$ and $hk0$ reflections indicated that, within the experimental error, x and y were the same, with $x = y = 0{\cdot}161\pm0{\cdot}003$. From similar considerations, it was determined that the z coordinates were given by $z = \pm0{\cdot}147\pm0{\cdot}003$, or $\frac{1}{2}\pm0{\cdot}147$.

Ambiguities arise in assigning z values to particular fluorine atoms. However, it is evident that z values may be chosen which will lead to planar or tetrahedral configurations of the fluorines about each bromine. Only one structure leads to reasonable F–F distances between neighboring configurations. This is shown in Fig. 1, where the potassium atom is now taken as the origin. The atomic positions and the symmetry are given by D_{4h}^{18}–$I4/mcm$, with

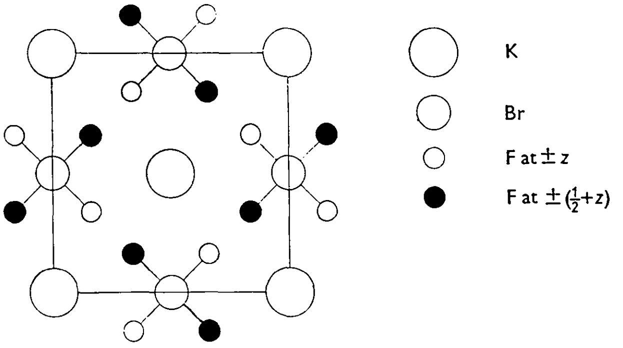

Fig. 1. Projection on c face of $KBrF_4$.

$$4\,K \text{ in } 0, 0, 0;\ 0, 0, \tfrac{1}{2};\ \tfrac{1}{2}, \tfrac{1}{2}, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}.$$

$$4\,Br \text{ in } 0, \tfrac{1}{2}, \tfrac{1}{4};\ 0, \tfrac{1}{2}, \tfrac{3}{4};\ \tfrac{1}{2}, 0, \tfrac{1}{4};\ \tfrac{1}{2}, 0, \tfrac{3}{4}.$$

$$16\,F \text{ in } (0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})+$$

$$x, \tfrac{1}{2}+x, z;\ \bar{x}, \tfrac{1}{2}-x, z;\ \tfrac{1}{2}+x, \bar{x}, z;\ \tfrac{1}{2}-x, x, z;$$

$$x, \tfrac{1}{2}+x, \bar{z};\ \bar{x}, \tfrac{1}{2}-x, \bar{z};\ \tfrac{1}{2}+x, \bar{x}, \bar{z};\ \tfrac{1}{2}-x, x, \bar{z};$$

$$\text{with } x = 0{\cdot}161\pm0{\cdot}003, \text{ and } z = 0{\cdot}147\pm0{\cdot}003\,.$$

The extent of agreement between observed and calculated intensities is shown in Table 1. The data of this table were taken with Cu radiation filtered with nickel foil. The observed intensities were deduced from microphotometer tracings and the calculated intensities have been corrected by the temperature factor $\exp(-2B\sin^2\theta/\lambda^2)$, with $B = 2\times10^{-16}$ cm.^{2}. Brackets surround poorly or improperly resolved lines, while the asterisk indicates interference by an impurity line.

The structure

The bromine atoms (Fig. 1) are surrounded by tetrahedral configurations of fluorine atoms with the two-fold axis of the tetrahedron parallel to the c axis. In the x–y plane, the F–F distance within any BrF_4^- tetrahedron is $2{\cdot}81\pm0{\cdot}04$ Å. In any other direction, the F–F distance is 3·03±0·04 Å. The tetrahedra are therefore elongated in the direction of the c axis. The Br–F distance is 1·81±0·04 Å, close to the value cited for BrF_3. (The sum of the tetrahedral radii is 1·75 Å.) All potassium atoms are bonded to 8 equidistant fluorines with K–8F = 2·84±0·03 Å. The coordination of the fluorines involves 4 fluorines at the corners of a square in a plane below the potassium and 4 fluorines similarily disposed in a plane above.

The structure is similar to $BeSO_4.4H_2O$ (Beevers & Lipson, 1932). The BrF_4^- ions are replaced by tetrahedral SO_4^{2-} ions while the K^+ ions are replaced by tetrahedral $(Be4H_2O)^{2+}$ groups. The space group is D_{2d}^{10} and no symmetry planes exist. Thus, the sulphurs do not lie on symmetry planes, as do the potassiums, and the sulphate ions can therefore be rotated from the position occupied by BrF_4^-. The rotation which is observed is slight. Otherwise the distribution of SO_4^{2-} ions about the $(Be4H_2O)^{2+}$ ions is similar to that observed for the BrF_4^- groups around K^+.

I am indebted to several members of the staff for the samples used in this study. Chemical preparations of the $KBrF_4$ samples and the filling of the capillaries were carried out by Dr I. Sheft and Dr A. Martin of the Chemistry Division. The density measurements, as well as the preparation of the narrow quartz capillary and the sample, were made by Mr G. Schnizlein of the Chemical Engineering Division.

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The Crystal Structure of Barium Dititanate, $BaO.2TiO_2$*

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The crystal structure of $BaO.2TiO_2$ has been determined by means of two-dimensional Patterson and Fourier syntheses. The unit cell is monoclinic with $a = 9{\cdot}410 \pm 0{\cdot}004$, $b = 3{\cdot}930 \pm 0{\cdot}001$, $c = 16{\cdot}892 \pm 0{\cdot}013$ Å, $\beta = 103^\circ\ 2' \pm 3'$, space group $A2/m$, and contains six formula units. The structural arrangement is discussed in relation to other baria–titania compounds.

Introduction

In the course of investigations of the phase diagram of the system $BaO–TiO_2$, Rase & Roy (1955) have observed the formation, in addition to the polymorphic forms of $BaTiO_3$, of the compounds $2BaO.TiO_2$, $BaO.3TiO_2$, $BaO.4TiO_2$, and $BaO.2TiO_2$ (or $3BaO.7TiO_2$).

The present paper is concerned with the structure of the last compound.

The compound is formed in mixtures of TiO_2 and $BaCO_3$ containing between 50 and 75 molar% of TiO_2 which have undergone prolonged heating at temperatures above 1210° C. Acicular crystals some 10 mm. long and 0·5 mm. in width grow readily on cooling a melt containing $62\frac{2}{3}$ molar% TiO_2.

Experimental

Crystals grown by Rase & Roy were examined by oscillation, rotation and Weissenberg photographs, using Cu $K\alpha$ radiation. They were found to be monoclinic with the b axis parallel to the needle length.

Accurate measurements of the cell dimensions were obtained by the method of Weisz, Cochran & Cole (1948). The values a, c, and β were found from X-ray photographs in which the b axis was rotation axis, and the value of b from photographs in which the a axis was rotation axis. The space group was derived from systematic absences observed on the zero, first, second and third b-axis Weissenberg photographs.

$0kl$ and $h0l$ intensities, recorded on zero-layer a- and b-axis Weissenberg photographs respectively, using Cu $K\alpha$ radiation, were measured by visual estimation. No correction for absorption was made in the latter case since the needle-shaped crystal was mounted with its length along the rotation axis and its cross-section was small. However, owing to the

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