CRYSTAL STRUCTURE OF BARIUM BROMOFLUORIDE

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ABSTRACT

BaBrF belongs to tetragonal space group P $(4/n)$ mm with $a = b = 4{\cdot}5097$ (9) Å, $c = 7{\cdot}4409$ (32) Å. The three dimensional X-ray data were collected using an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation. The least squares refinement based on 286 reflections led to an R value of 0·058.

INTRODUCTION

CRYSTALS of mixed dihalides of Ba, Sr and Pb constitute an important class of partially ionic compounds having interesting optical properties[1,2]. All of them crystallize in tetragonal space group P $(4/n)$ mm and are believed to be isostructural. The Pb ClF structure has been known from the powder diffraction data of Frevel *et al.*[3] Accurate cell parameters of SrClF have been measured by Brixner and Bierlein[4] and a preliminary determination of atomic parameters of BaClF has been obtained from $h0l$ Weissenberg photographs with an R factor of 0·178 by Nicklaus and Fischer[5]. Recently Sauvage[6] using the data from a PW 1100 automatic X-ray diffractometer has refined the structure of SrClF and BaClF to R factor values of 0·052 and 0·048 respectively. However, no precise data are available for other members of this family of crystals. During the course of our studies on some mixed dihalides grown in our laboratory (SrClF, BaBrF and SrBrF)[7], we had to determine the crystal structure of BaBrF and the results obtained are discussed in this paper.

EXPERIMENTAL AND RESULTS

An approximately cylindrical shaped specimen [radius varying from a minimum of 0·15 mm to a maximum of 0·17 mm, μr (Mo Kα) $\simeq$ 4] was selected for X-ray diffraction studies. This specimen was prepared by cutting and grinding the platy crystals obtained by the method of growth employed. The preliminary X-ray diffraction studies were carried out using Weissenberg technique. The diffraction data indicated the following systematic absences—$hk1$: no condition; $hk0$: $h + k = 2n + 1$; $0kl$: no condition; hhl: no condition. These identify the space group to be P $(4/n)$ mm with $Z = 2$ and this is in conformity with the generally accepted idea that all the mixed dihalides of the type ABF crystallize in the same space group. The cell parameters were refined for 14 high angle strong reflections by least-squares procedure. The refined cell parameters and their standard deviations are given in Table I. The corresponding values for SrClF and BaClF as determined by Sauvage[6] are also given in Table I for comparison. The calculated density for BaBrF (M = 236·28) is 5·18.

TABLE I

The refined cell parameters of BaBrF, BaClF and SrClF

Lattice parameters	BaBrF	BaClF	SrClF
$a = b$	4·5097 (9) Å	4·3939 (6) Å	4·1259 (8) Å
c	7·4409 (32) Å	7·2248 (9) Å	6·9579 (13) Å

X-ray intensity data were collected using an Enraf-Nonius CAD-4 diffractometer with Mo Kα-radiation. The data were corrected for polarization effects but not for absorption. The structure was refined isotropically by

TABLE II

Atomic positional coordinates and thermal parameters in BaBrF

(Origin at centre (2/m) at 1/4, $\bar{1}$/4, 0 from $\bar{4}$ m 2)

Atom	Position	x	y	z	$b_{11} \times 10^5$ Å^2	$b_{33} \times 10^5$ Å^2
Ba	2 (*c*)	0·25	0·25	0·19267 (15)	874 (27)	427 (13)
F	2 (*a*)	0·75	0·25	0	1682 (331)	448 (147)
Br	2 (*c*)	0·25	0·25	0·64948 (28)	1456 (53)	555 (26)

TABLE III

Interatomic distances in Å *in BaBrF, SrClF and BaClF*

No. of equivalent distances	BaBrF		SrClF		BaClF	
4	F–Ba	2·6679 (6)	F–Sr	2·4944 (10)	F–Ba	2·6491 (7)
4	F–F	3·1848 (6)	F–F	2·9175 (4)	F–I	3·1070 (3)
4	F–Br	3·4414 (16)	F–Cl	3·2291 (25)	F–Cl	3·3649 (41)
1	Ba–Br	3·3914 (24)	Sr–Cl	3·0715 (37)	Ba–Cl	3·1959 (55)
4	Ba–Br	3·3936 (8)	Sr–Cl	3·1117 (13)	Ba–Cl	3·2856 (18)
4	Br–Br	3·8819 (17)	Cl–Cl	3·5312 (26)	Cl–Cl	3·7655 (43)

full matrix least squares procedure to an R value of 0·073 for the 286 observed reflections [$I > 2\sigma(I)$]. The programme used was a full matrix structure factor least-squares programme, LALS, originally written by Gantzel, Sparks and Trueblood and modified by T. N. Bhat to suit IBM 360/44 system employed in the present study as well as to refine anisotropic temperature factor of the form $\exp -\{b_{11}(h^2 + k^2) + b_{33} l^2\}$. Using this programme the structure was refined to a final R value of 0·058. The scattering factors used were taken from the *International Tables for X-ray Crystallography*, Volume IV. The final atomic coordinates and anisotropic temperature factors are listed in Table II. The interatomic distances are given in Table III for the three crystals for comparison. A table of observed and calculated structure factors can be obtained from the authors.

From the analysis of the structure of BaBrF it is now confirmed that the crystal is isostructural with the other members belonging to the same family. A comparison of the fractional atomic coordinates given in Table II with those of other members[6] shows that there is only a very slight variation in their values which may be accounted for by the relative difference in the ionic radii of the constituent atoms. Accordingly one expects a very close similarity in their physical properties. In fact the dielectric and infrared data on SrClF, BaBrF and SrBrF are in agreement with their structural features[7, 8].

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