Preparation and Characterization of the System $BaBr_xCl_{2-x}$: The Structure of BaBrCl

STANISLAW A. HODOROWICZ,* EWA K. HODOROWICZ,* AND
HARRY A. EICK†

*Department of Chemistry, Michigan State University,
East Lansing, Michigan 48824*

The variations in the lattice parameters in the $BaBr_xCl_{2-x}$ system have been determined for the composition range $2.0 > x > 0.0$. All phases exhibit the $PbCl_2$-type orthorhombic structure and are assignable to space group *Pnma*. The crystallographic parameters of BaBrCl were determined by the Rietveld method from a line profile analysis of a digitized powder X-ray diffraction pattern. The anions are ordered with the bromide ion occupying the square pyramidal hole, and the chloride ion the smaller tetrahedral hole. Atomic coordinates are presented.

Introduction

Phase relationships in MBr_xCl_{2-x} and MBr_xI_{2-x} systems, where M = Pb and Sr, have been reported recently (*1–3*). All of these systems evidence $PbCl_2$-type orthorhombic symmetry, but over different composition ranges. The strontium bromide chloride system evidenced some unexpected narrow intermediate phase regions and anion ordering was apparent in some of the systems. Large variations in ion size and softness lead to differing cell geometries and to structural variation. This study on the $BaBr_xCl_{2-x}$ system was undertaken to determine if anion ordering occurred in the presence of a large, soft cation. The $BaBr_xCl_{2-x}$ system has been investigated marginally by Frit *et al.* (*4*) who report only that $BaBr_2$–$BaCl_2$ solid so-

lutions form the expected $PbCl_2$-type structure. We report detailed information regarding the variation of lattice parameters vs composition, the structure of BaBrCl, and the anion distribution in that structure.

Experimental

Starting materials were analytical-grade barium dibromide and barium dichloride obtained from Cerac, Inc., Milwaukee, Wisconsin. These substances were confined in recrystallized Al_2O_3 boats and were heated at 400°C under vacuum to remove occluded water, then were melted. X-Ray powder diffraction examination of the cooled products indicated only pure orthorhombic forms of both compounds (*5, 6*). The appropriate stoichiometric proportions of the reactants were pulverized and mixed intimately in a dry, argon-filled glove box. The samples (total weight of each sample was 1 g), again confined in

* On leave from Dept. of Chemistry Jagiellonian University, Poland.

† To whom correspondence should be addressed.

Al_2O_3 boats, were heated to 970°C, above the reported melting point of both reactants (7), and then cooled to room temperature at a constant rate of 0.1°C/min. All sample manipulations were effected in the glove box.

X-Ray diffraction measurements were taken on two instruments. Lattice parameter data were determined with a 100-mm evacuated Hägg–Guinier camera ($CuK\alpha_1$ radiation). Samples were protected by a film of paraffin oil during transfer to the camera. The X-ray photographs were calibrated internally by addition of platinum powder ($a = 3.9238 \pm 0.0003$ Å, 23°C) to the samples, and the lattice parameters were refined by a linear regression procedure based on coincidence-free reflections. Reflection intensity data were obtained on a Siemens diffractometer (Ni-filtered $CuK\alpha$ radiation). The pulverized sample was passed through a 325-mesh sieve and gently sifted onto a glass plate coated with paraffin oil. Special efforts were made both to minimize preferred orientation effects and to check for their absence. The spectrum, collected at a scan rate of $\frac{1}{4}$° 2θ/min, was digitized manually at 2θ intervals of 0.025°.

X-Ray powder diffraction intensities were calculated with the program ANIFAC (8). Scattering factors with appropriate dispersion correction terms were taken from the "International Tables" (9). Consistent with the geometry of the diffractometer and the Guinier camera, absorption terms were not included in the calculations. The digitized data were analyzed with a Rietveld line profile fitting program (10) reportedly modified to give correct standard deviations (11). Both the powder intensity and Rietveld calculations were effected on a CDC CYBER 750 computer.

Input to the Rietveld program consisted of lattice parameters derived from the Guinier data, atomic coordinates which were the average of the $BaCl_2$ and $BaBr_2$ parameters, and occupancy parameters of

unity for the cation and 0.5 for each anion, in each anion site. Relaxation factors were set at 0.95. Background correction was by interpolation among seven points spaced across the 20° $\leq 2\theta \leq$ 64° scan range. An asymmetry correction was made for angles less than 34°. Anion occupancy was refined with one variable so that each anion site was constrained only to a total anion occupancy of unity. In addition to atomic and isotropic thermal parameters, other variables included (a) the zeropoint, (b) preferred orientation parameters, (c) asymmetry parameters, (d) the scale factor, and (e) half-width parameters, a total of 18 in all.

The reaction product for the composition $x = 1.00$ was analyzed by atomic absorption spectroscopy. Specimens of this composition (supported on a holey carbon grid) were also examined at 100 kV in a Philips EM 300 electron microscope in diffraction mode.

Results and Discussion

Only the $PbCl_2$-type structure is observed throughout the entire system and every X-ray powder diffraction pattern can be indexed on the basis of orthorhombic lattice parameters close to those of $BaBr_2$ and $BaCl_2$. The variation of the lattice parameters and the cell volume vs composition is presented in Fig. 1; lattice parameter data for selected compositions are presented in Table I. In this structure all atoms occupy the fourfold special positions $4(c)$ of space group D_{2h}^{16}–$Pnma$ (1).

The atomic absorption spectroscopy data indicated the composition of the product from the reactants for which $x = 1.00$ to be $x = 0.990 \pm 0.005$. We interpret this close agreement between initial and final compositions as an indication that reactant was not lost during the preparatory procedure, and have reported data based upon the reactant composition.
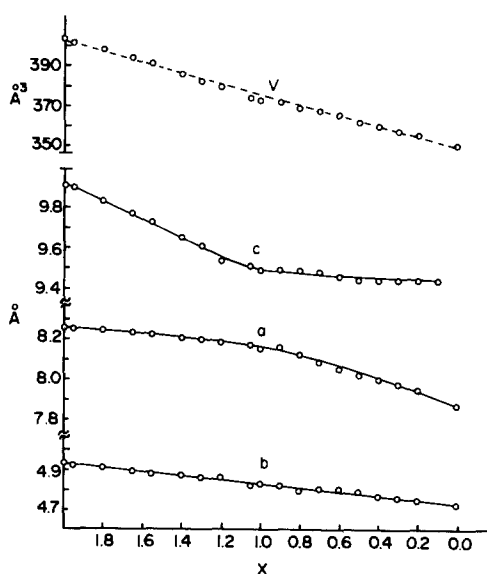
FIG. 1. Variation of lattice parameters and unit cell volume of $BaBr_xCl_{2-x}$ vs composition.

TABLE II

POSITIONAL PARAMETERS (SPACE GROUP *Pnma*) OF $BaBr_2$,[a] $BaCl_2$,[a] AND BaBrCl

	$BaBr_2$	$BaCl_2$	BaBrCl
Ba			
x	0.2447	0.2514	0.2673(7)
y	0.2500	0.2500	0.2500
z	0.1149	0.1209	0.1218(5)
$X(1)$			
x	0.1422	0.1504	0.136(2)
y	0.2500	0.2500	0.2500
z	0.4272	0.4130	0.436(2)
$X(2)$			
x	0.0284	0.0290	0.032(1)
y	0.2500	0.2500	0.2500
z	0.8401	0.8392	0.8266(8)

[a] Ref. (*6*).

Small BaBrCl crystallites were found to decompose quickly when exposed to the beam in the electron microscope. As a consequence, only larger crystallites could be examined and photographs were not taken of these. During the time span available for viewing the diffraction pattern on the microscope screen evidence of long-range order was never observed.

In this $PbCl_2$-type structure there are two anion positions, labeled in Table II as $X(1)$

TABLE I

LATTICE PARAMETERS FOR SELECTED $BaBr_xCl_{2-x}$ PHASES

	a (Å)	b (Å)	c (Å)	V (Å)[3]
$BaBr_2$	8.252(3)[a]	4.935(1)[a]	9.915(2)[a]	403.8
	8.276(8)	4.956(4)	9.919(8)	406.8[b]
$BaBr_{1.80}Cl_{0.20}$	8.242(4)	4.911(2)	9.830(2)	397.8
$BaBr_{1.40}Cl_{0.60}$	8.205(2)	4.873(1)	9.650(3)	385.8
BaBrCl	8.167(3)	4.825(1)	9.498(3)	374.3
$BaBr_{0.60}Cl_{1.40}$	8.051(3)	4.801(1)	9.461(1)	365.7
$BaBr_{0.20}Cl_{1.80}$	7.948(3)	4.750(2)	9.442(1)	356.4
$BaCl_2$	7.871(4)	4.730(2)	9.430(3)	351.0
	7.865(8)	4.731(4)	9.421(8)	350.5[b]

[a] Standard deviation of last digit.
[b] From Ref. (*6*).

and $X(2)$. The $X(1)$ anions are surrounded by four barium ions in a distorted tetrahedral configuration whereas the $X(2)$ anions, surrounded by five barium ions, occupy pyramidal holes. Hence, as a minimum, three structural models are possible: the bromine and chlorine atoms may independently occupy each of the two anion positions or these atoms may be distributed randomly between the two positions. Theoretical powder diffraction intensities were calculated for the $x = 1.00$ phase (program ANI FAC) from parameters derived by averaging those of $BaCl_2$ and $BaBr_2$ (*6*). The observed and calculated intensities of reflections found to be most sensitive to anion position, while in general giving poor agreement, indicated the best match for the ordered model. In addition, the nonlinear variation of the a and c parameters vs composition (Fig. 1) tends to support an ordered model.

As a check for partial anion ordering, powder diffraction intensities were calculated, using the same estimated atomic parameters, for position $X(1)$ occupancies of $Cl_yBr_{(1-y)}$ and $X(2)$ occupancies of $Cl_{(1-y)}Br_y$, with $y = 0.3$, 0.4, 0.6, and 0.7.

Ba–Cl	3.064 (18) Å
–2Cl	3.099 (12)
–Cl	3.159 (19)
–Br	3.407 (9)
–2Br	3.461 (7)
–2Br	3.508 (7)

None of these yielded improved intensity agreement.

In an effort to determine more accurate atomic parameters, the digitized intensity data were refined by the Rietveld line profile fitting procedure. The results of this analysis yielded the atomic parameters listed in Table II. The anion occupancy parameter refined quickly to a value of 0.99 ± 0.04, with $X(1)$, the tetrahedral hole, occupied by a chloride ion, and $X(2)$ by a bromide ion, indicative of a completely ordered structure at the 1:1 anion composition. The R_w value refined to 11.2, ($R = 8.45$) with $R_w = \Sigma w_i (y_{o_i} - y_{c_i})$. In this equation, $w_i = 1/y_{o_i}$, and y_{o_i} and y_{c_i} are the observed and calculated intensities, respectively, at the ith step. At the conclusion of the refinement process, shifts of atomic parameters had ceased, and those of thermal and other parameters were less than half the standard deviation.

Lattice parameters were refined initially, but were removed subsequently from refinement because these parameters are particularly sensitive to 2θ errors introduced by the digitizing procedure used. Initial refinements made with these parameters as variables indicated agreement, within experimental error, with the Guinier derived values. Eighteen variables remained when the lattice parameters were removed. The individual isotropic temperature factors hovered about 0; the overall temperature parameter refined to 6.3. The small thermal

parameter values are assumed to be the result of errors introduced in the data by the digitizing process and by preferred orientation effects.

Interatomic distances, with estimated standard deviations, derived by DISTAN (12) and presented in Table III, compare favorably with values expected from ionic radii data—3.15 and 3.30 Å, respectively, derived for the chloride and bromide using Shannon's ionic radii uncorrected for coordination number changes (13). It has been demonstrated that while thermal parameters derived by the Rietveld method may be in error, atomic parameters are generally correct (14). Indeed, refinements effected with occupancies fixed at unity and with selected reflections deleted were found to affect the thermal parameters, but not the positional parameters.

The atomic positional parameters are unexpectedly different from those of the parent species (6). The $BaCl_2$ and $BaBr_2$ structures were determined by refinement of powder diffraction peak intensity data. The interatomic distances reported for these phases are both much shorter and slightly longer than those reported for the corresponding atoms in this work. In view of the more reasonable interatomic distances reported herein, the $BaBr_2$ and $BaCl_2$ atomic parameters are suspect.

In this structure all the atoms lie on the mirror planes, perpendicular to the short b axis at $y = \pm 0.25$. The apparent abnormal expansion of the lattice in the a and c directions as a function of composition can be understood when viewed in terms of preferential occupancy of the anion sites (15). The observed and calculated d spacings of BaBrCl together with observed intensities derived by the Rietveld program and those calculated by ANIFAC are presented in Table IV. The one reflection whose observed and calculated intensities differ most significantly, (102), undoubtedly suffers from preferred orientation effects.

TABLE IV

OBSERVED AND CALCULATED POWDER
DIFFRACTION DATA FOR BaBrCl

hkl	d_{obs}	d_{calc}	I_{obs}[a]	I_{calc}[b]
011	4.302	4.302	8	7
102	4.100	4.105	55	43
200	4.071	4.084	11	8
111	3.803	3.806	47	43
201	3.752	3.751	4	4
112	3.123	3.127	43	44
210	}3.103	3.117	3	4
202		3.096	7	6
211	}2.959	2.961	100	100
103		2.952	13	12
013	2.646	2.647	30	30
301	2.616	2.617	12	11
113	2.516	2.518	35	32
020	2.410	2.412	32	35
004	2.373	2.374	16	14
302	2.361	2.362	36	33
311	2.299	2.300	11	15
213	2.220	2.221	15	15
122	2.079	2.080	15	15
220	2.070	2.074	3	3
303	2.064	2.064	5	5
204	2.055	2.052	9	8
400	2.042	2.042	8	7
222	1.9035	1.9033	2	3
313	1.8970	1.8979	2	1
410	1.8803	1.8803	4	5
123	1.8684	1.8682	4	6
105	1.8493	1.8502	2	3
321	1.7731	1.7740	5	6
412	1.7483	1.7483	1	1
115	1.7269	1.7276	5	5
024	1.6929	1.6924	8	9
322	1.6869	1.6879	19	22
314	1.6767	1.6779	4	6
215	1.6221	1.6221	10	11

[a] Data are observed values as summed by the Rietveld program.

[b] Calculated from ANIFAC.

The effects of preferred orientation on the intensities are difficult to assess. The platelike nature of the pulverized specimens causes them to pack preferentially with the b axis perpendicular to the specimen holder. Such packing was readily visible in the electron microscope.

The absence of long-range order in the electron diffraction patterns is consistent with the presence of an ordered structure. Although longer-range order might be anticipated and observed for anion compositions other than 1 : 1, beam degradation of the specimens precluded identification of such a region.

It is interesting to note that this phase fluoresces strongly when exposed to the X-ray beam, appearing pale blue. In view of the previous reports of fluorescence in barium compounds and especially in BaFCl, such an observation is not surprising (*16, 17*).

In summary, BaBrCl is found to be a completely ordered PbCl₂-type structure with the chloride ions occupying the tetrahedral hole and the bromide ions occupying the square pyramidal hole. The atomic parameters derived for BaBrCl differ appreciably from those of $BaCl_2$ and $BaBr_2$.

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