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An X-Ray Diffraction Study of the $SrBr_xI_{2-x}$ System

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The mixed halogen phases $SrBr_xI_{2-x}$, for which $2.00 > x > 0$ were prepared both by heating weighed masses of pure $SrBr_2$ and SrI_2 in sealed evacuated quartz ampoules and by cocrystallization from absolute ethanol. The reaction products were examined by X-ray powder diffraction methods. Five distinct regions were observed in the phase diagram. The crystallographic characteristics of phases representative of the single phase regions, $SrBr_2$–$SrBr_{1.60}I_{0.40}$, $SrBr_{1.40}I_{0.60}$–$SrBr_{0.80}I_{1.20}$, and $SrBr_{0.30}I_{1.70}$–SrI_2, are presented, and the anion distributions in the crystal structures are deduced on the basis of X-ray powder diffraction intensities.

Introduction

Recently Clink and Eick (*1*) in a study of the $EuBr_2$–$EuCl_2$ system identified two different phases for samples of the compositions $EuBr_{1.8}Cl_{0.2}$ and $EuBr_{1.5}Cl_{0.5}$. They reported structural details on an ordered $PbCl_2$-type (*2, 3*) structure for the latter phase. In view of the size similarities between Eu^{2+} and Sr^{2+} ions (*4*) and the isostructural nature of their bromides (*5, 6*), it seemed surprising that in the europium phase the anions were ordered, while in the strontium phase they were distributed randomly. Therefore, a study of the $SrBr_2$–$SrCl_2$ system (*7*) was undertaken, with the result that five unique phase regions were identified. Anions in phases represented by the compositions $SrBr_{1.60}Cl_{0.40}$ and $SrBr_{1.40}Cl_{0.60}$ assume an ordered arrangement while those in $SrBr_{0.30}Cl_{1.70}$ assume a random arrangement. The $SrBr_{1.60}Cl_{0.40}$ and $SrBr_{1.40}Cl_{0.60}$ structures may be regarded as $SrBr_2$- and $PbCl_2$-types, respectively, with Cl atoms in the tetrahedral positions.

The present research was initiated to determine if for the $SrBr_2$–SrI_2 system a similar complexity existed. Earlier studies of this system indicated solid solutions of the $SrBr_2$, $PbCl_2$, and SrI_2 structure types, but neither phase boundary limits nor selected anion occupancy was reported (*9*).

Experimental

The system $SrBr_xI_{2-x}$ was investigated over the composition range $2.00 > x > 0$. Starting materials were reagent grade $SrBr_2$ and SrI_2 (Cerac Inc., Milwaukee, Wis.) with a reported purity of at least 99.5%. The samples were weighed in a glove box filled with recirculated dry argon. Initially, the procedure outlined previously (*8*) was attempted. In this method $SrBr_2$ and SrI_2 powders in varying stoichiometric propor-

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tions were mixed and heated at 400°C. However, even after 2 weeks of heating some of the reactants were still present. An alternate procedure in which the reactants were prepared as before, but were heated to 650°C, above the reported melting points of both reactants (*10*), and then cooled slowly (0.1°C/min) to room temperature also failed. The reactants sublimed (*11*) from the heated zone of the furnace when the temperature was maintained >500°C for an appreciable length of time.

To keep the reactants confined two different procedures were used. In the first, appropriate mixtures were sealed in evacuated heavy-wall quartz tubes, heated to the melting point of $SrBr_2$, then cooled rapidly to 400°C. The samples were annealed at this temperature for 24 hr and were subsequently cooled (0.1°C/min) to room temperature.

In the second method the reaction was carried out from solution. First an approximate quantity of $SrBr_2$ was dissolved in absolute ethanol (*12*). To this $SrBr_2$ solution the required amount of SrI_2 was added with vigorous stirring. The yellow solutions obtained were evaporated under vacuum and then were heated in a dynamic vacuum at 200°C. When cocrystallization was attempted via the standard procedure in which the reagents in stoichiometric proportions are dissolved in hot solvent and subsequently cooled, one of the reagents crystallized out first. A similar phenomenon was recently reported for ammonium perchlorate–potassium perchlorate mixtures (*13*).

Most samples were subjected to X-ray powder diffraction analysis with a Guinier–Hägg forward-focusing camera and Cu$K\alpha_1$ (λ = 1.5405 Å) radiation. The samples were protected by a film of paraffin oil both during transfer to the camera and during diffraction analysis. For some samples the diffractograms were also obtained with an X-ray DRON-2 (USSR made) diffractometer with nickel-filtered copper radiation. Reflection intensity data were obtained from these patterns by measuring the area under the peaks.

Lattice parameters were refined by a least-squares treatment of d spacings recorded with the Guinier camera. The photographs were calibrated internally with Pt powder (a = 3.9238 ± 0.0003 Å, 25°C). X-Ray powder diffraction intensities for phases of selected composition were calculated on a CDC CYBER 750 computer with the program ANIFAC (*14*). Atomic scattering factors with appropriate dispersion correction terms were used (*15*). Consistent with the geometry of the Guinier camera and the diffractometer, an absorption correction was not included in the calculations.

For four reaction products (x = 1.8, 1.6, 1.0, and 0.3), the Sr : Br : I atomic ratio was determined by atomic absorption spectroscopy.

Results and Discussion

The atomic absorption spectroscopy data indicated that the composition of the products agreed to within ±0.002 of the atom ratio anticipated from the reactant mixture. We thus conclude that sample was lost neither by sublimation nor by reaction with the container. The products obtained from the absolute ethanol solution were identical in their behavior to those prepared by the fusion technique. However, specimens of all compositions were subsequently prepared by the latter procedure. X-Ray diffraction patterns of the SrI_2 reactant evidenced some unassignable reflections. D values greater than 9 Å were observed, suggestive that the SrI_2 contained a polyiodide contaminant (*16*). Polyiodides should decompose at high temperature (*17*), and indeed, after the SrI_2 had been heated in vacuum at 400°C for 3 hr, an X-ray powder pattern typical for pure SrI_2 was obtained. Heated SrI_2

samples were thus used for all preparations.

The X-ray powder diffraction data for the fused products as a function of composition are presented in Table I. Lattice parameters of $SrBr_2$ and SrI_2 after heat treatment at 650 and 400°C, respectively, agree well with the values reported from single crystal studies (*5, 18*). For the series $SrBr_xI_{2-x}$ ($2.00 > x > 0.0$) five phase regions were identified (see Table I and Fig. 1).

In the composition range $2.00 > x \geq 1.60$ the $SrBr_xI_{2-x}$ phase crystallizes in a tetragonal $SrBr_2$-type structure. The structure of $SrBr_2$ manifests many of the features common to that of SrI_2. The Br(1) and Br(2) atoms are trigonally and tetrahedrally coordinated to metal atoms, respectively, as are the two iodine atoms in SrI_2 (*18*). The remaining bromine atoms, designated as (3) and (4), occupy regular tetrahedral holes. On the basis of the anion distribution described above intensity data for the $SrBr_{1.80}I_{0.20}$ and $SrBr_{1.60}I_{0.40}$ phases were calculated for five models with the iodine atoms located (a) randomly in general anion positions Br(1) and Br(2), (b) only in the general position Br(1), (c) only in the general position Br(2), (d) randomly in general positions Br(1) and Br(2) and special positions Br(3) and Br(4), and (e) only in Br(3) and Br(4). In the intensity calculations atomic coordinates typical for the $SrBr_2$ structure (Table II) were used. The results obtained for selected reflections are presented in Table III. (Intensities calculated for I atoms located only on Br(3) and Br(4) differed markedly from the observed intensities and are not listed in the table.) In this table, the position designation R_g indicates random across the Br(1) and Br(2) positions, R_a indicates random across all anion positions, (1) indicates the Br(1) position, and (2) indicates the Br(2) position. The

TABLE I

CRYSTALLOGRAPHIC DATA FOR STRONTIUM BROMIDE–IODIDE PHASES, $SrBr_xI_{2-x}$.

x in $SrBr_xI_{2-x}$	Structure type	Lattice Parameters (Å) a	b	c	Volume of unit cell per Sr atom (Å³)
2.00		11.615(9)		7.133(8)	96.2
1.95		11.635(2)		7.142(5)	96.7
1.90		11.677(2)		7.174(0)	97.8
1.85	$SrBr_2$	11.706(6)		7.180(8)	98.4
1.80	(*P*4/*n*)	11.722(2)		7.195(5)	98.9
1.75		11.750(5)		7.208(0)	99.5
1.70		11.775(1)		7.224(8)	100.2
1.60		11.828(2)		7.251(6)	101.4
1.50	Two phases				
1.40	$PbCl_2$	9.675(7)	8.394(7)	4.825(1)	97.9
1.20	(*Pbnm*)	9.701(2)	8.430(8)	4.840(1)	98.9
1.00		9.720(8)	8.467(4)	4.859(2)	100.0
0.80		9.751(4)	8.524(0)	4.876(6)	101.3
0.70	Two phases				
0.60	Two phases				
0.40	Two phases				
0.30	SrI_2	15.150(1)	8.140(1)	7.805(4)	120.3
0.20	(*Pbca*)	15.189(1)	8.174(4)	7.840(2)	121.7
0.00		15.268(4)	8.251(1)	7.896(3)	124.3

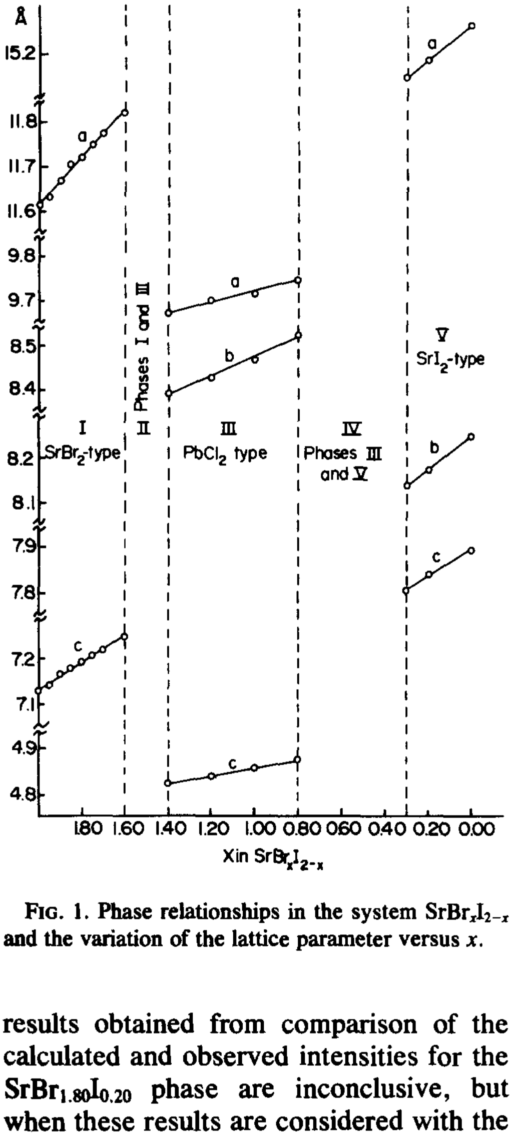

FIG. 1. Phase relationships in the system $SrBr_xI_{2-x}$ and the variation of the lattice parameter versus x.

results obtained from comparison of the calculated and observed intensities for the $SrBr_{1.80}I_{0.20}$ phase are inconclusive, but when these results are considered with the data for the $SrBr_{1.60}I_{0.40}$ phase, it is apparent that the iodine atoms are distributed statistically as might be expected from knowledge of the SrI_2 structure.

It is difficult to decide from the intensity data whether the iodine atoms are distributed statistically only in the general sites, or whether they are located in all the anion sites. We believe that based on structural comparisons a stronger argument can be made for iodine atom occupancy of only the general sites. Observed and calculated intensity data, based on such occupancy, and interplanar *d* spacings for $SrBr_{1.60}I_{0.40}$ are presented in Table IV. Lattice parameters observed in the composition region $2.00 > x \geq 1.60$ are larger than those reported previously by Frit *et al.* (*8*). The volume of the unit cell for $SrBr_{1.60}I_{0.40}$ phase is 1014.4 $Å^3$, while that for $SrBr_2$ is 962.3 $Å^3$, i.e., a 5.4% increase.

If the iodine atom concentration is increased beyond 0.40 a transition to a new phase occurs and for values of $x = 1.50$ a two-phase region is observed (see Table I and Fig. 1). Samples which possess the tetragonal ($SrBr_2$-type) form of the $SrBr_xI_{2-x}$ phases are colored off-white; after the transition, specimens exhibit a pale yellow color.

The X-ray powder patterns obtained for the products in the composition region $1.40 > x > 0.80$ are indexed on orthorhombic lattice parameters close to those reported for some of the mixed halide phases of lead (*18*) and for $EuBr_{1.5}Cl_{0.5}$ (*1*). Since the *a* lattice parameter is almost exactly 2 times the *c* parameter, one might infer that this phase is tetragonal rather than orthorhombic. However, two observed pairs of reflections for SrBrI (2.710, 2.695; 2.444, 2.429) can be indexed only on orthorhombic symmetry. In the isostructural $PbCl_2$ structure ($z = 4$) every atom is situated at equipoint 4*c* of space group *Pbnm*, No. 62 (*14*). Theoretical powder diffraction intensities were calculated for $SrBr_{1.40}I_{0.60}$ and SrBrI using the atomic coordinates (Table II) of $EuBr_{1.5}Cl_{0.5}$. In this structure there are two different anion positions, labeled (1) and (2) (see Table II) (*20*). Position (1) represents a pyramidal hole whereas position (2) represents a smaller tetrahedral hole. Three models were considered (a) with the iodine atoms randomly distributed between the two positions, and (b) with the iodine atoms independently occupying each of the two positions. The data obtained from $SrBr_{1.40}I_{0.60}$ and SrBrI for selected reflec-

TABLE II

ATOMIC PARAMETERS USED FOR CALCULATION OF X-RAY POWDER DIFFRACTION INTENSITIES OF SELECTED $SrBr_xI_{2-x}$ PHASES

Structural type and space group	Atom	Number and position notation	Coordinates		
			x/a	*y/b*	*z/c*
$SrBr_2$	Sr(1)	8*g*	0.1045	0.5856	0.2476
P4/n (No. 85)	Sr(2)	2*c*	0.25	0.25	0.8483
	Br(1) and I(1)	8*g*	0.1531	0.4590	0.6253
	Br(2) and I(2)	8*g*	0.3388	0.4572	0.0963
	Br(3)	2*a*	0.25	0.75	0
	Br(4)	2*b*	0.25	0.75	0.5
$PbCl_2$	Sr	4*c*	0.1215	0.2622	0.25
Pbnm (No. 62)	Br(1) and I(1)	4*c*	0.8317	0.0264	0.25
	Br(2) and I(2)	4*c*	0.4321	0.1448	0.25
SrI_2	Sr	8*c*	0.1105	0.4505	0.2764
Pbca (No. 61)	I(1) and Br(1)	8*c*	0.2020	0.1077	0.1630
	I(2) and Br(2)	8*c*	0.0341	0.2682	0.0054

tions (Table III) favor a random anion distribution. This observation is similar to that reported for PbBrI (*19*, *20*). Below $x = 0.70$ a two-phase region of $PbCl_2$- and SrI_2-type structures is observed.

For $x = 0.30$ the powder pattern was similar to that of SrI_2, and could be indexed on the basis of a unit cell with parameters close to those of SrI_2 (Table I), suggestive that the SrI_2 and the mixed halides of strontium in this composition range are isomorphous. The two iodine atoms in SrI_2 are structurally different (*18*). One iodine atom, I(1), is coordinated to three Sr atoms arranged in the form of a triangular plane and the other, I(2), is coordinated tetrahedrally by four Sr atoms. Theoretical X-ray powder pattern intensities were calculated for the three different distributions of the bromine atoms: random, in position (1), and in position (2). The results obtained show only very small intensity variations for the various models. Data for the reflections which showed the greatest intensity variations are listed in Table III. We are unable to conclude conclusively from these data which model is more plausible, but believe that, similar to the $PbBr_2$–PbI_2 system, a completely ordered phase is absent (*21*).

According to Shannon (*4*), the radii of Pb(II) and Sr(II), both CN=VIII, are 1.29 and 1.26 Å, respectively. Thus a comparison of this study with that of the $PbBr_xI_{2-x}$ system (*21*) is appropriate. Both systems contain three phases separated by two phase regions. The structures of the phases at both ends of the systems differ, but the intermediate phase region is similar in both. The two-phase regions are significantly longer in the lead system (0.3 and 0.8 in *x*) than in the strontium system (0.1 and 0.3, respectively). Thus, while the systems are globally similar, and structurally identical at the $MBr_{1.2}I_{0.8}$ composition, a significant

TABLE III

Observed and Calculated Intensities of Selected X-Ray Powder Diffraction Reflections for $SrBr_xI_{2-x}$ Phases

	SrBr₂-type										PbCl₂-type										SrI₂-type				
	$SrBr_{1.8}I_{0.2}$, Positions of iodine					$SrBr_{1.6}I_{0.4}$, Positions of iodine						$SrBr_{1.4}I_{0.6}$, Positions of iodine				SrBrI, Positions of iodine					$SrBr_{0.3}I_{1.7}$, Positions of bromine			
hkl	R_g	R_a	(1)	(2)	I_{obs}	R_g	R_a	(1)	(2)	I_{obs}	*hkl*	R_a	(1)	(2)	I_{obs}	R_a	(1)	(2)	I_{obs}	*hkl*	R_a	(1)	(2)	I_{obs}
001	7	7	3	12	5	6	6	0	22	4	110	2	0	8	—	2	1	20	1	200	5	10	2	8
011	11	11	16	7	10	9	10	22	2	10	200	1	0	4	—	1	0	8	—	210	100	100	100	100
111	6	6	5	7	5	5	5	2	8	4	101	1	0	6	—	1	1	11	—	211	12	13	10	10
021	3	3	3	2	1	2	2	4	1	—	220	9	9	8	10	46	34	63	40	102	20	17	22	21
211	38	40	35	41	40	23	30	17	30	20	211	96	85	100	100	94	87	100	90	220	32	34	29	35
130	8	9	10	7	6	9	10	15	8	10	121	100	100	92	100	100	100	97	100	202	43	45	41	44
131	100	100	100	100	100	95	92	92	98	93	130	23	19	27	20	31	22	42	26	221	31	28	35	28
212	50	51	51	50	50	100	99	100	100	100	301	33	25	41	30	42	26	63	40	022	49	51	46	50
											002	36	31	38	35	58	49	69	60					
											131	10	7	13	10	12	6	19	10					
											321	11	9	13	10	13	10	18	10					

Note. R_a indicated all anion positions; R_g indicates select anion positions.

TABLE IV

Observed and Calculated Powder Diffraction Data for $SrBr_{1.60}I_{0.40}$, SrBrI, and $SrBr_{0.30}I_{1.70}$

	$SrBr_{1.60}I_{0.40}$					SrBrI					$SrBr_{0.3}I_{1.7}$			
	Intensity		d_{hkl}			Intensity		d_{hkl}			Intensity		d_{hkl}	
hkl	Obs[a]	Calc[b]	Obs	Calc	*hkl*	Obs[a]	Calc[b]	Obs	Calc	*hkl*	Obs[a]	Calc[b]	Obs	Calc
001	4	6	7.261	7.251	110	1	2	6.387	6.384	200	8	5	7.567	7.575
011	10	9	6.183	6.181	220	40	46	3.190	3.192	210	100	100	5.546	5.545
111	4	5	5.476	5.478	211	90	94	3.184	3.184	211	10	12	4.525	4.520
211	20	23	4.270	4.273	121	100	100	3.030	3.032	102	21	20	3.774	3.779
130	10	9	3.740	3.740	310	25	27	3.025	3.026	311	15	17	3.761	3.760
012, 031	33	36	3.465	3.466	130	26	31	2.710	2.710	021	2	5	3.609	3.608

112, 131	93	95	3.327	3.326	301	40	42	2.693	2.695	220	35	32	3.588	3.585
022	12	13	3.092	3.090	221	4	6	2.665	2.668	121	17	15	3.512	3.510
212, 231	100	100	2.990	2.990	320	10	9	2.574	2.573	202	44	43	3.469	3.469
330	6	8	2.787	2.787	311	22	25	2.568	2.568	221	28	31	3.257	3.258
032, 411	100	99	2.666	2.668	230	25	28	2.444	2.440	411	38	36	3.141	3.143
240	60	65	2.644	2.644	400, 002	60	58	2.429	2.430	302	10	12	3.088	3.088
312, 331	55	58	2.605	2.603	131	10	11	2.367	2.367	321	2	6	2.936	2.936
241	30	30	2.484	2.484	410	1	3	2.336	2.335	312	2	4	2.886	2.887
232	2	4	2.433	2.432	321	10	13	2.273	2.273	022	50	49	2.817	2.816
042	10	13	2.293	2.291	330	2	4	2.128	2.128	420	20	22	2.770	2.772
142, 341, 051	10	10	2.249	2.249	240, 041	4	6	1.9407	1.9407	402	15	22	2.719	2.718
213	32	35	2.197	2.198	421, 222	4	5	1.9336	1.9335	222	18	25	2.642	2.640
521	15	16	2.102	2.102	510, 312	14	16	1.8945	1.8947	421	15	14	2.613	2.613
133	10	10	2.029	2.030	132	15	16	1.8092	1.8091	412	28	24	2.578	2.578
512, 351	2	4	1.9538	1.9539	501	3	5	1.8049	1.8049	230	4	6	2.553	2.554
233	10	10	1.9460	1.9459	241	1	3	1.8021	1.8022	113	10	8	2.445	2.445
522, 611	10	13	1.8786	1.8786	520, 322	8	10	1.7666	1.7666	231	10	9	2.429	2.427
					431, 232	30	37	1.7221	1.7220	610	22	21	2.411	2.411
										213	10	9	2.356	2.355
										611	25	30	2.304	2.304
										512	6	8	2.295	2.296
										313	5	8	2.224	2.224
										430	16	15	2.2058	2.2057
										123	22	19	2.1698	2.1695
										232	25	22	2.1374	2.1373
										612	8	10	2.0515	2.0515
										240	10	15	1.9652	1.9653

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[a] The observed intensity is the average of three independent measurements.
[b] The intensity calculated for random anion distribution.

difference that is not just a function of cation size is apparent. This difference might result from the lone pair of electrons that is present in the lead(II) ion and is known to have stereochemical effect (*22*).

The differences between this report and that of Frit *et al.* (*9*) are slight. We both observe the same three phases, but they report composition limits as $2.0 > x > 1.8$, $1.36 > x > 0.88$, and $0.36 > x > 0$ for the $SrBr_2$-, $PbCl_2$-, and SrI_2-structure types, respectively. We observe $2.0 > x > 1.8$, $1.4 > x > 0.8$, and $0.3 > x > 0$. The lattice parameters observed in this work are in all cases larger than those reported by Frit *et al.* This parameter difference may have resulted from a composition error on their part—we could not obtain homogeneous preparations by the procedure they reported. The analytical data obtained on selected specimens would seem to confirm the accuracy of our reported compositions.

The cell volume per strontium atom varies from 96.2 to 101.4 Å^3 for the $SrBr_2$-type structure. The comparable volumes of the first two structure types, and the great difference in the third structure type is indicative that in the iodide structure it is the anions which determine the structure type. The volume per strontium atom in the $PbCl_2$-type structure in the Sr–Br–Cl system varies from 79.9 to 96.4 Å^3, while in the Pb–Br–I system its range is 90.2 to 99.6 Å^3. It would thus appear that when the volume per cation exceeds a value of about 100 Å^3, the structure must rearrange.

In summary, five discrete regions are found in the $SrBr_2$–SrI_2 system. Three are single phase: region I exhibits the $SrBr_2$-, region III the $PbCl_2$-, and region V the SrI_2-type structure. The anion distribution is described best as random throughout the entire system. These principal regions are separated by two-phase regions. This observation suggests that the phase changes in this system are not connected with reordering or randomization of the anions.

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