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Phase Relationships in the System $SrBr_2-SrCl_2$

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Strontium bromide–chloride phases ($SrBr_xCl_{2-x}$) in the composition region $2.00 > x > 0$ were prepared and examined by the Guinier powder X-ray diffraction technique. Observed and calculated powder intensities for the compositions $x = 1.60$, 1.40, and 0.30 are presented. The anions assume an ordered arrangement at the first two compositions and a random arrangement at the third. Two previously unreported intermediate phases at the composition about $x = 1.50$ and $x = 0.60$, both of unknown structure, were identified and their d values are reported. $SrBr_2$ is found to be insoluble in $SrCl_2$.

Introduction

Recently Clink and Eick (*1*) studied the $EuBr_2$–$EuCl_2$ system at specific bromide and chloride ion activities. They identified two distinctly different X-ray powder diffraction patterns for samples of the composition $EuBr_{1.8}Cl_{0.2}$ and $EuBr_{1.5}Cl_{0.5}$ and reported structural details on an ordered $PbCl_2$-type structure for the latter phase. Earlier Frit *et al.* (*2, 3*) had studied the system $SrCl_2$–$SrBr_2$ and reported solid solutions of the CaF_2, $PbCl_2$, and $SrBr_2$ structure types. Although they observed in some instances noncontiguous phase limits, they reported neither the existence of new structures nor additional phases. In view of the size similarities between the Sr^{2+} and Eu^{2+} ions and the isostructural nature of their bromides, it seemed surprising that in the europium phase the anions were ordered, while in the strontium phase they were random (*4–7*). A systematic study of the $SrBr_2$–$SrCl_2$ system was therefore undertaken, and the results are presented below.

Experimental

The system $SrBr_xCl_{2-x}$ was investigated over the composition range $2.00 > x > 0$. The starting materials, analytical-grade strontium dibromide and strontium dichloride, were obtained from Cerac, Inc., Milwaukee, Wisconsin, and were used as received. Twenty-six samples (total weight of each sample was 2 g) were mixed intimately in varying stoichiometric proportions and either placed in recrystallized Al_2O_3 boats (*8*) or sealed in evacuated quartz ampoules. All sample manipulations were performed in a glove box whose recirculated argon atmosphere was purged of oxygen and water. The containers were heated to 860°C, above the reported melting point of both reactants (*9*), and then cooled to 600°C at a constant rate of 0.4°C/min through the melting tran-

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sition of $SrBr_2$. The samples were then annealed at this temperature for 12 hr and were subsequently cooled slowly (0.1°C/min) to room temperature.

To determine whether $SrBr_2$ vaporized from the Al_2O_3 boat into the vacuum system during heating, a sample was heated to the highest temperature used in the preparation and held there twice as long as was any reaction mixture. Mass loss was determined by difference.

Reaction products were subjected to X-ray powder diffraction analysis in a 100-mm evacuated Guinier–Hägg camera equipped with a quartz monochromator to provide clean Cu$K\alpha_1$ radiation. Platinum powder ($a = 3.9238 \pm 0.0003$ Å, 25°C) was used as an internal standard. The samples were protected by a film of paraffin oil, both during transfer to the camera and during diffraction analysis. Qualitative intensity data were obtained from the Guinier–Hägg films; quantitative data were obtained on a Siemens X-ray diffractometer with nickel-filtered copper radiation. The peak heights from a number of scans were averaged, and intensities are reported relative to that of the most intense reflection.

A specimen of the composition $x = 1.40$ was examined in a Philips EM300 transmission electron microscope in diffraction mode at 100 kV.

X-Ray powder diffraction intensities were calculated for phases of selected compositions on the basis of random and different ordered anion occupancies. Calculations were carried out on a CDC CYBER 750 computer with the program ANIFAC (*10*); atomic scattering factors with appropriate dispersion correction terms were obtained from the International Tables (*11*). Consistent with the geometry of the Guinier–Hägg camera and the diffractometer, absorption terms were not included in the calculations.

Powder diffraction data were reduced with the aid of a linear regression program written locally. The reported lattice parameters were derived from a refinement based on 20–30 coincidence-free reflections.

Results and Discussion

X-Ray diffractograms of the reactants indicated only reflections assignable to the pure phases; lattice parameters of these phases, after heat treatment at 680°C, are listed in Table I.

The mass loss experiment indicated that $SrBr_2$ did not sublime from the boat during the course of the heating. Thus the final composition was considered identical to the initial one.

Five phase regions were identified. The

TABLE I

CRYSTALLOGRAPHIC DATA FOR STRONTIUM BROMIDE–CHLORIDE PHASES, $SrBr_xCl_{2-x}$

x in $SrBr_xCl_{2-x}$	Lattice parameters (Å)			Space group and structure type
	a	*b*	*c*	
2.00	11.623(5)		7.133(3)	***P4/n***
1.95	11.590(7)		7.100(0)	$SrBr_2$
1.90	11.575(2)		7.091(1)	(ordered)
1.85	11.554(4)		7.070(0)	
1.80	11.513(4)		7.032(9)	
1.75	11.507(0)		7.027(7)	
1.70	11.504(0)		7.018(0)	
1.65	11.504(0)		7.019(2)	
1.60	11.503(7)		7.018(1)	
1.55				
1.50	Intermediate phase (II)			?
1.45				
1.40	9.308(0)	7.964(9)	4.670(8)	***Pbnm***
1.20	9.241(1)	7.945(2)	4.643(5)	$PbCl_2$
1.00	9.163(5)	7.922(1)	4.617(5)	(ordered)
0.80	9.116(9)	7.827(1)	4.585(2)	
0.70	9.090(1)	7.780(2)	4.586(1)	
0.65				
0.60	Intermediate phase (IV)			?
0.55				
0.50	9.075(4)	7.760(1)	4.586(4)	***Pbnm***
0.40	9.070(4)	7.728(8)	4.585(1)	$PbCl_2$
0.30	9.054(2)	7.704(2)	4.584(4)	(random)
0.20	Mixture of orthorhombic			
0.14	phase and $SrCl_2$			
0.10				
0.06				
0.00	6.975(2)			***Fm3m***, CaF_2

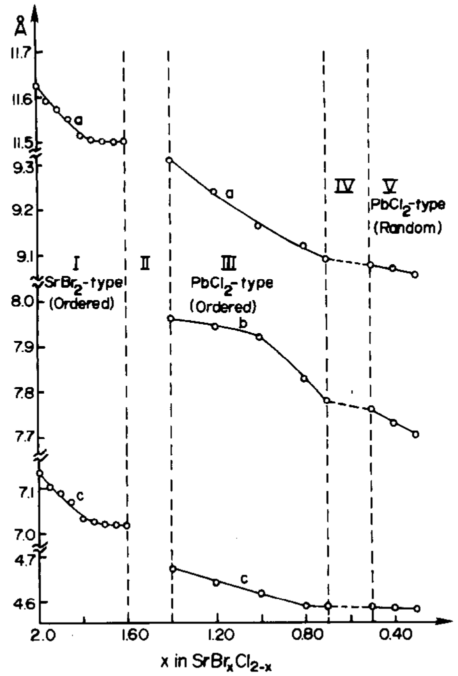

FIG. 1. Phase relationships in the system $SrBr_xCl_{2-x}$ and variation of the lattice parameter versus x.

crystallographic data and structure types for regions labeled I, III, and V, together with the lattice parameters expressed as a function of composition, are presented in Table I and Fig. 1.

For values of x between $2.00 > x \geq 1.60$ the $SrBr_xCl_{2-x}$ phase, designated I, crystallizes in a tetragonal $SrBr_2$-type structure. The strontium dibromide structure (*6*) contains three types of anion holes: one regular tetrahedral, as in $SrCl_2$, another distorted tetrahedral, and a third almost trigonal, as in SrI_2. The unit cell contains 10 formula units. Sixteen Br(1) and Br(2) atoms located in general positions 8*g* (space group No. 85, *P*4/*n*) (*12*) occupy the distorted tetrahedral and trigonal coordination sites, respectively, while the four Br(3) and Br(4) atoms (special positions 2*a* and 2*b*) occupy the regular tetrahedral holes. Intensity data were calculated for four models of the composition $SrBr_{1.60}Cl_{0.40}$:

(a) with the chlorine atoms located only in special positions 2*a* and 2*b*,

(b) with the chlorine atoms located randomly in general positions 8*g*,

(c) with the chlorine atoms located randomly in positions 8*g*, 2*a*, and 2*b*, and

(d) with the chlorine atoms located only in the general positions of Br(2).

A comparison of the observed and calculated intensities shows agreement only for the model in which all the chlorine atoms are located in the special positions 2*a* and 2*b*. Atomic coordinates for $SrBr_{1.60}Cl_{0.40}$ are listed in Table II, while observed and calculated intensity data, Miller indices, and interplanar *d* spacings are compiled in Table III. In this structure at this composition all the regular tetrahedral holes are filled with chlorine atoms, and the Br/Cl atomic ratio agrees exactly with the ratio of the number of the general positions to special ones, 4 : 1. Thus, over the composition region ($2.00 > x \geq 1.60$), the tetrahedral holes, special positions 2*a* and 2*b*, selectively fill with chlorine atoms. When the chlorine composition becomes greater than 0.4, chlorine atoms would have to occupy

TABLE II

ATOMIC PARAMETERS USED FOR CALCULATIONS OF X-RAY POWDER DIFFRACTION INTENSITIES FOR $SrBr_{1.60}Cl_{0.40}$, $SrBr_{1.40}Cl_{0.60}$, AND $SrBr_{0.30}Cl_{1.70}$

Phase	Atom	Number and position notation	Coordinates		
			x/*a*	*y*/*b*	*z*/*c*
$SrBr_{1.60}Cl_{0.40}$ ($SrBr_2$ type)	Sr(1)	8*g*	0.1045	0.5856	0.2476
	Sr(2)	2*c*	0.2500	0.2500	0.8483
	Br(1)	8*g*	0.1531	0.4590	0.6253
	Br(2)	8*g*	0.3388	0.4572	0.0963
	Cl(1)	2*a*	0.2500	0.7500	0.0000
	Cl(2)	2*b*	0.2500	0.7500	0.5000
$SrBr_{1.40}Cl_{0.60}$ ($PbCl_2$ type)	Sr	4*c*	0.1215	0.2622	0.2500
	Br(1)	4*c*	0.8317	0.0264	0.2500
	Br(2) Cl	4*c*	0.4321	0.1448	0.2500
$SrBr_{0.30}Cl_{1.70}$ ($PbCl_2$ type)	Sr	4*c*	0.1215	0.2622	0.2500
	Cl(1) Br(1)	4*c*	0.8317	0.0264	0.2500
	Cl(2) Br(2)	4*c*	0.4321	0.1448	0.2500

TABLE III

OBSERVED AND CALCULATED POWDER DIFFRACTION DATA FOR TETRAGONAL $SrBr_{1.60}Cl_{0.40}$ AND ORTHORHOMBIC $SrBr_{1.40}Cl_{0.60}$ AND $SrBr_{0.30}Cl_{1.70}$ PHASES

	$SrBr_{1.60}Cl_{0.40}$				$SrBr_{1.40}Cl_{0.60}$					$SrBr_{0.30}Cl_{1.70}$			
	Intensity		d_{hkl}		Intensity		d_{hkl}			Intensity		d_{hkl}	
hkl	Obs.[a]	Calc.	Obs.	Calc.	Obs.[a]	Calc.	Obs.	Calc.	*hkl*	Obs.[a]	Calc.	Obs.	Calc.
001	6	7.3	7.011	7.018	—	1.2	—	4.174	101	20	21.7	4.091	4.089
011	10	12.4	5.986	5.991	10	12.6	4.033	4.018	210	32	35.6	3.912	3.903
020	10	13.0	5.743	5.752	—	1.9	—	3.982	020	18	17.9	3.860	3.852
111	5	6.5	5.314	5.313	7	10.2	3.718	3.697	111	22	24.2	3.615	3.612
021	1	2.9	4.438	4.448	54	66.8	3.054	3.046	211	50	47.2	2.974	2.972
211	40	47.9	4.153	4.149	20	14.1	3.041	3.030	021	12	10.4	2.955	2.949
310	1	1.8	3.638	3.637		8.9		3.026	220	6	5.8	2.940	2.934
002	4	5.3	3.504	3.509	100	20.5	2.886	2.891	310	10	10.3	2.809	2.810
012	25	34.1	3.352	3.356		100.0		2.882	121	100	100.0	2.804	2.804
311	85	100.0	3.229	3.229	25	30.2	2.584	2.584	301	40	42.6	2.523	2.521
022	6	8.2	2.994	2.995	12	17.5	2.560	2.553	130	18	18.1	2.471	2.471
231	100	63.0	2.902	2.904	—	1.6	—	2.539	221				
112		51.6		2.899	20	25.0	2.465	2.458	311	30	34.6	2.396	2.396
330	2	6.9	2.711	2.711	1	2.8	2.448	2.447	320	3	2.5	2.375	2.376
411	100	87.6	2.592	2.593	30	37.2	2.342	2.335	002	40	39.7	2.289	2.292
032		30.1		2.589	10	13.3	2.328	2.327	400	18	16.7	2.265	2.263
240	50	61.2	2.572	2.572	20	26.6	2.306	2.306	230	30	33.3	2.235	2.234
312	42	53.4	2.525	2.525	7	10.7	2.242	2.240	131	20	21.0	2.174	2.175
241	25	31.1	2.416	2.415	10	14.0	2.169	2.168	321	22	22.9	2.109	2.109
322	4	5.2	2.359	2.360		4.2		2.018	212	11	11.6	1.9756	1.9764
510	4	4.6	2.256	2.256	10	0.7	2.020	2.015	022	6	5.9	1.9702	1.9697
042	9	11.0	2.225	2.224		2.5		2.015	411	—	0.3	—	1.9626
051	12	13.9	2.187	2.186		4.5		2.017	330	10	2.3	1.9550	1.9558
341									420		8.1		1.9515
023	1	2.0	2.164	2.167	—	2.8	—						
332	5	6.6	2.146	2.145	2	4.7	1.9923	1.9912	040	6	5.0	1.9260	1.9260
123	35	43.9	2.129	2.129	2	0.3	1.8508	1.8519	331	5	2.7	1.7998	1.8061
521	20	23.2	2.043	2.043		3.6		1.8488	222		2.1		1.7989
530	3	5.4	1.9737	1.9727	2	1.7	1.8314	1.8317	041	7	1.2	1.7741	1.7761
313	8	10.4	1.9674	1.9676		2.3		1.8307	240		1.4		1.7723
531	1	2.6	1.8981	1.8991	6	8.8	1.8169	1.8167	312		3.9		1.7761
233	8	9.4	1.8867	1.8865	1	2.7	1.8130	1.8127	510	—	1.7	—	1.7628
522	8	10.5	1.8248	1.8246	7	9.0	1.7236	1.7232	132	7	7.7	1.6788	1.6803
260	4	6.7	1.8188	1.8188	1	1.9	1.7049	1.7045	241	—	1.0	—	1.6530
143	1	1.9	1.7926	1.7926	1	1.7	1.6896	1.6899	511	5	4.2	1.6448	1.6453
261	6	8.6	1.7610	1.7606		1.4		1.6894	322	—	1.2	—	1.6495
423	1	3.2	1.7303	1.7306	1	2.6	1.6858	1.6844	520	—	2.2	—	1.6388
114	5	6.9	1.7151	1.7148	5	8.0	1.6487	1.6484	402	10	10.0	1.6094	1.6105
062	3	4.6	1.6830	1.6824	13	16.3	1.6418	1.6409	232	20	20.2	1.5984	1.5997
631	1	2.8	1.6657	1.6658	9	10.6	1.6383	1.6387	431	6	6.9	1.5921	1.5923
550 710	10	13.5	1.6271	1.6268	7	9.1	1.5861	1.5862	521	7	8.2	1.5432	1.5431

[a] The observed intensity is the average of three independent measurements.

the general position holes; but before this happens, the structure rearranges.

In the composition region (1.60 > x > 1.40) a previously unreported intermediate phase of unknown structure, designated II, is formed. In Table IV the interplanar d spacings with associated visually estimated intensities for one preparation, $SrBr_{1.50}Cl_{0.50}$, are presented. Some of the diffraction maxima obtained for this composition are broad, probably indicative that the I → II transition is a result of partial disorder in the $SrBr_2$-type ordered structure.

Electron diffraction patterns of some of the microcrystallites evidenced spotty ring formation, further substantiation of the disorder hypothesized from examination of the

TABLE IV

OBSERVED X-RAY INTERPLANAR *d* SPACINGS AND INTENSITIES FOR $SrBr_{1.50}Cl_{0.50}$ AND $SrBr_{0.60}Cl_{1.40}$

$SrBr_{1.50}Cl_{0.50}$		$SrBr_{0.60}Cl_{1.40}$	
Intensity	*d* spacings (Å)	Intensity	*d* spacings (Å)
Wb	8.106	Wb	7.878
Mb	7.366	Wb	7.129
Mb	5.880	Mb	5.643
Sb	4.189	MWb	5.206
VW	3.775	Ss	4.114
Sb	3.661	VW	4.009
Mb	3.641	Ms	3.948
Ws	3.478	VW	3.689
Ws	3.442	Ms	3.637
Ws	3.409	VW	3.514
Ms	3.276	VW	3.369
Ws	3.177	VW	3.252
VW	3.098	MWb	3.219
Sb	3.062	Ws	3.119
Mb	3.043	Ws	3.043
Mb	2.968	Ss	2.993
Sb	2.943	Ws	2.928
VW	2.778	Wb	2.886
Mb	2.743	Ss	2.837
Wb	2.727	Wb	2.804
Wb	2.646	Ms	2.707
Ms	2.624	Wb	2.669
Ws	2.606	VW	2.589
Ms	2.588	Ms	2.533
Ms	2.553	VW	2.482
Mb	2.443	Wb	2.457
Sb	2.396	Ms	2.409
Sb	2.321	Wb	2.382
Ws	2.246	MWs	2.373
Ws	2.157	Ws	2.340
Ms	2.148	Ms	2.294
Ws	2.123	MWs	2.275
Ms	2.062	Ms	2.260

Note. S: Strong; M: medium; W: weak; MW: medium weak; VW: very weak; b: broad; s: sharp.

Guinier data. Because the small crystallites either oxidized or hydrolyzed in the atmosphere of the microscope under high beam intensity, it was impossible to obtain single-crystal electron diffraction patterns.

A different X-ray powder diffractogram (phase III) was obtained for the composition $x = 1.40$ and was found to prevail over the composition region $1.40 > x > 0.70$. This powder pattern is identical to that of $EuBr_{1.5}Cl_{0.5}$ and is indexable on the basis of an orthorhombic $PbCl_2$-type cell (see Table I) with parameters about 0.1 Å larger than those of the europium phase (*1*). In the $EuBr_{1.5}Cl_{0.5}$ structure there are two anion positions, labeled (1) and (2), according to Baernighausen's notation (*13*) for $EuCl_2$. In this structure there are two types of anion holes—one tetrahedral and the other pyramidal. Position (2) represents the smaller tetrahedral hole; position (1) the pyramidal hole. Theoretical powder diffraction patterns were calculated for this strontium phase with the atomic coordinates reported for the europium analog, but with the chlorine atom occupancy (a) only in position (2) as reported for the europium phase, (b) only in position (1), and (c) randomly distributed between the two positions. The X-ray intensity calculations show definitely that the chlorine atoms occupy only position (2) and consequently that the anion distribution is ordered. Coordinates used for the calculations are listed in Table II; observed and calculated intensity data and interplanar *d* spacings are listed in Table III. This same-site occupancy pattern has been observed in other mixed halide phases, i.e., the PbClBr system (*14*).

The $EuBr_{1.5}Cl_{0.5}$ phase was found from single-crystal data to have one lattice parameter, *b*, doubled. It was assumed that the doubling reflected order in the Br(2)/Cl(2) position; in the true doubled cell the chlorine atoms occupy a unique set of positions as do the bromine atoms. Just as in the europium case, evidence for doubling of the cell could not be found in the Guinier powder data. A number of crystals were examined with the precession and Weissenberg cameras, but none was single. An obvious structural relationship which relates the phase terminus to composition is thus not apparent from the pseudocell.

Below $x = 0.70$ the diffraction pattern again changes. In Table IV the interplanar *d* spacings and their associated visually estimated intensities for $SrBr_{0.60}Cl_{1.40}$ are presented. This diffraction pattern could not be indexed in an orthorhombic system with lattice parameters extrapolated from those of phase III. Broadening of some of the reflections is suggestive that this new intermediate phase (designated IV) has characteristics similar to those of II.

Another diffraction pattern (phase V) became established at $x = 0.60$. Preparations of $SrBr_xCl_{2-x}$ for $0.60 > x > 0.30$ were also found to crystallize in an orthorhombic system of the $PbCl_2$ type, but reflection intensities differed significantly from those observed for III. Based on diffraction intensity calculations, the distribution of anions in V is statistical between the two positions of space group *Pbnm* (see Table II). In Table III the observed and calculated intensities for $SrBr_{0.30}Cl_{1.70}$ are compiled. If the $SrBr_2$ content of the reactants was decreased such that $x < 0.30$, the products showed diffraction lines characteristic of V and $SrBr_2$. A small content of the phase V was found even for a sample of the overall composition $x = 0.06$. On the basis of these observations and in contrast to the report of Frit *et al.* (*3*), we conclude that $SrBr_2$ is insoluble in $SrCl_2$. Our conclusion is consistent with that of Brauer and Knausenberger (*15*) for the miscibility of $PbCl_2$ and $EuCl_2$.

Clink and Eick (*1*) also hypothesized that in the europium system a phase of the composition $EuBr_{1.8}Cl_{0.2}$ existed. It is apparent that a strontium analog does not exist.

In summary, five unique phase regions were found in the $SrBr_2$–$SrCl_2$ system, with region I exhibiting the $SrBr_2$, and regions III and V the $PbCl_2$-type structure. In these regions, the anion distribution can be ordered or random and the ordering or randomness is related to the Br/Cl ratio. But while small concentrations of chloride ion will dissolve into the bromide lattice, occupying the tetrahedral holes, bromide ion will not dissolve into the chloride ion lattice. Between different principal regions intermediate areas (II and IV) are found. These intermediate areas are probably caused by reordering or randomization of anions.

Based on the results of selected literature data (*3, 15–17*) it can be concluded that phase situations similar to that described herein should be observed in other mixed halide systems. Further attempts to isolate single crystals for the $SrBr_xCl_{2-x}$ phases are underway.

Acknowledgments

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