Characterization of the CaCl$_2$–EuCl$_2$ and CaCl$_2$–SrCl$_2$ Systems by X-Ray Powder Diffraction

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The systems CaCl$_2$–SrCl$_2$ and CaCl$_2$–EuCl$_2$ were studied over the entire composition range by X-ray powder diffraction. The CaCl$_2$–XCl$_2$ (X = Sr, Eu) systems behave similarly and exhibit two single-phase regions with corresponding adjacent two-phase regions. The first single-phase region exhibits the SrI$_2$-type and the second the SrBr$_2$-type structure. The cation distribution is probably random throughout the systems. © 1987 Academic Press, Inc.

Introduction

Some recent studies of mixed alkaline earth and lanthanoid(II) chloride bromide systems indicate that these systems typically exhibit, as a minimum, both solid solution regions which match those of the parent phases and a discrete anion-ordered region. In the EuCl$_2$–EuBr$_2$ system (*1, 2*) a PbCl$_2$-type anion-ordered region was characterized by both X-ray single-crystal and powder diffraction procedures. In the SrBr$_2$–SrCl$_2$ system (*3*) a PbCl$_2$-type anion-ordered region was again found in addition to two more complex regions which have not yet been characterized satisfactorily.

The presence of anion ordering caused us to wonder if cation ordering might not also occur in mixed halide systems. Admittedly, the likelihood of cation ordering is less than that of anion ordering because cations are both smaller and less polarizable than anions. The possibility of cation ordering

would be enhanced by working with chloride or fluoride systems and by using relatively large cations. The radii of Sr(II) and Eu(II), CN = 8, are essentially equal, 1.40 and 1.39 Å, respectively (*4*), while that of Ca(II), CN = 8, is smaller, 1.26 Å. Although the size difference between these cations is not as great as that between the chloride and bromide anions, the cation ratio $r(Sr^{2+})/r(Ca^{2+})$ is greater than the anion ratio $r(Br^-)/r(Cl^-)$. Consequently, a study of the phase relationships among these halide systems seemed of potential interest.

Size considerations would dictate that systems such as SrCl$_2$–EuCl$_2$ exhibit random solid solution and, since the parent structures differ, one two-phase region (*5*). On the other hand, mixtures of these compounds with the smaller calcium ion might exhibit cation ordering.

Few reports of phase studies on related systems could be found. For MX_2–EuX_2 (M = Sr, Ca; X = F, Cl) systems, only EPR and luminescence data (*6–8*) are available. In view of both this dearth of data and the

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anion ordering observed in related systems, a systematic study of the title systems was undertaken.

Experimental

Each of the title systems was investigated over the full composition range. Reagents were analytical-grade $SrCl_2$ (AESAR, Johnson Matthey Inc., Seabrook, NH), anhydrous $CaCl_2$ (Mallinckrodt, St. Louis, MO), and Eu_2O_3 (99.99%, Research Chemicals, Phoenix, AZ). Pure europium trichloride was obtained by the ammonium halide matrix procedure (9, 10). The $EuCl_3$ was reduced under a stream of ultrapure hydrogen which was passed first over a palladium catalyst and then through a liquid nitrogen-cooled trap. All manipulations of reactants and products were effected in an argon-filled glove box which was continuously purged of water (molecular sieves) and oxygen (heated BASF catalyst).

Each of the reactants was melted under a $<1 \times 10^{-4}$ Torr vacuum prior to being examined for purity by X-ray powder diffraction in an evacuated Guinier–Haegg camera with CuK_{α_1} radiation. NBS calibrated silicon ($a = 5.43062(4)$ Å) was used as an internal standard.

The samples (total weight of each sample was 0.3 g) were prepared from reagents mixed intimately by grinding in an agate mortar in appropriate stoichiometric proportions according to Eq. (1) and were confined in previously outgassed quartz tubes:

$$(1 - x)MCl_2 + (x)EuCl_2 = M_{(1-x)}Eu_{(x)}Cl_2,$$
$$M = Sr, Ca. \quad (1)$$
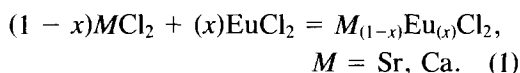
They were then melted under a 10^{-4} Torr vacuum with a hand-held torch, quenched, transferred to the glove box, pulverized, and then analyzed by X-ray powder diffraction. To verify that the quenching procedure did not preclude cation ordering, two

$EuCl_2$–$CaCl_2$ samples, one with 50 mole percent $EuCl_2$ and the other with 70 mole percent $EuCl_2$, were sealed in previously outgassed quartz tubes and inserted into a tube furnace. The furnace was heated to the melting point of the samples, then shut off and allowed to cool slowly to room temperature.

Theoretical X-ray powder diffraction intensities were calculated with either the program ANIFAC (11) or POWD12 (12) and compared with visually estimated intensities. Scattering factors were those of Cromer and Waber (13); unless stated otherwise, isotropic thermal (B) parameters were estimated to be ~1.0 for the cation and 1.5 for the anion. In the program POWD12, a correction was applied for polarization due to the quartz crystal monochromator of the Guinier camera. Because of the geometry of the Guinier camera, an absorption correction was not applied.

Results and Discussion

The X-ray diffraction data and the mass change that occurred upon reduction of $EuCl_3$ demonstrated that the $EuCl_2$ was of high purity.

Mass balance measurements on the mixed specimens verified that sample was not lost through either decomposition or vaporization during heating. Thus, the final compositions were considered identical to the mixed initial ones. The quartz containers were not attacked by $SrCl_2$ during the short interval that the samples were molten.

The X-ray diffractograms of the specimens which were allowed to cool slowly in the oven were identical to those of the quenched samples. The heating/quenching procedure was thus considered appropriate for these specimens.

An overview of these almost identical systems is presented graphically in Fig. 1.

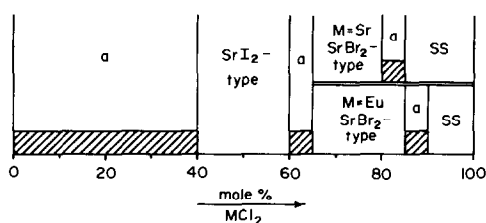The solubility of MCl_2 ($M = Sr, Eu$) in

FIG. 1. Schematic representation of the phase relationships in the systems $CaCl_2-MCl_2$, M = Sr and Eu, versus mole percent MCl_2. In this diagram a indicates a two-phase and ss a solid solution region.

the *Pnnm* $CaCl_2$ structure seems negligible. Thus a two-phase region prevails over the composition range 0–40 mole percent MCl_2. The second phase in this two-phase region is SrI_2-type $Ca_{0.6}M_{0.4}Cl_2$, the quantity of which increases with increasing

MCl_2 concentration. Finally, at approximately 40 mole percent MCl_2, the *Pnnm* reflections are no longer present in the X-ray powder diffractograms.

For the region of 40–60 mole percent MCl_2 only the orthorhombic SrI_2-type phase, typical of the high-pressure form of $CaCl_2$ (*14*), is observed. Lattice parameters for the 50 mole percent $EuCl_2$ and 55 mole percent $SrCl_2$ phases are presented in Table I. In this SrI_2-type structure there is one seven-coordinated cation site. Four chloride ions located on one side of the cation form a slightly deformed square while three chloride ions on the other side comprise a triangle. X-ray intensity calculations were effected with the positional and thermal parameters reported for SrI_2 (*15*) with the metal atom site occupied randomly by both

TABLE I

STRUCTURE TYPES AND LATTICE PARAMETERS OF THE PHASES OBSERVED IN THE $CaCl_2-EuCl_2$ AND $CaCl_2-SrCl_2$ SYSTEMS AS A FUNCTION OF COMPOSITION

Mole percent M cation	Structure type space group	CN	Lattice parameters (Å)			V ($Å^3/Z$)	Reference[a]
			a	b	c		
M = Eu							
0	$CaCl_2$	6	6.269(4)	6.431(6)	4.167(2)	84.00	
	Pnnm		6.264(1)	6.442(2)	4.181(1)	84.36	(*20*)
0	SrI_2	7	13.44(3)	7.07(2)	6.75(3)	80.2	
	Pbca		13.03(1)[b]	6.959(8)[b]	6.635(8)[b]	75.21[b]	(*14*)
50	SrI_2	7	13.38(1)	7.052(3)	6.800(4)	80.20	
	Pbca						
75	$SrBr_2$	8	10.861(6)	—	6.709(4)	79.14	(*16*)
	P4/n						
100	$PbCl_2$	9	8.962(3)	7.535(3)	4.507(2)	76.09	
	Pbnm		8.965(2)	7.538(1)	4.511(1)	76.21	(*19*)
M = Sr							
55	SrI_2	7	13.483(8)	7.074(2)	6.829(3)	81.42	
	Pbca						
70	$SrBr_2$	8	10.895(4)	—	6.742(3)	80.03	
	P4/n						
100	CaF_2	8	6.9792(4)			84.98	(*21*)
	Fm3m		6.978(1)			84.94	

[a] This work, except as noted.
[b] High-pressure modification.

TABLE II

Observed and Calculated Interplanar d-Spacings and Intensities of the SrI$_2$-Type Phase Found for Ca$_{0.5}$Eu$_{0.5}$Cl$_2$

h k l	d_{cal}	d_{obs}	I_{cal}	I_{obs}
2 0 0	6.690	6.743	10	1
2 1 0	4.857	4.866	13	2
1 1 1	4.597	4.612	5	1
2 1 1	3.950	3.957	100	10
0 2 0	3.526	3.534	12	2
0 0 2	3.400	3.406	20	3
4 0 0	3.345	3.351	7	1
3 1 1 1 0 2	3.297	3.299	9	1
1 2 1	3.048	3.051	6	1
2 0 2	3.031	3.031	10	1
2 2 1	2.835	2.842	12	2
2 1 2	2.785	2.785	20	3
4 1 1	2.762	2.764	31	3
3 0 2	2.704	2.708	9	1
0 2 2	2.448	2.448	40	5
4 2 0	2.427	2.427	24	3
4 0 2	2.384	2.387	27	4
4 2 1	2.286	2.286	17	2
2 3 0	2.218	2.219	25	3
1 1 3	2.130	2.131	10	1
2 1 3	2.054	2.054	15	1
6 1 1	2.030	2.031	31	3
4 2 2	1.975	1.975	4	1
0 2 3	1.907	1.908	2	1
1 2 3	1.887	1.885	6	1
2 3 2	1.857	1.860	11	1
0 4 1	1.706	1.704	3	1

cations. Since every weak reflection could be explained satisfactorily (see Table II) by this atomic arrangement, the possibility of cation ordering was dismissed. From the general agreement between observed and calculated reflection intensities, it was concluded that these phases are identical to the high-pressure SrI$_2$-type modification of CaCl$_2$ (14).

A two-phase region occurs again over the composition region 60 to 65 mole percent MCl_2. At ~65 mole percent MCl_2 an SrBr$_2$-type tetragonal phase region develops. This tetragonal phase region extends to 80 mole

percent MCl_2, M = Sr, and to 85 mole percent MCl_2, M = Eu. In Table III experimental and calculated interplanar d-spacings and intensity data for Ca$_{0.3}$Sr$_{0.7}$Cl$_{2.0}$ and Ca$_{0.3}$Eu$_{0.7}$Cl$_{2.0}$ are presented. Theoretical X-ray reflection intensities were calculated for these specimens by using the positional and thermal parameters reported for SrBr$_2$ (16). In these calculations three cation arrangements—two ordered and one random—were considered. The ten cation sites were occupied in the following manner: (a) random; (b) two Ca atoms in the twofold site and one Ca atom and seven M atoms in the eightfold site; and (c) two M atoms in the twofold site and three Ca and five M atoms in the eightfold site. The six

TABLE III

Observed and Calculated Interplanar d-Spacings and Intensities of SrBr$_2$-Type Structures Ca$_{0.3}$Sr$_{0.7}$Cl$_{2.0}$ and Ca$_{0.3}$Eu$_{0.7}$Cl$_{2.0}$

Ca$_{0.3}$Sr$_{0.7}$Cl$_{2.0}$					Ca$_{0.3}$Eu$_{0.7}$Cl$_{2.0}$			
d_{obs}	d_{cal}	I_{obs}	I_{cal}	h k l	d_{obs}	d_{cal}	I_{obs}	I_{cal}
7.733	7.704	vw	5	1 1 0	7.776	7.680	vw	2
6.752	6.742	vw	9	0 0 1	6.746	6.710	vw	4
5.757	5.733	w	17	1 0 1	5.744	5.710	w	9
5.095	5.074	vw	9	1 1 1	5.063	5.053	vw	5
4.257	4.237	vw	4	2 0 1	4.221	4.221	vw	3
3.950	3.949	s	100	2 1 1	3.934	3.934	s	100
3.863	3.852	vw	5	2 2 0	3.848	3.840	vw	6
3.457	3.445	vw	2	3 1 0	3.438	3.435	w	16
3.374	3.371	vw	8	0 0 2	3.356	3.355	w	14
3.228	3.220	w	22	1 0 2	—	—	—	—
3.076	3.068	m	57	3 1 1	3.062	3.057	w	11
2.871	2.866	w	23	2 0 2	2.855	2.854	vw	8
2.775	2.772	w	30	2 1 2	2.762	2.761	w	9
2.762	2.757	w	44	3 2 1	2.751	2.748	w	13
2.576	2.568	w	18	3 3 0	2.565	2.560	vw	4
2.464	2.460	m	65	4 1 1	2.454	2.452	m	26
2.438	2.436	m	57	4 2 0	2.432	2.429	m	19
2.413	2.410	m	77	3 1 2	2.401	2.400	m	31
2.296	2.291	w	20	4 2 1	2.284	2.284	vw	4
2.127	2.119	w	25	4 0 2	2.111	2.111	w	12
2.075	2.073	vw	7	5 0 1 3 4 1	2.068	2.067	vw	5
2.043	2.041	w	33	1 2 3	2.033	2.032	m	15
1.940	1.938	w	25	5 2 1	1.931	1.931	m	17
1.817	1.816	vw	6	6 0 0	1.810	1.810	vw	6
1.804	1.803	vw	6	3 2 3	1.647	1.645	vw	3
1.670	1.669	vw	6	6 2 1				
1.648	1.647	w	13	1 1 4				
1.598	1.598	vw	6	6 0 2				
1.579	1.579	vw	3	6 3 1				

reflections whose intensities were altered most significantly by these occupancy changes are presented together with the results of these calculations in Table IV. The results preclude case (b). The differences between the two remaining cases, (a) and (c), are relatively small and changes in the atomic positional parameters could shift the relative intensity values. However, based upon the assumptions made, the data seem to suggest that the cation occupancy is random.

Beyond the tetragonal phase region the systems differ. From 80 to ~85 mole percent $SrCl_2$, a two-phase region prevails; this region is followed by a fluorite-type solid solution region. This solid solution range is in good agreement with that reported by Brauer and Mueller (17), i.e., 19 mole percent $CaCl_2$ being soluble in $SrCl_2$. From 85 to 90 mole percent $EuCl_2$, a two-phase region prevails. Following this comes a $PbCl_2$-type solid solution region which continues to 100% $EuCl_2$.

It is of interest to view the system by examining the environment the average cation sees as the $MCl_2/CaCl_2$ ratio (R) increases. When this ratio R is zero, the cat-

ion sees a distorted octahedron of anions. As the ratio increases from zero, the coordination immediately changes from six to the seven of the SrI_2-type structure. Substitution of the larger cation effectively creates internal pressure which is sufficient to stabilize this high-pressure modification of $CaCl_2$. The presence of both modifications of $CaCl_2$ at $R = 0$ is an indication that the $CaCl_2$-type structure is but marginally stable with respect to the higher-coordinated SrI_2-type structure. Thus the addition of any cation larger than Ca(II) would stabilize the SrI_2-type structure; alternatively, addition of an anion larger than Cl^- should stabilize the $CaCl_2$-type structure. Furthermore, an increase in pressure, which favors higher coordination, will produce the SrI_2-type structure. A somewhat comparable situation exists in the $EuCl_2$–$EuBr_2$ system in that the $SrBr_2$-type $EuBr_2$ converts, upon substitution of the smaller chloride for the bromide anion (2), to the higher-coordinated $PbCl_2$-type structure which is also the high-pressure modification.

As the ratio R is increased further the structure converts to the $SrBr_2$ type in which there are two different cation sites. One of these sites has seven closely coordinated anions in an arrangement that is similar to that in the SrI_2-type structure, with an eighth anion somewhat further removed. The other site has square antiprismatic eightfold coordination, a slight distortion from the cubic eightfold coordination present in fluorite, but considerably different from the ninefold coordination present in $EuCl_2$. This $SrBr_2$ structure may be considered a hybrid with certain features of both the SrI_2 and $SrCl_2$ (fluorite) structures.

One criterion for structure type, albeit a poor one (18), is the radius ratio. For $Ca_{0.3}M_{0.7}Cl_2$ (M = Eu, Sr) it is possible to calculate a hypothetical CN = 8 cationic radius, 1.36 Å, and a hypothetical CN = 7 radius, 1.31 Å. From these values the expected coordination number for this struc-

TABLE IV

OBSERVED INTENSITIES OF SELECTED REFLECTIONS OF $SrBr_2$ TYPE $(Ca_{0.3}M_{0.7})Cl_2$ (M = Sr, Eu) COMPARED WITH INTENSITIES CALCULATED FOR RANDOM (I_r) AND ORDERED [I_{Ca}: Ca(II) OCCUPIES TWOFOLD POSITION; I_M: M(II) OCCUPIES TWOFOLD POSITION] ARRANGEMENTS

				I_{cal}				
		I_{obs}		I_r		I_{Ca}		I_M
$h k l$	M =	Sr	Eu	Sr	Eu	Sr	Eu	Sr	Eu
1 1 0		vw	vw	5	2	18	23	1	0
1 0 1		w	w	17	9	3	1	19	16
1 0 2		w	—	22	—	13	—	5	—
2 0 2		w	vw	23	8	20	14	13	7
3 3 0		w	vw	18	4	23	21	11	7
5 0 1 / 3 4 1		vw	vw	7	5	6	6	8	9

ture can be identified and is found to be consistent with the observed results.

The volume/cation data presented in Table I indicate further the difference between the two systems at the MCl_2 end. For the case $M = Eu$, there is a regular decrease in this volume as the larger Eu(II) ion is substituted for Ca(II) with a corresponding increase in coordination number. This volume decrease with increasing cation size is an indication of increased efficiency in packing. In the case $M = Sr$, the behavior is similar initially, with the volume value decreasing with increasing coordination number. But in this system when the fluorite structure with the same coordination number as that of the $SrBr_2$ structure grows in, there is an abrupt increase to a value slightly larger than that for $CaCl_2$, an indication of less efficient packing in the strontium than in the europium case.

Acknowledgment

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