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# Preparatory and X-Ray Diffraction Study of the $EuCl_2$–$EuBr_2$ System*

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The system $EuCl_xBr_{2-x}$, where $0 \leq x \leq 2$, has been examined by X-ray powder diffraction techniques. Three discrete regions were identified. From $0 \leq x \leq 0.10$ an $SrBr_2$-type anion-ordered structure is observed. From $0.30 \leq x \leq 2.0$ a $PbCl_2$-type anion-ordered structure is found. Between these two structure types a diphasic region exists. In the chloride-rich region an abnormal expansion of the *a* and *c* lattice parameters is observed. These results are compared to those obtained in a study of the $SrCl_xBr_{2-x}$ system, to a previous structural study of a single crystal of the composition $EuCl_{0.5}Br_{1.5}$, and to reported high pressure polymorphic modifications of the parent phases.

## Introduction

Clink and Eick reported the preparation of two Eu–Cl–Br phases of the composition $EuBr_{1.85}Cl_{0.15}$ and $EuBr_{1.5}Cl_{0.5}$. From a single crystal study of the latter phase they reported structural details on an ordered $PbCl_2$-type structure; for the former phase they hypothesized the existence of an anion-ordered compound of unknown structure (*1*). In a study of the strontium bromide–strontium chloride system five discrete phase regions were identified (*2*). The $Eu^{2+}$ and $Sr^{2+}$ ions frequently exhibit isostructural behavior; their ionic radii for octahedral coordination differ by only 0.01 Å (*3*). Both dibromides normally exhibit the tetragonal $SrBr_2$-type structure (*4, 5*), with the orthorhombic $PbCl_2$-type structure reported at high pressures (*6*). The normal chloride structures differ, as $EuCl_2$ (*7*) crystallizes in the orthorhombic $PbCl_2$-type structure while $SrCl_2$ (*8*) crystallizes in the $CaF_2$-type cubic structure. Two $PbCl_2$-type high pressure modifications have been reported for $SrCl_2$ (*6, 9*), with one said to be isostructural with $EuCl_2$ (*7*). However, X-ray intensity calculations effected with the atomic coordinates reported for $EuCl_2$ do not match the listed intensities and suggest that this report may be in error.

The bromine-rich mixed halide phase reported for the europium system was not observed in the strontium system. Hence, a systematic study of the $EuCl_2$–$EuBr_2$ system was undertaken.

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TABLE I

LATTICE PARAMETERS AND CELL VOLUME/CATION OF THE $EuCl_xBr_{2-x}$ PHASES AS A FUNCTION OF COMPOSITION

| $x$ | $a$ (Å) | $b$ (Å) | $c$ (Å) |
|---|---|---|---|
| 0 | 9.496[a] | 7.959[a] | 4.709[a] |
| 0 | 11.562(6) | | 7.087(6) |
| 0.05 | 11.530(3) | | 7.049(5) |
| 0.10 | 11.507(2) | | 7.020(8) |
| 0.15 | | | |
| 0.20 | | Two phase region | |
| 0.25 | | | |
| 0.30 | 9.323(9) | 7.917(5) | 4.667(1) |
| 0.40 | 9.244(6) | 7.888(4) | 4.631(8) |
| 0.46[b] | 9.230(5) | 7.890(4) | 4.613(3) |
| 0.60 | 9.181(2) | 7.871(6) | 4.595(2) |
| 0.80 | 9.142(5) | 7.850(6) | 4.567(2) |
| 1.00 | 9.075(1) | 7.822(3) | 4.540(1) |
| 1.20 | 9.052(4) | 7.765(0) | 4.521(6) |
| 1.40 | 9.013(5) | 7.730(2) | 4.523(4) |
| 1.60 | 9.005(1) | 7.659(4) | 4.527(5) |
| 1.80 | 8.989(2) | 7.604(9) | 4.530(1) |
| 2.00 | 8.974(3) | 7.542(7) | 4.512(7) |

[a] High pressure modification of $EuBr_2$ (*6*).

[b] Data from (*1*).

## Experimental

The dichloride and dibromide reactants were prepared by the method of Taylor and Carter from sesquioxide with, in the case of the chloride, subsequent reduction under a stream of ultrapure hydrogen which was passed first over a palladium catalyst and subsequently through a liquid nitrogen cooled trap (*10*). X-ray powder diffraction examination of the reactants indicated them to be of high purity. All manipulations of reactants and products were performed in a glove box whose recirculated argon atmosphere was purged of water.

Varying stoichiometric proportions of the reactants were mixed intimately in the glove box prior to being confined in pyrolytic graphite boats. The mixtures (total weight of each: 0.5 g) were heated to 750°C, above the reported melting point of both reactants (*11*), and then cooled to room temperature of a constant rate of 15°C/hr. The mass of each sample was checked before and after heating to determine if specimen vaporization had occurred.

X-ray powder diffraction patterns were obtained and analyzed as described previously (*2*, *12*). X-ray intensity data were obtained as described previously (*12*), with the exception that the specimen holder was covered with tape to minimize hydrolysis effects during exposure. Peak areas were determined from the mass of the cutout peaks; the reported intensities are the average of the three data sets. Theoretical X-ray powder diffraction intensities were calculated with the program ANIFAC (*13*) as described previously (*2*, *12*, *14*). Scattering factors with the appropriate dispersion corrections were taken from the *International Tables* (*15*). Numerous samples were examined in a Philips EM300 electron microscope operated at 100 kV in diffraction mode.

## Results and Discussion

The mass loss measurements verified that sample had not been lost during heating; the mass of the products was in all cases in excellent agreement with that of the reactants. The specimens slid easily from the pyrolytic graphite boats; there was no evidence of reaction with the container. The lattice parameters as a function of composition are listed in Table I and presented in Fig. 1. Lattice parameters of $EuCl_2$ and $EuBr_2$ agree well with literature values (*4*, *7*).

Three discrete regions were identified in this system. In the first region, which covers the composition range $0 \leq x \leq 0.10$, the $EuCl_xBr_{2-x}$ phase crystallizes in a tetragonal $SrBr_2$-type structure. In this structure the unit cell contains 10 formula units. Sixteen bromine atoms located in general positions occupy the distorted tetrahedral and

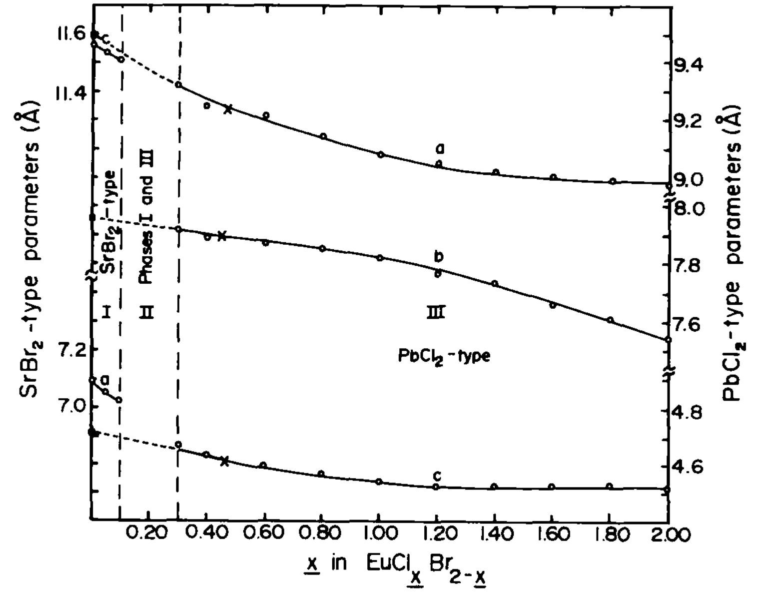

FIG. 1. Phase relationships in the system $EuCl_xBr_{2-x}$ and variation of the lattice parameters versus $x$. The dashed line extrapolates to high pressure $PbCl_2$-type lattice parameters.

trigonal coordination sites while four bromine atoms occupy the regular tetrahedral sites (*5*). By using the atomic coordinates reported for $SrBr_2$ (*5*), intensity data for the $SrCl_{0.10}Br_{1.90}$ phase were calculated as described previously (*2, 14*) for all possible locations of the chlorine atoms. The results indicate that of the three possible models which provided reasonable agreement, the one with the chlorine atoms randomly occupying only the regular tetrahedral sites fits best. Indexed $d$ spacings and intensities of the $EuCl_{0.10}Br_{1.90}$ phase are presented in Table II.

In the third region $0.30 \leq x \leq 2.0$, the X-ray diffractograms obtained for the products can be indexed on the basis of orthorhombic lattice parameters (Table I) close to those of $EuBr_{1.5}Cl_{0.5}$ (*1*) and $EuCl_2$ (*7*). In this $PbCl_2$-type structure there are two anion positions, one of which represents a square pyramidal, and the other a smaller, tetrahedral hole. Powder diffraction intensity data were calculated for three models, two ordered and one random, with the atomic coordinates reported for $EuBr_{1.5}Cl_{0.5}$. The data obtained for the $x = 1.00$ phase show agreement only for the ordered model in which the chlorine atoms are located exclusively in the tetrahedral holes. The interplanar $d$ spacings and calculated intensity data for EuClBr are also listed in Table II.

The region, $0.15 \leq x \leq 0.25$, is diphasic. Diffractograms of samples for the region could be indexed on the basis of the lattice parameters of the $EuCl_{0.10}Br_{1.90}$ and $EuCl_{0.30}Br_{1.70}$ phases.

In Fig. 1 the variation of the lattice parameters vs composition is presented. In the $SrBr_2$ region the lattice parameters decrease rapidly as chloride ion is substituted for bromide ion, with the cell volume decreasing from 947.6 to 929.7 Å³. In the $PbCl_2$-type region the lattice parameter variation is very similar to that observed in the $SrCl_xBr_{2-x}$ system (*2*). As bromine atoms substitute for chlorine atoms, the $b$ parameter initially increases rapidly while the $a$ and $c$ parameters remain relatively flat. At

TABLE II

OBSERVED AND CALCULATED POWDER DIFFRACTION DATA FOR TETRAGONAL $EuCl_{0.10}Br_{1.90}$ AND ORTHORHOMBIC EuClBr PHASES

| | $EuCl_{0.10}Br_{1.90}$ | | | |
|---|---|---|---|---|
| | $d_{hkl}$ | | Intensity | |
| *hkl* | Obs | Calc | Calc | Obs |
| 001 | 7.141 | 7.020 | 7 | 4 |
| 011 | 5.999 | 5.993 | 13 | 10 |
| 020 | 5.752 | 5.753 | 5 | 2 |
| 111 | 5.320 | 5.315 | 7 | 6 |
| 021 | 4.451 | 4.449 | 4 | 1 |
| 121 | 4.143 | 4.150 | 100 | 100 |
| 310 | 3.640 | 3.639 | 8 | 10 |
| 002 | 3.508 | 3.510 | 10 | 10 |
| 012 | 3.357 | 3.357 | 14 | 10 |
| 131 | 3.226 | 3.231 | 57 | 54 |
| 022 | 2.998 | 2.996 | 12 | 10 |
| 321 | 2.901 | 2.905 | 45 | 85 |
| 212 | | 2.900 | 39 | |
| 330 | 2.714 | 2.712 | 12 | 10 |
| 411 | 2.591 | 2.593 | 75 | 100 |
| 032 | | 2.589 | 21 | |
| 420 | 2.573 | 2.573 | 56 | 60 |
| 312 | 2.525 | 2.526 | 63 | 60 |
| 241 | 2.417 | 2.416 | 18 | 15 |
| 322 | 2.361 | 2.361 | 5 | 3 |
| 042 | 2.2244 | 2.2249 | 15 | 18 |
| 431, 051 | 2.1863 | 2.1869 | 16 | 15 |
| 332 | 2.1465 | 2.1462 | 8 | 6 |
| 123 | 2.1306 | 2.1301 | 43 | 40 |
| 251 | 2.0440 | 2.0442 | 29 | 25 |
| 252 | 1.8256 | 1.8252 | 4 | 2 |
| 620 | 1.8190 | 1.8194 | 5 | 3 |
| 621 | 1.7614 | 1.7612 | 5 | 3 |
| 114 | 1.7151 | 1.7155 | 7 | 4 |
| 062 | 1.6830 | 1.6830 | 5 | 3 |
| 170, 550 | 1.6274 | 1.6273 | 10 | 12 |

| | EuClBr | | | |
|---|---|---|---|---|
| | $d_{hkl}$ | | Intensity | |
| *hkl* | Obs | Calc | Calc | Obs |
| 101 | 4.056 | 4.060 | 9 | 6 |
| 210 | 3.928 | 3.925 | 46.8 | 40 |
| 020 | 3.908 | 3.911 | 11 | 10 |
| 111 | 3.606 | 3.604 | 43.6 | 40 |
| 211 | 2.970 | 2.969 | 40 | 35 |
| 021, 220 | 2.961 | 2.963 | 9.8 | 6 |
| 310 | 2.817 | 2.821 | 12 | 100 |
| 121 | | 2.817 | 100 | |
| 301 | 2.517 | 2.517 | 26.6 | 20 |
| 130 | 2.506 | 2.506 | 10 | 8 |
| 311 | 2.398 | 2.396 | 28.7 | 30 |
| 002 | 2.270 | 2.270 | 30.9 | 40 |
| 400 | | 2.269 | 15.5 | |
| 230 | 2.261 | 2.261 | 30 | 25 |
| 131 | 2.1943 | 2.1939 | 14.6 | 10 |
| 321 | 2.1166 | 2.1168 | 18 | 15 |
| 212, 411 | 1.9649 | 1.9650 | 16 | 16 |
| 232, 431 | 1.6018 | 1.6018 | 22.7 | 15 |

about the half-filled composition the trend reverses, with the *a* and *c* parameters increasing and the *b* parameter becoming relatively flat. Overall, the magnitude of change is about the same for each parameter. The same trend is apparent in the ordered $PbCl_2$-type region in both the $SrBr_2$–$SrCl_2$ (*2*) and the $BaCl_2$–$BaBr_2$ systems (*12*).

These diverse lattice parameter variations can be explained by examination of the $EuCl_2$ structure (*7*). In that structure the average Eu–*X*(2) (tetrahedral) distance is 2.94 ± 0.04 Å, while the Eu–*X*(1) (pyramidal) distance is 3.22 ± 0.20 Å. Thus substitution of a bromide ion into the *X*(1) position can take place with little effect on the interlayer distance (*c* parameter), but substitution of bromide ion into the smaller, almost tetrahedral and more rigid (as evidenced by thermal parameters) *X*(2) position causes the *c* parameter to increase.

The reasons for the *a* and *b* parameter changes are more subtle. In this structure zigzag layers of $X(1)$ anions runs parallel to the *b* axis. In $EuCl_2$ the anions are separated by 4.05 Å in the *b* direction and 8.95 Å in the *a* direction. Thus addition of bromide ion into the position initially affects the *b* parameter more significantly than it does the *a* parameter. One of the shortest anion distances in the $EuCl_2$ structure, 3.5 Å, is in a zigzag chain of $X(2)$–$X(1)$ atoms which runs parallel to the *a* axis. The final rapid increase in the *a* parameter results when bromide ions begin to fill this less flexible $X(2)$ position.

Clink and Eick (*1*) report interplanar *d* spacing for a sample of the composition $EuBr_{1.85}Cl_{0.15}$. These spacings are attributed to a mixture of $EuBr_2$ and an unknown discrete phase. It is clear from this work that the unknown phase is ordered $EuCl_xBr_{2-x}$. Indeed, their *d* values are very close to those observed in this work. The two phase mixture which these authors reported is an artifact of their preparatory procedure. They started with an $EuCl_3 \cdot NH_4Br \cdot H_2O$ slurry and obtained this phase when the slurry was heated initially under a stream of helium at 250°C for ~16 hr, then to about 370°C. (The $EuCl_{0.5}Br_{1.5}$ phase was obtained when the initial heating was effected at 200°C.) Since ammonium chloride sublimes at a lower temperature than ammonium bromide (340 vs 452°C) (*16*), the initial heating period preferentially caused loss of $NH_4Cl$ and resulted in a lower chloride content in the product. The low ultimate heating temperature (370° for 4 hr) precluded attainment of the equilibrium-ordered single phase. Thus a mixed halide phase and pure $EuBr_2$ resulted.

Clink and Eick also pointed out the presence of weak superstructure reflections at half integral values along 0*k*0. These reflections were hypothesized to result from ordering of the chloride and bromide ions in the 4*c* sites (*17*). As expected, examination of numerous crystals of the composition EuClBr in the electron microscope did not evidence any further ordering. Additional evidence of ordering would be expected as the $EuCl_{0.5}Br_{1.5}$ composition was approached.

A comparison of the results reported herein with those obtained for the $SrCl_xBr_{2-x}$ system is of interest. The $SrCl_xBr_{2-x}$ system contains five phases, while this system evidences only two. In contrast to the diphasic region identified in this system, discrete single phase regions were found in the $SrCl_xBr_{2-x}$ system to separate the $SrBr_2$- and $PbCl_2$-type structures, and the $PbCl_2$-type ordered and $PbCl_2$-type random structures. A comparison of the cell volume per metal atom for these europium and strontium mixed halide phases indicates a striking parallelism even though the number of phases observed in the systems is different. The volume/$Sr^{2+}$ ion in the dibromide structure is slightly larger than that per $Eu^{2+}$ ion, and the difference remains constant throughout the entire system, consistent with previous observations (*18*). Both systems exhibit the first transition from the $SrBr_2$-type structure at the same volume/metal ion ratio.

Comparison of these data with the high pressure work of Beck (*6*) illustrates that substitution of chloride ions for bromide ions creates internal pressure in the system, and this effect is tantamount to that of applying external pressure. The high pressure orthorhombic $PbCl_2$-type lattice parameters reported by Beck for $EuBr_2$ fit smoothly onto an extrapolation of the curves sketched in Fig. 1.

Since both dibromides and $SrCl_2$ transform to the $PbCl_2$-type structure under pressure, the presence of an extended $PbCl_2$ region is not surprising. Furthermore, if the structures are envisioned as being under pressure, then the larger square pyramidal hole should be occupied by the larger bromide ion, as is observed. However, other differences between the strontium and europium systems cannot be explained so easily. The onset of the $PbCl_2$-type structure occurs at 5% chloride ion concentration in $EuBr_2$ vs 20% in $SrBr_2$. Beck's data (*6*) imply the reverse situation should occur. Similarly, the multiplicity of phase regions observed in the strontium, but not the europium system, implies the existence of factors other than atomic radii and pressure effects.

## Acknowledgment

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