

## Preparation and Characterization of a Europium(II) Bromide-Chloride Phase $\text{EuBr}_{1.5}\text{Cl}_{0.5}$

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A divalent europium chloride-bromide phase,  $\text{EuBr}_{1.56(7)}\text{Cl}_{0.46(2)}$  has been prepared and identified on the basis of analytical, X-ray powder diffraction and single-crystal data. Although the phase is considered isostructural with  $\text{EuCl}_2$  ( $\text{PbCl}_2$  structure type,  $a = 0.9230$  (5),  $b = 0.7890$  (4),  $c = 0.4613$  (3) nm, space group  $Pbnm$ ), the single-crystal data indicate long-range order in the form of a superstructure which doubles the  $b$  parameter. In the pseudocell the square pyramidal anion sites are occupied principally by bromide ions, the tetrahedral sites almost equally by bromide and chlorine ions. Structural details and the long-range order are discussed. Evidence is presented for the existence of another europium(II) mixed halide phase,  $\text{EuBr}_{1.8(2)}\text{Cl}_{0.16(2)}$ .

### Introduction

Mixed halide phases which contain the fluoride ion have been known for some time for divalent elements such as Zn, Pb, and Sn, but only recently have these compounds been reported for lanthanide(II) elements (1-6). A number of reports of poorly characterized actinide trivalent and tetravalent mixed halide species can be found, and the Sr-Cl-Br system has been studied (7, 8). Neither Ln(II) nor Ln(III) mixed halide phases containing only chloride, bromide, or iodide ions have been reported, but Haschke (9) has predicted on the basis of structural relationships that such trivalent phases should exist. To enhance our understanding of lanthanide mixed halide chemistry we undertook a study of the europium(II) chloride-bromide system.

### Experimental

A number of potential preparatory reactions for mixed halide phases were attempted, but the most successful procedure involved the reaction of hydrated europium trichloride with ammonium bromide. The hydrated trichloride and ammonium bromide were mixed in aqueous solution in a 1:6 mole ratio, according to the method of Taylor and Carter (10) as modified by Hariharan (11). In this procedure the  $\text{EuCl}_3 \cdot \text{NH}_4\text{Br} \cdot \text{H}_2\text{O}$  slurry was confined in a carbon boat and heated under a deoxygenated helium stream at 200°C (or 250°C) for ~16 hr. Once excess water had evaporated, the temperature was increased to 370°C and heating was continued (~4 hr) until the orange phase which appeared initially had decomposed completely into a light grey powder. The sample was transferred to an argon-filled glove box and stored in a

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screw-capped vial which was subsequently sealed in plastic.

Powder diffraction patterns were obtained with a Haegg-type Guinier forward-focusing camera (radius 80 mm) and  $\text{CuK}\alpha$  radiation ( $\lambda = 0.154050$  nm) with a Pt internal standard ( $a = 0.39231$  (1) nm),  $t = 24 \pm 2^\circ\text{C}$ . The data were reduced with the linear regression program of Lindqvist and Wengelin (12).

#### Metal Analysis

Metal content was determined gravimetrically. Samples were weighed directly into constant-weight platinum crucibles and ignited to the sesquioxide at  $950^\circ\text{C}$  in a muffle furnace.

#### Halide Analysis

(a) Total halide analysis was effected by an amperometric procedure with a rotating Pt electrode (13, 14).

(b) Chloride analysis was effected by oxidation of  $\text{Br}^-$  to  $\text{Br}_2$  with subsequent removal by aeration, followed by amperometric titration.

The errors reported represent the standard deviations of at least three analyses of each sample. The empirical formula was calculated with the results of the metal, total halide, and chloride analytical data.

#### Single-Crystal Structural Determination

Single crystals were grown from the melt by slow cooling. A pulverized sample was sealed under vacuum ( $\sim 10^{-6}$  Torr) in an outgassed quartz ampule, heated to  $\sim 660^\circ\text{C}$ , cooled to  $300^\circ\text{C}$  at a rate of  $\sim 3^\circ/\text{hr}$ , and then quenched. The crystals were transferred in a glove box to a specially designed capped tube which was fitted with optical flats so that the product could be examined under the microscope. With a stream of dry argon flowing over the sample, a crystal fragment was selected and subsequently transferred into a capillary for mounting. Alignment was effected with a precession camera. The overall shape of this fragment approximated

that a rough-hewn triangular prism with basal faces  $\sim 0.08 \times 0.09 \times 0.09$  nm and with a height which varied between 0.10 and 0.16 mm.

From the precession data the symmetry of the crystal was determined to be orthorhombic, space group  $Pbnm$ . The cell parameters and the extinctions observed were similar to those reported for  $\text{EuCl}_2$  ( $a = 0.896$ ,  $b = 0.754$ ,  $c = 0.451$  nm, space group  $Pbnm$ , No. 62 (15)).

Two data sets were collected, the first by the  $\omega$ -scan technique ( $hkl$  and  $\bar{h}\bar{k}\bar{l}$  octants, scan range  $1.5^\circ$ , scan rate  $1.0^\circ/\text{min}$ ) with a computer-controlled Picker four-circle goniostat fitted with a graphite monochromator adjacent to the X-ray tube. This data set, which was not corrected for absorption, was reduced with programs provided by Zalkin (16). The second was collected by the  $\theta$ - $2\theta$  technique ( $hkl$ ,  $h\bar{k}\bar{l}$ ,  $hk\bar{l}$ , and  $\bar{h}kl$  octants) at Arizona State University and is described in detail below.

A set of 15 reflections in the range  $2\theta < 27^\circ$  was automatically centered on the autodiffractometer. Cell parameters were obtained from least-squares refinement of these reflections which were distributed among the four octants and are presented with other pertinent data in Table I. Examination of 12 low-angle reflections by  $\omega$  scans verified that the crystal was single and of excellent quality. The intensity data were corrected for absorption by an analytical procedure (17).

The structure was solved with the first data set by using the atomic coordinates of  $\text{EuCl}_2(\text{PbCl}_2$  structure type, position  $4(c) \pm (x, y, \frac{1}{4}), \pm(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{4})$ ) for least-squares refinement (18). In the  $\text{EuCl}_2$  structure there are two different anion positions, labeled (1) and (2) according to Baernighausen's notation (15). Insertion of chlorine atoms into both of these positions yielded marginal refinement with negative anion temperature factors. When a bromine atom was substituted for the chlorine atom in position 2, the

TABLE I  
CRYSTAL AND COLLECTION DATA FOR  
EuCl<sub>0.46(2)</sub>Br<sub>1.56(7)</sub>

$a = 0.9230$ (5) nm	$\rho$ (calc) = 5.72 g cm <sup>-3</sup>
$b = 0.7890$ (4) nm	$Z = 4$
$c = 0.4613$ (3) nm	Mol. wt. = 292 (3) g mole <sup>-1</sup>
$V = 0.3359$ nm <sup>3</sup>	Temp. = 23 ± 2°C
Space group	$Pbnm$ [No. 62, $D_{2h}^{16}$ ]
Diffractometer	Syntex P1
$2\theta$ range	8–60°
Scan speed	1°/min in $2\theta$
Scan range	$[2\theta(\text{MoK}\alpha_1) - 0.7^\circ] \rightarrow$ $[2\theta(\text{MoK}\alpha_2) + 0.7^\circ]$
Standards	Four measured after each 100 reflections. Percentage deviation of measurements varied from 0.4 to 1.5; no correction was applied.
Absorption coeff.	387.1 cm <sup>-1</sup>
Radiation (nm)	MoK $\lambda_{\alpha_1} = 0.070926$ $\lambda_{\alpha_2} = 0.071354$

structure refined to  $R \sim 0.08$ , but the thermal parameter of anion (1) was still negative. Subsequently, structures of 60, 70, 80, and 100 mole% bromine were refined with the thermal parameter of the bromine atom in position (1) reset to that of the atom in position (2) after each cycle of refinement. A least-squares fit of  $R$  as a function of mole% bromine ( $x$ ) yielded the equation:  $R = 70.9 - 1.76x + 0.0117x^2$ . This equation gives a minimum at 75.2 mole% bromine, and an empirical formula of EuCl<sub>0.5</sub>Br<sub>1.5</sub>. Refinement subsequently effected at this composition with the real part of the scattering factors of neutral atoms (19), isothermal temperature parameters, and 305 nonzero reflections gave an unweighted  $R$  value of 0.076.

Refinement of the second data set was initiated with the parameters derived above. Of the 2102 reflections collected, 192 were rejected as systematically extinct, but for a few of these, such as (010) and (001) ( $|F_0|^2 > 200$ ), and (034), (201), (00 $\bar{1}$ ), (011), and (09 $\bar{2}$ ) ( $|F_0|^2 > 100$ ), the  $|F_0|^2$  values were

$> 10\sigma_F$ . The 1910 remaining reflections were merged to a 548 unique reflection set. For refinement data were weighted according to  $w = 1/\sigma_F^2$ , where  $\sigma_F = 0.025|F_0| + [C + (B_1 + B_2)k^2]^{1/2}R/2|F_0|Lp$ . In this expression  $C$  is the total count in a scan taken at the rate  $R$  and  $k$  ( $= 4$ ) is the ratio of scanning time to the time for background counts  $B_1$  and  $B_2$ . Four strong reflections with  $|F_0| > 1370$ , and 36 weak reflections with  $|F_0| < 45$  were deleted. All calculations were effected with the program set CRYSTALS adapted for the UNIVAC 1110 (20). Scattering factors in exponential form for Eu<sup>2+</sup> and X<sup>-</sup> ions were used throughout, with both the real and imaginary parts applied in the last cycles of refinement (21). In the least-squares refinement,  $\sum w(|F_0| - |F_c|)^2$  was minimized, and  $R_w = [\sum w(|F_0| - |F_c|)^2 / \sum w|F_0|^2]$ . In addition to an examination by both precession and Weissenberg techniques a region of reciprocal space was step-scanned with the diffractometer in search of superstructure reflections.

## Results

### Analytical

Two divalent europium mixed halide phases were identified. The light grey hygroscopic powder obtained when the initial heating temperature was  $> 250^\circ\text{C}$  had an empirical formula, EuCl<sub>0.16(4)</sub>Br<sub>1.85(15)</sub>. Metal, chloride, and total halide analytical results are presented in Table II. The X-ray powder diffraction pattern presented in Table III contains reflections assignable to EuBr<sub>2</sub>. Single crystals of this phase, designated phase 1, could not be grown.

The light grey hygroscopic powder obtained when the initial heating period was at a temperature  $\leq 200^\circ\text{C}$  had an empirical formula EuCl<sub>0.46(2)</sub>Br<sub>1.56(7)</sub>. The analytical results of this phase, designated phase 2, are also presented in Table II.

TABLE II  
 ANALYTICAL DATA

Species	Moles/gram of sample	Moles of halide/mole of Eu ion
Phase 1		
Total halide	$(6.6_3 \pm 0.5_0) \times 10^{-3}$	$2.0_1 \pm 0.1_5$
Chloride	$(5.3 \pm 1.3) \times 10^{-4}$	$0.16 \pm 0.04$
Bromide	$(6.1_0 \pm 0.5_1) \times 10^{-3}$	$1.8_5 \pm 0.1_5$
Eu(II)	$(3.30 \pm 0.08) \times 10^{-3}$	
Phase 2		
Total halide	$(7.1_2 \pm 0.2_7) \times 10^{-3}$	$2.02 \pm 0.07$
Chloride	$(1.62 \pm 0.07) \times 10^{-3}$	$0.46 \pm 0.02$
Bromide	$(5.4_9 \pm 0.2_8) \times 10^{-3}$	$1.56 \pm 0.07$
Eu(II)	$(3.512 \pm 0.005) \times 10^{-3}$	

*Structural Studies of EuCl<sub>0.46(2)</sub>Br<sub>1.56(7)</sub>*

The scan of a region of reciprocal space indicated the presence of weak superstructure reflections at half-integral values along  $0k0$ . These reflections were not observed in

the heavily exposed precession or Weissenberg photographs. Since their low intensity indicated little probability of determining the true structure, refinement of the  $\text{PbCl}_2$  sub-cell was effected.

The second data set refined initially to an unweighed  $R$  value of 11.4%. In subsequent cycles of refinement the occupancy factors of both anion sites were refined with an anisotropic temperature factor for each anion site and the metal ion. In the refinement the  $U[13]$  and  $U[23]$  terms were set to zero (21). Since temperature and occupancy factors were varied simultaneously, it was necessary to include in the least-squares equations the composition constraint observed experimentally. The error limit was set at  $3 \times$  the standard deviation. The final discrepancy indices were  $R = 9.11\%$ .  $R_w = 11.78\%$ .

The final difference Fourier indicated a few small peaks. Two peaks of  $\sim 3 \text{ e}/\text{\AA}^3$

 TABLE III  
 OBSERVED X-RAY POWDER DIFFRACTION PATTERN FOR  $\text{EuBr}_{1.85(15)}\text{Cl}_{0.16(4)}$ 

Intensity	Interplanar $d$ -spacings		Intensity	Interplanar $d$ -spacings	
	Observed (nm)	Calculated for $\text{EuBr}_2^a$ (nm)		Observed (nm)	Calculated for $\text{EuBr}_2^a$ (nm)
3	0.425		4	0.2178	
4	0.419	0.418	3	0.2141	0.2152
4	0.407		1	0.2050	
4	0.400		1	0.2023	
4	0.324	0.325	1	0.1985	
4	0.307		1	0.1857	
4	0.304	0.302	3	0.1829	
4	0.292	0.293	1	0.1660	
5	0.289		3	0.1647	
5	0.260	0.261	1	0.1536	
4	0.258	0.258	1	0.1515	
4	0.255	0.255	1	0.1505	
4	0.254		3	0.1486	
1	0.2429	0.2431	3	0.1457	
4	0.2355		3	0.1443	
4	0.2307		1	0.1324	
3	0.2243	0.2243			

<sup>a</sup>  $\text{EuBr}_2$  intensities from Ref. (23);  $d$  values calculated for tetragonal cell,  $a = 1.1574$ ,  $c = 0.7098$  nm.

TABLE IV  
 POSITIONAL AND THERMAL PARAMETERS FOR  $\text{EuCl}_{0.5}\text{Br}_{1.5}$ 

Atom	OCC	$x/a$	$y/b$	$z/c$		
Eu	1.0	0.1215 (2)	0.2622 (2)	0.2500		
Cl(1)	0.503 (25)	0.4321 (5)	0.1448 (5)	0.2500		
Br(1)	0.497 (25)					
Cl(2)	0.026 (26)	0.8317 (3)	0.0264 (4)	0.2500		
Br(2)	0.974 (26)					
	$U(11)$	$U(22)$	$U(33)$	$U(23)$	$U(13)$	$U(12)$
Eu	0.0207 (9)	0.0162 (8)	0.0200 (8)	0	0	0.0030 (5)
X(1)	0.0217 (22)	0.0226 (20)	0.0254 (23)	0	0	-0.0005 (16)
X(2)	0.0184 (15)	0.0159 (14)	0.0237 (15)	0	0	-0.0022 (10)

were situated about  $0.8 \text{ \AA}$  (at  $z \approx 0.40$ ) above the metal atom and were centered around a pseudo twofold axis at  $y = 0.25$ . A channel of electron density was parallel to the  $z$  axis at  $y \sim 0.65$ ,  $x \sim 0.10$ , with a maximum of  $\sim 2 \text{ e}/\text{\AA}^3$  on the mirror plane about  $1.4 \text{ \AA}$  from both anions 1 and 2. Attempts to improve the refinement by allowing these sites to be partially occupied with europium and bromide or chloride ions, respectively, did not significantly improve the discrepancy index.

The final fractional position and anisotropic thermal parameters, with estimated standard deviation of the last digits in parentheses, are presented in Table IV. Interatomic distances around the Eu ion are presented in Table V.

 TABLE V  
 INTERATOMIC DISTANCES AROUND EU IN  $\text{EuCl}_{0.5}\text{Br}_{1.5}$ 

Bond	No.	Distance (nm)
Eu-X (1)	1	0.3013 (5)
-X (1)	1	0.3059 (5)
-X (1)	2	0.2986 (3)
-Br (2)	1	0.3259 (3)
-Br (2)	2	0.3270 (3)
-Br (2)	2	0.3444 (2)

## Discussion

The presence of ammonium halide has long been known to prevent hydrolysis of hydrated lanthanide halide phases (9, 22). The mechanism of the reaction is still unknown; hence it is difficult to rationalize a temperature dependence of the products. It is reasonable to assume, though, that under the preparatory conditions used here the high thermodynamic activity of the bromide ion relative to that of the chloride ion determined that the phases would be bromide rich. The final composition of the phases probably depends primarily upon the activities of the bromide and chloride ions—which in turn are affected by the heating temperatures.

A europium(III) mixed halide phase could not be prepared. Although the Taylor-Carter preparatory procedure is normally nonreducing, the presence of Eu(II) is consistent with previous observations that a Eu(III)-bromide-containing phase is unstable to decomposition at  $200^\circ\text{C}$  (23, 24).

The crystal whose structure was solved was representative of the sample since excellent agreement was obtained between the observed diffraction pattern and that calculated from the single crystal results. Although each phase could be prepared reproducibly, the analytical results for phase 1 were not so

reproducible as were those for phase 2. The presence of lines in the X-ray powder diffraction photograph assignable to the tetragonal form of  $\text{EuBr}_2$  explains some of this variation. The observed diffraction intensities, when compared to those expected for pure  $\text{EuBr}_2$ , do indicate line overlap. Unassigned lines cannot be ascribed to  $\text{EuCl}_{0.5}\text{Br}_{1.5}$ , the phase expected if phase 1 were but a mixture. The work of Frit *et al.* (8) on the Sr-Cl-Br ternary system indicates that the proposed  $\text{EuBr}_{1.85}\text{Cl}_{0.16}$  phase should exhibit the  $\text{SrBr}_2$ -type structure. This unexpected result might be caused by the presence of trace amount of  $\text{Eu(III)}$ .

It is interesting to compare bond distances in this structure with those in  $\text{EuCl}_2$ . In both structures nine anions are coordinated around the metal ions in a tricapped trigonal prismatic arrangement. In  $\text{EuCl}_2$  there is one metal-chlorine bond length of 0.3046, 0.2994, and 0.2916 nm each and two metal-chlorine bond lengths of 0.3440, 0.2925, and 0.3090 nm each. There are two types of anion holes—square pyramidal and tetrahedral. The M-Cl bond distances greater than 0.3 nm are for those chloride ions in square pyramidal holes. As is expected, in  $\text{EuBr}_{1.5}\text{Cl}_{0.5}$  the larger square pyramidal hole is filled completely, within the limits of the esd of the occupancy factor, with bromide ions; the tetrahedral hole is partially filled with bromide ions. The bond distances observed here are on the average 0.010 nm larger than those reported for  $\text{EuCl}_2$ ; the square pyramidal (bromide-filled) hole averages  $\sim 0.012$  nm larger, while the tetrahedral hole averages only  $\sim 0.007$  nm larger, consistent with the observed occupancy.

Frit *et al.* (8) report a  $\text{PbCl}_2$ -type structure for  $\text{SrCl}_{0.6}\text{Br}_{1.40}$  with lattice parameters of 0.9251, 0.7928, and 0.4657 nm. The volume of their cell is about 2% larger than that observed for  $\text{EuCl}_{0.5}\text{Br}_{1.5}$ . The radius of  $\text{Eu}^{2+}$  is 0.001 nm smaller than that of  $\text{Sr}^{2+}$  (for CN=8 and 9), consistent with this change (25). But the greater bromine

content ( $\text{Br}_{1.5}$  vs  $\text{Br}_{1.4}$ ) should cause the reverse effect. This apparent discrepancy might be the result of different anisotropic characteristics of the ions or might indicate the presence of a trace amount of  $\text{Eu}^{3+}$  in the lattice.

The tetragonal  $\text{SrBr}_2$ -type phase is reported for compositions more bromine rich than  $\text{SrCl}_{0.36}\text{Br}_{1.64}$ , but the region of bromine content between 1.36 and 1.64 has not been discussed (8). While our data indicate a superstructure for this intermediate region, the superstructure is so subtle that it cannot be detected by ordinary Guinier powder techniques, and one must wonder if the superstructure extends to less bromine rich compositions.

Only the  $\text{SrBr}_2$ -type structure has been reported for  $\text{EuBr}_2$  at normal pressures. For  $\text{SmBr}_2$  both the  $\text{SrBr}_2$  and the  $\text{PbCl}_2$ -type structures are known (15). The  $\text{PbCl}_2$ -type structure is stable when  $\text{SmBr}_2$  is in equilibrium with elemental samarium; the  $\text{SrBr}_2$ -type is stable when  $\text{SmBr}_2$  is in equilibrium with  $\text{Sm}_6\text{Br}_{13}$  (26, 27). The presence of some  $\text{Sm(III)}$  in the  $\text{SmBr}_2$  lattice appears to decrease the effective cationic radius and cause the structural change. Substitution of the smaller chloride ions for  $\sim 25\%$  of the bromide ions in  $\text{EuBr}_2$  has the same effect as substituting  $\text{Sm(III)}$  for  $\text{Sm(II)}$  in  $\text{SmBr}_2$ . Here the effective anionic radius is decreased, and the crystal energetics change to stabilize a  $\text{PbCl}_2$ -type nine-coordinate structure.

The rather high final value of the discrepancy index, the presence of peaks in the difference Fourier, and the observation of reflections that should be extinct are reflective of the fact that a pseudocell has been refined. Undoubtedly some of the reasons for the high  $R$  value stem from the absorption correction process. The absorption coefficient is large and the irregular shape of the crystal with reentrant angles present made the definition of boundary planes inexact. But the collection of data for

one-half of the sphere of reflection should compensate for errors introduced in the absorption correction process. We believe that the chloride and bromide ions are present in an ordered arrangement and cause the unit cell to be double that of the  $\text{PbCl}_2$  cell.

The two small peaks present in the difference Fourier about  $0.8 \text{ \AA}$  above (and below) the europium atom may be indicative of some further disorder in the crystal. The coordination polyhedron of europium contains two anions of type 1 in the tricapped position, and one in the basal plane. These positions are arranged such that a string of type 1 anions runs in the staggered arrangement, basal plane, capped position, basal plane, etc., parallel to the  $z$  axis. The peaks adjacent to the europium atom are located in a plane which includes this tricapped type 1 anion. If two chloride ions occupy these chain positions the europium might move up (or down) and out into a somewhat lower energy position, in the process pushing the smaller tricapped chloride ion from its normal site. This phenomenon could occur much more easily if the metal ion were tripositive rather than dipositive.

It is interesting to speculate on compositions that might yield the observed stoichiometries. If a bromide ion were substituted in seven-ninths of the anion positions, the empirical formula would be  $\text{EuCl}_{0.44}\text{Br}_{1.56}(\text{Eu}_9\text{Br}_{14}\text{Cl}_4)$ ; if a bromide ion were substituted in three-fourths of the anion positions, the empirical formula would be  $\text{EuCl}_{0.5}\text{Br}_{1.5}$ ,  $[\text{Eu}_8\text{Br}_{12}\text{Cl}_4]$ . Both are consistent with the analytical results. The first single-crystal data set indicated a minimum  $R$  value at the composition,  $\text{EuCl}_{0.5}\text{Br}_{1.5}$ ; the second set at the value  $\text{EuCl}_{(0.53 \pm 0.07)}\text{Br}_{(1.47 \pm 0.09)}$ . Since for the true cell  $z \geq 8$ , the formula of the phase must be  $\text{EuCl}_{0.5}\text{Br}_{1.5}$ .

Substitution of bromide ions in eight of the nine coordination positions around euro-

pium yields the empirical formula  $\text{EuCl}_{0.22}\text{Br}_{1.78}$ , suspiciously analogous to that observed for Phase 1,  $\text{EuCl}_{(0.16 \pm 0.04)}\text{Br}_{(1.85 \pm 0.15)}$ .

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