

An X-ray Powder Diffraction Study of the Chloride-Bromide Systems of Trivalent Gadolinium, Terbium, and Ytterbium

MONIKA OLEJAK-CHODAN, WIESLAW LASOCHA,
AND HARRY A. EICK*

*Department of Chemistry, Michigan State University,
East Lansing, Michigan 48824*

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The lanthanoid mixed halide systems, MCl_3 - MBr_3 , for $M = \text{Gd, Tb, and Yb}$, have been prepared by mixing and fusing the pure reactants and have been examined by X-ray powder diffraction procedures. For $M = \text{Gd}$, UCl_3 , ($P6_3/m$)-, $PuBr_3$ ($Cmcm$)- and $AlCl_3$ ($C2/m$)-type solid solution regions were found. For $M = \text{Tb}$, $PuBr_3$ - and $AlCl_3$ -type solid solution regions were found. For $M = \text{Yb}$, $AlCl_3$ - and $FeCl_3$ - ($R\bar{3}$)-type solid solution areas were observed. Pure $TbBr_3$ appears to be isostructural with $GdBr_3$ rather than with $DyBr_3$. These systems are discussed and compared to related systems. © 1988 Academic Press, Inc.

Introduction

The lanthanoid trichlorides exhibit three structural types at normal pressures—the hexagonal UCl_3 type, the orthorhombic $PuBr_3$ type, and the monoclinic $AlCl_3$ type—with coordination numbers of 9, 8, and 6, respectively (*1*). Most binary mixed lanthanoid trichloride systems have been examined by DTA and both melting points as a function of composition and solubility limits are characterized (*1-6*). Those binary lanthanoid trichloride systems which involve the three different structural types, $TbCl_3$ - $DyCl_3$, $TbCl_3$ - $HoCl_3$, $GdCl_3$ - $DyCl_3$, and $GdCl_3$ - $TbCl_3$, have also been examined by X-ray powder diffraction (*1*). In addition, enthalpy of mixing data are reported for the $LaCl_3$ - $YbCl_3$ and $LaCl_3$ - $GdCl_3$ systems (*6*).

These binary trichloride systems are characterized by two types of equilibrium phase diagrams. The first type which entails a continuous solid solution region is found for systems in which the parent components possess isomorphous structures. The second type, which is observed when the parent phases are not isomorphous, typically exhibits a eutectic and may or may not exhibit a distinct two-phase region. Other factors such as cationic size and lattice energy differences also affect the equilibrium temperature-composition diagrams.

The lanthanoid tribromide systems exhibit three structural types at normal pressures—the UCl_3 and the $PuBr_3$ types similar to those reported for the trichlorides and the rhombohedral $FeCl_3$ type which has a coordination number of 6 (*7*). Reports of mixed binary lanthanoid tribromide systems could not be found, but since two of the structure types are similar to those re-

* To whom correspondence should be addressed.

ported for the trichlorides, the behavior of some of the mixed tribromide systems is expected to be comparable to that of the related mixed trichloride systems.

Mixed binary lanthanoid trichloride-tribromide systems are better characterized than are the mixed tribromide systems. Some $Ln(\text{Cl}, \text{Br})_3$ matrices have been used in spin relaxation studies (8), and $Ln\text{Cl}_3$ doped with $Ln\text{Br}_3$ has been used as a matrix for spectroscopic studies on other lanthanoids (9). The enthalpy of mixing of LaCl_3 - LaBr_3 has been determined (6) and the $M\text{Cl}_3$ - $M\text{Br}_3$ systems, $M = \text{La}$ and Nd , have been studied by X-ray powder diffraction procedures (10). In the LaCl_3 - LaBr_3 system a continuous solid solution region prevails, whereas in the NdCl_3 - NdBr_3 system a two-phase region separates the parent phases. This behavior is consistent with that reported for mixed binary lanthanoid trichloride systems. Isomorphous substances yield solid solutions, whereas non-isomorphous substances yield a two-phase region.

Beck and Gladrow have examined lanthanoid trihalide systems at high pressures (11-13). They note that at intermediate pressures the AlCl_3 -type trichlorides HoCl_3 through LuCl_3 can be converted into the rhombohedral RhF_3 -type structure, a structure not observed for trichlorides at normal pressures. At higher pressures the trichlorides DyCl_3 through YbCl_3 can be converted into the PuBr_3 -type structure (13). The FeCl_3 -type tribromides DyBr_3 through HoBr_3 can also be converted into the PuBr_3 -type structure at high pressures (11, 12). It has been demonstrated that the internal pressure created in mixed halide systems in some cases is adequate to convert the structure to the high-pressure modification and to cause the anions to order when different sized anion sites are available (14).

A detailed preparatory and X-ray diffraction study of representative binary

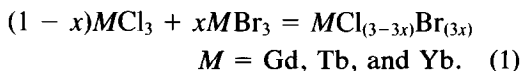
mixed trichloride-tribromide systems was deemed of interest for the following reasons: (a) mixed halide systems frequently exhibit structures of known high-pressure polymorphs, (b) when two or more unique anion sites are available in the crystal, mixed halide systems frequently exhibit anion ordering, and (c) there is a reasonable chance to obtain as yet uncharacterized phases. The systems chosen: GdCl_3 - GdBr_3 , TbCl_3 - TbBr_3 , and YbCl_3 - YbBr_3 , represent at room temperature, respectively, UCl_3 ($P6_3/m$)- AlCl_3 ($C2/m$)-, PuBr_3 ($Cmcm$)- FeCl_3 ($R\bar{3}$)-, and AlCl_3 - FeCl_3 -type structures which have the respective coordination number differences of 3, 2, and 0. Pure TbCl_3 is reported to exhibit $C2/m$ symmetry at elevated temperatures (1). The results of a systematic study of these systems are presented below.

Experimental

The lanthanoid trihalides were prepared by the ammonium halide matrix procedure (15, 16). The 99.9% pure lanthanoid sesquioxides, Gd_2O_3 (Michigan Chemical Co.), and Ln_2O_3 , $\text{Ln} = \text{Tb}, \text{Yb}$ (Research Chemicals, Inc., Phoenix, AZ), were combined with NH_4Cl (Fisher Scientific, ACS reagent grade) in a 1:6 molar ratio and with NH_4Br (Matheson, ACS reagent grade) in a 1:8 molar ratio. These mixtures were dissolved completely in the appropriate hydrohalic acid. The solutions were then evaporated slowly to dryness, and the dried mixtures were transferred to Pyrex tubes and heated slowly to 350°C under a vacuum of $\sim 10^{-3}$ Torr. Analysis was effected by X-ray powder diffraction as described below. All manipulations of both reactants and products were effected in a glove box whose Ar atmosphere was purged continuously of water (molecular sieves) and oxygen (heated BASF catalyst).

Each binary system was investigated over the full composition range. Mixed tri-

halide specimens, each of which had a total weight of 0.3 g, were intimately ground in an agate mortar in the desired stoichiometric ratio according to the equation



After transfer to previously outgassed quartz tubes the $\text{YbCl}_3\text{--YbBr}_3$ samples were melted with a hand-held torch under a vacuum of $\sim 10^{-4}$ Torr, then quenched to room temperature. The quartz tubes containing the $\text{GdCl}_3\text{--GdBr}_3$ and $\text{TbCl}_3\text{--TbBr}_3$ mixtures were sealed under a $\sim 10^{-4}$ Torr vacuum, placed in a tube furnace, heated rapidly to the melting point of the mixture, and then cooled slowly to room temperature over a period of 1 to 3 days.

Both the initial reactants and the pulverized products were analyzed by X-ray powder diffraction. To protect the samples from hydrolysis during transfer to the evacuable 114.6-mm Guinier camera they were coated (soaked) with dried paraffin oil and covered with Scotch tape. Copper $K\alpha$ radiation ($\lambda_{\alpha_1} = 1.54050 \text{ \AA}$) obtained from a quartz monochromator and the mixing of NBS certified silicon powder ($a = 5.43062(4) \text{ \AA}$) with the sample assured consistent and accurate interplanar d spacings. Because the samples were sprinkled lightly on tape, preferred orientation effects were negligible.

The observed $1/d^2$ values were indexed with the program ITO9 (17) and refined by least-squares treatment with locally written programs. Theoretical X-ray powder reflection intensities for selected compositions were calculated with the program POWD12 (18). For these calculations polynomial scattering factors were used with isotropic thermal parameters of 1.0 for the cations and 1.5 for the anions. The atomic positional parameters used are indicated by reference. To check for anion ordering when two unique crystallographic sites are present in the structure theoretical X-ray powder intensities were calculated for ordered

anion arrangements. Bond distances were determined with the program BONDLA (19).

Consistent with the geometry of the Guinier camera an absorption correction was not included in the calculations, but a correction was included for the incident beam quartz monochromator.

Results

Mass balance confirmed that the final composition could be considered identical to the mixed composition. There was no apparent attack of the quartz container during the short interval that the samples were molten.

Phase relationships in all three systems are presented schematically in Figure 1. It is apparent that a systematic progression of the phases occurs as the size of the cation is varied. Lattice parameters of the parent phases and of selected mixture compositions are presented in Table I.

Discussion

The $\text{GdCl}_3\text{--GdBr}_3$ System

The X-ray diffraction pattern of every mixed gadolinium trihalide which contained more than 45% tribromide exhibited broad, diffuse reflections characteristic of very small particles and/or microstrains. Extended annealing did not appear to improve the X-ray diffraction pattern quality. This observation is consistent with a previous report that gadolinium tribromide gave very poor X-ray diffraction patterns (20). As a consequence, neither precise lattice parameters nor high quality intensity data could be obtained for the bromide-rich specimens.

Pure GdBr_3 crystallized in the AlCl_3 -type ($C2/m$) structure (21). Gadolinium trichloride exhibited the UCl_3 -type ($P6_3/m$) structure (22, 23), and is reported to undergo a

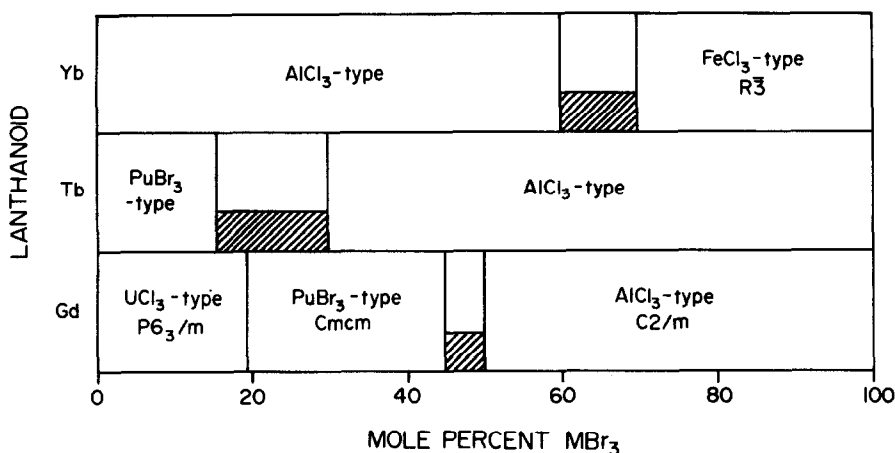


FIG. 1. Schematic representation of the MCl_3 - MBr_3 mixed halide phase diagrams for $M = Gd, Tb$, and Yb . The cross-hatched area represents a two-phase region.

UCl_3 - $PuBr_3$ -type transition at $100^\circ C$ (24). But both slowly cooled and quenched $GdCl_3$ crystallized only in the UCl_3 -type structure, consistent with more recent reports (1). Lattice parameter data for these pure phases are presented in Table I.

In the mixed halide system a UCl_3 -type solid solution is observed from 0 to 17 mole% $GdBr_3$. The lattice parameters increased as expected over this region and produced a 2.6% volume expansion of the unit cell (Table I). Between 20 and 45 mole% $GdBr_3$ a $PuBr_3$ -type phase prevailed. Anion substitution causes a 5.4% volume increase across the region.

From 45 to 50 mole% $GdBr_3$ a two-phase region was found. Beyond this region came a large $AlCl_3$ -type solid solution area which continued to pure $GdBr_3$, i.e., from 50 to 100 mole% $GdBr_3$.

A two-phase region was not observed between the $P6_3/m$ - and the $Cmcm$ -type structures. Mixtures of 10 and 15 mole% $GdBr_3$ exhibited only $P6_3/m$ symmetry, one mixture of the nominal composition 17 mole% $GdBr_3$ evidenced only the $P6_3/m$ structure; another of the same composition yielded only the $Cmcm$ structure. Mixtures of 20, 25, and 35 mole% $GdBr_3$ evidenced only the

$Cmcm$ structure. Thus if a two-phase region exists between the two structure types it must be exceedingly narrow. It is pre-

TABLE I
LATTICE PARAMETER DATA FOR THE MCl_3 - MBr_3 SYSTEMS FOR $M = Gd, Tb$, AND Yb

Composition	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	Ref ^a
$GdCl_3$	7.366(2)		4.106(1)		(23)
$P6_3/m$	7.366(9)		4.106(4)		
$GdCl_{2.49}Br_{0.51}$	7.455(1)		4.1134(4)		
$GdCl_{2.4}Br_{0.6}$	3.9033(9)	12.065(7)	8.652(4)		(21)
$GdCl_{1.8}Br_{1.2}$	3.923(2)	12.420(8)	8.813(9)		
$GdCl_{1.2}Br_{1.8}$	7.13(3)	12.40(5)	6.75(12)	110.9(2)	
$GdBr_3$	7.22(1)	12.52(2)	6.87(4)	110.7(1)	
$C2/m$	7.224(5)	12.512(5)	6.84(1)	110.6(2)	
$TbCl_3$	3.846(1)	11.766(5)	8.515(3)		(28)
$Cmcm$	3.847(2)	11.771(5)	8.516(4)		
$TbCl_{2.7}Br_{0.3}$	3.854(2)	11.85(1)	8.574(7)		
$TbCl_{0.9}Br_{2.1}$	7.10(2)	12.30(2)	6.65(1)	110.3(1)	
$TbBr_3$	7.167(3)	12.410(6)	6.829(3)	110.47(1)	
$C2/m$					(20)
$R\bar{3}$	7.159(4)		19.16(1)		
$YbCl_3$	6.738(2)	11.671(6)	6.383(4)	110.49(1)	(7)
$C2/m$	6.73	11.65	6.44	110.4	
$YbCl_{2.7}Br_{0.3}$	6.748(4)	11.693(9)	6.410(1)	110.38(1)	
$YbCl_{2.4}Br_{0.6}$	6.781(3)	11.755(6)	6.490(7)	110.34(1)	
$YbCl_{1.5}Br_{1.5}$	6.859(3)	11.882(4)	6.628(4)	110.05(4)	
$YbCl_{1.35}Br_{1.65}$	6.877(2)	11.910(4)	6.663(4)	109.98(4)	(20)
$YbCl_{0.9}Br_{2.1}$	6.902(5)		18.90(3)		
$YbCl_{0.6}Br_{2.4}$	6.94(1)		19.09(3)		
$YbBr_3$	6.973(5)		19.138(1)		
$R\bar{3}$	6.981(2)		19.115(6)		

^a This work, except as noted.

sumed that the reason for which apparently identical compositions can yield different structure types relates to slight differences in either composition or rate of cooling.

In the PuBr_3 structure (space group $Cmcm$) there are two anion sites; one fourfold (4c) and the other eightfold (8f) (25). Since cation-anion distances calculated for these anion sites with PuBr_3 coordinates (25) differ by only ~ 0.02 Å, it was thought that anion ordering might occur at the 1:2 or 2:1 anion compositions. Theoretical intensities were calculated with these coordinates for $\text{GdCl}_{1.8}\text{Br}_{1.2}$ with three models: one with random anion occupancy, one with the 4c site occupied by bromide ions, and the other with the 4c site occupied by chloride ions. In each of these latter cases the 8f site contained both chloride and bromide ions. These results are presented in Table II. Because of the diffuse nature of the reflections it is difficult, if not impossible, to decide among the three arrangements. But because in a diffuse spectrum the intensities of low-angle reflections can be determined more accurately than those of high angle reflections, it would seem that occupancy of the 4c site—the site with the shorter cation-anion distance—by only bromide ions can be rejected. Indeed, random occupancy would seem to be favored by the data. It is possible, but unlikely, that the coordinates in the mixed halide are altered such that none of the models chosen is representative of the specimen.

Reflection intensities of diffraction patterns for specimens with a Br/Cl ratio of 2, i.e., in the AlCl_3 solid solution region, could not be estimated with an accuracy sufficient to draw conclusions regarding anion distribution, and precluded a Rietveld structural analysis being effected on the powder.

The appearance of the PuBr_3 -type structure at 20 mole% tribromide is consistent with radius ratio considerations. Under normal pressure conditions the only lanthanoid trichloride to exhibit the PuBr_3 -type

structure is TbCl_3 with the (crystal) radius ratio, $r_a/r_c = 1.42$ (26, 27). At 20 mole% GdBr_3 a hypothetical radius ratio can be calculated as $[0.20(1.82) + 0.8(1.67)]/1.193$ and gives an essentially identical value, 1.42. Probably because internal pressure effectively decreases the Br^- anion size, this PuBr_3 -type region extends beyond what would be expected from simple radius ratio considerations.

The observed phase behavior correlates well with that found in the GdCl_3 - DyCl_3 system (1). This similar structure type system exhibited a UCl_3 -type solid solution, a two-phase region, and a PuBr_3 -type solid solution. At elevated temperatures the latter region converts to an AlCl_3 -type region. Thus identical phases are present in both systems. The differences are the absence of a two-phase region between the $P6_3/m$ and $Cmcm$ structures, the presence of a two-phase region between the $Cmcm$ and the

TABLE II

X-RAY POWDER DIFFRACTION INTENSITIES CALCULATED FOR 40 MOLE% GdBr_3 [$\text{GdCl}_{1.8}\text{Br}_{1.2}$] AS A PuBr_3 -TYPE STRUCTURE FOR RANDOM AND TWO ORDERED ANIONIC ARRANGEMENTS TOGETHER WITH OBSERVED AND CALCULATED INTERPLANAR SPACINGS

<i>h k l</i>	<i>d</i> spacing (Å)		Intensity			
	Obs	Calc	Obs	Rand	Cl4c	Br4c
0 2 0	6.194	6.210	s	78	100	48
0 0 2	4.411	4.406	m	30	20	43
0 2 2	3.593	3.594	w	23	27	16
1 1 1	3.440	3.443	m	28	33	21
1 1 2	2.854 ^a	2.852	vw	16	13	17
1 3 0		2.848		15	22	7
1 3 1	2.707	2.710	s	100	94	100
0 2 3	2.657	2.655	vw	23	26	19
0 4 2	2.537	2.538	vvw	29	38	17
1 1 3	2.313 ^a	2.310	s	56	75	32
1 3 3	2.043 ^a	2.045	w	26	30	32
1 5 1		2.042		26	34	16
2 0 0	1.962	1.962	m	19	21	16
0 6 2	1.874	1.874	vvw	22	22	20

Note. The designation "Rand" indicates a random arrangement, "Cl4c" indicates chloride ion occupancy of the 4c site, and "Br4c" indicates bromide ion occupancy of the 4c site. In each of these latter instances the 8f site contains both Cl^- and Br^- anions.

^a Indicates broad reflection.

$C2/m$ structures, and the fact that in the mixed trichloride system the $C2/m$ structure is observed only at elevated temperatures. The presence in the Br^- -containing system of the $C2/m$ structure at room temperature is the result of anion size effects. In this system the larger anion forces the cation to become 6-coordinate; in the chloride system thermal vibrations at elevated temperature increase the anion size and produce the same effect. Reasons for the two-phase region differences are more obscure, but must be the result of anion size constraints.

The TbCl_3 - TbBr_3 System

Pure TbCl_3 exhibited the expected PuBr_3 -type structure (26); lattice parameters are in excellent agreement with literature values (28). But TbBr_3 , on the other hand, produced a diffraction pattern whose intensities did not agree well with those expected for a $R\bar{3}$ FeCl_3 -type structure (20). In fact, the observed reflection positions and intensities match those reported for $C2/m$ GdBr_3 very closely (21). In the $R\bar{3}$ model the $(210)_R$ 3.123 and $(321, 123)_R$ 2.38 Å reflections calculate to be the most intense (20), but neither of these reflections is observed. Our TbBr_3 thus appears isostructural with GdBr_3 . Observed interplanar d spacings and intensities of TbBr_3 are compared in Table III with values calculated for a $C2/m$ structure. The coordinates reported for YCl_3 (29) were used for these calculations rather than those reported for GdBr_3 because the latter parameters were derived on the basis of spatial considerations, whereas the former were derived from a single crystal. The data in Table III reveal that two low-angle reflections (110) and $(\bar{1}11)$, whose intensities calculate to be 28 and 14, respectively, are not observed. A comparable situation prevails for GdBr_3 (21). Calculations effected with the spatially derived GdBr_3 coordinates indicate the intensity of these reflections to be 22 and 9 (rather than 28

and 14), respectively, but reflection (110) still should be observed and is not. The calculated $R\bar{3}$ powder diffraction pattern is, of course, almost identical to that reported for TmBr_3 in (20) and is not tabulated here. Since Tb^{3+} and Y^{3+} have approximately the same ionic radii (27), different positional parameters might be expected for different halides. Although most reflection positions can be accounted for on either the $R\bar{3}$ or the $C2/m$ models, the absence of the very strong 2.877 Å reflection in the $R\bar{3}$ model, as well as other intensity mismatches, favor the $C2/m$ model. Lattice parameters of the pure terbium phases are presented in Table I.

The mixed halide system consists of two solid solution regions. The first, PuBr_3 -type, extends from 0 to ~15 mole% TbBr_3 . The second, AlCl_3 -type, continues from ~30 to 100 mole% TbBr_3 . A two-phase region separates the $Cmcm$ and $C2/m$ -type solid solutions. The extended $C2/m$ solid solution region was expected; that symmetry is exhibited by the trichloride at elevated temperatures and by the tribromide at room temperature. Furthermore, in the mixed trichloride system, TbCl_3 - DyCl_3 , the high temperature $C2/m$ transition occurs at progressively lower temperatures as Dy content increases. Increasing the Dy content in that mixture increases the radius ratio, r_a/r_c , just as does addition of a larger anion. Thus the behavior of this system is consistent with that observed in the GdCl_3 - GdBr_3 and the TbCl_3 - DyCl_3 systems.

Mixed halide systems with 80 to 90 mole% TbBr_3 exhibited diffraction patterns identical to that of TbBr_3 . The 70 mole% TbBr_3 mixture yielded a pattern which included the missing (110) and $(\bar{1}11)$ reflections, but in all other respects was identical to the TbBr_3 pattern. This same pattern continued through the 40 mole% TbBr_3 composition. Interplanar d spacings and intensities for the 70 mole% TbBr_3 phase are also presented in Table III.

TABLE III

OBSERVED INTERPLANAR d SPACINGS AND INTENSITIES FOR TbBr_3 AND $\text{TbBr}_{2.1}\text{Cl}_{0.9}$ COMPARED WITH THOSE CALCULATED FOR A $C2/m$ STRUCTURE WITH POSITIONAL PARAMETERS FROM (29)

TbBr_3					$\text{TbBr}_{2.1}\text{Cl}_{0.9}$				
Obs		Calc ^a		$h\ k\ l$	Obs		Calc ^a		
d value (Å)	I	d value (Å)	I		d value (Å)	I	d value (Å)	I	
6.404	s	6.398	39	0 0 1	6.280	s	6.240	52	
6.205	w	6.205	13	0 2 0	6.132	w	6.150	5	
—	—	5.906	28	1 1 0	5.837	m	5.857	28	
—	—	5.211	14	1 1 1	5.138	m	5.121	20	
—	—	—	—	0 2 1	4.369	w	4.380	5	
3.529	m	3.522	26	$\begin{Bmatrix} 1\ 3\ 0 \\ 2\ 0\ 1 \end{Bmatrix}$	3.490	ms	$\begin{Bmatrix} 3.491 \\ 3.483 \end{Bmatrix}$	$\begin{matrix} 16 \\ 14 \end{matrix}$	
3.352	w	3.356	8	1 3 1	3.310	w	3.315	2	
3.208	w	3.199	2	0 0 2	—	—	—	—	
2.877	vs	2.871	100	$\begin{Bmatrix} 1\ 3\ 1 \\ 2\ 0\ 2 \end{Bmatrix}$	2.838 ^b	vs	$\begin{Bmatrix} 2.834 \\ 2.817 \end{Bmatrix}$	$\begin{matrix} 66 \\ 34 \end{matrix}$	
2.626	vvw	2.619	10	1 3 2	2.570	w	2.570	8	
2.136	vvw	2.177	11	$\begin{Bmatrix} 1\ 3\ 2 \\ 2\ 0\ 3 \end{Bmatrix}$					
2.068	m	2.068	37	$\begin{Bmatrix} 3\ 3\ 1 \\ 0\ 6\ 0 \end{Bmatrix}$	2.049	s	2.050	41	
1.991	w	1.994	36	$\begin{Bmatrix} 2\ 0\ 2 \\ 1\ 3\ 3 \end{Bmatrix}$	1.963	vvw	1.962	10	
1.968	vw	1.968	14	$\begin{Bmatrix} 3\ 3\ 0 \\ 3\ 3\ 2 \\ 0\ 6\ 1 \end{Bmatrix}$	1.947	w	$\begin{Bmatrix} 1.949 \\ 1.952 \\ 1.943 \\ 1.948 \end{Bmatrix}$	$\begin{matrix} 23 \\ 9 \\ 4 \\ 6 \end{matrix}$	
1.784	vw	$\begin{Bmatrix} 1.784 \\ 1.782 \end{Bmatrix}$	$\begin{matrix} 5 \\ 2 \end{matrix}$	$\begin{Bmatrix} 4\ 0\ 1 \\ 2\ 6\ 1 \end{Bmatrix}$	1.763	vvw	$\begin{Bmatrix} 1.769 \\ 1.767 \end{Bmatrix}$	$\begin{matrix} 1 \\ 5 \end{matrix}$	
1.736	vvw	1.736	1	$\begin{Bmatrix} 3\ 3\ 1 \\ 3\ 3\ 3 \\ 0\ 6\ 2 \end{Bmatrix}$					
1.721	vvw	1.721	2	3 5 1					
1.679	w	1.678	19	$\begin{Bmatrix} 1\ 1\ 4 \\ 4\ 0\ 0 \\ 2\ 6\ 2 \end{Bmatrix}$	1.661	m	$\begin{Bmatrix} 1.665 \\ 1.657 \end{Bmatrix}$	$\begin{matrix} 6 \\ 15 \end{matrix}$	
1.600	vw	1.599	6	0 0 4					

Note. Intensities for $\text{TbBr}_{2.1}\text{Cl}_{0.9}$ were calculated with an ordered arrangement as is described in the text.

^a Except where observed, reflections with $I < 10$ are omitted.

^b Two close reflections.

Intensity calculations were effected by using the spatially determined coordinates (21) for two ordered and one random anion arrangement. As might be expected from cation-anion distance constraints, the ordered arrangement in which the Cl anions occupy only the 4i site in space group $C2/m$

could be rejected. The arrangement in which the Cl anions occupy both sites randomly or occupy only the 8j site matched observed intensities relatively well, with the ordered arrangement matching somewhat more closely. The halide anions are thus assumed to be ordered at this composi-

tion, and intensities for the ordered arrangement are reported.

The reason for the abrupt appearance of the two expected, but absent, reflections at the 70 mole% composition is not apparent. The diffuse nature of the reflections causes uncertainty in the interpretation of the data and it appears that an exact structural refinement will be necessary to clarify the problem definitively.

The YbCl_3 – YbBr_3 System

Pure YbCl_3 exhibited the reported AlCl_3 ($C2/m$)-type (7) and pure YbBr_3 the expected FeCl_3 ($R\bar{3}$)-type (20) structure. The lattice parameters observed for YbBr_3 differed slightly from literature values, but cell volumes are identical. This level of parameter deviation is characteristic of that observed when different individuals read the same Guinier film.

The observed phase behavior is similar to that of other mixed halide systems. From 0 to 60 mole% YbBr_3 a solid solution of $C2/m$ symmetry prevails. From 70 to 100 mole% a FeCl_3 -type solid solution exists. A two-phase region which spans the composition range 60 to 70 mole% YbBr_3 separates these solid solution areas. There is no comparable mixed lanthanoid(III) chloride system to which this one can be compared as there was with the other mixed chloride–bromide systems.

Within the lanthanoid(III) species it is difficult to identify a precise radius ratio at which the $C2/m$ phase region should terminate because LuCl_3 exhibits the $C2/m$ structure while the much smaller ScCl_3 exhibits the $R\bar{3}$ structure. From an examination of the lanthanoid(III) tribromides, however, one can determine a "starting point" of the $R\bar{3}$ structure. If it is assumed that the $R\bar{3}$ structure appears first at DyBr_3 , as our TbBr_3 data lead us to believe, then the radius ratio (27) at which this phase appears is $r_a/r_{\text{Dy}^{3+}} = 1.73$. A hypothetical radius ratio computed as $[0.70(1.82) + 0.30(1.67)] \text{ \AA}$

for the 70 mole% bromide composition yields $r_a/r_{\text{Yb}^{3+}} = 1.76$, reasonably consistent with the observed value when one considers that due to parameter adjustment and polarization the mixed anions will not pack as ideally as would a common anion.

In the $C2/m$ structure the halogen atoms occupy two nonequivalent positions (29), one fourfold and the other eightfold. The fourfold anion is surrounded by two equidistant ($\sim 2.6 \text{ \AA}$) cations and three anions in a distorted trigonal bipyramid, whereas the eightfold ion is surrounded by one cation at $\sim 2.5 \text{ \AA}$, a second cation at $\sim 2.6 \text{ \AA}$, and one anion in a trigonal arrangement. Thus, again three structural models are possible: the bromide ion could preferentially occupy either the fourfold (4i) or, less likely because of distance constraints, the eightfold (8j) site, or could occupy both sites ran-

TABLE IV
MILLER INDICES AND OBSERVED X-RAY POWDER
DIFFRACTION INTENSITIES FOR 45, 50, AND 55
MOLE% YbBr_3 MIXED YTTERBIUM
TRICHLORIDE–YTTERBIUM TRIBROMIDE SPECIMENS
COMPARED WITH VALUES CALCULATED FOR A $C2/m$
STRUCTURE WITH POSITIONAL PARAMETERS
FROM (21)

<i>h k l</i>	Observed intensity mole% YbBr_3			Calculated intensity		
	45	50	55	Rand	Br4i	Cl4i
0 0 1	s	s	vs	96	87	89
0 2 0	w	m	m ⁺	19	7	36
1 1 0	m	m ⁺	m [−]	46	50	40
$\bar{1}$ 1 1	m ⁺	m	s	25	48	9
0 2 1	w [−]	w	m	12	10	14
$\bar{1}$ 1 1	vvw	vw	w	15	6	26
$\bar{2}$ 2 2	vvw	w	vw	5	2	10
$\bar{2}$ 4 0						
$\bar{1}$ 5 1	vw	w	w	6	12	4

Note. The designation "Rand" indicates a random arrangement, "Cl4i" indicates the 4i site is occupied only by chloride ions, and "Br4i" indicates that 4i site is occupied only by bromide ions. In each of these latter instances the 8j site is occupied by both ions.

domly. The observed intensities of the first six and two other reflections for the 45, 50, and 55 mole% tribromide mixtures are compared in Table IV with those calculated for $\text{YbCl}_{1.5}\text{Br}_{1.5}$ with the positional parameters reported in (21). For these calculations the thermal parameters were varied by approximately 30%, but the calculated intensities remained essentially constant. Intensities were also calculated with the positional parameters reported in (29) and with the values reported by Wyckoff (30). Although the calculated intensities are very sensitive to positional parameter changes, the results are the same in all cases. The data rule out the ordered arrangement of chloride ion occupancy of the 4i site; reflection ($\bar{1}11$) calculates far too weak and ($\bar{2}22$) too intense. The calculated difference between (110) and ($\bar{1}11$) and the intensity of ($\bar{1}11$) rule out the random arrangement. Consistent with cation-anion distance constraints, only the ordered arrangement of bromide ion occupancy of the 4i site satisfies the observed intensities. However, an aura of uncertainty must remain because intensity is very sensitive to positional parameter variation.

In the $R\bar{3}$ region symmetry requirements dictate that the anions be arranged randomly.

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