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An X-Ray Powder Diffraction Study of the $YbCl_2$–YbI_2 System

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The $YbCl_2$–YbI_2 system has been investigated over the entire composition range by examining at room temperature both slowly cooled and quenched fused samples of the reactants. The system may be described in terms of mole% YbI_2, Y, as follows: for $Y = \sim 85$ to 100, a YbI_2 (CdI_2-type) solid solution region prevails; for $Y = \sim 55$ to ~ 85, "$YbCl_{0.3}I_{1.7}$," $YbCl_2$, and 6R-"$YbCl_{0.5}I_{1.5}$" are found; for $Y = 10$ to ~ 55, the $YbCl_2$ and 6R-"$YbCl_{0.5}I_{1.5}$" phases coexist; and for $Y = 0$ to 10, a $YbCl_2$ solid solution region is found. The unusual behavior of the system is discussed and compared with that of related systems.

Introduction

Numerous studies of mixed halide systems of divalent elements such as Eu, Pb, and the alkaline earths, Sr and Ba (*1–7*) have pointed out some general principles which typically describe the behavior of 9-coordinate cation systems (*8*). However, mixed chloride–bromide systems of Ca and Yb, unlike their larger divalent congeners, exhibit only solid solutions without discrete mixed anion phase formation (*7, 8*). Although their 8-coordinate ionic radic differ by only 0.02 Å, $YbCl_2$ exhibits the SrI_2- and $CaCl_2$ the pseudorutile ($CaCl_2$-) type structure (*7, 9, 10*). The CdI_2-type structure is common to both iodides (*7, 11*). *Ln*ClI·*n*THF phases for *Ln* = Yb, EU, and Sm have been hypothesized to be the by-product of an organometallic reaction, but have not been characterized either by chemical or physical means (*12*).

The compounds $CaCl_2$ and CaI_2 exhibit only minimal solubility in each other; a two-phase region prevails between the compositions $CaCl_{1.95}I_{0.05}$ and $CaCl_{0.10}I_{1.90}$. From ionic radii considerations and the similarities between the chloride–bromide systems $YbCl_2$ and YbI_2 would be expected to be immiscible. However, in view of the differences between the chloride structures, the previous observation that chloride–iodide systems are frequently more phase rich than chloride–bromide systems (*8*), and the absence of reported high-pressure polytypes for the ytterbium halides which might serve as a guide to mixed-halide behavior, a phase study of the title system was deemed of potential interest.

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Experimental

Ytterbium(III) chloride was prepared from the oxide by the HCl–NH_4Cl route. A 6× molar excess of NH_4Cl was added to oxide dissolved in HCl. The dried mixture was confined in Pyrex and heated slowly under vacuum over a 2-day period to ~400°C to remove first the coordinated water and then to decompose the resulting $(NH_4)_3YbCl_6$ (*13, 14*). Ytterbium dichloride was prepared by reduction of $YbCl_3$(s) with Yb(s). The reactants were confined either in evacuated, outgassed quartz ampoules or tantalum tubes which were welded under an Ar atmosphere and then heated slowly to 900°C. Ytterbium diiodide was prepared by reaction of metal and excess HgI_2 confined in an evacuated Pyrex ampoule for 7 days at 365°C (*8, 15*). All manipulations of reactants and products were effected in a glove box whose Ar atmosphere was purged continuously of water (molecular sieves) and oxygen (heated BASF catalyst).

Mixed halide samples were prepared by grinding in an agate mortar the appropriate stoichiometric quantities such that the pulverized specimens had a mass of about 1 g. Some specimens were placed in pyrolytic graphite boats which were then situated in previously outgassed quartz boats to ensure physical stability. The mixture was transferred to the quartz heating assembly with a transfer apparatus designed to keep the sample blanketed with Ar. The mixture, maintained at $<10^{-5}$ Torr in a dynamically pumped vacuum, was heated with a tubular furnace to ~780°C so that the melting point of at least one reactant was exceeded (*16*). Other specimens were sealed in previously outgassed quartz ampoules, pressurized to atmospheric pressure with Ar, melted with a hand torch, and then quenched.

The reaction products were transferred under dry Ar to the glove box and after grinding in an agate mortar, were analyzed by X-ray diffraction with Cu*Kα* ($\lambda\alpha_1$ = 1.5405 Å) radiation in a 114.59-mm Guinier–Haegg camera evacuated to $\sim 10^{-3}$ Torr. NBS certified Si [a_0 = 5.43082(3) Å] served as an internal standard. Samples were placed on Scotch tape-backed planchets which were covered first with paraffin oil maintained over Na and then with wafers of borosilicate glass broken from thin glass bubbles to protect them from hydration or hydrolysis during transfer to the camera. Film measurements were effected with a Charles Supper reader; intensities were estimated visually and recorded on a scale of 1 to 100. One 40 mole% YbI_2 specimen which oxidized slightly during exposure was examined on a Philips APD 3720 diffractometer system equipped with a sample spinner and θ-compensating slit. These data were corrected for the θ-compensating slit by multiplying the observed intensity by the factor, $1/\sin\theta$.

Lattice parameters were determined and refined by the programs TREOR (*17*) and LATCON (*18*); calculations were effected on a VAX 11/750 computer. X-ray powder diffraction intensities were calculated with the program POWD12 (*19*). In an effort to confirm the polytype composition, reflection intensities were calculated for 25, 50, 75, 80, 85, and 100 mole% iodide concentrations and at each iodide concentration with anion z parameters of 0.245, 0.25, 0.255, and 0.26 (position 6c, space group $R\bar{3}m$). For these calculations the following isotropic thermal parameters were used: Yb, 1.0; I, 1.25; and Cl, 1.50. An absorption correction was not included in the calculations; a correction for the incident/diffracted beam monochromator was included.

Results

The data are presented schematically in Fig. 1. A CdI_2-type solid solution region was found only over the composition range 100 to ~85 mole% YbI_2. Specimens with

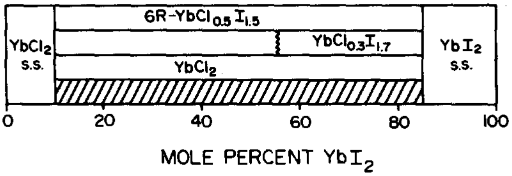

FIG. 1. A schematic representation of the $YbCl_2$–YbI_2 system. The cross-hatched area represents the multiphase region; the bands indicate the region over which the various phases are observed.

compositions between ~85 and ~55 mole% iodide exhibited in addition to the YbI_2-type "$YbCl_{0.3}I_{1.7}$," two identifiable phases, $YbCl_2$ and a YbI_2-type polytype designated 6R-"YbClI," as is described in the succeeding paragraph, and of the probable composition, $YbCl_{0.5}I_{1.5}$. From ~55 to 10 mole% iodide 6R-"YbClI" and $YbCl_2$ were observed, and from 10 to 0 mole% iodide, a $YbCl_2$-type solid solution region was apparent. Lattice parameter data for all observed phases are presented in Table I together with volume/cation data of the YbI_2 and the 6R polytype phases and literature values for the parent phases.

X-Ray diffraction reflections which could not be assigned to either $YbCl_2$, 2H-YbI_2, or any known oxide, oxide–halide, or halide–hydrate were always present for iodide mole% concentrations of greater than 10 and less than 90. Even though numerous synthetic procedures were utilized, neither a composition nor preparatory procedure that would yield a phase which exhibited only the extra reflections could be found. Since polytypism is characteristic of the layered CdI_2-type structure, an attempt was made to assign these reflections to a YbI_2-polytype (*20*).

Reflections which could be assigned to either YbI_2 or $YbCl_2$ were deleted from the

TABLE I

LATTICE PARAMETERS AND VOLUME/CATION DATA AT SELECTED COMPOSITIONS IN THE $YbCl_2$–YbI_2 SYSTEM

Mole% YbI_2	Phase(s) observed	Lattice parameters (Å) *a*	*b*	*c*	Volume/cation (Å^3)	Ref.[a]
0	$YbCl_2$	13.148(4)	6.955(3)	6.698(2)		
		13.14(1)	6.948(9)	6.698(9)		(*10*)
10	$YbCl_2$	13.166(5)	6.966(2)	6.703(2)		
40	$YbCl_2$[b]	13.175(3)	6.961(1)	6.702(2)		
	"YbClI"[b]	4.449(1)		20.828(9)	59.50	
	"YbClI"	4.456(1)		20.81(1)	59.64	
50	$YbCl_2$	13.167(3)	6.956(2)	6.702(2)		
	"YbClI"	4.455(2)		20.870(5)	59.78	
	$YbCl_2$	13.168(6)	6.962(3)	6.703(3)		
60	"YbClI"	4.453(2)		20.861(8)	59.70	
	YbI_2	4.453(2)		6.957(4)	59.75	
75	YbI_2	4.457(5)		6.96(1)	59.9	
80	YbI_2	4.463(3)		6.97(1)	60.1	
90	YbI_2	4.494(2)		6.963(5)	60.89	
100	YbI_2	4.508(2)		6.974(3)	61.35	
		4.503(3)		6.972(4)	61.20	(*11*)

Note. Observed structure types are: $YbCl_2$ (*Pbca*), YbI_2 ($P\bar{3}m1$), and 6R-"YbClI" ($R\bar{3}m$).

[a] This work except as noted.

[b] Sample quenched by being plunged into cold water.

TABLE II

Observed (40 mole% Iodide Specimen) and Calculated Interplanar d-Spacings and Intensity Data Assignable to 6R-"YbClI"

			I_o		I_{calc} for given mole% I					
					$z = 0.25$			$z = 0.255$		
d_o (Å)	d_c (Å)	$h\ k\ l$	C	D	75	80	85	75	80	85
6.936	6.943	0 0 3	~60[a]	100[b]	42	40	38	53	51	49
3.786	3.789	1 0 1	30	37	34	32	31	31	30	29
3.611	3.614	0 1 2	5	—	1	2	3	1	2	3
3.096	3.097	1 0 4	100	80	100	100	100	100	100	100
2.825	2.828	0 1 5	15	19	17	16	15	11	11	10
2.315	2.314	0 0 9	3	38[a]	3	3	3	2	1	1
2.224	2.224	1 1 0	45	30	42	42	42	42	42	42
2.157	2.157	0 1 8	30	34	38	38	38	37	37	37
2.118	2.118	1 1 3	20br	22	16	15	15	20	19	18
1.922[c]	1.918	0 2 1	7	—	6	6	6	6	5	5
1.8066	1.8068	0 2 4	25	18	23	23	23	23	23	23
1.7498	1.7485	2 0 5	3	—	5	4	4	3	3	3
—	1.6993	0 1 11	1	—	4	4	4	8	8	8
1.5477	1.5486	2 0 8	~5	12	14	15	15	14	14	14

Note. Calculated intensity data are presented for 75, 80, and 85 mole% iodide compositions and for two anion z parameters. C indicates Guinier camera and D diffractometer data.

[a] Reflections with $d < 1.8066$ are diffuse; intensity measurements are difficult.

[b] Reflection intensities enhanced by preferred-orientation effects.

[c] Reflection overlapped Si standard; intensity measured on film without Si.

reflection list. The remaining reflections were analyzed by the program TREOR (*17*). Three solutions were obtained, one each in tetragonal, hexagonal and orthorhombic symmetry. The orthorhombic solution with lattice parameters suggestive of a higher symmetry system had the lowest figure of merit (*21*). It was not considered further. The tetragonal and hexagonal solutions were transformable into each other. The hexagonal solution yielded a figure of merit of 26 with $a = 4.449(1)$ and $c = 20.829(9)$ Å.

The X-ray intensity calculations on the 6R polytype indicated that the 25, 50, and 100% models could be rejected. For the 100% model the (003) and (101) reflections calculated less intense than either the (110) or (018) reflections. For the 50% model the observed (012) reflection calculates to be extinct. Intensities calculated for the 25% model for the reflection pairs, (003) and (110) and (101) and (018), which have comparable observed intensities, differ for this model by a factor of >1.5.

The reflections (003), (015), (113), and (01 11) are particularly sensitive to the anion z parameter with calculated intensities varying by a factor of 2 to 3 for a z parameter change from 0.24 to 0.26. Since these values correspond to Yb–I distances of about 2.99 and 3.22 Å, respectively, such intensity changes for selected reflections are not surprising and do permit an estimate of both composition and anion parameter to be made. Results for the remaining models are presented in Table II.

Discussion

The volume/cation data (Table I) support the hypothesis that the two phases, 2H-

YbI_2 and 6R-"YbClI," are essentially identical as would be expected for polytypism, but not for discrete phases. Reflections ultimately assigned to the polytype were found initially to be always present with two other phases, in apparent violation of phase rule considerations when the composition range was greater than ~55 and less than ~85 mole% iodide. However, if the extra phase is a polytype of essentially the same stability as the hexagonal phase, it is easy to understand why the structures coexist. The stability of the 2H form must increase with increasing iodide content, though, since that form becomes the stable phase.

The polytype parameters are close to those reported for 6H and 6R PbI_2 polytypes ($a = 4.557$, $c = 20.937$ Å), even though the Pb^{2+} ion is ~15% larger than the Yb^{2+} ion (*9*, *22*). To determine if any other PbI_2 polytype structure would satisfy the ytterbium mixed-halide data, X-ray powder intensity calculations were effected with the positional parameters and space groups reported by Wyckoff (*22*) for 6H, 4H, and 12R polytypes. Calculated intensities for the 6H modification indicated the strongest reflection to be (013) ($d = 3.374$ Å), an unobserved reflection. The 12R and 4H models could also be rejected because in each case reflections calculated to be intense were unobserved. The 6R ($R\bar{3}m$) model reproduced the observed positional distribution satisfactorily. In this modification (hexagonal setting) with the cation located in position $3a$ (0, 0, 0), and the anion in position $6c \pm (0, 0, z)$, a random anion distribution must be assumed. Comparison of the 0.245, 0.25, and 0.26 z parameter data for the 75, 80, and 85 mole% iodide calculations favors the value of $z = 0.25$, or a slightly refined value of 0.252. At this z value compositions which range between 75 and 85 mole% fit the observed data almost equally well.

The chloride ion content of the polytype could not be determined directly since the phase could not be prepared in pure form, but was assumed to be approximately 75 mole% iodide for the following reasons:

(a) The composition must be equal to or less than the solubility limit, ~85 mole% iodide.

(b) The polytype volume/cation decreases slightly below that of 80 mole% composition and then remains constant within experimental error.

(c) The 75 and 80 mole% iodide X-ray intensity calculations yield good, but not definitive, agreement with the observed results.

(d) Since it becomes the final stable phase over the entire two-phase region, it must have a slightly lower iodide content than does the 2H form.

The principal reason for the less than desirable intensity agreement between the diffractometer and Guinier data is preferred orientation. Reflections (003) and (009), for example, were observed to be significantly more intense in the diffractometer data than either the calculations or the Guinier data suggested they should be. This effect arises primarily because while the Guinier technique requires only a few sample particles dusted onto tape, the diffractometer specimen must be relatively thick and compact, yielding preferred orientation.

The $YbCl_{0.3}I_{1.7}$ (85 mole%) composition was established in the following manner. The most intense polytype reflection could be observed readily in the X-ray diffraction pattern of the 80, but not the 90, mole% specimen. The most intense $YbCl_2$ reflection was barely visible in an overexposed X-ray pattern of the 90 mole% material and clearly present (along with a second reflection) in a pattern of an 80 mole% specimen. These observations suggest a 90 mole% solubility limit. On the other hand, the cell volume data (Table II) support a solubility limit closer to 80 mole%. Since it is possible that the $YbCl_2$ reflection from the 90 mole% specimen resulted from incomplete fusion, the solubility limit was estimated to be 85 mole%.

The observation that the rapidly quenched 40 mole% iodide specimen is slightly more chloride rich, as indicated by the lattice parameters, than is the slowly cooled sample is taken as an indication that the high temperature chloride ion solubility is greater than the room temperature solubility. Such an increase would be expected since thermal vibrations would tend to decrease size difference effects.

It is interesting to consider whether polytypism is characteristic of other mixed chloride–iodide systems. It has not been observed in the Sr–Cl–I, Eu–Cl–I, or Sn–Cl–I systems (*6, 23*), all of which exhibit variants of the $PbCl_2$-type structure. However, none of these systems has a CdI_2-type parent phase. This structure is exhibited by diiodides of first row transition elements and Mg, Ca, Ge, and Pb, among others (*24*). The Pb–Cl–I system has been examined twice; both reports confirm that PbClI exhibits the $PbCl_2$-type structure, with two-phase regions separating PbClI from both parent phases (*5, 25*). However, PbI_2 polytype stabilities differ from those of YbI_2. Both the 2H and the 4H forms of PbI_2 have been reported, based upon experimental results, to be the thermodynamically stable room temperature variant (*5, 26*). It is argued that impurities stabilize the 4H modification of PbI_2 (*26*). For YbI_2 the 2H modification appears to be the only stable form, and it is evident from this work that impurities stabilize the higher polytype of YbI_2 (*11*). As has been indicated, the ionic radius of Pb^{2+} is significantly larger than that of Yb^{2+}, and as such, comparisons between these systems may not be meaningful.

Although the ionic radius of calcium is almost identical to that of ytterbium, 1.14 Å vs 1.16 Å, the chloride and iodide are almost immiscible (*7, 9*). Another factor such as difference in hardness (acidity) of the cations must enter into consideration when mixed halide systems are considered. The ionic radius of Cd^{2+} is about 6% less than that of Yb^{2+} (1.09 Å vs 1.16 Å), both ions have *d*-electrons and thus might be expected to behave more closely than do ytterbium and calcium. $CdI_{(2-x)}Cl_x$ phases grown by vapor deposition exhibit principally 4H and 12R polytypes (*27*). Other CdI_2-type mixed-halides may form polytypes, but no other definitive study could be found.

In the cadmium mixed-halide system the presence of the smaller anion was postulated to cause the anion layers to rotate. This rotation generated the polytypism and is consistent with the hypothesis that an impurity ion helps to stabilize polytypes (*26, 27*). If such a mechanism prevails in the present situation, the anions may be in an ordered rather than random arrangement as has been assumed. Such ordering, which would lower the symmetry of the 6R modification, could only be characterized with a complete structural study.

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