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# Synthesis of $YbBr_2$ and $YbCl_2$ and an X-Ray Diffraction Study of the System $YbBr_2$–$YbCl_2$

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Ytterbium dichloride was prepared in pure form by the oxidation of elemental ytterbium by $ZnCl_2$ with subsequent removal of the zinc impurities by sublimation. Ytterbium dibromide in the orthorhombic $SrI_2$-type structural form was prepared in a sealed tantalum container by reduction of the tribromide with elemental ytterbium at a temperature not exceeding 960°C for 15 min. The dihalides, mixed intimately in appropriate molar ratios in a glove-box and contained in pyrolytic graphite boats, were melted under vacuum. These two halides form a solid solution with the $SrI_2$-type structure. Lattice parameters are reported as a function of composition. © 1987 Academic Press, Inc.

## Introduction

Recent investigations of europium(II)-, strontium-, and barium-mixed halide systems (*1–6*) have indicated that:

(1) if a structure contains two different sized anion sites, the larger anion will preferentially occupy the larger site to produce anion ordering;

(2) if the mixed halide system exhibits a structure type different from that of the parent phases, it is usually characteristic of the high pressure form of one of the parent species;

(3) the nine-coordinate $PbCl_2$-type structure is frequently one of the structure types observed when larger cations are involved;

(4) bromide–iodide systems are usually more phase-rich than either chloride–bromide or chloride–iodide systems.

With this background in mind a study of ytterbium mixed halide systems was deemed to be of special interest because the ionic radius of Yb(II), while relatively close to that of Ca(II), 1.14 (CN8) vs 1.12 Å (CN8), respectively, is significantly different from that of Eu(II), 1.25 Å (CN8). Furthermore, in the system $CaCl_2$–$CaBr_2$ only the $CaCl_2$ pseudorutile-type structure prevailed even though at high pressure $CaCl_2$ exhibits a $SrI_2$-type structure and $CaBr_2$ an $\alpha$-$PbO_2$-type structure (*7, 8*). Thus the behavior of the ytterbium(II) mixed halide system might be expected to differ from those of the lighter lanthanides and be more closely related to that of calcium.

Further complexity might be expected for this system because ytterbium dibromide is reported to exhibit four temperature-dependent structure types (*9, 10*). Listed in order of the reported increasing temperature of formation these structure types are: $SrI_2$ (<207°C); $\alpha$-$PbO_2$ (<267°C); $CaCl_2$ (<447°C), and rutile (<477°C).

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## Experimental

Ytterbium(II) chloride was prepared by two procedures. The first procedure was unique to $YbCl_2$; the second, a conventional procedure, was used for both $YbCl_2$ and $YbBr_2$. In the first procedure elemental ytterbium (99.9%, Research Chemicals, Phoenix, AZ) was oxidized by $ZnCl_2$ according to the equation

$$Yb(s) + ZnCl_2(l) \rightarrow YbCl_2(s) + Zn(g). \quad (1)$$

The reaction was carried out in a quartz tube outgassed previously by heating to 1000°C in high vacuum. Small pieces of ytterbium and approximately two times the molar amount of $ZnCl_2$ required according to (1), previously sublimed and maintained in a glove-box whose Ar atmosphere was continuously circulated through a molecular sieve drying tower, were sealed under high vacuum. The tube was heated at 550°C for 12 hr, then slowly removed from the furnace over the course of a day to effect partial separation of the Zn and $ZnCl_2$. The partially purified product was removed from the quartz tube in the glove-box, placed in a pyrolytic graphite boat, and was transferred under a blanket of argon to a tube furnace. It was heated at 540°C for 15 min to remove excess Zn and $ZnCl_2$. Preparation of $YbBr_2$ by the same procedure was attempted with $ZnBr_2$ being substituted for $ZnCl_2$.

In the second procedure the trihalide prepared either by reaction of the metal with $HgX_2$ (*11*) or by reaction of the oxide with $HX$ and $NH_4X$ (*12*) was confined in welded tantalum containers with the stoichiometric amount of Yb metal required for reduction to the dihalide. It was heated by induction in different experiments at temperatures up to 1000°C for the chloride and 1040°C for the bromide, maintained at temperatures for about 15 min, then quenched. The containers were opened in the glove-box and the samples were stored in carefully outgassed screw cap vials until use.

The mixed halide samples were prepared by grinding in the glove-box in an agate mortar, the appropriate stoichiometric quantities such that the pulverized specimen had a mass of about 1 g. These were placed in pyrolytic graphite boats which were then situated in either previously heated quartz or alundum boats to ensure physical stability. The mixture was transferred to the quartz heating assembly with a transfer apparatus designed to ensure that the sample remained blanketed with Ar. The mixture, maintained under a $10^{-5}$ Torr dynamically pumped vacuum, was heated with a tubular furnace so that the temperature exceeded the melting point of at least one, and sometimes both, of the reactants. It was quenched by removing the heating tube from the furnace.

To check for potential loss of one reactant during heating, the 50 and one of the 25 mole percent $YbBr_2$ mixtures were given special treatment. The quartz heating assembly was dynamically evacuated to $2 \times 10^{-8}$ Torr, the tube furnace was preheated to 650°C, and then, over the course of a 5-min period, the sample was heated to above the melting temperature. The sample was removed from the furnace and quenched; when the furnace temperature had cooled to ~600°C, the sample was reinserted to permit annealing as the furnace cooled slowly to room temperature over the course of 12 hr.

The reaction products were transferred under a blanket of dry argon to the glove-box where they were ground in an agate mortar and subjected to X-ray diffraction analysis with CuK$\alpha$ ($\lambda\alpha_1 = 1.5405$ Å) radiation in a Guinier-Haegg camera evacuated to $\sim 10^{-3}$ Torr. NBS certified Si [$a_0 = 5.43082(3)$ Å] was mixed with the specimens in the glove-box, and the 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 a thin glass bubble to protect the specimens from oxidation or hydrolysis during transfer to the camera. Film measurements were effected with a Charles Supper reader; intensities were estimated visually.

To check for anion ordering X-ray powder diffraction intensity calculations were effected with the program POWD12 (*13*) for the 25, 55, and 75 mole percent bromide specimens. In these calculations the atomic positions and isotropic thermal parameters reported for $YbCl_2$ (*14*) were used together with the polynomial scattering factors integral to the program (*13*) and the lattice parameters derived in this work. The 75 mole percent $YbBr_2$ calculations were also performed with atomic and thermal parameters derived for $DyBr_2$ (*10*), since such parameters should more closely approximate those of $YbBr_2$. Neither a dispersion nor an absorption correction was applied in these calculations, but the effect of the incident beam monochromater was considered. Three structural arrangements were considered:

(1) random occupancy of the anion sites by both ions,

(2) the bromide ion preferentially in the tetrahedral site, and

(3) the bromide ion preferentially in the trigonal site.

In the 55 and 75 mole percent calculations, preferential site occupancy means that the designated site is completely occupied by bromide ions; the other site is partially occupied by bromide ions.

## Results and Discussion

The synthesis of $YbCl_2$ according to Eq. (1) yielded a product pure by X-ray diffraction in 90% yield. The lattice parameters of the orthorhombic $SrI_2$-type $YbCl_2$ listed in Table I are in good agreement with literature values (*15*).

TABLE I

LATTICE PARAMETERS AND VOLUME FOR THE $YbBr_2$–$YbCl_2$ SYSTEM

| Mole percent $YbBr_2$ | *a* | *b* | *c* | Volume | Ref. |
|---|---|---|---|---|---|
| 0 | 13.1578(7) | 6.960(3) | 6.708(3)Å | 614.18Å$^3$ | |
| | 13.150 | 6.942 | 6.693 | | (*15*) |
| 25 | 13.316(8) | 7.045(5) | 6.759(8) | 634.07 | |
| | 13.332(8) | 7.047(3) | 6.749(4) | 634.07* | |
| 50 | 13.500(4) | 7.136(2) | 6.809(1) | 655.95* | |
| 55 | 13.547(9) | 7.178(5) | 6.882(5) | 669.16 | |
| 65 | 13.579(9) | 7.213(5) | 6.944(6) | 679.94 | |
| 75 | 13.630(7) | 7.255(4) | 6.998(5) | 691.85 | |
| 85 | 13.708(10) | 7.330(7) | 7.063(4) | 709.59 | |
| 95 | 13.764(7) | 7.336(5) | 7.073(4) | 714.08 | |
| 100 | 13.797(7) | 7.361(3) | 7.092(3) | 720.26 | |
| | 13.786(2) | 7.357(2) | 7.087(2) | | (*10*) |

*Note*. The * indicates preparations effected under conditions of $10^{-8}$ Torr vacuum and minimum time at temperature. The numbers in parentheses indicate the standard deviation of the least significant digits.

Attempts to synthesize $YbBr_2$ by oxidation of Yb with $ZnBr_2$ were unsuccessful. Regardless of the precautions taken in purifying the reagents and outgassing the quartz reaction vessel, the X-ray diffraction pattern of the product evidenced a few weak reflections assignable to YbOBr along with reflections assignable to $CaCl_2$-type $YbBr_2$ and a few reflections assignable to $SrI_2$-type $YbBr_2$. It is presumed that the YbOBr results from the molten $YbBr_2$–$ZnBr_2$ mixture attacking the quartz container. This synthesis procedure for $YbCl_2$ is related to, but is much less complicated than, that of DeKoch and Radtke (*16*). In their procedure the reactants are the sesquioxide, $NH_4Cl$, and $ZnCl_2$. Zinc is added subsequently as a reducing agent. The procedure reported herein, while not utilized to prepare either $EuCl_2$ or $SmCl_2$, is expected to work satisfactorily in either case.

The second procedure ($YbCl_3$ + Yb sealed in Ta and heated by induction) initially yielded incomplete reaction. The Ta tube expanded, the product yielded a complicated diffraction pattern characteristic of a mixture, and ytterbium metal remained. Initial attempts to prepare $YbBr_2$ by this procedure also failed. When a bromide preparation was heated in excess of 1000°C, the product was contaminated with tantalum bromides, unreacted ytterbium metal remained, and the 9.5-mm OD sealed tantalum container had expanded, indicative of a very high internal pressure. However, during one preparation a large temperature rise was noted in the base of the Ta cylinder as energy was being applied, the container was observed to swell abruptly, to release pressure, and then to cool to the set temperature. The resultant bromide product was red, and its X-ray diffraction pattern was also exceedingly rich in reflections. It was deduced that the $YbBr_3$ had oxidized the tantalum container almost explosively to yield $TaBr_x$ phases, some of which were gaseous at the reaction temperature (*10*). The pressure rise associated with the formation of these gaseous species caused the container to swell, and then to rupture and release pressure. Unreacted Yb metal remained since the $YbBr_3$ had reacted with the Ta first. Once the reaction was over, no further pressure rise occurred. The numerous X-ray diffraction reflections resulted from nonvolatile tantalum bromides formed in the reaction (*10*).

To alleviate this problem subsequent bromide-metal mixtures were heated slowly to a maximum temperature of 960°C, 4° above the reported melting point of $YbBr_2$ (*17*). The reaction product then was a light yellow-green powder whose X-ray diffraction pattern could be indexed completely on the basis of a $SrI_2$-type structure and a few dark particles which collected on top of the yellow-green product. A pulverized sample of the apparently less dense dark particles also produced a powder diffraction pattern characteristic of an $SrI_2$-type structure, but in addition had a couple of exceedingly weak reflections which could not be assigned to any expected compound. The lattice parameters listed in Table I for this dibromide are in good agreement with those indicated both in a preliminary report (*9*) and in Bossert's dissertation (*10*). In subsequent experiments the reaction was found to proceed exothermically at temperatures of about 700°C as long as the container was heated slowly so that the trihalide reacted with the elemental ytterbium before it reacted with the Ta. Once reduction was complete the dihalide could be heated to a higher temperature since ytterbium dihalides do not appear to react with tantalum.

The observation that a $CaCl_2$-type $YbBr_2$ structure and a trace of YbOBr were the products of the Yb + $ZnBr_2$ reactions is consistent with the hypothesis that the $CaCl_2$-type structure results when dibromide is contaminated with a small amount of the trivalent ion (*18*).

In the melt experiments typically ~75% of the material inserted into the boat was recovered. Spattering occurred for some specimens when the temperature appreciably exceeded the melting point. Some specimens were difficult to remove completely from the delicate pyrolytic graphite boats and could not be recovered quantitatively. However, neither evidence of attack of the graphite boat, as evidenced by its mass remaining constant, nor decomposition of the sample was apparent. In the two $YbBr_2$ experiments during which sample time at temperature was severely limited, 96 and 89%, respectively, of the initial sample was recovered.

At a temperature of 700°C the vapor pressure of $YbBr_2$ is estimated to be 13× that of $YbCl_2$ (*19*, *20*), so the melt could become slightly enriched in chloride. However, such enrichment is not apparent in the data presented in Fig. 1. The two experiments for which 89 and 96% sample recovery was achieved do not differ appreciably from the others in lattice parameters; in fact, their cell volumes are identical.

Every X-ray diffraction pattern contained reflections which could be indexed on the basis of the $SrI_2$-type structure. Some very weak to weak reflections were found in the X-ray diffractograms of every

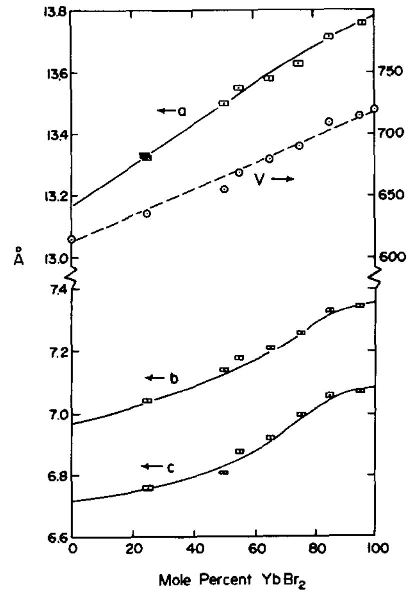

FIG. 1. Plot of lattice parameters and volume of the $YbBr_2$–$YbCl_2$ system as a function of composition.

specimen for which the pyrolytic graphite boat was supported on alundum. That outgassing of the alundum occurred was evidenced by a pressure rise in the system. These extra reflections were not assignable to oxide, oxide–bromide, or oxide–chloride. They were too few in number to attempt to index by computer (*21*). When the alundum was replaced by quartz, extra reflections were no longer observed. The lattice parameters and volume are presented as a function of composition in Table I and graphically in Fig. 1.

It is apparent from Fig. 1 that although the volume has an almost linear relationship with composition, the individual parameters deviate somewhat from linearity particularly at the bromide-rich end of the curve. Although the reasons for this deviation are not known, it was thought initially that it might result from anion ordering. The $SrI_2$-type structure possesses two types of anion sites, one coordinated tetrahedrally and the other trigonally (*14*). The results of the intensity calculations for three compositions are presented in Table II. Intensities calculated for the 75 mole percent $YbBr_2$ composition with the $DyBr_2$ atomic parameters did not deviate significantly from the values listed; an indication both of the insensitivity of the intensities to slight atomic parameter shifts and of their probable accuracy. On the basis of these intensity calculations it is clear that at all compositions bromine anions do not preferentially occupy the tetrahedral hole, and it is probable that they do not preferentially occupy the trigonal site. The occupancy appears to be random. The absence of the larger bromide ion in only the trigonal site is not surprising since in the $YbCl_2$ structure the average Yb–Cl distance for the trigonal site is 0.07 Å less than that in the tetrahedral site, but the lack of ordering in the tetrahedral site is somewhat surprising.

On the basis of this work the behavior of the ytterbium mixed halide systems would seem to differ significantly from those of its lighter lanthanide divalent congeners and would seem to resemble that of calcium.

TABLE II

COMPARISON OF OBSERVED AND CALCULATED INTENSITIES FOR LOW ANGLE REFLECTIONS IN THE $YbBr_2$–$YbCl_2$ SYSTEM AT SELECTED COMPOSITIONS

| | | Intensity | | | |
|---|---|---|---|---|---|
| Composition | *hkl* | Obs | Random | Br in $X(1)$ (trigonal) | Br in $X(2)$ (tetrahedral) |
| 0.75 $YbCl_2$–0.25 $YbBr_2$ | 200 | vw | 4 | 0 | 10 |
| | 210 | w | 8 | 11 | 5 |
| | 111 | vw | 2 | 3 | 1 |
| | 211 | vvs | 100 | 100 | 100 |
| 0.45 $YbCl_2$–0.55 $YbBr_2$ | 200 | w | 4 | 0 | 17 |
| | 210 | m | 8 | 15 | 3 |
| | 111 | vw | 2 | 4 | 1 |
| | 211 | vvs | 100 | 100 | 100 |
| 0.25 $YbCl_2$–0.75 $YbBr_2$ | 200 | w-m | 5 | 0 | 11 |
| | 210 | m | 8 | 12 | 5 |
| | 111 | vw | 2 | 3 | 2 |
| | 211 | vvs | 100 | 100 | 100 |

*Note.* At the 0.75 $YbBr_2$ composition the Br ion completely occupies the designated trigonal or tetrahedral site.

## Acknowledgment

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