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AN INVESTIGATION OF SOME LANTHANIDE CARBON,
NITROGEN, CHALCOGEN AND HALOGEN SYSTEMS AT
ELEVATED TEMPERATURES

Progress Report

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Harry A. Eick, Heinrich Luke,
Carol G. Biefeld, Robert M. Biefeld,
Beatrice L. Clink, John T. Richards

Michigan State University
East Lansing, Michigan 48824

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The following constitutes the technical progress report of work performed under Contract AT(11-1)-716 during the year 1974-75. Following the summary of the years activities are a series of brief documents, each of which bears the name of the investigator.

The following reprints are ~~appended~~.

1. "The Incongruent Vaporization of Europium(III) Oxide Chloride," by A. V. Hariharan and H. A. Eick, High Temp. Sci., 5, 269 (1973) (C00-716-080).
2. "Sublimation Thermodynamics of EuSe," by A. V. Hariharan and H. A. Eick, J. Chem. Thermodynamics, 6, 373-378 (1974) (C00-716-081)

During the academic year the principal investigator devoted fifteen percent of his effort to the research described in this report. During the summer he devoted forty percent of his effort to his research. Considerable effort was devoted to making the 11th Rare Earth Research Conference, of which the principal investigator was chairman, a success.

The present positions of doctoral students trained under this grant are:

1. Gordon L. Galloway, Ph.D., 1962, Associate Professor of Chemistry, Denison University, Granville, Ohio
2. Richard A. Kent, Ph.D., 1963, Staff Member, Los Alamos Scientific Laboratory, Los Alamos, New Mexico
3. George D. Sturgeon, Ph.D., 1964, Associate Professor of Chemistry University of Nebraska, Lincoln, Nebraska.
4. Robert E. Gebelt, Ph.D., 1965, Associate Professor of Chemistry, Mankato State University, Mankato, Minnesota

5. Philip A. Pilato, Ph.D., 1968, Xerox Corporation, Rochester, New York.
6. Dennis B. Shinn, Ph.D., 1968, Sylvania El. Prod. Co., Danvers, Massachusetts.
7. Kenneth J. Manske, Ph.D., 1969, Associate Professor of Chemistry, Mars Hill College, Mars Hill, North Carolina.
8. A. Duane Butherus, Ph.D., 1969, Bell Telephone Laboratories, Murray Hill, New Jersey.
9. John J. Stezowski, Ph.D., 1969, Associate Professor, Institute for Organic Chemistry and Biochemistry, University of Stuttgart, Germany.
10. John M. Haschke, Ph.D., 1969, Assistant Professor of Chemistry, University of Michigan, Ann Arbor, Michigan.
11. Norman A. Fishel, Ph.D., 1970, Monsanto Chemical Company, St. Louis, Missouri.
12. Robert L. Seiver, Ph.D., 1971, Esso Research and Development Corporation, Linden, New Jersey.
13. Dale E. Work, Ph.D., 1972, Sylvania El. Prod. Co., Danvers, Massachusetts.
14. Alleppey V. Hariharan, Ph.D., 1972, CEQ Institute de Energia Atomica, Sao Paulo, Brazil.
15. Carol G. Biefeld, Consultant, Sandia Laboratories, Albuquerque, New Mexico.
16. Robert M. Biefeld, Sandia Laboratories, Albuquerque, New Mexico.

The present position of masters students trained under this grant are:

1. Sandra Leonard, M.S., 1971, unemployed.
2. John Richards, M.S., 1974, Eastman Kodak Corporation, Rochester, New York.
3. Beatrice Clink, M.S., 1974, Great Lakes Chemical Company, West Lafayette, Indiana.

The present position of postdoctoral associates trained under this grant are:

1. Dr. John Smeggil, 1970, General Electric Co., Schenectady, New York.
2. Dr. Conrad Ayasse, 1972, Dow Canada, Sarnia, Ontario, Canada.

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Vaporization Reactions in the Ytterbium Fluoride System

Robert M. Biefeld

Introduction

The phases SmCl_3 , EuCl_3 , YbCl_3 , and EuBr_3 have been shown to decompose at high temperatures to the condensed divalent halide and the respective halogen.^{1,2} At still higher temperatures the divalent halides are reported to vaporize congruently according to (1).³⁻⁶

However, unlike the heavier analogues both EuF_2 and EuF_3 are reported to vaporize congruently.^{7,8} In an effort to understand better the differences observed in the europium-halogen systems and to increase our understanding of the stability relationships between the divalent and trivalent lanthanide halides, a thermodynamic examination of the vaporization reactions in the Yb-F system was undertaken. Since $\text{YbF}_3(\text{s})$ was reported to vaporize congruently,⁸ we originally focused only on the high temperature behavior of YbF_2 . However, in the course of the investigation it was noted both in our laboratory and in that of Petzel's,⁹ that neither YbF_2 nor YbF_3 vaporized congruently. Discrepancies in the vaporization thermodynamics of other lanthanide trifluorides as reported by McCreary and Thorn,¹⁰ and reports of the reduction of lanthanide trifluorides by tantalum containers^{11,12} suggested that the vaporization of YbF_3 be reexamined.

Experimental Methods

Hydrated YbF_3 was prepared by precipitation of Yb_2O_3 (99.9%, American Potash and Chemical Corp., West Chicago, Ill.) with HF. A mixture of the

hydrated trifluoride and ammonium fluoride (1:6 molar ratio), confined in Pt, was heated slowly to 875 K under continuous flow of dry He.¹³ Phases with $2 < \text{F:Yb} < 2.4$ (c.f. Tables I and II) were prepared by reduction of the appropriate amounts of YbF_3 with Yb (distilled, 99.9%, Research Chemicals, Phoenix, Ariz.).¹⁴ The reactants, confined in Ta thimbles sealed by arc welding in an Ar atmosphere, were heated under high vacuum ($\approx 10^{-5}$ - 10^{-6} torr) to 1875-1975 K, maintained at that temperature for one to three h and then cooled to room temperature over a one to three h period.

The fluoride products were analyzed for ytterbium content before and after some vaporization experiments by conversion to Yb_2O_3 with a steam hydrolysis procedure.¹⁴ Weighed amounts of the fluoride (0.05-0.2 g) contained in Pt were heated first to 1273 K and held at that temperature for three to six h under a continuous flow of steam; then cooled to 1173 K in air and held at that temperature for two to six h to remove adsorbed CO_2 .

X-Ray powder diffraction photographs were obtained before and after all vaporization and residue analysis experiments and after metal analyses with a Haegg-type Guinier camera [internal Pt standard ($a = 0.39238(1) \text{ nm}$)¹⁵] and Cu K α radiation.

The vapor species were investigated over a temperature range of 1075-1825 K with a time-of-flight mass spectrometer described previously.¹⁷ An assymetric Mo Knudsen cell with a knife edge orifice [$(347.7 \pm 1.5) \times 10^{-5} \text{ cm}^2$ as determined by planimeter measurements of photomicrographs] was used in two separate experiments. In the first experiment a sample of $\text{YbF}_{2.01}$ was vaporized partially; a portion of the residue was removed for analysis, and the remainder returned to the spectrometer and vaporized

completely. In the second experiment a sample of $\text{YbF}_{3.00}$ was vaporized partially.

An ionizing electron beam of 45 ± 5 V was used; ionization efficiency curves were recorded over the range 5 to 50 V. Appearance potentials were obtained by linear extrapolation to zero ion current¹⁸ using as a standard the ionization potential of Hg, 10.44 V.¹⁹ Assignment of the peaks was effected by use of isotopic distributions, relative time-of-flight as compared with Hg, and shutterability.

Equilibrium vapor pressures in the Yb-F system were determined by a target collection technique. Knudsen effusion experiments were carried out on a number of samples with different compositions and under varied experimental conditions (Table I). In Experiments 5-10, 20 to 30 mass percent of an initial $\text{YbF}_{2.01}$ sample had been vaporized. Two different target collection systems were utilized. For experiments 4 and 11-16 a Vycor-Pyrex apparatus similar to that described by Ackermann *et al.*²⁰ was used, while in experiments 1-3 and 5-10 the system used was that described by Hariharan.²¹ Residual system pressures were always less than 10^{-5} torr in the glass system and 10^{-6} torr in the metal system. Radiation from an inductively heated W + Mo alloy oven was used in experiments 1-4 and 11-16 to heat the symmetric Knudsen cells, while in experiments 5-10 the cells were heated directly by induction. For experiments 5-10, a tight fitting 0.18 mm thick Mo cap with a 3.175 mm diameter hole was fitted onto the cell to minimize temperature gradients. The effusate was condensed on liquid nitrogen-cooled (experiments 1-4 and 11-16) or water-cooled (experiments 5-10) aluminum-backed Pt targets, which were analyzed quantitatively for Yb by X-ray fluorescence as described previously.⁵

Several mass-loss vaporization experiments were carried out for the purposes of residue analysis (Table II). In a typical experiment a sample of known mass percent Yb confined in a symmetric Mo Knudsen cell was heated by induction at a specified temperature for several hours. The sample would be quenched, weighed and analyzed for mass percent Yb and by X-ray powder diffraction.

A distillation experiment was carried out on $\text{YbF}_{3.00}$ by introducing a temperature gradient along the walls of an asymmetric graphite Knudsen cell fitted with a channel orifice. The YbF_3 was placed in an open graphite crucible in the bottom of the Knudsen cell and the effusate was collected on the cooler lid.

Complete vaporization of three samples of YbF_3 (0.28, 0.34, and 0.36 g) and YbF_2 (0.42, 1.58 and 2.25 g) at a maximum temperature of 1800 K resulted in average mass losses of (100.1 ± 0.3) and $(99.8 \pm 0.8)\%$ respectively.

Temperatures were measured with either a Leeds and Northrup or a Micro-Optical disappearing filament optical pyrometer. Corrections were made for absorptions by the optical windows and prisms used and the pyrometers were intercompared with an N.B.S. calibrated Leeds and Northrup instrument (IPTS 1948).

Results

The results of a series of preparation and mass-loss experiments are presented in Table II. Lattice parameters for cubic $\text{YbF}_{2.01}$ [$a = 0.5600(3)$ nm] and orthorhombic $\text{YbF}_{3.00}$ [$a = 0.4435(1)$, $b = 0.6788(3)$, $c = 0.6218(3)$ nm] agree with literature values.^{22,23} The pseudo-tetragonal [$a = 0.3932(3)$ nm, $c = 0.5586(4)$ nm] and -rhombohedral [$a = 0.686_4(1_2)$ nm, $\alpha = 33.22(7)^\circ$]

modifications of and the contraction of the cubic fluorite lattice reported here are similar to those observed in the Sm- and Eu-F systems.^{14,24}

The residue of experiments 1, 4, and 16, contained traces of YbOF or $\text{Yb}_4\text{O}_3\text{F}_6$.²⁵ However, these impurities cannot explain the unidentified lines present in the X-ray photographs of both the freshly prepared pseudo-tetragonal and -rhombohedral phases and the residues of certain experiments (Table II).

The results of the mass loss experiments illustrate the incongruent vaporization behavior of both YbF_2 and YbF_3 . A sample of $\text{YbF}_{2.01}$, upon heating, converts initially to a contracted cubic fluorite phase, and then to the pseudo-tetragonal phase with loss of Yb. Vaporization of the pseudo-tetragonal phase, $\text{YbF}_{2.32}$, produces a pseudo-rhombohedral modification, $\text{YbF}_{2.40}$, still by an incongruent reaction. The congruent behavior of $\text{YbF}_{2.40}$ is indicated by the lack of composition or structural change upon continued vaporization, and is supported by the presence of Yb enriched residues after the partial vaporization of $\text{YbF}_{2.49}$ and $\text{YbF}_{2.60}$ both of which contain orthorhombic $\text{YbF}_{3.00}$. Upon vaporization $\text{YbF}_{3.00}$ yields a slightly Yb enriched residue, as indicated by the presence of two [(222) and (211)] reflections of the pseudo-rhombohedral phase in the X-ray diffraction photographs. There is no significant crucible interaction. Furthermore, the incongruent vaporization behavior of $\text{YbF}_{2.01}$ and $\text{YbF}_{3.00}$ is support for the observed congruent vaporization of $\text{YbF}_{2.40}$.

Mass spectrometric analysis of the effusate from $\text{YbF}_{2.01}$ indicated only Yb^+ at temperatures up to 1477 K. When the sample temperature was elevated the Yb^+ intensity increased initially (Fig. 1); but with time decreased.

Time-dependence of the Yb^+ ion intensity is typical of the behavior expected for a non-stoichiometric solid.²⁶ Since the vapor is enriched in Yb the composition of the sample changes with time. The ionization efficiency curve recorded for Yb^+ at 1335 K yields an appearance potential of $(7.7 \pm 1.9)\text{V}$ [cf. literature value: $(5.9_0 \pm 0.1_0)^{27}$ and $(6.25 \pm 0.01)^{28}$ V]. Ion currents were observed for YbF^+ and YbF_2^+ at 1477 K and higher temperatures. In figure 2 the behavior of the intensity fractions of Yb^+ , YbF^+ and YbF_2^+ vs time at 1653 K are presented. Analysis of a portion of this sample after the intensities had become reproducible with time and temperature (33.8 h) indicated the composition, $\text{YbF}_{2.39}$, and the presence of the pseudo-rhombohedral phase. The congruent vaporization of the pseudo-rhombohedral phase was confirmed by the ion intensities which remained reproducible until the sample had evaporated completely. Ionization efficiency curves (Fig. 3 and 4) were obtained for Yb^+ , YbF^+ , and YbF_2^+ from this sample before (15-16)h and during (42-44)h heating in the reproducible region. The complex behavior of these curves which were obtained by a least squares four parameter equation fit of the data is similar to that observed for other reduced lanthanide fluorides.⁸ The most probable explanation of the inflection points is the presence of two or more molecular precursors for the ions. Second appearance potentials for some ions were estimated from the inflection points and these values are assigned an arbitrarily chosen error of ± 5 V. The appearance potentials are reported in Table III.

Examination of the effusate of $\text{YbF}_{3.00}$ by mass spectrometry yielded results similar to those reported by Zmbov and Margrave.⁸ The absence of any observable inflection points in the ionization efficiency curves

indicates YbF_3 (g) to be the only Yb-containing species. The Yb-containing ion current intensities and their ratios were reproducible with time and temperature. Appearance potentials and relative ratios are also listed in Table III. In the mass range of 16 to 480 no other shutterable ion current ($I^+ \leq 1\% I(\text{YbF}_2^+)$) was observed. From the results of the distillation experiment (Table II) and with the assumptions that $\text{YbF}_{3.00}$ vaporizes to yield YbF_3 (g) and $\text{YbF}_{2.40}$ (s, ℓ) which then vaporizes congruently, reaction (2) can be established.

Comparison of the relative intensities and second appearance potentials for the ions from the effusate of $\text{YbF}_{2.40}$ with those from $\text{YbF}_{3.00}$ indicates YbF_3 (g) to be one of the molecular precursors present in the $\text{YbF}_{2.40}$ effusate. The presence of YbF_2 (g) is indicated by the first appearance potential for YbF_2^+ (10.6 ± 2.4) V, a number significantly less than the value for YbF_2^+ (14.4 ± 1.1) V over $\text{YbF}_{3.00}$. Since for YbF^+ and Yb^+ one and two appearance potentials were observed over $\text{YbF}_{2.40}$, respectively, we assume that neither Yb(g) nor YbF (g) is present. The YbF^+ ion is expected to produce the most intense ion current in the fragmentation pattern for YbF_2 (g) and should mask out the much weaker contribution from YbF_3 (g).²⁹

The congruent vaporization of $\text{YbF}_{2.40}$ (s, ℓ) is represented by (3)

in accordance with the requirement that the mole fractions of $\text{YbF}_2(\text{g})$ and $\text{YbF}_3(\text{g})$ are 0.60 and 0.40, respectively. Use of this relationship allows the partial pressures of $\text{YbF}_2(\text{g})$ and $\text{YbF}_3(\text{g})$ to be calculated from the effusate data. In accordance with previous work^{5,21,30} the condensation coefficients of gaseous lanthanide dihalide and trihalide were assumed to be unity. The natural logarithm of the equilibrium constant for (3) for 94 data points from experiments 1-10 along with the five corresponding unweighted linear least-squares equations from Table IV are presented in Fig. 5. [In all calculations, activities of solids = 1, activities of gases = partial pressures in atmospheres. The first four data points from experiment 1 represent pressures for $\text{Yb}(\text{g})$ before the $\text{YbF}_{2.40}$ composition has been reached. Changes in cell material from Mo to graphite or changes in sample composition from $\text{YbF}_{2.28}$ (residue composition of experiment 1) to $\text{YbF}_{2.51}$ (initial sample composition of experiment 2) have little effect on the equilibrium constant.

From the slope-intercept data of experiments 5-10 the following thermodynamic values with errors indicative of standard deviations are calculated at the median temperature for (3): $\Delta H^\circ_{1597} = (96.8 \pm 1.1) \text{ kcal gfw}^{-1}$ and $\Delta S^\circ_{1597} = (36.8_2 \pm 0.6_8) \text{ cal gfw}^{-1} \text{ K}^{-1}$.

To effect data reduction, thermodynamic functions for $\text{YbF}_2(\text{s})$ were estimated by the method of Hariharan et al. From the heat capacity data of $\text{CaF}_2(\text{s})$,³¹ $\text{Ca}(\text{s})$,³² and $\text{Yb}(\text{s})$ ³³ the heat capacity of $\text{YbF}_2(\text{s})$ at 298 K is estimated as $(17.3 \pm 0.5) \text{ cal mol}^{-1} \text{ K}^{-1}$. The heat capacity of $\text{YbF}_2(\text{s})$ at its melting point, 1680 K,³⁴ is estimated to be $21.75 \text{ cal mol}^{-1} \text{ K}^{-1}$.³⁵

On the assumption of linear variation of C_p° with temperature

$$C_p^\circ(\text{YbF}_2, s) = [(16.4 \pm 0.5) + (3.19 \times 10^{-3})T] \text{ cal mol}^{-1} \text{ K}^{-1}; (298-1680) \text{ K} \quad (4)$$

A heat capacity of $(29.2 \pm 0.7) \text{ cal mol}^{-1} \text{ K}^{-1}$ for $\text{YbF}_2(\ell)$, assumed constant over the entire liquid range, and an enthalpy of fusion for $\text{YbF}_2(s)$ of $(7.5 \pm 1.0) \text{ kcal mol}^{-1}$ were estimated for YbF_2 by analogy with values for CaF_2 .³¹

Thermodynamic functions were derived for $\text{YbF}_{2.40}$ at each temperature by combining in the ratio of 0.4:0.6 the values reported for $\text{YbF}_{3.00}$ ¹¹ with those estimated for $\text{YbF}_{2.00}$.

The standard entropies, $S_{298}^\circ(\text{YbF}_2, s)$ and $S_{298}^\circ(\text{YbF}_3, s)$ are taken as $(22.5_0 \pm 0.5_0)$ and $(26.5_6 \pm 0.5_0) \text{ cal mol}^{-1} \text{ K}^{-1}$, respectively, from the schemes of Westrum³⁶ and Latimer.³⁷ The F^- contribution to $S_{298}^\circ(\text{YbF}_3, s)$ was estimated from the difference of the experimental value for $\text{CeF}_3(s)$ ³⁸ and the value recommended for Ce(III) .³⁶ From these values, $S_{298}^\circ(\text{YbF}_{2.40}, s)$ is calculated as $(24.1_2 \pm 0.5_0) \text{ cal mol}^{-1} \text{ K}^{-1}$.

Thermodynamic functions for $\text{YbF}_2(g)$ and $\text{YbF}_3(g)$ are calculated from the measured and estimated molecular constants.³⁹ A non-linear geometry with a F-Yb-F angle of $(140 \pm 10)^\circ$ ⁴⁰ and a Yb-F distance of $0.210(5) \text{ nm}$ ^{5,41} are assumed for $\text{YbF}_2(g)$. A non-planar geometry with a F-Yb-F angle of $(117 \pm 10)^\circ$ ⁴² and a Yb-F distance of $0.203(5) \text{ nm}$ ⁴³ are used for $\text{YbF}_3(g)$. For $\text{YbF}_2(g)$ wave numbers, $\nu_1 = (476 \pm 10)$, $\nu_2 = (114.5 \pm 5.0)$ and $\nu_3 = (462 \pm 10) \text{ cm}^{-1}$,⁴² were used with a ground state statistical weight of one by analogy with the value for Lu^{3+} . For $\text{YbF}_3(g)$ wave numbers, $\nu_1 = (584 \pm 10)$, $\nu_2 = (100 \pm 5)$, $\nu_3 = (565 \pm 10)$, and $\nu_4 = (144 \pm 5) \text{ cm}^{-1}$,⁴² where ν_2 and ν_3 are doubly degenerate, were used with a ground state statistical

weight of eight.³⁶ The uncertainty in the entropy and the free energy functions which results from the errors in the molecular constants and the statistical weights is ± 1.3 cal mol⁻¹ K⁻¹.

Reduction of the slope-intercept (second law) data of experiments 5-10 for reaction (3) was accomplished by the Σ' method of Cubicciotti.⁴⁴ For each data point a value of $\Sigma' = R \ln K - \Delta(H^\circ_T - H^\circ_{298})/T + \Delta(S^\circ_T - S^\circ_{298})$ was calculated. A fit of Σ' vs. $1/T$ is described with standard deviations by unweighted linear least-squares equation (5) where $\Sigma' = (\Delta H^\circ_{298})/T - \Delta S^\circ_{298}$.

$$\Sigma'(\text{cal K}^{-1}) = (110.7 \pm 1.0) \times 10^3/T - (50.8_5 \pm 0.6_4) \quad (5)$$

Contributions to the uncertainties in ΔH°_{298} and ΔS°_{298} from the measured and estimated thermodynamic functions are 1.3 kcal mol⁻¹ and 1.6 cal mol⁻¹ K⁻¹, respectively.

Combination of the experimental pressures with free-energy functions yields, by the third-law procedure, $\Delta H^\circ_{298} = (109.8 \pm 2.4)$ kcal gfw⁻¹ for reaction (3). From $S^\circ_{298}(\text{YbF}_{2,g})$, $S^\circ_{298}(\text{YbF}_{3,g})$ and the $\ln K$ vs. $1/T$ derived ΔS°_{298} for (3), $S^\circ_{298}(\text{YbF}_{2.40,s}) = (23.8 \pm 3.3)$ cal gfw⁻¹ K⁻¹.

The natural logarithm of the equilibrium partial pressures (atm) of $\text{YbF}_3(g)$ (60 temperature-pressure data points, two corresponding unweighted linear least-squares equations (Table IV)) is presented in Fig. 6. As expected, the change of cell material from Mo to graphite has little effect upon the equilibrium pressures of $\text{YbF}_3(g)$. The stoichiometry of reaction (2) requires the partial pressures of $\text{YbF}_3(g)$ and $\text{F}(g)$ in the Knudsen cell be related according to (6). From (6) and the thermodynamic

$$P_F/[(M_F)^{1/2}(0.03)] = P_{\text{YbF}_3}/[(M_{\text{YbF}_3})^{1/2}(0.95)] \quad (6)$$

data for $F_2(g)$ and $F(g)$,⁴⁵ the pressures of $F_2(g)$ at the experimental temperatures are negligible. The equilibrium constant for reaction (2) when calculated from the relationship in (6) and the data from experiments 11-15 is represented by (7). From (7) the following thermodynamic values are found for reaction (2): $\Delta H^\circ_{1568} = (91.1_9 \pm 0.4_1) \text{ kcal mol}^{-1}$ and

$$\ln K(2) = ((-4.58_8 \pm 0.2_0) \times 10^3)/T + (18.7_6 \pm 0.1_3) \quad (7)$$

$\Delta S^\circ_{1568} = (37.2_8 \pm 0.2_6) \text{ cal mol}^{-1} \text{ K}^{-1}$. The errors represent the standard deviations of the least-squares fit. The Σ' vs. $1/T$ fit of the slope-intercept data is described by the unweighted linear least-squares equation (8) with standard deviations. Combination of the calculated equilibrium

$$\Sigma'(\text{cal K}^{-1}) = (111.0_5 \pm 0.4_4) \times 10^3/T - (56.1_7 \pm 0.2_9) \quad (8)$$

constant with the free-energy functions yields, by the third-law procedure, a value of $\Delta H^\circ_{298} = (107.0 \pm 3.0) \text{ kcal mol}^{-1}$ for reaction (2). From $S^\circ_{298}(\text{YbF}_3, g)$, $S^\circ_{298}(\text{YbF}_{2.40}, s)$, $S^\circ_{298}(F, g)$ and the $\ln K$ vs. $1/T$ derived ΔS°_{298} for reaction (2), $S^\circ_{298}(\text{YbF}_3, s) = (23.9 \pm 3.5) \text{ cal mol}^{-1} \text{ K}^{-1}$.

The difference in the enthalpies of formation at 298 K for $\text{YbF}_3(s)$ ⁴⁶ and $\text{YbF}_{2.40}(s)$ (difference estimated as $0.6[\Delta H^\circ_f(\text{YbF}_3, s) - \Delta H^\circ_f(\text{YbF}_2, s)]$), the enthalpy of formation for $F(g)$ ⁴⁵ and the enthalpy for reaction (2) are combined to yield for (9): $\Delta H^\circ_{298} \text{ (2nd law)} = (113.3 \pm 2.0) \text{ kcal mol}^{-1}$ and $\Delta H^\circ_{298} \text{ (3rd law)} = (109.0 \pm 3.4) \text{ kcal mol}^{-1}$.

Also for (9) from the absolute entropies for $\text{YbF}_{2.4}(\text{s})$, $\text{YbF}_3(\text{g})$ and $\text{F}(\text{g})$ in combination with ΔS°_{298} for (2) yield $\Delta S^\circ_{298} = (58.1 \pm 1.6)$ cal mol⁻¹ K⁻¹. From ΔS°_{298} for (9) and $S^\circ_{298}(\text{YbF}_3, \text{g})$, $S^\circ_{298}(\text{YbF}_3, \text{s}) = (23.8 \pm 3.6)$ cal mol⁻¹ K⁻¹.

The enthalpies and entropies for reactions (9), (3) and (10)

[estimated as $\Delta H^\circ_{298} = (0 \pm 2)$ kcal gfw⁻¹ and $\Delta S^\circ_{298} (0.0 \pm 1.2)$ cal gfw⁻¹ K⁻¹] are used to obtain for (11) ΔH°_{298} (2nd law) = (109.0 ± 8.5) kcal mol⁻¹, $\Delta S^\circ_{298} = (46.0 \pm 5.6)$ cal mol⁻¹ K⁻¹ and ΔH°_{298} (3rd law) = (111.0 ± 8.3) kcal mol⁻¹.

From ΔS°_{298} for (11) and S°_{298} for $\text{YbF}_2(\text{g})$, $S^\circ_{298}(\text{YbF}_2, \text{s}) = (23.5 \pm 7.0)$ cal mol⁻¹ K⁻¹.

Discussion

The vaporization reactions and the vapor pressures observed in the Yb-F system are illustrated in a pressure-composition diagram, fig. 7. The greater total pressures from YbF_2 and YbF_3 when compared with those from $\text{YbF}_{2.40}$ are evidence for the incongruent vaporization of YbF_2 and YbF_3 and the congruent vaporization of $\text{YbF}_{2.40}$. The vaporization reactions of $\text{YbF}_{2.40}$ and YbF_3 have been characterized and their thermodynamics determined. Because of the dependence of the equilibrium vapor pressures on composition and temperature in the composition region YbF_{2+x} ($0.00 \leq x < 0.40$), the measurements that were carried out in this region represent non-equilibrium values.

The vaporization behavior observed in the Yb-F system is unique among the lanthanide-halogen systems that have been studied. However, several analogies can be drawn with other systems. Ytterbium trichloride is known to decompose at high temperatures to yield $\text{Cl}_2(\text{g})$ and $\text{YbCl}_2(\text{s})$. At somewhat lower temperatures, EuBr_3 decomposes to yield $\text{Br}_2(\text{g})$ and $\text{EuBr}_2(\text{s})$. The YbF_3 system behaves in a similar manner with decomposition to an Yb-enriched solid, $\text{YbF}_{2.40}$, an indication of the greater stability of the reduced phase. However, vaporization occurs to yield both $\text{F}(\text{g})$ and $\text{YbF}_3(\text{g})$. Since a study of the vaporization behavior of EuF_2 ⁷ indicates that no change in the composition of the residue occurs, it is likely that EuF_3 undergoes an incongruent vaporization reaction similar to that of YbF_3 . This interpretation is consistent with the results, but not the interpretation of Zmbov and Margrave⁸ for the sublimation of $\text{EuF}_3(\text{s})$. The enthalpies for reaction (11) depend on the difference in the enthalpies

of formation of the fluorides. By use of estimated enthalpies^{45,46} for (12) $\Delta H^\circ_{298}(\text{Yb}) = (115 \pm 14) \text{ kcal mol}^{-1}$ and $\Delta H^\circ_{298}(\text{Eu}) = (110 \pm 14) \text{ kcal mol}^{-1}$. Reaction (12) which is similar to the vaporization behavior of YbF_3 is more favorable for EuF_3 by 5 kcal mol^{-1} than for YbF_3 . The dissimilar vaporization reactions of EuF_2 and YbF_2 can be explained in terms of the differences in the enthalpies of formation of the fluorides and the enthalpies of sublimation for the metals. By use of estimated enthalpies, values^{32,46} for reaction (13) can be derived [$\Delta H^\circ_{298}(\text{Eu}) = (160 \pm 35)$ and $\Delta H^\circ_{298}(\text{Yb}) = (124 \pm 35)$]. Reaction (13) is 36 kcal less favorable for

Eu than for Yb. Since reaction (13) is similar to the decomposition of YbF_2 , our work agrees with the difference in the reported enthalpies.

If the data from Zmbov and Margrave²⁷ for the vapor pressures of $\text{YbF}_3(\text{g})$ are treated in the manner described above, the following values are derived for reaction (2): $\Delta H^\circ_{1362} = (83.7 \pm 1.4) \text{ kcal mol}^{-1}$, $\Delta S^\circ_{1362} = (34.5 \pm 1.0) \text{ cal mol}^{-1} \text{ K}^{-1}$, $\Delta H^\circ_{298}(\text{2nd law}) = (98.5 \pm 2.9) \text{ kcal mol}^{-1}$, $\Delta H^\circ_{298}(\text{3rd law}) = (105.9 \pm 3.4) \text{ kcal mol}^{-1}$, $\Delta S^\circ_{298} = (49.8 \pm 2.5) \text{ cal mol}^{-1} \text{ K}^{-1}$. The disagreement between second- and third-law derived values for Zmbov and Margrave's data, $-7.4 \text{ kcal mol}^{-1}$, is slightly larger than our difference, $+4.3 \text{ kcal mol}^{-1}$, and opposite in sign. The vapor pressure for $\text{YbF}_3(\text{g})$ observed by Zmbov and Margrave at 1362 K is 3.3 times greater than that observed in the present study. Because Zmbov and Margrave used only one pressure-temperature data point determined by one mass-loss experiment to calibrate their data over a limited temperature range, we feel that our vapor pressures and thermodynamic values more closely represent the equilibrium values.

The derived values for the enthalpy and entropy of congruent sublimation of $\text{YbF}_3(\text{s})$ [$\Delta H^\circ_{298} = (113.3 \pm 2.0)$ and $(109.0 \pm 3.4) \text{ kcal mol}^{-1}$ and $\Delta S^\circ_{298} = (58.1 \pm 1.6) \text{ cal mol}^{-1} \text{ K}^{-1}$] when compared with the values of other lanthanide trifluorides^{10,47} (Table V) reveal no significant differences. The derived values for the enthalpy and entropy of sublimation of YbF_2 [$\Delta H^\circ_{298} = (109.0 \pm 8.5)$, $(111.0 \pm 8.3) \text{ kcal mol}^{-1}$ and $\Delta S^\circ_{298} = (46.0 \pm 5.6) \text{ cal mol}^{-1} \text{ K}^{-1}$] when compared with the values of EuF_2 and the alkaline earth fluorides^{7,48,49} (Table V) support the previously observed correspondence of their thermodynamic properties.^{5,49} The similarity of the entropies of sublimation of YbF_2 ($\Delta S^\circ_{298} = 46.0 \pm 5.6 \text{ cal mol}^{-1} \text{ K}^{-1}$)

and YbCl_2 ($\Delta S^\circ_{298} = 48.0 \pm 1.1 \text{ cal mol}^{-1} \text{ K}^{-1}$)⁵ is consistent with the constant entropy change observed for the congruent sublimation at 298 K for the europium dihalides.⁴⁹

The reported uncertainties in the thermodynamic values were determined as follows: The error in the sublimation entropies and enthalpies derived by the Σ' method are the sum of the standard deviation of the least-squares analysis and the uncertainties in the solid and gaseous heat capacities. The errors in the enthalpies of sublimation of $\text{YbF}_3(\text{s})$ and $\text{YbF}_2(\text{s})$ are the sums of the reported errors for the enthalpy values used. The errors in the third-law derived values are the standard deviations plus the uncertainty in the Gibb's functions for solids and gases.

The thermodynamic approximations for YbF_2 and $\text{YbF}_{2.40}$ used in the data reduction are internally consistent. This consistency is observed in the close agreement between values derived by the Σ' and third-law methods for reaction (3) and in the temperature independence of the third-law derived values. Also, the estimated standard entropy for $\text{YbF}_{2.40}$ is in good agreement with the Σ' value. Although the agreement in the above values for reaction (2) is somewhat less, they are still within the reported errors.

Knudsen numbers⁴⁸ for $\text{YbF}_2(\text{g})$ and $\text{YbF}_3(\text{g})$ [estimated to have diameters of $(0.64_2 \pm 0.1_0)$ and $(0.63_0 \pm 0.1_0)$ nm] varied between 231 and 3.9 for $\text{YbF}_2(\text{g})$ and 601 and 0.34 for $\text{YbF}_3(\text{g})$ for the largest and smallest orifices at the lowest and highest temperatures, respectively. The values for $\text{YbF}_2(\text{g})$ are within the limits accepted for molecular flow.⁴⁸ While some values for $\text{YbF}_3(\text{g})$ are on the borderline of acceptability, the vapor pressures do not deviate significantly from the least-squares fit and no correction was made.

This study presents well-determined thermodynamic values for reactions (2) and (3). When better thermodynamic functions for $\text{YbF}_2(\text{s}, \ell)$ and the enthalpies of formation of $\text{YbF}_2(\text{s})$ and $\text{YbF}_3(\text{s})$ are determined, more accurate values for the sublimation of $\text{YbF}_2(\text{s})$ and $\text{YbF}_3(\text{s})$ could be derived from the above results.

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Table I. Experimental Conditions for Vaporization Runs in the Ytterbium Fluoride System

Exp.	% Yb ¹	(F/Yb) ²	Set-up ⁴	Cell	Orifice Area ⁵	T Range
1	81.9	2.01	M + O	Mo	$7.90 \times 10^{-3} \text{ cm}^2$	1293-1592 K
2	78.4	2.51	"	Mo	1.14	1547-1696
3	78.9	2.44	"	Mo	7.59	1520-1673
4	----	2.4 ³	G + O	C(gr)	5.01	1504-1609
5-7	----	2.4 ³	M	Mo	1.12	1566-1742
8-10	----	2.4 ³	"	Mo	7.28	1452-1640
11-13	75.2	3.00	G + O	Mo	8.33	1342-1620
14,15	"	"	"	Mo	1.11	1511-1794
16	"	"	"	C(gr)	1.10	1521-1667

¹ Average error for all analyses before vaporization = $\pm 0.3 \%$

² Composition error = ± 0.04

³ Estimated value

⁴ M = metal vacuum line; O = W-Mo oven; G = glass vacuum line

⁵ Estimated error = $\pm 0.10 \times 10^{-3} \text{ cm}^2$

Table II. Results of Mass Loss Experiments for Ytterbium Fluoride Samples Confined in Mo

Before Vaporization		Temperature of Vaporization	After Vaporization		
Composition ¹ (F/Yb)	Structure(s) ²		Mass Loss	Composition ¹ (F/Yb)	Structure(s) ²
2.01	C a = 0.5600(1) nm	1097 K	1 %	2.01	C a = 0.5597(3) nm
"	"	1450	15	2.19	T + C + U a = 0.5585(1)
"	"	1800	27	2.35	H + T + U'
"	"	1800	45	2.39	H + U''
2.29	T + U	1700	31	2.39	H + U''
"	"	1700	45	2.37	H + U''
2.44	H + U''	1673	20	2.37	H + U''
2.51	H + O + U''	1696	37	2.46	H + U''
2.60	H + O + U''	1712	41	2.55	H + O + U''
3.00	O	1560	17	2.96	O + H
"	"	1725	37	2.99	O + H

¹ Average error in composition is ± 0.04

² C = cubic, T = tetragonal, H = hexagonal, O = orthorhombic YbF₃, U, U' and U'' = unidentified lines (superstructure)

Table III. Appearance Potentials of the Ions Detected in the Ytterbium Fluoride System

Condensed Composition ¹	T (K)	Ion	Relative Intensity ²	1st A.P. (volts)	2nd A.P. (volts)
YbF ₂	1335	Yb ⁺	100	7.7 ± 1.9	-----
YbF _{2+x}	1667	Yb ⁺	100	8.8 ± 2.5	-----
"	"	YbF ⁺	66	8.5 ± 1.7	-----
"	"	YbF ₂ ⁺	35	11.4 ± 2.2	20 ± 5
YbF _{2.40}	1735	Yb ²⁺	26	10.0 ± 5.0	23 ± 5
"	"	YbF ⁺	56	10.8 ± 2.5	-----
"	"	YbF ₂ ⁺	100	10.6 ± 2.4	15 ± 5
YbF ₃	1673	Yb ⁺	14	25.3 ± 1.5	-----
"	"	YbF ⁺	8	19.1 ± 1.7	-----
"	"	YbF ₂ ⁺	100	14.4 ± 1.1	-----

¹ 0.00 ≤ x < 0.40² Ionization energy of 45 ± 5 volts

Table IV. Results of Linear Least-Squares Analyses of Vaporization Reactions in the Ytterbium Fluoride System

Exp.	Slope	Intercept	Range
$\text{YbF}_{2.40}(\text{s},\ell) = 0.60 \text{ YbF}_2(\text{g}) + 0.40 \text{ YbF}_2(\text{g})$ $\ln K \text{ vs. } 10^4/T$			
1	$-4.5_3 \pm 0.1_9$	17.0 ± 1.2	1466-1592 K
2	$-3.8_1 \pm 0.3_3$	12.7 ± 2.0	1572-1728
3	$-4.19_5 \pm 0.08_7$	$14.8_8 \pm 0.5_5$	1520-1673
4	$-4.9_4 \pm 0.1_4$	$19.1_8 \pm 0.8_8$	1504-1609
5-10	$-4.87_4 \pm 0.05_4$	$18.5_3 \pm 0.3_4$	1452-1742
$\text{YbF}_{3.00}(\text{s},\ell) = 0.05 \text{ YbF}_{2.40}(\text{s},\ell) + 0.95 \text{ YbF}_3(\text{g}) + 0.03 \text{ F}(\text{g})$ $\ln p(\text{YbF}_3(\text{g})/\text{atm}) \text{ vs. } 10^4/T$			
11-15	$-4.68_2 \pm 0.02_1$	$19.2_9 \pm 0.1_4$	1342-1794
16	$-4.40_0 \pm 0.08_8$	$17.3_7 \pm 0.5_3$	1548-1703

Table V. Thermodynamic Data for Selected Metal Fluorides

Fluoride	Ref ¹	ΔH_{298}° (kcal mol ⁻¹) ²	ΔS_{298}° (cal mol ⁻¹ K ⁻¹) ³
$MF_n(s) = MF_n(g)$			
EuF ₂	7	101	50
SrF ₂	47	100	46
CaF ₂	46	102	47
LaF ₃	45-b	108	57
CeF ₃	10-b	106	54
PrF ₃	45-a	106	54
GdF ₃	10-a	108	52

¹ See references 11, 40, 48 for thermodynamic functions for LnF₃

² Average error for $\Delta H_{298}^{\circ} = \pm 2.5$ kcal mol⁻¹

³ Average error for $\Delta S_{298}^{\circ} = \pm 1.9$ cal mol⁻¹ K⁻¹

Figure 1. Intensity of Yb^+ from YbF_{2+x} ($0.00 \leq x < 0.40$) Confined in Mo vs. Time [O ($T = 1396$ K); X ($T = 1338$ K)]

Figure 2. Fractional Ion Intensities of Yb^+ ($\square$), YbF^+ ($\times$) and YbF_2^+ ($\diamond$) from YbF_{2+x} ($0.00 \leq x \leq 0.40$) Confined in Mo vs. Time ($T = 1653$ K)

Figure 3. Ionization Efficiency Curves for Yb^+ ($\square$), YbF^+ ($\times$) and YbF_2^+ ($\diamond$) from YbF_{2+x} ($0.00 \leq x < 0.40$) Confined in Mo ($T = 1667 \text{ K}$)

Figure 4. Ionization Efficiency Curves for Yb^+ ($\square$), YbF^+ ($\times$) and YbF_2^+ ($\diamond$) from $\text{YbF}_{2.40}$ Confined in Mo ($T = 1735$ K) (displaced abscissa: 0 to 60 V for YbF_2^+ , -5 to 55 V for YbF^+ , -10 to 50 V for Yb^+)

Figure 5. Natural Logarithm of the Equilibrium Constant for the Congruent Vaporization of $\text{YbF}_{2.40}$ [Exp. 1($\circ$), 2(Δ), 3($\ominus$), 4($\blacksquare$), 5($\square$), 6($\times$), 7($\blacktriangledown$), 8($\diamond$), 9(∇) and 10(∇)] and the Pressure of Yb(g) from YbF_{2+x} ($0.00 \leq x < 0.40$) [Exp. 1($\boxtimes$)] vs. Reciprocal Temperature

Figure 6. Natural Logarithm of the Equilibrium Partial Pressure of $\text{YbF}_3(\text{g})$ from $\text{YbF}_3(\text{s}, \ell)$ [Exp. 11($\square$), 12($\times$), 13($\diamond$), 14(∇), 15($\circ$) and 16($\blacktriangledown$)] vs. Reciprocal Temperature

Figure 7. Qualitative Pressure-Composition Diagram for the Yb-F System ($T = 1500\text{ K}$)

The Vaporization and Sublimation Thermodynamics of Samarium and Thulium Fluorides

Robert M. Biefeld

The vaporization and sublimation reaction for the samarium and thulium fluoride systems have been investigated at high temperatures by mass loss, X-ray powder diffraction and elemental analysis.

The divalent halide, $\text{SmF}_{2.00}$ decomposes when heated to give metal rich vapors and a metal deficient residue until the composition $\text{SmF}_{2.40}$ is reached. The behavior in this system is similar to that in the Yb-F system. Thulium metal partially reduced TmF_3 , but a reduced thulium fluoride was not isolated. Partially reduced thulium fluoride specimens decomposed when heated to yield a metal rich vapor and TmF_3 as the residue.

The following vaporization reactions were established:

Target collection Knudsen effusion techniques were used to obtain equilibrium vapor pressures for these reactions over the temperature ranges of 1369-1791 K for $\text{SmF}_{2.40}$, 1352-1746 K for $\text{SmF}_{3.00}$ and 1348-1809 K for $\text{TmF}_{3.00}$.

The following second-law enthalpy and entropy changes with associated standard deviations were derived at the median temperatures: $\text{SmF}_{2.40}$,

$\Delta H^\circ_{1580} = (90.5 \pm 2.2) \text{ kcal mol}^{-1}$ and $\Delta S^\circ_{1580} = (37.2 \pm 1.4) \text{ cal mol}^{-1} \text{ K}^{-1}$; $\text{YbF}_{2.40}$, $\Delta H^\circ_{1597} = (96.9 \pm 1.1) \text{ kcal mol}^{-1}$ and $\Delta S^\circ_{1597} = (36.8_3 \pm 0.6_7) \text{ cal mol}^{-1} \text{ K}^{-1}$; $\text{SmF}_{3.00}(\text{s})$, $\Delta H^\circ_{1462} = (95.0 \pm 2.0) \text{ kcal mol}^{-1}$ and $\Delta S^\circ_{1462} = (42.8 \pm 1.4) \text{ cal mol}^{-1} \text{ K}^{-1}$; $\text{SmF}_{3.00}(\text{l})$, $\Delta H^\circ_{1669} = (83.2 \pm 4.7) \text{ kcal mol}^{-1}$ and $\Delta S^\circ_{1669} = (34.8 \pm 2.8) \text{ cal mol}^{-1} \text{ K}^{-1}$. Estimated and reported thermodynamic functions were employed to reduce the thermodynamic values to

298 K. The following values with estimated uncertainties were derived

by the Σ' method: $\text{SmF}_{2.40}(\text{s})$, $\Delta H^\circ_{298} = (100.2 \pm 3.4) \text{ kcal mol}^{-1}$ and $\Delta S^\circ_{298} = (46.2 \pm 2.8) \text{ cal mol}^{-1} \text{ K}^{-1}$; $\text{SmF}_{3.00}(\text{s})$, $\Delta H^\circ_{298} = (101.7 \pm 2.0) \text{ kcal mol}^{-1}$ and $\Delta S^\circ_{298} = (52.5 \pm 1.7) \text{ cal mol}^{-1} \text{ K}^{-1}$; and $\text{TmF}_{3.00}(\text{s})$, $\Delta H^\circ_{298} = (108.2 \pm 1.5) \text{ kcal mol}^{-1}$ and $\Delta S^\circ_{298} = (55.4 \pm 1.3) \text{ cal mol}^{-1} \text{ K}^{-1}$.

The following ΔH°_{298} values with estimated uncertainties were derived by the third-law procedure: $\text{SmF}_{2.40}(\text{s})$, $(104.4 \pm 3.0) \text{ kcal mol}^{-1}$; $\text{SmF}_{3.00}(\text{s})$, $(101.7 \pm 2.6) \text{ kcal mol}^{-1}$ and $\text{TmF}_{3.00}(\text{s})$, $(107.5 \pm 2.3) \text{ kcal mol}^{-1}$.

The derived thermodynamic values were used with estimated and reported values for the enthalpies of formation and standard entropies S°_{298} , to calculate the enthalpies and entropies for the hypothetical congruent sublimation reactions of $\text{SmF}_2(\text{s})$ and $\text{SmF}_3(\text{s})$ at 298 K. Values are as follows: $\text{SmF}_2(\text{s})$, $\Delta H^\circ_{298} = (99.5 \pm 9.3) \text{ kcal mol}^{-1}$, $\Delta S^\circ_{298} = (40.9 \pm 6.8) \text{ cal mol}^{-1} \text{ K}^{-1}$ and $\Delta H^\circ_{298} \text{ (3rd law)} = (106.5 \pm 9.1) \text{ kcal mol}^{-1}$ and $\text{SmF}_3(\text{s})$, $\Delta H^\circ_{298} = (101.2 \pm 2.5) \text{ kcal mol}^{-1}$, $\Delta S^\circ_{298} = (54.1 \pm 1.9) \text{ cal mol}^{-1} \text{ K}^{-1}$ and $\Delta H^\circ_{298} \text{ (3rd law)} = (101.2 \pm 3.2) \text{ kcal mol}^{-1}$. Boiling points and associated enthalpies of congruent vaporization are listed in Table 1.¹

A comparison of the thermodynamic data derived for SmF_2 with comparable data for other fluorides is presented in Table II.²⁻⁵

Qualitative pressure-composition diagrams are presented in Figures 1 and 2.

The results presented here are in general agreement with those of Zmbov and Margrave.⁶

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Table 1. Thermodynamic Values for the Congruent Vaporization of Selected Metal Fluorides at Their Boiling Points

Fluoride	T_b (K)	ΔH_v° (kcal mol ⁻¹)	ΔS_v° (cal mol ⁻¹ K ⁻¹)
SmF ₂ ¹	(2715 ± 5)	(79.1 ± 9.3)	(29.2 ± 6.8)
SmF ₂ ²	(2555 ± 5)	(87.5 ± 9.1)	(34.2 ± 3.6)
SmF ₂ ³	(2700)	(78)	(29)
SmF ₃ ¹	(2420 ± 5)	(65.5 ± 2.5)	(27.1 ± 1.9)
SmF ₃ ²	(2420 ± 5)	(65.5 ± 3.2)	(27.1 ± 1.3)
SmF ₃ ³	(2600)	(62)	(24)
YbF ₂ ¹	(3045 ± 5)	(79.6 ± 8.4)	(26.1 ± 6.1)
YbF ₂ ²	(3015 ± 5)	(82 ± 10)	(27.2 ± 3.3)
YbF ₂ ³	(2650)	(75)	(28)
YbF ₃ ¹	(2490 ± 5)	(82.7 ± 1.8)	(33.2 ± 1.4)
YbF ₃ ²	(2580 ± 5)	(77.6 ± 4.1)	(30.1 ± 1.6)
YbF ₃ ³	(2500)	(60)	(24)
TmF ₃ ¹	(2580 ± 5)	(72.0 ± 1.5)	(27.9 ± 1.3)
TmF ₃ ²	(2600 ± 5)	(71.0 ± 2.3)	(27.3 ₁ ± 0.8 ₈)
TmF ₃ ³	(2500)	(60)	(24)

¹Second-law derived values with estimated uncertainties

²Third-law derived values with estimated uncertainties

³Brewer's estimates; reference 1

Table 2. Thermodynamics for the Congruent Sublimation of Selected Metal(II) Fluorides

Metal ¹	ΔH_{298}° (kcal mol ⁻¹) ²	ΔS_{298}° (cal mol ⁻¹ K ⁻¹) ²	ΔH_{298}° (kcal mol ⁻¹) ³	ΔS_{298}° (est) (cal mol ⁻¹ K ⁻¹)
Ca	(103.2 ₆ ± 0.2 ₃)	(48.3 ₀ ± 0.1 ₅)	(101.5 ₃)	(47.1 ± 2.5)
Ca	(102.5)	(48.1)	(101.0)	(47.1 ± 2.5)
Sr	(100)	(46.4)	-----	-----
Ba	(90)	(45.8)	-----	-----
Eu	(100.8 ₄ ± 0.9 ₂)	(48.9 ₂ ± 0.6 ₀)	(98.3)	(47.3 ± 2.0)
Sm	(99.5 ± 9.3)	(40.9 ± 6.8)	(106.5 ± 9.1)	(45.5 ± 2.5)
Yb	(109.0 ± 8.4)	(46.0 ± 6.1)	(11.1 ± 1.0)	(47.0 ± 2.5)

¹References 2, 3, 4 and 5

²Second-law derived values with associated uncertainties

³Third-law derived values with associated uncertainties

Figure 1. Qualitative Pressure-Composition Diagram for the Sm-F System ($T = 1500 \text{ K}$)

Figure 2. Qualitative Pressure-Composition Diagram for the Tm-F System ($T = 1500\text{ K}$)

Intermediate Phases in the YbCl_2 - YbCl_3 System

Heinrich Luke

Introduction

Although a considerable number of intermediate phases besides $\text{GdCl}_{1.5}$ are known to exist in the rare earth metal-rare earth trihalide systems,^{1,2} the structure of not one of these phases has been investigated. For ytterbium, a phase intermediate between YbCl_2 and YbCl_3 with the approximate composition $\text{YbCl}_{2.28 \pm 0.02}$ has been reported and characterized by its X-ray powder diffraction diagram.² This report deals with the attempted growth of single crystals of this phase and their X-ray investigation.

Experimental

1. Materials

Ytterbium trichloride was prepared from a mixture of $\text{YbCl}_3 \cdot x\text{H}_2\text{O}$ and NH_4Cl according to the method of Cox and Fong.³ The product was purified by high vacuum sublimation and by heating the sublimed product under a Cl_2 atmosphere in order to assure complete oxidation to YbCl_3 .

Zinc granules (reagent grade) were freed mechanically from most of their oxide coating by cutting or filing away a ca. 1 mm thick surface layer.

Hydrogen (Matheson, prepurified grade, purity greater than 99.9%) was used without further treatment.

Commercial THF (analytical reagent grade) was dried over Na and filtered before use.

2. Preparation

a. H₂ Reduction. An about 100 mg sample of YbCl₃ was sealed under 600 torr of H₂ into a small quartz ampoule (5 mm i.d., ca. 100 mm long) and heated as fast as possible (in about 30 min.) to 1000°C. It was maintained at this temperature for about 5 min. and shaken several times in order to assure complete exposure of the melt to hydrogen. The mass was then allowed to solidify by lowering the temperature to 500°C, after which the temperature was elevated to the melting point (560-570°C). The ampoule was kept at the melting point overnight, then cooled slowly at a rate of 10°/hr. to about 530°C. Finally the furnace was turned off and the ampoule was cooled to room temperature.

The product consisted of large, green crystals embedded in a matrix of unreacted YbCl₃. The ampoule was opened under Ar and the YbCl₃ was removed with dry THF. The remaining product was a clear, coarse, crystalline powder.

b. Zinc Reduction. An about 200 mg sample of YbCl₃ was sealed under 1 atm of Ar into a small quartz ampoule (5 mm i.d., 50 mm length) along with the amount of Zn calculated for reduction to compositions which varied between YbCl_{2.20} to YbCl_{2.50}. The reaction was carried out as described above, but different temperatures were applied. The respective temperature steps were applied in the order: 1000°, 400°, 470°, and 430°C. Excess YbCl₃ and the byproduct, ZnCl₂, were dissolved in THF.

3. Analysis

The product was dissolved in water; chlorine content was determined as AgCl. Excess Ag⁺ was removed from the filtrate with HCl and Yb³⁺ was precipitated as the hydroxide, which was subsequently calcined to the sesquioxide at 1000°C.

X-Ray powder diffraction patterns were taken on an 80 mm Haegg-type Guinier camera with CuK_α radiation; Pt powder served as an internal standard.

Single crystal isolation was effected in a Schlenk tube under a flow of Ar. Crystals of the appropriate size (0.05-0.2 mm) were removed from the YbCl_3 or the $\text{YbCl}_3/\text{ZnCl}_2$ matrix. (The ability to remove the byproduct by THF-extraction was discovered after this research had been performed and has not been used for isolation of single crystals). Crystals were selected for further study with the aid of a long glass rod to which they adhered electrostatically; they were then dropped into a quartz or Lindemann glass capillary which was attached to a T-shaped glass tube. The Schlenk tube was closed, evacuated, refilled with Ar, and the capillary was sealed with a flame. The crystals were investigated subsequently by precession and Weissenberg techniques.

Results

Examination of the product under the microscope showed it to consist entirely of clear, green crystals nominally 0.01-0.1 mm. The crystals showed sharp extinctions under polarized light, but no irregularities could be detected. Compared to YbCl_3 the crystals were hard and could be cleaved only with difficulty. They are rather stable in air, but dissolve instantly in water to give a green-yellow solution. Preparations made by the H_2 reduction procedure yielded a composition of $\text{YbCl}_{2.18}$. Those formed by the Zn reduction procedure yielded the composition $\text{YbCl}_{2.11}$. The width of the phase region could not be established.

Although the product seemed completely single-phased by optical means, the single crystals photographs show clearly that the "single crystals" always contained two intergrown phases, and are always twinned. The overlapping is so extensive that a structural determination of either one of the phases on the diffractometer is almost impossible. It is possible to separate the overlapping reciprocal lattices and to derive at least tentatively the lattice constants and possible space groups. These data are presented in Table 1.

Discussion

The results described above resemble somewhat the situation observed in the YbF_2 - YbF_3 system.⁴ In that system investigation of single crystals of the intermediate phase $\text{YbF}_{2.4}$ indicates the possibility of a whole band of intergrown fluoride phases with the comparably difficult structural problems. The chloride system should be more favorable for study because only two phases are known to exist. The larger chloride ion apparently is able to dominate the structure. To obtain more structural information a method to separate these two phases must be found, but all attempts effected to date have failed. Efforts to recrystallize the product from molten, anhydrous ZnCl_2 resulted in the formation of colorless crystals later identified as YbCl_2 .

An attempt to grow crystals by dissolving YbCl_3 in excess ZnCl_2 and reducing the solution by distilling zinc vapor slowly into the melt yielded in some cases large green crystals, which later X-ray investigation showed to be diphasic as before. In another preparation CaCl_2 and YbCl_3 were melted together in the molar ratio of 4:1 in order to replace Yb^{2+} .

(0.94 Å) with Ca^{2+} (0.99 Å). Even though the atomic radii are slightly different, the halides of Yb^{2+} resemble those of Ca^{2+} to a great extent. The similarity is clearly not so close as in the well-known Eu^{2+} - Sr^{2+} case in which Sr^{2+} can form mixed crystals with Eu^{2+} . Only simple CaCl_2 crystals were isolated. Another preparation utilized as the reactant YbCl_2 which was partially oxidized by gaseous Cl_2 generated by terminal decomposition of K_2PtCl_6 . The crystals derived from this preparatory procedure were too small, but I am planning to repeat the experiment. The principal problem apparently is choice of temperature conditions such that only one of the described phases is formed. The temperature conditions utilized may have induced the formation of two phases, but such conditions appeared necessary to induce crystallization since the melt tended to supercool. Every attempt to grow single crystals by slowly cooling of the melt resulted in an almost amorphous product - apparently as a result of sudden solidification of the supercooled mass.

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Table 1
Tentative Crystal Data of Two Intermediate Phases in the
 $\text{YbCl}_2\text{-YbCl}_3$ System

Phase I

monoclinic, probable space group $P2/c$ or Pc

$$a = 20.50 \text{ \AA} \quad b = 6.54 \text{ \AA} \quad c = 6.99 \text{ \AA} \quad \beta = 91^\circ$$

Phase II

monoclinic, probable space group $P2_1/m$ or $P2_1$

$$a = 20.37 \text{ \AA} \quad b = 6.99 \text{ \AA} \quad c = 13.02 \text{ \AA} \quad \beta = 99^\circ$$

Reaction Between Ytterbium Halides and Quartz

Heinrich Lücke

Introduction

In 1973 Ayasse and Eick¹ reported the synthesis and structural determination of the ytterbium chlorosilicate, $\text{Yb}_3(\text{SiO}_4)_2\text{Cl}$. Brandt and Diehl² also prepared this phase and reported its powder diffraction pattern. This phase drew considerable attention at the 10th Rare Earth Research Conference, probably because of potential use of materials of this kind either for IR-visible upconversion or as laser materials. The anhydrous rare earth halides which can be used for these purposes are very air and moisture sensitive and are difficult to handle.³ This report describes several attempts to synthesize with different starting materials new ytterbium-halide-silicate phases.

1. YbOCl

a. Experimental

An attempt was made to synthesize both $\text{Yb}_3(\text{SiO}_4)_2\text{Cl}$ and a second phase which had been obtained by Ayasse and Eick¹ as a byproduct of that preparation. Solid YbOCl was prepared by heating $\text{YbCl}_3 \cdot x\text{H}_2\text{O}$ slowly to 480°C in a stream of Ar.⁴ The product was sealed into a quartz ampoule under 1 atm of chlorine and heated at 1100°C for 4 days.

b. Results

While most of the mass was still amorphous and had not reacted, a minor amount of crystalline material was found in the form of very thin sheets sticking to the upper part of the ampoule. The material was

readily identified as YbOCl ,⁵ apparently transported by the Cl_2 . No silicate phase could be found.

2. $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$

a. Experimental

The compound was prepared by dissolving Yb_2O_3 in HCl and evaporating the solution to dryness.⁶ The product was sealed into a quartz ampoule under 1 atm of Cl_2 and heated to 1000°C for 6 days, checked for crystals, and heated again for three more days.

b. Results

Most of the mass had not reacted, but a ring of tiny clear crystals which adhered very tightly to the wall was found. These crystals were broken off, investigated by precession techniques, and identified as $\text{Yb}_2\text{Si}_2\text{O}_7$.⁷ All crystals were twinned. The unreacted residue after exposure to air showed the powder pattern of $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$.

3. Anhydrous YbCl_3

a. Experimental

Ytterbium trichloride was prepared from a mixture of $\text{YbCl}_3(\text{aq})$ and NH_4Cl according to the method of Taylor and Carter.⁸ The trichloride was sealed under one atmosphere of Cl_2 and heated overnight to 1000°C .

b. Results

After 12 hours of heating the reaction was virtually complete. The product consisted of large clear plates and rods, some almost 1 mm long. The product was identified on the precession camera as $\text{Yb}_2\text{Si}_2\text{O}_7$.

4. Anhydrous YbCl_3 and Br_2

a. Experimental

Ytterbium trichloride was sealed under Ar into a small (3 mm I.D.) quartz ampoule, the tip of which was pulled out and bent back to form a thin U-shaped capillary. Bromine was sealed into another ampoule of similar shape. The quantity of Br_2 used was three times that amount necessary to replace all 3 Cl-atoms by Br. Both of these small ampoules were then sealed under Ar into a larger quartz cylinder. The capillary tips of the small ampoules were fractured by forcibly contacting them against the interior wall of the outer cylinder; the large cylinder was then heated for 24 hours at 1050°C .

b. Results

Some of the material had reacted with the quartz wall and formed clear crystals which were identified by their powder diffraction pattern as $\text{Yb}_2\text{Si}_2\text{O}_7$.

5. Anhydrous YbCl_3 and I_2

a. Experimental

The technique described in 4 was used for the reaction of anhydrous YbCl_3 with I_2 with a Cl:I ratio of 1:1. The ampoule was heated for 12 hours at 1050°C .

b. Results

Reaction with the quartz wall could not be detected. The YbCl_3 , however, had become deep yellow-brown, and showed large yellow single crystals. Upon exposure to air these crystals decomposed with the liberation of deep brown spots of iodine. Some of the crystals which were isolated

in capillaries were investigated on the precession camera and showed an expanded, highly disordered lattice of YbCl_3 ,⁹ apparently the result of solid solution of iodine in the YbCl_3 lattice. No silicate phase was observed.

Discussion

The results show that in the temperature range studied (1000-1100°C) $\text{Yb}_2\text{Si}_2\text{O}_7$ is the most stable phase. It is interesting that large single crystals of this phase can be obtained easily by reacting the halide with quartz whereas preparation of such crystals from the oxide requires very high reaction temperatures (1500°C).⁷ Preparation of phases other than $\text{Yb}_2\text{Si}_2\text{O}_7$ apparently requires temperatures higher than 1100°C. Brandt and Diehl² assume that the formation of the chlorosilicate, $\text{Yb}_3(\text{SiO}_4)_2\text{Cl}$, is brought about by cleavage of the $\text{Si}_2\text{O}_7^{6-}$ group by YbOCl according to the reaction

This compound must be stable with respect to disproportionation into YbCl_3 and $\text{Yb}_4(\text{SiO}_4)_3$. This somewhat unexpected behavior suggests that despite the failure of the preparations described above some other halo-silicates may exist at temperatures in excess of 1100°C - temperatures at which formation of the monosilicate group, SiO_4^{4-} , is favored over that of the disilicate group, $\text{Si}_2\text{O}_7^{6-}$.

Another possibility that has not been investigated is the formation of the phases with mixed valency states of ytterbium.

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An X-Ray Structural Investigation of an Ytterbium(III)
Oxidechloride Phase

John T. Richards

Introduction

The goal of this project was the preparation of a crystalline sample of the phase $\text{YbCl}_{2.26}$ for structural and thermodynamic study. One preparation yielded a crystal suitable for a structural investigation. As a result of structural analysis, I deduce that the crystal contains some oxide contaminant. A complete refinement could not be effected.

Experimental

Two reaction procedures were followed for the preparation of the intermediate phase $\text{YbCl}_{2.26}$: 1) a mixture of ytterbium metal and ytterbium trichloride confined in a sealed ampoule was heated to temperatures between 550 and 1450°C (various runs) and 2) a mixture of ytterbium dichloride and trichloride confined in a sealed tantalum ampoule was heated to a temperature of 800°C. These temperatures were chosen as being less than, equal to and greater than the melting points of the reactants (the metal, dichloride and trichloride melt in the range 700 to 865°C).

A consistent heating procedure was used in all preparations. The reactants were cycled to temperature over a period of eight hours, heated at temperature for periods of time which varied from 1.5 to 13 days, then cooled to room temperature over a period of eight hours. In some preparations carried out by the first procedure, a very small amount of iodine was included to serve as a transport agent; iodine was present in all preparations carried out by the second procedure.

Ytterbium trichloride was prepared according to the method of Taylor and Carter.¹⁰ The overall reaction is as follows:

Ytterbium dichloride was prepared according to the method of DeKock and Radtke.¹¹ The overall reaction is:

Zinc metal and zinc chloride are added to YbCl_3 to provide a reducing melt (mole ratios: $\text{ZnCl}_2/\text{YbCl}_3 = 1.2$, $\text{NH}_4\text{Cl}/\text{YbCl}_3 = 12$, $\text{Zn}/\text{YbCl}_3 = 2$). The reaction temperature is increased to over 500°C and maintained at that temperature for more than an hour until a clear melt is obtained. The crude product was purified by sublimation at 1300°C under high vacuum.

Routine analyses of the trichloride and dichloride prepared by these methods were effected by an X-ray powder diffraction technique. An 80 mm Guinier forward focusing camera which employed $\text{CuK}\alpha$ radiation was used. Platinum powder ($a = 0.39237(3)$ nm) was included as an internal standard in the samples for powder diffraction analysis.

X-Ray fluorescence experiments were performed with a Norelco spectrometer (see first report in this document). Three backing targets were used: platinum, aluminum and quartz. Quantitative analyses were not attempted, only the qualitative presence of metals was examined.

Both the ytterbium dichloride and trichloride are hygroscopic materials¹ and must be isolated from atmospheric moisture. Additionally, it was assumed that all intermediate phases in the dichloride-trichloride system

would behave similarly. All transfer of materials was performed in a dry box under a dried argon atmosphere and at all other stages of experimental work precautions were taken to isolate the experiment from atmospheric moisture.

Results

The results of the preparations were examined visually under a microscope. Typically, the Yb/YbCl_3 reaction products included unreacted ytterbium metal, a black compound of unknown composition and colorless to light green crystals of no repetitive morphology. The results of the $\text{YbCl}_2/\text{YbCl}_3$ preparations were unclear, the product being composed of the same green crystals (YbCl_2) and white powder (YbCl_3) that were the reactants. Seven preparations were run, five of the Yb/YbCl_3 type and two of the $\text{YbCl}_2/\text{YbCl}_3$ type.

When suitable crystals were found, they were mounted on an X-ray precession camera for preliminary investigation. A suitable crystal was taken as one that was visibly single and was of an unrecognized structural type.

One of the colorless crystals was chosen first for examination and was eventually identified from the unit cell parameters and space group as YbCl_2 . This result, together with the ytterbium metal observed in the product, indicates incomplete reaction in these preparations.

Close examination of all the samples prepared showed only one to contain crystals of a type different from YbCl_2 . This preparation consisted of metal and trichloride mixed in $\text{Cl:Yb} = 2.26$ stoichiometric

proportions with a small chip of iodine (mole ratio: total Yb/I₂ > 300) added to the tantalum ampoule before it was welded shut. The temperature was raised to 1000°C and held there for two hours, then maintained at 800°C for five days. Aside from the unreacted metal and the recognizable dichloride, there was a small number of green plate-like crystals. The total yield of this type of crystal was estimated to be approximately a milligram.

The majority of these crystals could be seen as twinned by means of the platelets being stacked on top of each other. Several others were only verified as twinned by precession X-ray photography. One good crystal was found for a structural determination (0.24 X 0.14 X 0.056 mm) and was mounted and sealed in a glass capillary.

The precession photographs of this crystal were found to be consistent with a hexagonal unit cell with lattice parameters $a = 0.617(4)$ and $c = 1.96(6)$ nm. Neither any general nor any specific extinction condition was found to limit the possible reflections. There are five space groups of hexagonal symmetry which have no general or special extinction conditions: $P6_{22}$, $P6_{mm}$, $P\bar{6}m2$, $P\bar{6}2m$ and $P6/mmm$. Of these five, only $P6/mmm$ is centrosymmetric.

Single crystal diffraction measurements of this crystal were effected on a computer controlled (program FACS I), four circle, Picker goniometer with Mo K α radiation and a perpendicular graphite monochromator. Room temperature during the data collection was $22 \pm 3^\circ\text{C}$. Preliminary examination confirmed that the crystal has hexagonal symmetry and that it has no general or special extinction conditions. A least squares lattice

parameter fit of twelve data points gave the following values: $a = 0.6187(1)$, $c = 1.976(1)$ nm. Table I lists pertinent data collection parameters.

In correcting the raw data for background radiation, the observed intensity was defined to be zero if the raw intensity was less than two sigma. Sigma, a measure of the uncertainty in the reflection intensity, was calculated from counting statistics by the method of Ibers.² An empirical absorption correction was applied to the data to reflect the fact that the crystal is not spherical and at different orientations the incident X-ray beam had different pathlengths to travel. Strong reflections were chosen and the crystal was rotated full-circle around the ϕ angle. Rotating a crystal 360° through the X-ray beam, as described, necessarily results in a sinusoidal empirical absorption curve.

The absorption correction was determined after the reflection data had been collected. To achieve a sinusoidal correction the diffractometer had to be realigned. Phi curves around the $\bar{1}20$ and the $\bar{3}60$ were collected and averaged for the empirical absorption correction.

The raw data set contains two equivalent sets of reflections: the hexagonal symmetry requires that the sets hkl and $kh\bar{l}$ be equivalent because they are related by a mirror plane. Examination of the absorption corrected data shows that the reflections which are supposed to be equivalent do not differ from each other by more than three sigma. These two sets of data were averaged together to give 378 independent reflections.

Structure Determination

A three dimensional Patterson function was calculated for the data set after the absorption correction had been applied to the data and the

equivalent reflections averaged. The centrosymmetric space group $P6/mmm$ was used in the synthesis. Table 2 lists the positions, relative peak heights and assignments to the vectors observed in the map.

The largest vector peaks were found in six levels of the Patterson map: fractional w coordinates 0.000, 0.155, 0.187, 0.310, 0.337 and 0.500. These levels were interpreted as being the six distances of separation of planes of metal atoms along the long axis of the unit cell. There are only three types of vector positions in the map: $u, 0, w$; $1/3, 2/3, w$ and $0, 0, w$. Two image seeking functions³ were used on the map to establish possible real fragments of the heavy atom positions - $(1/3, 2/3, z$ and $2/3, 1/3, z)$ and $0.325, 0, z$; $0, 0.325, z$ and $0.675, 0.675, z)$. The image seeking functions indicated the $1/3, 2/3, z$ position was real and the $x, 0, z$ position was probably real, but for more than one value of x .

The requirement for strong peaks at the level $w = 0.187$ was found to be satisfied by two eclipsed sets of $x, 0, z$ positions separated by that increment in z . These positions disallowed the space group $P622$ because the only levels possible for $x, 0, z$ positions in this symmetry are $z = 0$ and $z = 1/2$, a separation of $z = 0.500$. The space group $P\bar{6}m2$ was rejected for the same reason. Space groups $P6mm$ and $P6/mmm$ were not considered because the $x, 0, z$ positions in these two symmetries require placing six metal atoms in the same x, y plane. With six metals in the same plane, the best metal-metal separation in $x, 0, z$ positions would be $2.06 \text{ \AA}$, less than half the Yb-Yb separation found in YbCl_2 , for example.

Of the five possible space groups listed previously, $P\bar{6}2m$ is the only one consistent with the Patterson results. All the major peaks in the

Patterson map are accounted for by placing metal atoms in the positions shown in Table 3.

The metal atoms are located in the unit cell in three sets of special positions. Two sets are $x,0,z$ positions around $z = 0.000$ and $z = 0.500$ ("staggered" to each other with $x = 0.638$ and $x = 0.369$) which account for the Patterson peaks at $0,0,0.187$ and $1/3,2/3,0.187$ - each $x,0,z$ set is split by symmetry into two eclipsed subsets with an average spacing between them of $z = 0.187$. Between the staggered sets are average distances of $z = 0.310$ and $z = 0.500$. The third set of metal atoms occupies the positions $1/3,2/3,z$ at $z = \pm 0.251$. Between this third set and the first two are average distances of z equal to 0.155 and 0.337 .

Some metal to anion vectors are found in the Patterson map at low peak heights. The $x,0,z$ sets of metal atoms are spaced an average of $z = 0.094$ above and below the levels of $z = 0.000$ and $z = 0.500$. Thus the vector peaks at $0,0,0.098$ and $1/3,2/3,0.098$ are interpreted to mean that anions are located at the zero and $1/2$ levels in positions eclipsed to the surrounding metal atoms. The $u,0,w$ vector positions at $w = 0.255$ and 0.405 confirm that the anions at the zero and one-half levels are in $x,0,z$ positions in real space.

Scattering factor tables and a correction for anomalous dispersion were included in the least squares refinement. The scattering factors computed by Cromer and Waber⁴ were used for the ytterbium and chloride ions, those of Tokonami⁵ were used for the oxide ion. The anomalous dispersion corrections of Cromer⁶ were used. The scattering factor tables allow corrections for an atom interacting with the incident X-ray

beam as a function of the scattering angle. Anomalous dispersion is an effect by which an atom that is absorbing radiation strongly will scatter radiation with different phase changes than the other atoms in the structure.

With only the metal atoms in the refinement and with isotropic temperature factors, an R value of 0.196 was attained. Employing anisotropic motion gave an R value of 0.136 for the metal atoms alone. For the final refined parameters listed in Table 3 and Table 4, an R value of 0.101 was achieved.

Discussion

After the metal atom positions of the unit cell had been determined, it was seen that the phase being investigated contained atoms other than just ytterbium and chlorine. From a consideration of the closest packing of hard spheres with radii equal to the crystal radius of the chloride anion ($1.81 \text{ \AA}$),⁷ calculations show that between six and seven layers of three chloride ions each can be packed within the dimensions of the unit cell. Allowance for negative deviations from this crystal radius allows for up to eight or nine layers, or a maximum of 27 negative charges in the unit cell. Even the assumption that all 16 metal positions are filled by divalent ytterbium leaves a deficiency of five negative charges.

This problem may be solved by recognizing oxygen as a likely contaminant. Ytterbium oxide chloride is known¹ to form in ytterbium chloride systems when a trace of water is present. From a single crystal structural study⁸ the following lattice parameters are reported for hexagonal YbOCl :
 $a = 0.3726$, $c = 2.7830 \text{ nm}$. The atomic positions of YbOCl all lie on the

z-axis of the unit cell, forming linear anion-metal-anion interactions. The Patterson and Fourier maps in this study indicate linear anion-metal-anion interactions, parallel to the z-axis of the unit cell. An oxide anion has a much smaller crystal radius ($1.40 \text{ \AA}$)⁷ than does the chloride anion. The double negative charge on the oxide anion also requires that fewer of these anions be put in the unit cell. However, a combination of space group symmetry and closest packing considerations still restricts to three the number of oxide anions that can be placed in any x,y plane.

The final refinement listed in Tables 3 and 4 identifies four anion positions. Anions 1, 2 and 4 were assigned the oxide anion scattering factor table during the least squares refinement; Anion 3 was assigned the chloride anion scattering table. This assignment was made in earlier cycles of refinement; with more than four anion positions occupied, Anion 3 had metal-anion distances closer to those of Yb-Cl than Yb-O (see below). With just four anion positions occupied, the metal-anion distances of separation have readjusted to different values, so no definite identification of the anions should be made from metal-anion separation distances until after the structure has been completed.

Conclusion

The intent of this research was to characterize a mixed oxidation state in the ytterbium(II)-ytterbium(III) chloride system. Based on ionic size considerations and observed metal-anion distances from the partial structure refinement that was possible, the phase probably contains oxygen atoms.

Sixteen ytterbium atoms are contained in the unit cell in two types of special positions: two six-fold $x,0,z$ positions and a four-fold $1/3,2/3,z$ position. Moreover, anions occupy only these two types of positions as indicated by the Patterson map, Fouriers and difference Fouriers, and the partial refinement of three metal and four anion positions. As a necessary consequence of space group $P\bar{6}2m$, these sets of ions are located in a layered pattern along the long c -axis of the unit cell, in good agreement with the plate-like morphology of the phase.

The ytterbium positions and the partial set of refined anion positions may be interpreted in terms of three possible models for the complete crystal structure. All three models assign both $x,0,z$ sets of metal atoms to Yb_2O_3 structural units. The first model consists of the $1/3,2/3,z$ metal atoms as part of linear units of $YbCl_2$, the second puts $YbOCl$ units in these positions, and the third has YbO units in the four-fold position.

These three models require a linear group around the four-fold position. Of the three possibilities, YbO units must be linear, units of $YbOCl$ are reported⁸ to be linear, and units of $YbCl_2$ are reported⁹ to have a bent configuration. Because the oxide chloride is a known¹ contaminant in ytterbium chloride systems, the model chosen for the complete structure is the one having $YbOCl$ units in the four-fold positions. The final structure by this model would consist of sesquioxide and oxide chloride units to build the $Yb_{16}O_{22}Cl_4$ unit cell, or $(Yb_2O_3)_6(YbOCl)_4$. This formula was used to calculate a density and linear absorption coefficient for the crystal.

Figures 1-3 show three projections of this structural model. Figure 1 is a projection of the refined metal atom positions on the (001) plane, Figure 2 is a projection of the refined anion positions on the (001) plane. Numbering of positions on both figures corresponds to the numbering system of the final refinement (Table 3). Figure 3 is a projection of the $\text{Yb}_{16}\text{O}_{22}\text{Cl}_4$ model on the (010) plane. The darker circles of Figure 3 represent atomic positions in the (010) plane, the fully dashed circles represent anion positions that are not refineable. Figure 2 shows the near-eclipsing of x,0,z anion positions, Figure 3 shows the layered packing of ions in the unit cell.

The unit cell for the above model may be considered to be derived from the hexagonal symmetry of YbOCl with that of the cubic symmetry exhibited in ytterbium sesquioxide.

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Table 1: X-ray Diffraction Data Collection

Mo radiation

$\lambda = 0.70926 \text{ \AA}$, no filter, kV = 40, ma = 18

ω Scanned

$1^\circ/\text{min.}$, no attenuator, background time = 20 sec.

Perpendicular graphite monochromator, $d = 3.354 \text{ \AA}$

$\sin\theta/\lambda$: $0.03691 \text{ \AA}^{-1}$ to $1.15494 \text{ \AA}^{-1}$

662 reflections measured, 107 absent

Empirical absorption correction applied

$V = 655.4 \text{ \AA}^3$

$\rho(\text{calc}) = 8.3 \text{ g/cc}$

$\mu = 598 \text{ cm}^{-1}$

Table 2: Patterson Map

P6/mmm Positions	u	v	w	Relative Height	Assignment
1a	0.000	0.000	0.000	999	Origin
2c	0.333	0.667	0.000	505	Yb-Yb in same x,y plane
2e	0.000	0.000	0.098	66	Yb(x,0,z) - Anion(x,0,z+ 0.098)
4h	0.333	0.667	0.098	13	Yb(x,0,z) - Anion(0,x,z+ 0.098)
12n	0.325	0.000	0.155	195	Yb(x,0,z) - Yb(1/3,2/3,z+ 0.155)
2e	0.000	0.000	0.187	387	Yb(x,0,z) - Yb (x,0,z)
4h	0.333	0.667	0.187	178	Yb(x,0,z) - Yb (0,x,z)
12n	0.325	0.000	0.255	16	Yb(1/3,2/3,z) - Anion(x,0,z+ 0.255)
12n	0.350	0.000	0.310*	104	Yb(x,0,z) - Yb (x,0,z+0.310)
12n	0.325	0.000	0.337*	195	Yb(x,0,z) - Yb (1/3,2/3,z+0.337)
12n	0.325	0.000	0.405	19	Yb(x,0,z) - Anion (x,0,z+0.405)
1b	0.000	0.000	0.500	171	Yb(1/3,2/3,z) - Yb(1/3,2/3,z+ 0.500)
2d	0.333	0.667	0.500	96	Yb(1/3,2/3,z) - Yb(2/3,1/3,z+ 0.500)
6k	0.350	0.000	0.500	238	Yb(x,0,z) - Yb (x,0,z+0.500)

*Strongly overlapping peaks

Table 3: Refined Atom Positions in Space Group $P\bar{6}2m$

Atom	x	y	z
Anion 1	0.5957	0.0000	0.0000
Yb 1	0.6383	0.0000	0.0962
Anion 2	0.5892	0.0000	0.1900
Yb 2	0.3333	0.6667	0.2513
Anion 3	0.3716	0.0000	0.2902
Anion 4	0.3333	0.6667	0.3578
Yb 3	0.3609	0.0000	0.4073

Table 4. Temperature Factors

Atom	B11 or B	B22	B33	B12	B13	B23
Anion 1	-2.44					
Yb 1	-1.53	-0.81	0.65	-0.81	-0.02	0.00
Anion 2	-1.74					
Yb 2	-1.00	-1.00	1.34	-1.00	0.00	0.00
Anion 3	4.96					
Anion 4	0.23					
Yb 3	-1.20	-1.27	1.56	-1.27	0.21	0.00

Figure 1. Projection of Metal Atom Positions on (001) Plane

Figure 2: Projection of Anion Positions on (001) Plane.

Figure 3. Projection of $\text{Yb}_{16}\text{O}_{22}\text{Cl}_4$ on (010) Plane.

Mixed Halide Phase of Europium and Ytterbium

Beatrice L. Clink

Introduction

The goal of this project was the preparation and characterization of some europium and ytterbium mixed halide phases. Since the thermodynamic properties of EuCl_2 , EuBr_2 and EuCl_3 were well characterized, the initial efforts of the study were directed to combinations of these elements.

Preparation

1. Anhydrous Lanthanide Trichlorides

Both europium and ytterbium trichloride were prepared according to the method of Taylor and Carter¹ as modified by Hariharan.²

The product was transferred to a glove box, where the sample was stored in a screw capped vial, which was then sealed in plastic under a dry argon atmosphere.

2. Anhydrous Lanthanide Chloride Bromide Phases

Based on the known thermodynamics for the europium trichloride and tribromide systems, and thermodynamic functions for a mixed halide phase assumed to lie linearly between those of the pure phases, methods that use $\text{Cl}_2(\text{g})$ or $\text{Br}_2(\text{g})$ to chlorinate or brominate the desired lanthanide trihalide are unfavorable for the preparation of pure mixed halide phases. However, the reaction (1) involving ammonium bromide and europium trichloride seemed favorable.

$$(\Delta G = -9.0 \text{ kcal mol}^{-1})^{2-4}$$

The sealed bomb preparation was based on these calculations.

The acidic nature of ammonium halide is believed to prevent hydrolysis of the lanthanide trihalide in the Taylor-Carter preparation.¹ It is my belief that there is an exchange of halide ion between the ammonium halide and the intermediate phase, but no investigation presently available defines this reaction pathway. The pseudo Taylor-Carter preparation of the mixed halide is based on the assumption of a halide ion exchange between the ammonium halide and the europium halide hydrate or other decomposition intermediate.

a. Sealed Bomb Preparation

A 1:1.25 mole ratio of anhydrous europium trichloride to dried ammonium bromide was heated in an outgassed quartz tube under vacuum at 395°C for four days. The sealed bomb was cooled over a period of ~ 6 h, transferred to the glove box, opened, and the contents removed. The various colored phases were separated according to color and stored in screw-capped vials sealed in plastic.

An attempt was made to remove the excess ammonium halide by heating the sample in vacuum over a temperature range of 170-200°C for a period of ~ 24 h.

b. Pseudo Taylor-Carter Preparation

This preparatory method is similar to that described earlier for the anhydrous lanthanide trichlorides. The anhydrous lanthanide trichloride and ammonium bromide, in a 1:6 mole ratio, were mixed in aqueous solution which was subsequently evaporated to dryness. The lanthanide trihalide hydrate-ammonium bromide matrix was transferred to a carbon boat and heated under a deoxygenated helium stream at 200°C

(or 250°C) for ~ 16 h. Once excess water appeared to have evaporated, the temperature was raised to 370°C and heating continued (~ 4 h) until the orange phase had completely decomposed into a light grey powder. The sample was cooled and treated as described earlier.

3. Single Crystal Preparation

Single crystals of mixed halides (obtained from the pseudo Taylor-Carter preparation) were crystallized from the liquid melt by slow cooling.

The mulled sample was sealed in an outgassed quartz tube under vacuum (10^{-6} torr), heated to a liquid melt ($\sim 660^\circ\text{C}$), and then cooled to a temperature of 300°C over a period of several days at $\sim 20^\circ\text{C}/8$ h. The sample was cooled rapidly from 300°C and transferred to the glove box in the sealed quartz tube.

Elemental Analyses

1. Metal Analysis

The metal content was measured gravimetrically. Samples were weighed directly into constant weight platinum crucibles and ignited to the sesquioxide at 950°C in a muffle furnace.⁵

2. Halide Analysis

a. Total halide analysis was effected by an amperometric procedure with a rotating Pt electrode.

b. Chloride analysis was effected by oxidation by Br^- to Br_2 , with subsequent removal by aeration, followed by amperometric titration.

3. Data Reduction

The empirical formula was calculated with the results of the metal, total halide and chloride analytical results.

X-Ray Diffraction Analyses

1. Powder Diffraction Analysis

Diffraction patterns of powdered samples were obtained with a Haegg Type Guinier forward focussing camera (radius 80 mm) and $\text{CuK}\alpha$ radiation, Pt internal standard ($a = 0.39231 \text{ nm}$), $t = 24 \pm 2^\circ\text{C}$. Guinier techniques have been described in previous reports and in detail by Stezowski.⁶

With platinum powder as the internal standard, the diffraction data were reduced with the least squares regression program of Lindqvist and Wengelin.⁷

2. Single Crystal X-Ray Diffraction Analysis

a. Crystal Mounting

Crystals were transferred to a special capped transfer tube (Figure 1) in the glove box. The procedure used to select a crystal has been described earlier in this report by Lücke.

It was necessary to seal the capillary as close to the crystal as possible in order that it would be locked in place. The tube was then mounted in clay on the goniometer head.

b. Equipment and Parameters

Lattice parameters and intensity data measurements were made at a temperature of $23 \pm 3^\circ\text{C}$ with a computer-controlled, four-circle, Picker goniostat with $\text{Mo K}\alpha$ radiation ($\lambda = 0.07093 \text{ nm}$), and a graphite monochromator mounted adjacent to the X-ray tube.

The ω -scan technique was used for data collection with a scan range of 1.5° and a scan rate of $1.0^\circ/\text{min}$. Both the hkl and $\bar{h}\bar{k}l$ octants were collected.

Cell constants were obtained from a least squares refinement of 12 reflections which were hand-centered on the goniostat. Reflections from the $\bar{h}\bar{k}l$ and hkl octants were centered. The crystal data are presented in Table 1.

PKCORR, an adaption of NUFACS written by Ibers,^{8,9} was used to correct the intensity measurements for background. An empirical absorption correction around the ϕ curve was applied using EMPASS. Lorentz and polarization corrections were effected with the program INCOR provided by A. Zalkin. This program had been modified to include a correction for the graphite monochromator. The least squares refinement program was also provided by Zalkin.

Results

1. Phase 1

a. Elemental Analyses

The pseudo Taylor-Carter preparation in which the initial heating period was at a temperature less than 200°C yielded a white hydroscopic powder. Halide and metal analysis showed the product to be

$\text{EuCl}_{0.46}\text{Br}_{1.56}$. Results of the analysis are listed in Table 2.

b. Single Crystal X-Ray Diffraction Analysis

From precession measurements and intensity data collected by use of a four circle goniostat, the unit cell was determined to be orthorhombic with lattice parameters: $a = 0.7880(3)$, $b = 0.9198(4)$, and $c = 0.4611(2)$ nm.

Because of the close similarity between the unit cell and extinctions observed in the intensity data of the mixed halide phase and that of EuCl_2 ($a = 0.751$, $b = 0.893$, $c = 0.450$ nm),² an attempt was made to solve the structure based on least squares refinement of the atomic coordinates of EuCl_2 (PbCl_2 structure type) with various concentrations of bromide ion substituted for chloride ion.

The positions used for the calculations were those of the space group Pbnm , no. 62, as given by Baernighausen⁹ with x and y being interchanged according to the choice of the principle axis. In this setting all atoms are in special positions defined by the symmetry relationships:

$$x, y, z$$

$$1/2 - x, 1/2 + y, 1/2 + z$$

$$1/2 + x, 1/2 - y, z$$

$$-x, -y, 1/2 + z$$

The chloride ions have two different points of symmetry. Negative thermal parameters arose when a chloride ion was refined in position two, an indication that the electron density was too low. A bromide ion was substituted for the chloride ion in this position. The electron density was then increased further by progressively replacing the chloride ion scattering curve with that of a bromide ion until the R factor was minimized (and thermal parameters maximized). By plotting R as a function of the mole % bromide of the total halide and finding the best least squares parabola to fit the data, one finds the minimum at 75.1% bromide, which corresponds to an empirical formula of $\text{EuCl}_{0.498}^{\text{Br}}1.502$.

2. Phase 2

a. Elemental Analyses

The white hygroscopic powder obtained from the pseudo Taylor-Carter preparation (initial heating temperature greater than 250°C) had the empirical formula $\text{EuCl}_{0.16}\text{Br}_{1.85}$. Results of the metal and halide analyses are listed in Table 3.

Discussion

A single crystal structure determination of EuCl_3 was done by Morosin.¹⁰ Four of the chloride ions in the metal ion coordination sphere have metal-chloride bond distances of 0.4492 nm, two have bond distances of 0.2835 nm, and there is one with a M-Cl bond distance of 0.2919 nm. The ionic radius of Eu(III) is 0.0950 nm,¹¹ while Pauling lists the ionic radius of bromide ion as 0.195 nm. The sum of the ionic radii is 0.290 nm. A bromide ion could easily substitute for the four chloride ions with bond distances of 0.4492 nm. The empirical formula for such a compound would be $\text{EuCl}_{1.28}\text{Br}_{1.72}$. There is the possibility of further substitution of a bromide ion for the chloride ion with a metal bond distance of 0.2919 nm. The empirical formula of this compound would be $\text{EuCl}_{0.86}\text{Br}_{2.14}$. In either case, we would expect the bromide ion to be the reducing ion, and the final divalent halide, from the decomposition of these trivalent europium mixed halide phases, to be richer in chloride than either phase prepared.

A similar study of the EuCl_2 structure shows one metal-chloride bond each of 0.3046, 0.2994, and 0.2916 nm and two metal-chloride bonds of 0.3440 and 0.2925 nm. The ionic radius of Eu^{2+} is reported to be between

0.121 and 0.129 nm depending on the anion.⁹ In this structure 56% of the chloride ions lie in the center of a square pyramid of metal ions and 44% lie in a tetrahedral hole. As would be expected, the M-Cl bond distances greater than 0.3 nm are for those chloride ions in the tetrahedral holes. If a bromide ion were substituted for seven of the nine chloride ions in the coordination sphere, the empirical formula for such a compound would be $\text{EuCl}_{0.44}\text{Br}_{1.56}$. The R function in the single crystal analysis of Phase 1 was minimized for a compound with the empirical formula $\text{EuCl}_{0.5}\text{Br}_{1.5}$ with bromide ion substituted entirely for the chloride ion in position two. The elemental analyses showed Phase 1 to be $\text{EuCl}_{(0.46 \pm 0.02)}\text{Br}_{(1.56 \pm 0.07)}$. For bromide ions in eight of the nine positions, the empirical formula of such a compound would be $\text{EuCl}_{0.22}\text{Br}_{1.78}$, analogous to Phase 2, $\text{EuCl}_{(0.16 \pm 0.04)}\text{Br}_{(1.85 \pm 0.04)}$.

The reduction of the anhydrous europium trichloride to the dichloride is not known to be significant under the experimental conditions used in this work. One would not expect EuCl_2 to be a major intermediate, yet the structure may be used to account for the particular phases obtained. It is interesting to note that even with the high concentration of bromide ion, the unit cell appears to retain its orthorhombic symmetry.

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Table 1. Crystal Data for $\text{EuCl}_{0.46(s)}\text{Br}_{1.56(7)}$

$$\text{EuCl}_{0.46(2)}\text{Br}_{1.56(7)}, \underline{M} = 239(6) \text{ g mol}^{-1}$$

$$\underline{a} = 0.7880(3), \quad \underline{b} = 0.4611(2), \quad \underline{c} = 0.9198(4) \text{ nm}$$

Systematic Absences: $0k\ell, k + \ell = 2n + 1; h k 0, h = 2n + 1$

Space Group: $Pnma$, No. 62

$$\underline{Z} = 4, F(000) = 502(11) \text{ e}, \underline{V} = 334.2(3) \text{ \AA}^3$$

$$\mu = 387.1 \text{ cm}^{-1} \text{ (Mo } K\alpha)$$

$$D = 4.75 \text{ g cm}^{-3}$$

$$(\text{Mo } K\alpha, \text{ graphite monochromator}) = 0.07093 \text{ nm}$$

Table 2. Analysis of Phase 1 ($\text{EuCl}_x\text{Br}_{2-x}$)

Species	Moles/Gram of Sample	Moles of Halide/Mole of Eu Ion
Total Halide	$7.1_2 \pm 0.27 \times 10^{-3}$	2.02 ± 0.07
Chloride	$1.6_2 \pm 0.07 \times 10^{-3}$	0.46 ± 0.02
Bromide	$5.4_9 \pm 0.28 \times 10^{-3}$	1.56 ± 0.07
Eu Ion	$3.51_2 \pm 0.005 \times 10^{-3}$	

Table 3. Analysis of Phase 2 ($\text{EuCl}_x\text{Br}_{2-x}$)

Species	Moles/Gram of Sample	Moles of Halide/Mole of Eu Ion
Total Halide	$6.6_3 \pm 0.50 \times 10^{-3}$	2.01 ± 0.04
Chloride	$5.3_0 \pm 1.3 \times 10^{-4}$	0.16 ± 0.04
Bromide	$6.1_0 \pm 0.51 \times 10^{-3}$	1.85 ± 0.04
Eu Ion	$3.3_0 \pm 0.08_3 \times 10^{-3}$

- A. Glass rod
- B. Viewing window
- C. Transfer tube (flat bottom)
- D. Vacuum stopcock
- E. Mounting apparatus
- F. Capillary protection tube
- G. Vapor inlet from F
- H. Capillary
- I. Closing tube

Figure 1. Single crystal mounting apparatus.