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

Progress Report

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The following constitutes the technical progress report of work performed under Contract AT(11-1)-716 during the year 1973-74. Following the summary of the years activities are a series of brief preprints, each of which bears the name of the investigator. Documents produced since the last technical progress report have been submitted as separate items and are tabulated below. Six copies of reprints published since the last technical progress report ~~are included as a separate attachment, and~~ are listed below.

The following documents have been or will be submitted for publication.

1. "The Incongruent Vaporization of Europium(III) Oxide Chloride," by A. V. Hariharan and H. A. Eick, *High Temp. Sci.*, 5, 269 (1973) (COO-716-080).
2. "Sublimation Thermodynamics of EuSe," by A. V. Hariharan and H. A. Eick, *J. Chem. Thermodynamics*, in press (COO-716-081).
3. "Synthesis and Crystal Structure of Triytterbium Chloroorthosilicate, $Yb_3(SiO_4)_2Cl$," by C. Ayasse and H. A. Eick, presented at the 10th Rare Earth Conference, 1973 (COO-716-082).
4. "Sublimation and Vaporization Thermodynamics of Ytterbium(II) Fluoride," by R. M. Biefeld and H. A. Eick, submitted to *High Temp. Sci.* (COO-716-083).

The following reprints are also appended.

1. "Vaporization Thermodynamics of EuI_2," by A. V. Hariharan and H. A. Eick, *High Temp. Sci.*, 4, 379 (1972) (COO-716-073).
2. "Vaporization Thermodynamics of $YbCl_2$," by A. V. Hariharan, N. A. Fishel, and H. A. Eick, *High Temp. Sci.*, 4, 405 (1972) (COO-716-074).
3. "The Sublimation Thermodynamics of Zinc(II) Fluoride," by R. M. Biefeld and H. A. Eick, *J. Chem. Thermodynamics*, 5, 353 (1973) (COO-716-075).
4. "Preparation, Characterization, and Some Thermodynamic Properties of Lanthanum Oxide Carbide, $La_2O_2C_2$," by A. Duane Butherus and H. A. Eick, *J. Inorg. Nucl. Chem.*, 35, 1925 (1973) (COO-716-077).
5. "Synthesis and Crystal Structure of Triytterbium Chloroorthosilicate, $Yb_3(SiO_4)_2Cl$," by C. Ayasse and H. A. Eick, *Inorg. Chem.*, 12, 1140 (1973) (COO-716-078).

6. "The Incongruent Sublimation of Europium(III) Oxochloride," by A. V. Hariharan and H. A. Eick, *High Temp. Sci.*, **5**, 269 (1973) (COO-716-080).

During the academic year the principal investigator devoted twenty percent of his effort to the research described in this report. During the summer he devoted sixty percent of his effort to this research.

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.
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3. George D. Sturgeon, Ph.D., 1964, Associate Professor of Chemistry, University of Nebraska, Lincoln, Nebraska.
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The present position of masters students trained under this grant are:

1. Sandra Leonard, M.S., 1971, Instructor, Eastern Michigan University, Ypsilanti, Michigan.

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The Thermodynamic Characterizations of the Sublimation and Vaporization Reactions of $YbF_2(s)$ and $YbF_3(s)$

Robert M. Biefeld

Introduction

The sublimation and/or vaporization reactions of $EuF_2(s,l)$, $EuF_3(s)$, and $YbF_3(s)$ have been characterized by Knudsen effusion,[1,2] matrix isolation[3,4] and electric deflection techniques,[5] while the sublimation reaction of $YbF_2(s)$ has been characterized by only the latter two methods.[4,5] Some of these reactions have been reported to procede congruently according to (1)

$$MF_x(s) = MF_x(g) \qquad (1)$$

where M = Eu or Yb and x = 2, 3. Although it is unusual to observe more than one congruently vaporizing composition in binary systems[6] this investigation was undertaken originally not to determine the vaporization and sublimation reactions, but to determine precisely the thermodynamics of the congruent vaporization and sublimation reactions of $YbF_2(s,l)$ and $YbF_3(s,l)$. In the course of this investigation it was noted both in this laboratory and in that of Petzel's[7] that neither YbF_2 nor YbF_3 appeared to vaporize congruently under the experimental conditions. For this reason the emphasis of the investigation shifted to determination of the vaporization and sublimation mode of $YbF_2(s,l)$ and $YbF_3(s,l)$. Knudsen effusion experiments have been carried out on the $YbF_x(s,l)$ systems by a target collection technique; however, characterization of the sublimation and vaporization reactions in the YbF_x systems by analysis of effusion residues and effusates and by mass-spectral experiments has been only partially completed.

Experimental

Preparation. The preparations of $YbF_3(s)$ and $YbF_2(s)$ were carried out as described previously.[8]

Analysis. The fluorides of ytterbium were analyzed for metal content by conversion to the oxide. A weighed amount of the fluoride was placed in a Pt boat and heated under steam over a two hour period to 1275 K, held at that temperature for six to twelve hours, then cooled to 1175 K and held at that temperature for six to twelve hours.

X-Ray powder diffraction photographs were obtained on a Haegg-type Guinier camera with an internal Pt standard (a = 0.39238(1) nm[8]), by use of Cu Kα radiation.

Effusion Experiments. Knudsen effusion experiments were carried out on YbF_2(s,l) confined in Mo and graphite cells (T = 1452-1742 K) and on YbF_3 contained in Mo, graphite, W, and ThO_2 cells (T = 1300-1750 K).

The residues in all cases were examined by X-ray powder diffraction and in some cases by chemical analysis. The effusates were collected on Pt and graphite targets and in some cases analyzed by X-ray powder diffraction. In other cases the effusate was analyzed quantitatively for Yb by X-ray fluorescence at the Yb $L\alpha_1$ peak maximum.[9]

Distillation experiments were carried out on YbF_2(l) and YbF_3(l) by introducing a temperature gradient along the walls of a graphite Knudsen cell fitted with a channel orifice and by collecting the distillate on the cooler top. The trifluoride contained in Pt and graphite boats was also heated under a liquid nitrogen dried stream of He for a number of one hour periods at 1475 K.

Mass-Spectrometric Experiments. Preliminary mass-spectral experiments conducted with a Bendix TOF model 12-107 mass spectrometer equipped with a Mo Knudsen cell have been carried out on YbF_2(s,l) from 1075-1825 K.

Results

Ytterbium Trifluoride

Preparations of YbF_3(s) yielded a pure white powder (orthorhombic, $\underline{a}$ = 0.6207(8), $\underline{b}$ = 0.6788(4), $\underline{c}$ = 0.4439(6) nm) in agreement with the literature reports.[10] Chemical analysis for Yb: observed 75.2 ± 0.2; calculated, 75.22 mass %.

When YbF_3 is heated in Mo cells *in vacuo* two new reflections are observed in the X-ray powder diffraction photographs of the residues. These reflections with interplanar d-values of 0.3226(5) and 0.2791(5) nm, have been assigned as the (222) and (211) reflections of a Yb-F phase of rhombohedral symmetry in agreement with observations in the Sm-F and Eu-F systems.[11,12] From them a rhombohedral cell with $\underline{a} = 0.6834(5)$ nm and $\underline{\alpha} = 33.36(6)^\circ$ is calculated. Chemical analysis of the residues yielded 75.5 ± 0.2 mass % Yb. Similar experiments carried out with graphite crucibles, yielded two different reflections with d-spacings of 0.3134(5) and 0.2744(5) nm, assignable as the (101) and 002) tetragonal reflections of a Yb-F phase with cell parameters $\underline{a} = 0.3820(5)$ and $\underline{c} = 0.5465(5)$ nm. These same reflections were observed in X-ray diffraction photographs of YbF_3 distilled from graphite cells, heated *in vacuo* in W or ThO_2 crucibles or heated in Pt or graphite boats under He. Distilled YbF_3 analyzed as 75.4 ± 0.2 mass % Yb.

Linear least-squares analysis of the ytterbium pressures calculated from the results of 5 effusion experiments of 10 targets each performed in Mo cells yielded (2),

$$\log[p(YbF_3(g))/atm] = -19{,}745 \pm 82/T + 8.474 \pm 0.056 \quad (1301\text{-}1722\ K) \qquad (2)$$

while least squares analysis of ytterbium pressures from one experiment performed in a graphite crucible yielded (3)

$$\log[p(YbF_3(g))/atm] = -19{,}1_{40} \pm 4_{27}/T + 7.9_5 \pm 0.2_7 \quad (1501\text{-}1647\ K)\ . \qquad (3)$$

To neither equation (2) nor (3) has a window or prism temperature correction been applied.

Ytterbium Difluoride

Preparations of $YbF_2(s)$ yielded green crystals with the cubic fluorite structure [$\underline{a} = 0.5598(5)$ nm] in agreement with literature reports.[13]

Chemical analysis for Yb: observed, 81.9 ± 0.3; calculated, 82.0 mass %. After six consecutive effusion experiments conducted in Mo cells the lattice parameter had decreased [$\underline{a}$ = 0.5592(7) nm] and chemical analyses indicated only 81.6 ± $1._4$ mass % Yb. Two new reflections, with d-spacings of 3.138(7) and 2.730(9) nm, were observed in the powder diffraction photographs, and appeared assignable to the tetragonal phase observed when YbF_3 was heated.

Distillation of the difluoride from a graphite Knudsen cell at 1650 K for 6h yielded a grey-green condensate ($\underline{a}$ = 0.5584(1) nm) with 81.7 ± 0.3 mass % Yb. This condensate was heated in graphite and molybdenum crucibles for varying time periods at different temperatures and the contents of the cell were examined by X-ray powder diffraction at the end of each period. The data are presented in Table I. In two experiments this condensate was heated at 1625 K in a graphite Knudsen cell and the effusate was collected on a liquid nitrogen-chilled graphite target. The effusate ultimately exhibited 2 phases, one cubic ($\underline{a}$ = 0.5584(4) nm) with the parameter varying as effusion progressed; the other which was observed only in one photograph exhibited the (101) tetragonal reflection.

Ytterbium pressures calculated from six independent vaporization experiments (52 pressure-temperature pair determinations) with YbF_2 confined in a Mo crucible yielded least squares equation (4),

$$\log[p(YbF_2(g))/atm] = (-21169 \pm 233)/T + (8.33 \pm 0.15) \qquad (1452\text{-}1742\ K). \tag{4}$$

One experiment (5 temperature-pressure pairs) conducted in a graphite crucible yielded (5)

$$\log[p(YbF_2(g))/atm] = (-20859 \pm 560)/T + (8.33 \pm 0.35) \qquad (1538\text{-}1619\ K). \tag{5}$$

Mass spectrometric analysis of the effusate from freshly prepared YbF_2 indicates only $Yb^+(g)$ at 1350 K. The observed appearance potential, 7.2 ± 1.8 V, agrees well with the reported value of 7.1 V for elemental Yb.[14] As the temperature of the sample was eleviated the $Yb^+(g)$ intensity naturally increased. But, with time, the $Yb^+(g)$ intensity decreased and, consequently, was not reproducible with temperature. Ion currents for $YbF^+(g)$ and $YbF_2^+(g)$ were first observed at 1635 K. As heating progressed over a 2 h period the $I_{Yb^+(g)}:I_{YbF^+(g)}:I_{YbF_2^+(g)}$ changed as indicated in Table II. (Intensities subsequently became reproducible.) The appearance potential for the species Yb^+, YbF^+, and YbF_2^+ were 13.5 ± 4.3, 13.1 ± 1.9, 12.6 ± 2.5 eV respectively at 1780 K. The appearance potential of Hg^+ at 1780 K was found to be 9.9 + 1.1 V, in comparison with the accepted value of 10.39 V.[14] A plot of 33 $\log I^+T$ vs $1/T$ data points yielded for the vaporization of $YbF_2(s)$ least squares equation (6)

$$\log(I^+T) = (-19071 \pm 0.0926)/T + (15.16 \pm 0.52) \quad (1698\text{-}1837\ \mathrm{K}). \tag{6}$$

Discussion

The X-ray and chemical analyses of the residues and effusates of effusion experiments carried out on $YbF_3(s,l)$ indicate that with the containers used $YbF_3(s)$ does not vaporize according to (1), but undergoes reduction. The difference between the vapor pressure of $YbF_3(s,l)$ in a graphite crucible as compared to that in a Mo cell, although barely significant, may result from the greater reducing power of graphite. Graphite has been reported to reduce SmF_3 to the difluoride, whereas Mo will not.[15] Additional support for reduction by graphite is the rhombohedral phase which appears when YbF_3 is heated in Mo in contrast to the tetragonal phase observed when it is heated in graphite, the tetragonal phase being indicative of greater reduction.[11,12] The fact that when $YbF_3(s)$ is heated to 1475 K in a Pt or graphite boat under He the tetragonal phase grows in may be indicative that $YbF_3(l)$ undergoes reduction whether or not vaporization is occurring. Present evidence indicates that $YbF_3(s,l)$ vaporizes congruently, but is reduced through reaction with the container material. The vapor pressures measured in Mo are considered to be experimentally indistinguishable from the actual vapor pressures.

In the case of YbF_2 all evidence is against congruent vaporization and sublimation. X-Ray and chemical analyses indicate that the residues of the effusion experiments were no longer YbF_2, but an oxidized Yb-F phase, $YbF_{2.1 \pm 0.2}$. The non-reproducible vapor pressures over the YbF_2-$YbF_{2+\underline{x}}$ composition range indicate that a continuous decomposition takes place in that region yielding Yb(g). However, the ultimate reproducibility of the vapor pressure over $YbF_{2+\underline{x}}(s)$ indicates that it vaporizes congruently according to (7).

$$YbF_{2+\underline{x}}(s) = (1-\underline{x})YbF_2(g) + \underline{x}YbF_3(g) \qquad (7)$$

This type of reaction should be supported by chemical analyses of residues after partial vaporization, and by the temperature and time dependence of the vapor pressure. In addition, the appearance potential of $Yb^+(g)$ at 1780 K indicates that its parent species is not Yb(g). The ratios of the ion intensities are different from what would be expected for YbF_2; the YbF_2^+ intensity being larger than the YbF^+ intensity.[9,16] The ratio also differs greatly from that reported for YbF_3.[2] Thus (7) is proposed as the most likely vaporization mode for $YbF_{2+\underline{x}}$. Lack of crucible interaction is concluded from the similarity of the vapor pressures when $YbF_{2+\underline{x}}$ is vaporized from graphite or Mo crucibles. The reported data from the target collection and mass spectrometric experiments are in substantial agreement when corrections have been made to account for the enthalpy of fusion of YbF_2 at 1680 K, estimated as 7.5 kcal/mol. Thus from the data already collected on $YbF_2(s)$ thermodynamic values for the sublimation reaction can be determined once $\underline{x}$ has been established.

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Table I

Phases Observed When Distilled YbF_2 is Heated to Different Temperatures for Varying Periods of Time

Temperature K	Time h	Crucible	Phases Present in Residue
1175	1.5	Graphite	C*(*a* = 0.5584(1) nm) gr-grey
1375	2	"	C
1425	4	"	C + T*(101)
1425	2	"	C + T(101)
1475	2	"	C + T(101),(002),A
1675	2	"	-
1525	1	"	{C(*a* = 0.5579(1) nm) +T(101),A} gr-black
1550	1	Mo	C(*a* = 0.5584(1) nm)
1675	0.25	Mo	-
1550	0.75	Mo	-
1375	1	Mo	{C(*a* = 0.5585(1) nm) + T(101),A +Yb_2O_3}

*C = cubic fluorite structure, T = tetragonal phase, A = unidentified lines

Table II

Variation in the $Yb^+(g):YbF^+(g):YbF_2^+(g)$ Ion Intensities With Temperature Over a 2 h Period (Ionizing Energy = 44.5 eV)

$I_{Yb^+(g)}$	$I_{YbF^+(g)}$	$I_{YbF_2^+(g)}$	Temperature (K)	Comment
10	1	1	1635	
13	4	1	1675	
12	2	1	1725	
1	1	1	1790	
7	10	14	1780	reproducible
2	3	5	1700	reproducible
11	15	27	1830	reproducible

Mixed Halides of Europium

Beatrice L. Clink

Introduction

The study of mixed halide lanthanide compounds of the formula MX_nY_{3-n} and MXY has significance from both a structural and thermodynamic viewpoint. Detailed structural and vaporization data for such compounds would help establish stability relationships of the transition from MX_3 to MY_3,metal-halogen bond strengths,and the effect of anion size on packing. For these reasons, the work initiated by A. V. Hariharan was continued.[1]

The stabilities of the divalent and trivalent states of europium open the possibility of comparing the mixed halide effects in various oxidation states. The difficulty, however, is in developing a method in which side reactions and numerous decomposition products are kept to a minimum.

Experimental

The first preparatory method attempted involved a metathesis reaction (1)

$$EuCl_3 + NH_4Br \xrightarrow{\Delta} EuCl_2Br + NH_4Cl. \qquad (1)$$

A 1:1.25 mole ratio of the anhydrous lanthanide halide to dried ammonium bromide was heated in an outgassed quartz tube at 395°C. Four various colored phases were obtained: a dark yellow powder, a light yellow powder, a dark grey powder and dark gray crystals. The dark yellow and dark grey phases were heated under vacuum ($\sim10^{-6}$ torr) at 188°C for 12 h to remove the ammonium halide present. The dark yellow phase decomposed into a dark grey phase at this temperature. The diffraction patterns of all four phases were significantly different from those of $EuCl_2$, $EuBr_2$, $EuCl_3$, $EuBr_3$ and the various europium oxohalides.

The second preparatory method involved a pseudo Talyor, Carter preparation[2] in which anhydrous europium trichloride and ammonium bromide

(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 for 16 h. An orange phase which formed decomposed into a light grey powder after continued heating for 4 h at 370°C. The apparently homogeneous hydroscopic powder exhibited a diffraction pattern different from that of known europium halides and oxohalides.

A portion of the light grey product was melted to a dark brown liquid in a sealed outgassed quartz tube (650-675°C) and cooled slowly. The clear colorless crystals obtained upon solidification had a diffraction pattern identical to that of the powder coincident with apparent lattice parameters of $\underline{a} = 9.23(2)$, $\underline{b} = 7.862(7)$, $\underline{c} = 4.588(4)$ Å. Chemical analysis of the product is currently in progress.

The second method was repeated substituting ammonium chloride for the ammonium bromide. Anhydrous europium trichloride was recovered.

Discussion

The formation of a product other than the tri- or dichloride of europium in method two suggests there is an exchange of halide ion between the ammonium halide and metal in the Taylor Carter preparation. These results and the known fact that europium trichloride hydrate more readily evolves hydrochloric acid than water[3] is evidence for the feasibility of the following reaction pathway (2)

$$EuCl_3 . 6H_2O \xrightarrow[\Delta\ 200^\circ C]{\substack{-H_2O \\ -HCl}} EuOCl \xrightarrow[\Delta\ 200^\circ C]{NH_4Br} EuClBr_2 + 2NH_3 + H_2O \xrightarrow[\Delta\ 370^\circ C]{-Br_2} EuClBr \tag{2}$$

The color, hydroscopic nature, melting point and lattice parameters (see Table 1) suggest the product is a mixed europium dihalide. Further analyses are needed to confirm this hypothesis. There is also the possibility that the reaction is proceeding through an ammonium complex rather than the oxohalide and mixed trihalide.

The above suggests that for preparation of anhydrous lanthanide trichlorides from the hydrated trichlorides a chlorinating agent is more necessary than a dehydrating agent.

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Table 1[4]

EuX_2	Color	Space Group and No.	Structure Type	Lattice Parameters		
				a	b	c
$EuCl_2$	white	Pbnm, 62	orthorhombic $PbCl_2$	8.93	7.51	4.50
$EuBr_2$	white	P4/n, 85	tetragonal $SrBr_2$	11.574		7.098
Unknown	lt grey			9.23(2)	7.862(7)	4.588(4)

A New Phase in the Ytterbium Chloride System

John T. Richards

Introduction

In the ytterbium chloride system, in addition to ytterbium di- and trichloride which are well characterized and which can be synthesized routinely in the laboratory,[1] an intermediate phase has recently been reported.[2]

This work was undertaken to isolate and to characterize this intermediate phase. Instead of the expected product, a few single crystals of an apparently new phase were found. One of these crystals has been submitted to X-ray diffraction analysis to characterize it.

Experimental

Ytterbium metal (99% pure, Research Chemicals, Phoenix, Arizona) and ytterbium trichloride prepared by the NH_4Cl and $YbCl_3.xH_2O$ matrix technique in the ratio $YbCl_3/Yb = 3.08$ were sealed in a tantalum ampoule with a small chip of iodine (<0.0003 g) included to hasten transport of the ytterbium. After the ampoule had been heated at 550° for seven days, at least three phases were recovered: unreacted metal, a black powder and a few clear, colorless crystals. Some of the crystals were observed to grow from the surface of the ytterbium metal.

X-Ray diffraction studies undertaken by the precession technique with molybdenum radiation indicate a unit cell of no more than tetragonal symmetry with lattice parameters of $\underline{a} = 6.94$ and $\underline{c} = 13.02$ Å.

Discussion

Since the metal was used "as obtained" it probably has an oxide coating. There is thus a reasonable probability that the crystals isolated are not pure chlorides, but have oxide incorporated in them. But comparison of the observed lattice parameters with those reported by Beck[3] for orthorhombic $YbCl_2$, $\underline{a} = 13.18$, $\underline{b} = 6.96$, $\underline{c} = 6.70$ Å indicate a marked similarity between the phases and a high probability that the colorless crystals are either those of $YbCl_2$ or a closely related structure. Additional work is in progress to characterize the remaining phase.

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Ternary Systems of Lanthanide(III) Fluorides

Carol G. Biefeld

Introduction

We have found previously[1] that, as expected, the ternary lanthanide(III) fluoride phases are isostructural with the parent fluorides as long as the component fluorides are of the same structure-type, but a phase (or phases) whose structure is unidentifiable by X-ray powder diffraction methods is obtained when the fluorides are of different structure types. Recently published results on the LaF_3-YF_3 system[2] have established the phase diagram. In agreement with our results for the LaF_3-ErF_3 system, an extensive LaF_3 structure-type solid solution was found for LaF_3-rich mixtures, as was evidence for a low temperature hexagonal compound, which exhibited a considerable composition range. In addition a restricted cubic solid solution was observed for YF_3-rich mixtures. No lattice parameters were reported for any of these phases. Since we have found more than one phase when equimolar compositions of LaF_3 and ErF_3 are mixed, (comparable results have been found for 1:1 mixture of LaF_3-YF_3) we are continuing our investigation into the identification and structural characteristics of this region of the phase diagram.

Experimental

A 1:1 molar ratio of ErF_3:GdF_3 and 2:1 molar ratio of LaF_3:ErF_3 were mixed and placed in a platinum ampoule which was sealed under argon *via* arc welding. The platinum was then sealed into an outgassed evacuated quartz tube and heated to 925° for a period of 2 months. The tube was quenched in water, and the contents of the ampoules examined by X-ray powder diffraction. Single-crystals from a 1:1 molar ratio LaF_3:YF_3 prepared analogously to those described above were examined by precession techniques.

Results and Conclusions

a. ErF_3GdF_3 and $2LaF_3 \cdot ErF_3$

These two phases were found to have powder patterns identical to those observed previously[1] for samples contained in unsealed platinum inside the evacuated quartz tubes. These results conclude the general study of lanthanide fluoride mutual solubility. These solid solutions of lanthanide fluorides may prove useful as fluoride fluxes for utilization in the electroslag process when a more detailed knowledge of the melting points and electrical conductivity of the solutions and of the compounds formed in the case of the mixtures of nonisostructural fluorides is available.

b. $LaErF_6$ Single Crystal[3]

An attempt to refine occupancy factors for the metal positions was only partially successful; however, there are indications that a greater percentage of the erbium atoms are present at the (2/3, 1/3, 1/2) metal position. This result would mean that $LaErF_6$ has neither a completely ordered nor disordered structure. In order to determine to what extent disordering of the metal atoms and possibly the fluorine atoms occurs, much more precise intensity data will be needed.

c. $LaYF_6$ Single Crystal

Since an accurate solution of the light-atom structure of $LaErF_6$ is made difficult by the presence of two heavy atoms, single-crystals of $LaYF_6$ have been examined in an attempt to partially alleviate this problem. All the crystals thus far examined have been multiple twins. We believe that the twinning has affected our lattice parameter measurements since no lattice parameters could be obtained which will produce d-spacings consistent with those calculated for the powder patterns. We are still attempting to find a single-crystal of this material.

References

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3. C. G. Biefeld and H. A. Eick, U.S. Atomic Energy Commission Report, COO-716-079.