

The magnetic properties of HfI_3 reported previously³ are at variance with those given here, apparently because of gross contamination of the earlier samples. The earlier results indicated $10^6\chi_g$ values of about 15.5 (green) to 11.2 (black) at 300°K and 5.2 kG, in contrast with only 0.27 found here for $\text{HfI}_{3.3}$ at 5.05 kG. The prior values of χ also showed a broad maximum near 120°K and substantially larger field and temperature dependencies. However, the samples employed were the residues from the incomplete reduction of HfI_4 with aluminum followed by sublimation of HfI_4 and AlI_3 , and aluminum was evident in the powder patterns (together with seven unidentified lines.) In fact, the HfI_3 yield was only 5–10% for the green product and 12% for the black,¹⁸ and the triiodide at best comprised 59–84% of the residue after sublimation. The hafnium analysis of the water-

soluble portion was also quite low. Therefore it would appear that the high susceptibilities originated from more than HfI_3 and aluminum, perhaps hafnium–aluminum intermetallic phases. The present data for the triiodide phase are rather comparable with those obtained by Lewis, *et al.*,¹⁹ for the zirconium(III) halides at only room temperature, which correspond to effective moments of about 0.4 β . The temperature-independent character of the small paramagnetism for the hafnium iodide phase is rather typical.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MICHIGAN STATE UNIVERSITY,
EAST LANSING, MICHIGAN 48823

Phase Analyses of Lanthanide Oxide Fluorides

BY DENNIS B. SHINN¹ AND HARRY A. EICK

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Approximate composition limits and lattice parameters of the rhombohedral and tetragonal phases observed in the system $\text{LnO}_{1-x}\text{F}_{1+2x}$ ($\text{Ln} = \text{Nd, Gd, Er}$) are reported. Variation of the c/a ratio of the tetragonal phase with atomic number is noted and discussed. The rhombohedral to cubic transition temperatures of $\text{LnO}_{1-x}\text{F}_{1+2x}$ ($\text{Ln} = \text{La, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, and Er}$) determined from differential thermal analysis are reported and the transition is discussed. Thermal expansion data are reported for NdOF and its mode of thermal decomposition is indicated.

Introduction

Lanthanide oxide fluorides are often encountered as contaminants in metal trifluoride investigations, yet they have been studied only infrequently.^{2–15} Zachariasen² reported for yttrium and lanthanum two oxide fluoride phases which he prepared by pyrohydrolysis of the fluorides: a rhombohedral LnOF and

a tetragonal $\text{LnO}_{1-x}\text{F}_{1+2x}$ ($0.0 \leq x \leq 0.3$). From an X-ray powder diffraction study he deduced that these phases were superstructures based upon fluorite in which the oxygen and fluorine atoms are ordered into distinct sites. In the bimolecular rhombohedral unit cell of LaOF , space group $R\bar{3}m$, he found the metal atoms to be at $\pm(XXX)$, where $X(\text{La}) = 0.242$, and postulated that the anions were also situated along the threefold axis with $X(\text{O}) = 0.370$ and $X(\text{F}) = 0.122$. The value of α was 33.01° in contrast with the 33.56° value for fluorite based on a rhombohedral cell. Templeton³ later concluded from a lattice energy calculation that the oxygen and fluorine positions should be interchanged. This rhombohedral structure has been observed^{9,11–15} for most lanthanide oxide fluorides and values of α that vary between 33.0 and 33.3° have been reported.

The tetragonal phases exhibit space group $Pnmm$ symmetry, and alternate layers of oxygen and fluorine atoms are normal to the c axis. The c/a ratios reported² for the lanthanum and yttrium tetragonal phases deviate slightly from 1.414, the value for cubic

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fluorite referred to a tetragonal cell. Excess anions apparently occupy interstitial sites as they do in solutions of YF_3 in CaF_2 .^{16,17} These fluoride-rich tetragonal phases have been given little consideration.

Cubic lanthanide oxide fluorides in which a disordered arrangement of anions is generally assumed have been reported by several investigators.⁴⁻⁷ Zachariasen attempted unsuccessfully to obtain cubic YOF and LaOF by quenching. However, he postulated that the cubic disordered phases would exist at high temperatures. The present project was initiated both to check this rhombohedral-cubic transition hypothesis and to investigate further the tetragonal phases.

Experimental Section

The lanthanide trifluorides were prepared by treating 99.9% pure sesquioxide specimens (Michigan Chemical Co.) with excess ammonium fluoride (J. T. Baker Chemical Co.) These mixtures were heated under a flow of helium to about 450° in platinum boats situated in a Vycor tube. Completeness of conversion to the trifluoride was established by weight increase of the lanthanide phase (always >99% of theoretical conversion) and by X-ray powder diffraction identification. Samples of composition $\text{LnO}_{1-x}\text{F}_{1+2x}$ ($-0.1 \lesssim x \lesssim 0.5$ and Ln = La, Nd, Sm-Gd, Dy-Ho) were prepared by heating the appropriate mixtures of oxide and fluoride at 1050° for 4-5 hr in an inert atmosphere and then cooling them slowly. TbOF was prepared by pyrohydrolysis of TbF_3 at 500°.

Metal content of the phase was determined either by direct ignition or by dissolution in hot sulfuric acid, precipitation of the oxalate, and subsequent ignition to the oxide. Fluorine content was determined by neutron activation analysis. Analytical data obtained on X-ray pure specimens are presented in Table I.

TABLE I
ANALYTICAL RESULTS
(a) Metal Analyses in $\text{LnO}_{1-x}\text{F}_{1+2x}$

Ln	x	% Ln		Samples
		Calcd	Found	
La	~0	79.86	80.2 ± 0.3	2 ^a
Nd	~0	80.43	80.45 ± 0.1	2
Sm	~0	81.13	81.13 ± 0.1	3
Eu	~0	81.28	81.08 ± 0.1	2
Gd	~0	81.79	81.79 ± 0.1	3
Tb	~0	81.98	81.4 ± 0.3	2 ^a
Dy	~0	82.22	82.7 ± 0.3	2 ^a
Ho	~0	82.49	82.9 ± 0.1	2
Er	~0	82.69	82.54 ± 0.1	2
Y	~0	71.67	71.69 ± 0.1	4
Nd	0.27 ± 0.02	77.9	78.2 ± 0.3	2 ^a
Gd	0.28 ± 0.02	79.3	79.1 ± 0.3	2 ^a
Dy	0.23 ± 0.02	80.2	79.5 ± 0.3	2 ^a
Er	0.20 ± 0.02	80.9	80.82 ± 0.1	2

(b) Fluorine Analyses in $\text{LnO}_{1-x}\text{F}_{1+2x}$

Ln	x	% F		F/Ln
		Calcd	Found	
Nd	0.02 ± 0.02	11.1	11.1 ± 0.3	1.05 ± 0.04
Nd	0.27 ± 0.02	15.8	15.9 ± 0.3	1.54 ± 0.04
Gd	0.28 ± 0.02	14.9	14.9 ± 0.3	1.56 ± 0.04
Dy	0.23 ± 0.02	13.7	13.6 ± 0.3	1.46 ± 0.04
Er	0.20 ± 0.02	13.0	12.9 ± 0.3	1.41 ± 0.04

^a Determined by oxalate precipitation. Probable errors based on variance found in all analyses.

These phases were examined both by X-ray powder diffraction and by thermal-analysis techniques. X-Ray diffraction phase analyses were made with 114.59-mm Debye-Scherrer powder cameras, while lattice parameters were calculated from data collected with a Siemens diffractometer.

Structural transitions in rhombohedral LnOF were observed with an MRC high-vacuum X-ray diffractometer attachment mounted on the Siemens diffractometer. Pressures monitored with an ionization gauge mounted on the vacuum main varied between 4 and 8×10^{-6} Torr, but the pressure in the camera was undoubtedly higher since sample hydrolysis was observed below 1000°. Specimen temperatures were calculated from the observed lattice parameter of platinum, the internal standard, by use of the thermal expansion data tabulated by Campbell.¹⁸ The lattice parameter of this standard was determined from the (311) reflection after the diffractometer had been aligned to $\pm 0.01^\circ$ in 2θ . Probable errors in temperature measurements are estimated to be $\pm 20^\circ$.

The differential thermal analysis apparatus was constructed in this laboratory.¹⁹ One of the lanthanide sesquioxides was used as an inert reference. Temperature measurements were made with calibrated iron-constantan thermocouples (encased in Inconel shields) situated in the samples. A probable error of $\pm 2^\circ$ was estimated for these measurements. Heating rates between 1 and 3°/min were employed.

A sample of rhombohedral $\text{NdO}_{1-x}\text{F}_{1+2x}$, $x \approx 0.05$, was heated under vacuum in a tantalum crucible to constant weight at temperatures maintained between 1475 and 1600°. The decomposition reaction was analyzed from weight loss data and from X-ray diffraction analyses of the products. A similar sample confined in a Knudsen cell was heated to 1700° and the vapor species was examined with a Bendix Model 12-107 time-of-flight mass spectrometer.

Results

The phases identified by X-ray powder diffraction in the systems $\text{LnO}_{1-x}\text{F}_{1+2x}$ ($-0.1 \lesssim x \lesssim 0.5$ and Ln = Nd, Gd, and Er) were oxide and rhombohedral phase for $x \approx -0.1$, rhombohedral phase for $x = 0.0$, the rhombohedral plus a tetragonal phase for $0.0 \lesssim x \lesssim 0.1$, a tetragonal phase for $0.1 \lesssim x \lesssim 0.3$, and a tetragonal phase plus the trifluoride for $x \approx 0.4$. The tetragonal gadolinium phase has a smaller composition range, $0.2 \sim x \lesssim 0.3$, than that observed for Nd or Er. A tetragonal dysprosium phase, $x \approx 0.23$, and La, Sm, Eu, Dy, Tb, Ho, and Y rhombohedral phases ($x \approx 0.0$) were also prepared.

Lattice parameters for the tetragonal oxide fluorides obtained by extrapolation with Vogel and Kempter's²⁰ least-squares routine are listed in Table II together with values for Ln = La and Y reported by Zachariasen. Diffraction patterns of the erbium phase contained several lines which could not be indexed.

A rhombohedral to cubic structural transition was observed both by high-temperature X-ray diffraction and by differential thermal analysis for every LnOF specimen examined. In diffraction experiments, both phases were perceptible over a 30° range about the transition temperature. The presence of a temperature gradient throughout the sample probably accounted for part of this range. For slow rates of temperature change hysteresis effects were not apparent within

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TABLE II
LATTICE PARAMETERS FOR TETRAGONAL $\text{LnO}_{1-2x}\text{F}_{1+2x}$

Ln	x	$a, \text{\AA}$	$c, \text{\AA}$	c/a	$V/\text{mol}, \text{\AA}^3$
La ^a	0.0	4.091 (1) ^b	5.837 (1)	1.427 (1)	48.84 (2)
La ^a	0.3	4.106 (2)	5.852 (4)	1.425 (2)	49.34 (8)
Nd	~0.15	3.999 (2)	5.704 (3)	1.426 (2)	45.61 (7)
Nd	0.27	4.014 (3)	5.720 (4)	1.425 (2)	46.08 (9)
Gd	0.28	3.977 (1)	5.528 (1)	1.390 (1)	43.72 (2)
Dy	0.23	3.933 (1)	5.451 (1)	1.386 (1)	42.16 (2)
Y ^a	0.0	3.910 (5)	5.43 (1)	1.389 (4)	41.5 (2)
Y ^a	0.3	3.930 (5)	5.46 (1)	1.389 (4)	42.2 (2)
Er	~0.15	3.893 (1)	5.400 (2)	1.387 (1)	40.92 (4)
Er	0.20	3.907 (1)	5.385 (1)	1.387 (1)	41.10 (2)

^a Parameters reported by Zachariasen (converted from kX units). ^b Standard deviations in last digit given in parentheses.

the limit of error in temperature measurement. However, in the Nd, Sm, and Eu cases the cubic phase could be quenched at least partially by rapid cooling. In the differential thermal analysis results there was some evidence of hysteresis since the transition temperature was generally 10–20° lower in the cooling than in the heating cycle. Smaller differences were observed in the temperatures corresponding to initiation of the conversion. The rhombohedral–cubic transition temperatures reported in Table III are the average of values obtained in heating and cooling cycles.

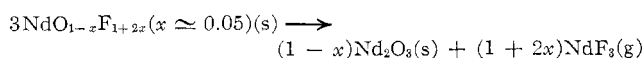
TABLE III
RHOMBOHEDRAL LANTHANIDE OXIDE FLUORIDE
TRANSITION TEMPERATURES

Approx stoichiometry	$T_{\text{rhomb} \rightarrow \text{cub}}, ^\circ\text{C}$	Approx stoichiometry	$T_{\text{rhomb} \rightarrow \text{cub}}, ^\circ\text{C}$
LaOF	494	GdO _{0.9} F _{1.2}	608
NdO _{1.1} F _{0.8}	526	TbOF	551
NdOF (prepn 1)	517	DyOF	558
NdOF (prepn 2)	524	YOF	571
NdO _{0.93} F _{1.14}	524	HoOF	588
SmOF	524	ErO _{1.1} F _{0.8}	586
EuOF	513	ErOF	592
GdO _{1.1} F _{0.8}	605	ErO _{0.9} F _{1.2}	598
GdOF	606		

^a Average values obtained from differential thermal analyses.

The volume of the sample increased by 0.7–1.0% at the transition. This increase in molecular volume is illustrated in the NdOF thermal expansion data (Figure 1). The molecular volume of quenched cubic samples of EuOF and NdOF was also greater than that of the corresponding rhombohedral phases at the same temperature.

Neodymium oxide fluoride was observed to decompose according to the equation



The observed weight loss (39%) of the unfused solid agreed with the calculated value (39.4%). In addition, the only peaks observed in the mass spectrum of the decomposition products were $\text{NdF}_2^+(\text{g})$ and $\text{Nd}^+(\text{g})$. The appearance potential of the $\text{Nd}(\text{g})$ was 24 ± 1 eV, in good agreement with the value

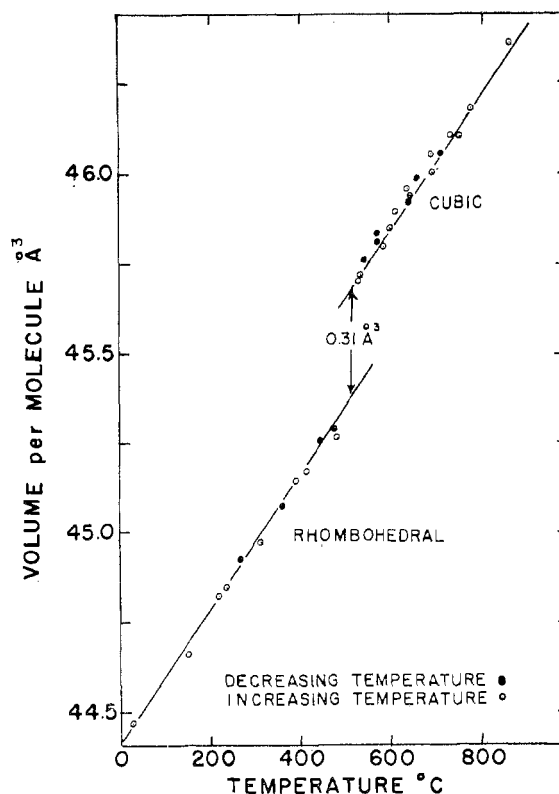


Figure 1.—Thermal expansion of NdOF.

reported by Zmbov and Margrave for the vaporization of NdF_3 .²¹ These fragments, which would be expected if the vapor species were NdF_3 , substantiate further the weight loss data. No $\text{NdO}(\text{g})$ was observed.

Discussion

An interesting aspect of the structural data is that for the La and Nd species the c/a ratio is greater than 1.414 while for the Gd–Er species it is less than 1.414, the value expected for a tetragonal cell derived from fluorite. This variation may be related to packing of the anions. Anion–anion contact is expected along the $\langle 001 \rangle$ and $\langle 110 \rangle$ directions if the cation to anion radius ratio is less than 0.73. From the reported Ln^{3+} radii⁹ and a 1.38-Å anion radius, radius ratios of 0.77, 0.72, 0.68, and 0.64 are calculated, respectively, for La, Nd, Gd, and Er. On this basis, anion–anion contact appears most probable for the Gd–Er oxide fluorides. However, according to Zachariasen the oxygen and fluorine atoms are in separate layers normal to the c axis. Since the oxygen atoms are larger than the fluorine atoms, the alternating layers should pack more tightly than do the oxygen atoms within any layer. That is, the c/a ratio should be less than 1.414, as observed. In the La and Nd cases, anion contact is probably effective only in the oxygen layer and the larger lanthanide separates the oxygen and fluorine layers, producing $c/a > 1.414$.

The molecular volumes of the cubic samples examined were always larger than those of the analogous

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rhombohedral phases. No significant change in the rhombohedral angle of neodymium oxide fluoride ($\alpha = 33.03 \pm 0.05^\circ$) was observed in the thermal expansion data below the transition point.

Bevan, *et al.*,¹⁵ have reported for the erbium system a fluorite-related orthorhombic phase. The extra lines observed in the erbium X-ray diffraction photographs could be explained by this phase.

The rhombohedral-cubic transitions are evidently associated with order-disorder of the oxygen and fluorine atoms. As is characteristic for such transitions, the high-temperature form has a larger molecular volume and higher symmetry, and the down-temperature transition is somewhat sluggish. The disordering process must involve migration of the anions through the interstitial holes. Anion migration has been observed¹⁷ *via* the interstices in CaF_2 and $\text{YF}_3 \cdot \text{CaF}_2$ solids. This migration is expected to become more difficult as the metal ion size decreases since the unit cell shrinks. On this basis one might predict that the transition temperature would increase with decreasing metal ion size. The observed transition temperatures increase from 494° for LaOF to 592° for ErOF . The

temperature observed for GdOF , 606° , is the most obvious deviation from a gradual increase in transition temperature. The transition temperature has only a slight composition dependence (Table III), not enough to account for its unexplainable anomalous value.

Attempts to observe a tetragonal-cubic transition by high-temperature X-ray diffraction and differential thermal analysis were unsuccessful. No transition was observed below 1000° , but hydrolysis apparent above 800° confused the observations. The absence of a transition at these temperatures is surprising in light of the mobility of the anions in fluorite structures. However, it was noted that the molecular volume of the tetragonal phases was larger than that of the corresponding cubic and rhombohedral phases, and a transition with a volume decrease would be somewhat unusual.

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CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY,
UNIVERSITY OF CALIFORNIA, LOS ALAMOS, NEW MEXICO 87544

Lattice Constants of Actinide Tetrafluorides Including Berkelium¹

By T. K. KEENAN AND L. B. ASPREY

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The lattice constants of ThF_4 , PaF_4 , UF_4 , NpF_4 , PuF_4 , AmF_4 , and CmF_4 were redetermined using modern experimental and computational methods. Lattice parameters for the isostructural BkF_4 were obtained in a similar manner. Trends and volume changes in these tetrafluorides and other series of tetravalent actinide fluoride complexes are discussed.

Introduction

Following our preparation of BkF_4 earlier this year,² the lattice constants and volume of this compound were compared with other actinide tetrafluorides or fluoride complexes involving a tetravalent actinide. Penneman has pointed out the significance of the "volume/fluoride" ratio in fluoride compounds³ and noted certain discontinuities when he plotted the actinide tetrafluoride data with those for LiMF_5 ⁴ and $\text{Na}_7\text{M}_6\text{F}_{31}$.⁵ The volumes of the highly charged tetravalent actinide may be neglected along with the volume of the lithium ion for such calculations. The values for the sodium compound have been corrected for the volume of the sodium ion (7 \AA^3). This in-

formation is shown in Figure 1. It can be seen that our berkelium data do not fit the curve for MF_4 . Furthermore, that curve is much steeper than those of the complex fluorides. In fact, an extrapolation of that curve apparently will cross those of LiMF_5 and $\text{Na}_7\text{M}_6\text{F}_{31}$. While not impossible, such behavior did not appear in harmony with recent studies from this laboratory on systems of these types of compound.

From independent considerations of the molar refractivity of ThF_4 , Penneman⁶ also suspected that the lattice constants of the thorium compound were too large. If this were true, and the slope of the curve is less steep, our berkelium value falls into place more neatly.

The published values for the MF_4 compounds date from 1949 through the mid 1950's, and significant advances in manipulative techniques, equipment, and computer data reduction have been made since then.

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