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Nonstoichiometry in the Samarium(II) Fluoride–Samarium(III) Fluoride System[1,2]

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An examination of the samarium(II) fluoride–samarium(III) fluoride system has indicated nonstoichiometry in the region SmF_2–$SmF_{2.5}$. Phases in this composition region, prepared from the element and its trifluoride, display structural modifications of the fluorite unit cell exhibited by stoichiometric $SmF_{2.00}$. Three phases have been found by Guinier forward-focusing X-ray diffraction techniques: a cubic phase whose lattice parameter decreases in a linear manner ($a = 5.867 \pm 0.001$ to $a = 5.841 \pm 0.001$ Å) as the composition is changed from $SmF_{2.00}$ to $SmF_{2.14}$, a tetragonal phase $SmF_{2.35}$ ($a = 4.106 \pm 0.002$ Å and $c = 5.825 \pm 0.003$ Å), and a rhombohedral phase which also displays variable lattice parameters ($a = 7.124 \pm 0.002$ Å, $\alpha = 33.40 \pm 0.02°$ to $a = 7.096 \pm 0.002$ Å, $\alpha = 33.23 \pm 0.02°$) as the composition is varied from $SmF_{2.41}$ to $SmF_{2.46}$. The measured density increases as the F:Sm atomic ratio is increased from 2.00 to 3.00 and is compatible with an interstitial anion description of the lattice modifications. Several similarities are noted between the fluoride phases and those reported for the UO_2–UO_3 system.

Introduction

The preparation of $SmF_{2.29}$ by reduction of SmF_3 with hydrogen has been reported by Asprey, *et al.*,[3] who postulated for the phase a cubic fluorite lattice of variable composition. This proposed variable composition together with the nonstoichiometry recently observed in ternary lanthanide oxide fluoride systems[4] indicated that reduction of SmF_3 might produce a nonstoichiometric Sm(II)–Sm(III) system which might exhibit both a variable cationic oxidation state and interstitial anion behavior. Kirshenbaum and Cahill[5] have indicated that graphite, molybdenum, and tungsten are less effective reducing agents for SmF_3 than hydrogen. Thus, the reaction between elemental samarium and SmF_3 was investigated.

Experimental Section

Preparation of Samarium Trifluoride.—Samarium trifluoride was prepared by reaction of calcined Sm_2O_3 (99.9%, Michigan Chemical Corp.) with gaseous HF (99.9%, The Matheson Co., Inc.) diluted with nitrogen. The sample was confined in a platinum boat and situated in a platinum-lined nickel tube which was flushed thoroughly with nitrogen before the mixed HF–N_2 atmosphere was established. It was heated to 500° for approximately 10 hr, weighed, recycled until a constant weight was attained, and stored in platinum in an evacuated desiccator. The preparation was analyzed both by chemical methods for samarium and by powder X-ray diffraction techniques.

Preparation of Reduced Samarium Fluorides.—Samarium metal shavings (99.6%, Michigan Chemical Corp.) were chipped with a carbon steel cold chisel from an ingot confined under xylene (steel particles were removed with a permanent magnet), rinsed with trichloroethane, and stored under argon in a glove box until needed (but never more than 1 week). The metal and trifluoride (or reduced fluoride prepared by this procedure) were inserted into tantalum thimbles (6.2- or 9.0-mm i.d., 0.4-mm wall thickness) which had been outgassed by induction heating under vacuum (~10^{-6} Torr, at >2100°) until metallic tantalum deposited on the vacuum jacket. All sample manipulations were effected in a glove box whose argon atmosphere was recirculated over activated alumina to remove water and over BASF Catalyst R3-11 (Badische Anilin- & Soda-Fabrik AG) to remove oxygen. The open end of the tantalum thimble was crimped and sealed by arc welding in a zirconium-gettered argon atmosphere. (If a very shiny weld was not obtained, the capsule was discarded.)

The capsules were heated under vacuum (10^{-6} Torr or less) to 1600–1900°, depending upon sample composition, maintained at temperature for about 5 min, either quenched or cooled to 1200°, maintained at that temperature for about 8 hr, and then brought to room temperature with stepwise cooling over a period of about 50 hr. They were then opened in the glove box and the sample was placed in glass vials which were subsequently sealed with paraffin.

One sample was placed in a tightly crimped outgassed tantalum thimble, confined in the vacuum system, heated for 5 min at 1150°, quenched, and immediately placed in the glove box. Both the effusate which collected on the water-cooled jacket of the vacuum line as a result of this heating and portions of a number of other samples were treated with 6 *N* HCl.

Analysis.—All fluoride-containing products were analyzed for samarium by steam hydrolysis to the sesquioxide. Two or three 0.2-g samples confined in platinum boats were placed in a 25-mm Vycor reaction tube which was heated to 1000° and maintained at that temperature for 6 hr as steam was slowly swept through the tube. The samples were subsequently placed in a 900° muffle furnace to drive off absorbed carbon dioxide, cooled in a vacuum desiccator, and weighed. Several samples were checked for constant weight by recycling.

Two sets of samples together with a CaF_2 "standard" were submitted to the National Spectroscopic Laboratories (Cleveland, Ohio) for oxygen analysis by the platinum-fusion technique.

A Guinier forward-focusing Haegg-type X-ray powder diffraction photograph (Cu Kα radiation, $\lambda\alpha_1$ 1.54051 Å) calibrated with annealed KCl ($a = 6.2930$ Å, at $24 \pm 1°$) was obtained for each sample. Lattice parameters were obtained by the method of least regression with a computer program written by Lindqvist and Wengelin.[6] Both crystalline and pulverized samples were viewed with a Leitz polarizing microscope under both reflected and transmitted light.

Results

Samarium Trifluoride.—Several white, powdery samples of samarium trifluoride were prepared. Both

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[1] Abstracted from the Ph.D. thesis of J. J. Stezowski submitted to the Graduate College of Michigan State University, 1968.

[2] Presented at the 7th Rare Earth Conference, San Diego, Calif., Oct 1968.

[3] L. B. Asprey, F. H. Ellinger, and E. Staritzky, "Rare Earth Research," Vol II, K. S. Vorres, Ed., Gordon and Beach, New York, N. Y., 1964, pp 11–20.

[4] D. B. Shinn, Ph.D. Thesis, Michigan State University, East Lansing, Mich., 1968, pp 62–104.

[5] A. D. Kirshenbaum and J. A. Cahill, *J. Inorg. Nucl. Chem.*, **14**, 148 (1960).

[6] O. Lindqvist and F. Wengelin, *Arkiv Kemi*, **28**, 179 (1967).

the weight change during reaction and the samarium analyses (72.4 ± 0.2% found, 72.51% calcd) were indicative of complete conversion to the trifluoride. Guinier diffraction photographs obtained from these samples displayed lines assignable to both the hexagonal and orthorhombic crystal modifications.[7,8]

The Reduced Samarium Fluorides.—Twenty-two different compositions were analyzed for samarium and the F:Sm ratio of the preparations varied from 1.83 to 2.54. Even though the oxygen analytical results indicated 0.31 ± 0.12% oxygen, the high results obtained for the CaF_2 standard indicate this value is the upper limit of the oxygen concentration. On the basis of these data, the concentration of oxygen was assumed insignificant.

As the F:Sm atomic ratio of the powdered samples exposed to 6 *N* HCl solutions decreased to 2, a definite increase in the rate of gas evolution was noted, but this rate was considerably more vigorous when the ratio was less than 2. Vigorous gas evolution was also noted when the coating which deposited on the vacuum line was treated with acid.

The color of opaque fragments of the reduced samarium fluorides ranged from purple (composition near SmF_2) to dull burgundy red (composition $SmF_{2.5}$). Upon powdering, the difficulty of which increased as the fluoride content decreased, the purple fragments appeared blue to blue-green; the burgundy-colored samples appeared lighter. Microscopic examination with transmitted light indicated the powder was opaque, while examination with reflected light revealed an apparently regular change in color as a function of composition. The fragments exhibited sharp faces, but recurrent morphology was not observed. A graph of density *vs.* composition is presented in Figure 1.

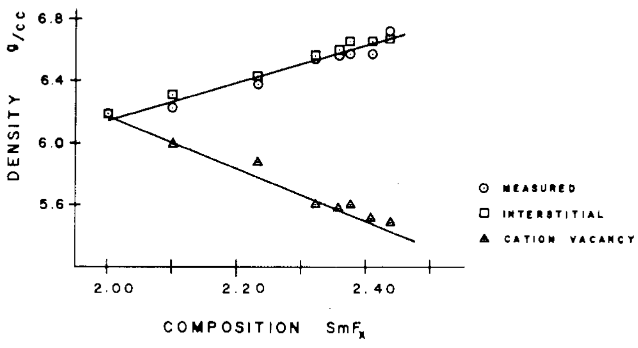

Figure 1.—A graph of density *vs.* composition for the samarium–fluorine system.

All the Guinier powder X-ray diffraction patterns were reasonably similar to that of face-centered cubic SmF_2, but a detailed examination indicated considerable line splitting and additional extra lines. With the exception of their sharpness, patterns of quenched and annealed samples were identical. The Guinier photographs obtained for samples with an F:Sm atomic ratio of less than 2.00 were also generally diffuse, but they yielded within the limit of error the same lattice parameters as those obtained from stoichiometric SmF_2.

The cubic lattice parameter decreased linearly as the F:Sm atomic ratio was varied from 2.00 to 2.14, and its behavior is describable by the linear equation determined by least squares: $L = -0.2008x + 6.274$, in which L is the lattice parameter in Å and x is the composition in SmF_x. Typical standard deviations are ±0.002 Å.

Samples of the composition $SmF_{2.17}$ yielded photographs which displayed doublets for the normally single lines. Similar powder patterns for which a trend in relative line intensities was noted were obtained until, at F:Sm = 2.35 ± 0.02, a second phase, indexable on tetragonal symmetry with lattice parameters of $a = 4.106 \pm 0.002$ and $c = 5.825 \pm 0.003$ Å, was obtained in pure form. The lattice parameter of the cubic phase remained invariant throughout this two-phase region at $a = 5.841 \pm 0.002$ Å. A number of very weak reflections (Table I), observable throughout the latter half of the two-phase region, were unassignable to this tetragonal unit cell.

Table I

Interplanar *d* Spacings and Relative Intensities of Pseudotetragonal $SmF_{2.35}$ and Rhombohedral $SmF_{2.41}$

$SmF_{2.35}$					$SmF_{2.41}$				
h	*k*	*l*	Intens	*d* value, Å	*h*	*k*	*l*	Intens	*d* value, Å
			1	3.627[a]	0	0	6	6	3.365[a]
			1	3.566	0	1	2	10	3.342
1	0	1	10	3.355	1	0	4	6	2.901
0	0	2	7	2.913	0	1	8	5	2.054
1	1	0	7	2.899	1	1	0	8	2.047
			1	2.782	1	0	10	...	(1.754)[b]
			1	2.761	1	1	6	6	1.748
1	1	1	1	2.599	2	0	2	6	1.747
			1	2.580	0	0	2	4	1.680
			1	2.464	0	1	14	4	1.334
1	0	2	2	2.398	0	2	10	4	1.332
			1	2.331					
			1	2.163					
			1	2.129					
1	1	2	5	2.058					
2	0	0	7	2.051					
			1	1.975					
0	0	3	1	1.951					
			3	1.359					
1	0	3	5	1.757					
2	1	1	7	1.750					
2	0	2	5	1.678					
2	2	2	2	1.451					
			3	1.343					
2	1	3	3	1.334					
			3	1.287					

[a] Estimated error ±0.005. [b] Observed only when F:Sm ≥ 2.43.

The diffraction pattern of a sample of composition F:Sm = 2.39 contained, in addition to the lines assignable to the tetragonal phase, another set indexable on rhombohedral symmetry (Table I). Thus, the composition range of the tetragonal phase is very narrow. The lines attributable to rhombohedral symmetry remained invariant only until F:Sm = 2.41 ± 0.02. From this composition to F:Sm = 2.46, the rhombo-

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(7) A. Zalkin and D. H. Templeton, *J. Am. Chem. Soc.*, **75**, 2453 (1953).

(8) I. Oftedal, *Z. Physik. Chem.*, **B5**, 272 (1929); **B13**, 190 (1931).

TABLE II

PHASE REGIONS OBSERVED IN THE SAMARIUM(II) FLUORIDE–SAMARIUM(III) FLUORIDE SYSTEM

x in SmF_x	Phase(s) obsd	Lattice parameters, Å
<2.00	Metal + SmF_2	...
$2.00 < x < 2.14$	Homogeneous cubic	$5.867\ (1) > a > 5.841\ (1)^a$
$2.14 < x < 2.34$	Cubic + tetragonal	...
2.35	Pseudotetragonal	$a = 4.106\ (2)$; $c = 5.825\ (3)$
$2.36 < x < 2.40$	Tetragonal + rhombohedral	...
$2.41 < x < 2.46$	Rhombohedral	$7.124\ (2) > a > 7.096\ (2)$ $33.40\ (2)^\circ > \alpha > 33.23\ (2)^\circ$
$2.46 < x < 3$	Rhombohedral + SmF_3	...

[a] Standard deviation.

hedral unit cell volume decreased regularly ($a = 7.124 \pm 0.002$ Å, $\alpha = 33.40 \pm 0.02°$ to $a = 7.096 \pm 0.002$ Å, $\alpha = 33.23 \pm 0.02°$).

The Guinier photograph of a sample of composition F:Sm = 2.54 displayed lines assignable both to the rhombohedral phase, whose lattice parameters were identical with those of $SmF_{2.46}$, and to the hexagonal and orthorhombic forms of samarium trifluoride.

A summary of the phases observed and their compositions and lattice parameter limits is presented in Table II.

Discussion

The reaction between samarium and samarium trifluoride produced a samarium(II) fluoride–samarium(III) fluoride system which displays a minimum of three discrete phases, two of which have a variable composition region and one of which appears stoichiometric. The similarity of the diffraction patterns obtained throughout the entire composition range is indicative of a continual modification of the parent fluorite SmF_2 lattice.

Two models whose basis is this lattice may be proposed for a description of this system: (a) an interstitial anion model and (b) a cation vacancy model with a constant anion lattice. The theoretical densities calculated with the observed unit cell volumes for each of these models, also presented in Figure 1, indicate the interstitial model is consistent with the observed data. The volume–composition behavior of this model is governed by (a) substitution of a smaller, more highly charged cation for its divalent analog and (b) addition of a fluoride ion into an interstitial site. The observed volume decrease indicates dominance of the substitution step. The regular decrease in the cubic lattice parameter probably indicates that a random substitution mechanism prevails as the stoichiometry deviates from F:Sm values of 2.00–2.14 and the two-phase region between the cubic and tetragonal phases may represent a transition from a random to an ordered substitution mechanism. However, the insensitivity of the X-ray technique to the detection of closely related phases whose lattice parameters deviate only slightly prevents preclusion of an ordered substitution process.

The weak lines which remained unassigned in the tetragonal powder pattern indicate that the phase is only pseudotetragonal and that the true symmetry is lower. Since the samarium electrons are the major contributor to the X-ray structure factors, cation symmetry must be nearly tetragonal and the observed superstructure lines probably reflect the long-range ordering of the fluoride lattice.

The Guinier photographs and samarium analyses indicate the fluoride-rich boundary to be near $SmF_{2.46\pm0.02}$, but the rhombohedral geometry of the lattice is more consistent with the composition $SmF_{2.50}$ if the true unit cell contains only two samarium ions. One ion may be located at the body center and the other shared between adjacent unit cells. If one of these ions is Sm^{3+}, the composition of the cell would be Sm_2F_5 or $SmF_{2.50}$. The decrease in the rhombohedral angle, α, is consistent with the placing of a trivalent samarium ion in the body-centered position but the probable location of the extra ion cannot be predicted. Since samarium trifluoride is observed on the fluoride-rich side of this rhombohedral phase, the rhombohedral phase must be the last in the series.

It is frequently possible to represent the phases observed in a nonstoichiometric system by a homologous series. The phase boundaries observed in this system may be represented within experimental error by the general formula Sm_nF_{3n-6}, in which $6 < n < 11$ (Table III). One boundary predicted by this scheme has not been detected, $SmF_{2.25}$, but its absence is not inconsistent with observations made of other similar phases.[9,10] Furthermore, the very narrow composition range of the tetragonal phase is represented by one value, 2.33. Since this series is related to phase boundaries, and not to discrete phases, all of which have narrow compositions, its significance may be questioned. However, it may indicate structural changes occurring in the lattice which are too minute to be detected by the X-ray technique employed.

TABLE III

COMPARISON OF OBSERVED STOICHIOMETRIES AND THOSE CALCULATED FOR THE Sm_nF_{3n-6} HOMOLOGOUS SERIES

	$(3n-6)/n$			$(3n-6)/n$	
n	Calcd	Obsd	n	Calcd	Obsd
6	2.00	2.00	9	2.33	2.35
7	2.14	2.16	10	2.40	2.41
8	2.25	...	11	2.45	2.46

Uranium dioxide also possesses the cubic fluorite structure and upon oxidation yields many discrete phases. A lattice parameter and density study of the UO_2–UO_3 system by Lynds, *et al.*,[11] has produced results somewhat similar to those reported here. The crystal radius of U^{4+} (0.97 Å) calculated from the lattice parameter of stoichiometric UO_2 ($a = 5.740 \pm 0.001$ Å) is relatively close to the value calculated for Sm^{2+} (1.18 Å) in a similar manner from SmF_2. However, since a fluoride ion is smaller than an oxide ion, the more important radius ratio would indicate

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[9] L. Eyring and B. Holmberg, Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, p 46.

[10] E. S. Makarov, *Proc. Acad. Sci. USSR, Chem. Sect.*, **139**, 720 (1961).

[11] L. Lynds, W. A. Yong, J. S. Mohl, and G. G. Libowitz, Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, p 58.

that the systems would differ considerably. Lynds, *et al.*,[11] presented two equations to describe the decrease in the lattice parameter as the oxide content of the lattice increases: one for the composition range UO_2–$UO_{2.125}$ and another for the range $UO_{2.17}$–$UO_{2.25}$. The first equation characterizes the behavior of a nonstoichiometric UO_2 phase while the second characterizes that of a U_4O_9 phase ($UO_{2.25}$). The first of these has a clear counterpart in the samarium fluoride system but the second does not, probably because a clearly defined $SmF_{2.25}$ analog could not be found. However, a single-crystal study by Belbeoch, *et al.*,[12] has demonstrated that the unit cell of $UO_{2.25}$ contains 64 nominally fluorite unit cells arranged in a 4 × 4 × 4 array. The superstructure observed in the latter half of the cubic–tetragonal two-phase region and assigned to the tetragonal unit cell may, in fact, correspond to a similar type of cell and an $SmF_{2.25}$ phase may exist. The concurrence of a phase boundary at $SmF_{2.16}$ and $UO_{2.17}$ provides some support for the existence of a phase at $SmF_{2.25}$.

Another phase in the uranium–oxygen system, $UO_{2.33}$ (U_6O_{14}), a member of a homologous series (U_nO_{2n+2}) reported for this system by Makarov,[10] has a similar analog in the samarium system, $SmF_{2.35}$. Hoekstra, *et al.*,[13] have reported that this uranium phase possesses body-centered tetragonal symmetry with $a = 3.78$ and $c = 5.55$ Å. As in the samarium phase, the a parameter is less than half the face diagonal of a cube with edge c. A modification of this tetragonal cell in which $a = 3.84$ and $c = 5.40$ Å has been observed for only the uranium–oxygen system.

The next phase in the homologous series, $UO_{2.40}$ (U_5O_{12}), has been reported to be tetragonal with $a = 5.364$ and $c = 5.531$ Å. The phase $SmF_{2.41}$, which has been indexed on a rhombohedral lattice, seems to be related to this uranium analog.

The samarium analog of $UO_{2.5}$ (U_4O_{10}) may correspond to $SmF_{2.46}$, but the relationship is not so well defined. The uranium compound has been examined by single-crystal techniques and has been found to be orthorhombic.[10] It seems apparent that while many of the same stoichiometries are involved, the lattice modifications are different for the two systems. The uranium system displays at least one more phase, with several crystal modifications, before the lattice collapses to that of UO_3, and thus appears to be more complicated at the anion-rich end of the nonstoichiometric region. This complexity probably results from the different charges and sizes of the ions.

It is apparent from the above discussion that the nonstoichiometry displayed by these two systems is the result of similar modifications of the fluorite lattice. The present investigation has been unable to establish the nature of these changes and has indicated that single-crystal studies must be undertaken to clarify some of the observations.

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(12) B. Belbeoch, C. Piekarski, and P. Perio, *Acta Cryst.*, **14**, 837 (1961).

(13) H. R. Hoekstra, A. Santoro, and S. Seigel, *J. Inorg. Nucl. Chem.*, **18**, 166 (1961).

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The Crystal and Molecular Structure of Dinitrosylbis(triphenylphosphine)iridium Perchlorate, $[Ir(NO)_2(P(C_6H_5)_3)_2][ClO_4]$

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The structure of dinitrosylbis(triphenylphosphine)iridium perchlorate, $[Ir(NO)_2(P(C_6H_5)_3)_2][ClO_4]$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the space group C_{2h}^6-$C2/c$ of the monoclinic system with four molecules in a unit cell of dimensions $a = 17.090$ (16) Å, $b = 12.413$ (13) Å, $c = 17.165$ (17) Å, and $\beta = 108.02$ (11)°. The observed and calculated densities are 1.69 (±0.02) and 1.68 g/cm³, respectively. Least-squares refinement of the structure has led to a final value of the conventional R factor (on F) of 0.043 for the 1597 independent reflections having $F^2 > 3\sigma(F^2)$. The crystal structure consists of well-separated, discrete, monomeric ions. The coordination geometry around the iridium atom is only approximately tetrahedral; the N–Ir–N angle, 154.2 (7)°, is much larger than expected. Possible reasons for this distortion are discussed. The iridium–nitrogen–oxygen bond angle of 164 (1)° deviates considerably from linearity. The perchlorate anion is disordered about two positions and has been refined as a rigid group, with normal tetrahedral angles of 109° 28′ and chlorine–oxygen bond lengths of 1.43 Å.

Introduction

Crystal structure studies of $[IrX(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$ (X = Cl or I)[1-3] showed that in each compound the metal–nitrosyl geometry was very different from that previously observed in reliable structural studies of transition metal–nitrosyl complexes. Whereas the usual transition metal–nitrosyl geometry involves a short metal–nitrogen bond and a linear or nearly linear metal–nitrogen–oxygen bond angle,

(1) D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Am. Chem. Soc.*, **90**, 4486 (1968).

(2) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968).

(3) D. J. Hodgson and J. A. Ibers, *ibid.*, **8**, 1282 (1969).