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The Crystal Structure and Nonstoichiometry of Rare Earth Oxyfluoride

Koichi Niihara and Seishi Yajima
The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai

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Oxyfluoride phases for the rare earth Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Y have been prepared by heating a mixture of lanthanon fluorides, LnF_3, and lanthanon oxides, Ln_2O_3. Three phases were identified. The rhombohedral phases, LnOF, have a stoichiometric composition, and the tetragonal phases, $Ln_4O_3F_6$, have a comparatively large nonstoichiometric composition range. The third cubic phase, with a fluorite-type structure, was observed in the SmOF-$Sm_4O_3F_6$ region after quenching from a high temperature. This establishes that both the rhombohedral SmOF and the tetragonal $Sm_4O_3F_6$ transform to the cubic phase and form a complete solid solution in the high-temperature range. It is postulated that the rhombohedral and tetragonal phases are pseudo-cubic from the fact that the diffraction patterns of these two phases are closely similar to that of the fluorite type.

Relatively few data on the chemical properties of the rare earth oxyfluorides exist in the literature; there is an adequate reason for this. Similar in size to the fluoride ion, the oxide ion may be substituted through a wide concentration range in these heavy metal fluorides. Therefore, the compositional variability of the rare earth oxyfluorides with respect to the anionic ligands is very extensive. Accurate property data are, consequently, very limited. Research problems connected with those materials require mainly information concerning the extent of the oxide-fluoride miscibility before other data may be obtained. If the generally indiscrete composition of the solid phases can be well understood, attempts to obtain other accurate data will be stimulated.

Oxyfluorides of lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, and yttrium have been prepared using several techniques.[1-6] Zachariasen[1] prepared two types of crystal structures of LaOF and YOF by the hydrolysis of LaF_3 and YF_3 at 900°C and 500°C respectively, one being rhombohedral and the other tetragonal. The rhombohedral phases were observed to have stoichiometric compositions, LaOF and YOF. The tetragonal phases appeared with an increase in the fluorine in the LaO_xF_{3-2x} system $(0.7<x<1)$. Zachariasen related all the structures to the fluorite-type structure. He postulated that the rhombohedral and tetragonal forms result from a complete ordering of the oxygen and fluorine atoms into distinct sites of the unit cell.

Hund[2] prepared tetragonal and cubic YOF by heating a mixture of Y_2O_3 and YF_3 in a high vacuum at 900°C for several hr.

Popov[3] and other Russian workers[4] prepared rare earth oxyfluorides (La through Er) by heating their metal fluorides in a muffle furnace in dry air or in a stream of moist air. All the compounds except CeOF, which was cubic, were found to exhibit rhombohedral symmetry.

Thus, there are various structures which have been reported for the rare earth oxyfluorides. The main purpose of this study is to elucidate the relation between the crystal structure and the nonstoichiometric composition of the rare earth oxyfluorides, and to give precise lattice parameters.

Experimental

The anhydrous lanthanon trifluorides, SmF_3, EuF_3, GdF_3, DyF_3, HoF_3, ErF_3, TmF_3, and YbF_3 were prepared by converting the 99.9% pure Ln_2O_3 to fluoride according to the following chemical reaction:

$$Ln_2O_3 + 6NH_4\cdot HF_2 = 2LnF_3 + 6NH_4\cdot F + 3H_2O.$$

A mixture containing excess $NH_4\cdot HF_2$ was heated at 350°C

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[1] W. H. Zachariasen, *Acta Crystallogr.*, **4**, 231 (1951).

[2] F. Hund, *Z. Anorg. Allg. Chem.*, **265**, 62 (1951); *ibid.*, **273**, 212 (1953).

[3] A. I. Popov, *J. Amer. Chem. Soc.*, **76**, 4734 (1954).

[4] L. R. Batsanona, *Zh. Neorg. Khim.*, **9**(2), 330 (1964).

[5] K. S. Vorres, "Rare Earth Research III," ed. by Eyring., Gordon and Breach, New York, N. Y., (1964), p. 521.

[6] W. H. Zachariasen, *Z. Krystallogr.*, **80**, 137 (1931).

for 10 hr in a platinum boat, which was placed in an Inconel tube situated in an electric furnace. The resulting water, HF, and NH_4F were evacuated by an aspirator during the reaction. The trifluoride sample thus obtained was degassed in another furnace by careful heating in a high vaccum, *i. e.*, by raising the temperature to 600°C at a rate of 5°C/min and by then maintaining the temperature these for 5 hr.

The lanthanon trifluoride was mixed with lanthanon sesquioxide in various ratios. The fully homogenized mixtures were compacted into pellets, about 10 mm in diameter and 10—30 mm thick. These pellets were reacted in a high vacuum or in an inert gas atmosphere at 1000—1200°C for 5—10 hr, and then quenched or slowly cooled to room temperature. This method of preparing the oxyfluoride is very convenient in studying the nonstoichiometry if enough attention is paid to the weight loss during the reaction and to the anhydrolysis of the rare earth oxides and fluorides.

The nonstoichiometric compositions of the lanthanon oxyfluorides can be expressed as follows:

$$a\mathrm{LnF}_3 + b\mathrm{Ln}_2\mathrm{O}_3 = (a+2b)\mathrm{LnO}_x\mathrm{F}_{3-2x} \quad (x=3b/a+2b)$$

If the amount of either LnF_3 or Ln_2O_3 exceeds the nonstoichiometric composition given by this formula, the excess amount of either LnF_3 or Ln_2O_3 can be determined by X-ray. The pellets thus obtained were pulverized after heat treatment and were examined by X-ray powder diffraction using copper *Kα* radiation and a 114.6 mm-diameter Debye-Scherrer powder camera. Chemical analysis was performed by direct ignition to the oxide.

Experimental Results

The oxyfluorides of samarium, europium, gadolinium, dysprosium, holmium, erbium, thulium, and ytterbium were prepared by the above-described method. The results of the identification of the reaction products cooled slowly in the furnace are shown in Fig. 1; they indicate that there are two oxyfluoride phases. According to the interpretation of the X-ray diffraction patterns, one phase is tetragonal, and the other, rhombohedral. Only in the SmF_3-Sm_2O_3 system, were phases of the fluorite type observed upon quenching from 1200°C. However, in the other system, LnF_3-Ln_2O_3, efforts to obtain a phase of the fluorite type by quenching were unsuccessful.

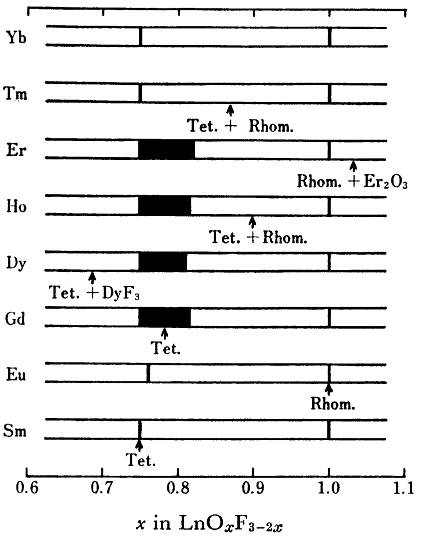

Fig. 1. Phase regions of rhombohedral and tetragonal oxyfluorides.

Rhombohedral-phase LnOF. In all cases, the rhombohedral phases were found to be a single phase only when $x=1$. In the regions of $x>1$ and $x<1$, the diffraction lines of both Ln_2O_3 and the tetragonal oxyfluoride occurred, as well as the rhombohedral phase. No variation in the unit-cell dimensions of this rhombohedral phase was observed. Therefore, it may be concluded that the chemical composition of the rhombohedral phase is sharply defined and corresponds exactly to LnOF. The diffraction data of SmOF and ErOF are shown in Table 1. The diffraction data of EuOF, GdOF, DyOF, HoOF, TmOF, and YbOF are good similar to those of SmOF and ErOF.

Zachariasen[1] found, for LaOF, the space group $R\bar{3}m$ with two molecules in the unit cell; he reported atomic positions which were satisfactory for YOF as well. The data for SmOF, EuOF, GdOF, DyOF, ErOF, TmOF, and YbOF obtained in the present research

TABLE 1. DIFFRACTION DATA FOR RHOMBOHEDRAL SmOF AND ErOF

hkl	I (obsd)	SmOF $\sin^2\theta$ (obsd)	SmOF $\sin^2\theta$ (calcd)	ErOF $\sin^2\theta$ (obsd)	ErOF $\sin^2\theta$ (calcd)
111	vw	—	0.0141	0.0152	0.0151
100	vvw	—	0.0534	0.0512	0.0571
222	s	0.0567	0.0565	0.0605	0.0605
110	vs	0.0588	0.0581	0.0626	0.0621
211	s	0.0776	0.0770	0.0822	0.0823
221	w	0.0919	0.0911	0.0977	0.0974
333	m	0.1284	0.1273	0.1372	0.1361
322			0.1289		0.1378
$33\underline{2}$	s	0.1527	0.1524	0.1636	0.1629
101	s	0.1565	0.1555	0.1674	0.1662
$21\underline{0}$	vvw	—	0.1696	0.1814	0.1813
111	m	0.2087	0.2089	0.2230	0.2232
433			0.2096		0.2234
321	s	0.2129	0.2120	0.2273	0.2266
200			0.2136		0.2283
444	vvw	0.2269	0.2264	0.2419	0.2419
220	m	0.2324	0.2325	0.2487	0.2484
443	w	0.2412	0.2420	0.2581	0.2586
311	vvw	—	0.2466	0.2642	0.2635
432	m	0.2833	0.2828	0.3027	0.3023
331			0.2843		0.3039
422	m	0.3079	0.3079	0.3290	0.3290
544	w	0.3173	0.3175	0.3389	0.3393
555	vw	—	0.3537	0.3775	0.3780
$55\underline{4}$	vw	—	0.3599	0.3826	0.3846
201	vw	0.3647	0.3644	0.3883	0.3894
442			0.3645		0.3895
211	m	0.3692	0.3691	0.3948	0.3944
543	w	0.3817	0.3818	0.4077	0.4080
310	w	0.3880	0.3880	0.4146	0.4146
533	vvw	—	0.3975	0.4247	0.4247
320	vvw	—	0.4021	0.4282	0.4297
421	vw	—	0.4398	0.4703	0.4701

SmOF $a=6.863\pm0.002$Å, $\alpha=33.10\pm0.02°$
ErOF $a=6.639\pm0.001$Å, $\alpha=33.10\pm0.01°$

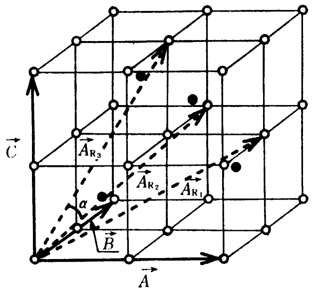

Fig. 2-a. The relation between rhombohedral and fluorite type unit cell.
A, B, C: fluorite type
A_{R1}, A_{R2}, A_{R3},: rhombohedral

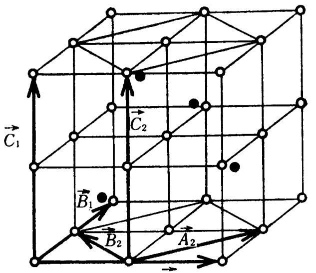

Fig. 2-b. Tetragonal unit cell.
A_1, B_1, C_1,: this research
A_2, B_2, C_2: Zachariasen

can be interpreted in a similar way, as the X-ray diffraction data agree well with those observed by Zachariasen for LaOF and YOF. The structure is a superlattice based upon a slightly distorted CaF_2-type structure. For the undistorted structure, α is 33.56°. The relation between the rhombohedral cell and the fluorite cell is shown in Fig. 2-a. The lattice constants, unit cell volume, and X-ray density obtained are listed in Table 2, where they are also compared with the previous data.[1,7–9] The change in the molecular volume against the atomic number of rare earth elements plotted in Fig. 3 is characteristic of the well-known lanthanide contraction.

TABLE 2. LATTICE PARAMETER OF RHOMBOHEDRAL RATE EARTH OXYFLUORIDES

Compound	Lattice parameter		Unit cell volume in Å³	X-Ray density (g/cc)
	a in Å	α in degree		
YOF[a]	6.697	33.20	79.4	5.18
LaOF[a]	7.132	33.01	95.9	6.02
PrOF[b]	7.016	33.03	91.3	6.40
NdOF[b]	6.953	33.04	88.9	6.69
SmOF	6.863±0.002	33.10±0.02	85.8	7.17
EuOF	6.828±0.002	33.05±0.02	84.3	7.37
GdOF	6.801±0.001	33.05±0.01	83.3	7.67
TbOF[c]	6.751	33.09	81.6	7.89
DyOF	6.719±0.003	33.02±0.02	80.2	8.18
HoOF	6.687±0.001	33.02±0.02	79.0	8.40
ErOF	6.639±0.001	33.10±0.01	77.7	8.65
TmOF	6.604±0.002	33.06±0.02	76.2	8.93
YbOF	6.569±0.002	33.04±0.02	75.0	9.25

a) Zachariasen, Ref. 1
b) Baenzigh, Ref. 7
c) Templeton, Ref. 8

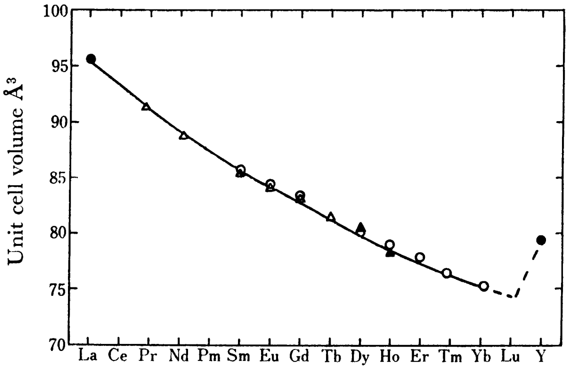

Fig. 3. Unit cell volume of rhombohedral rare earth oxyfluorides, LnOF, as a function of atomic number of rare earth element.

○ this work ○ Zachariasen, Ref. 1
△ Baenziger, Ref. 7 ▲ Vorres, Ref. 9

Tetragonal-phase $Ln_4O_3F_6$ ($Ln_2O_3\cdot 2LnF_3$). The tetragonal phases were observed as mono-phases in the fluorine-rich region. Generally, the chemical composition of the phase throughout its homogeneity range can be expressed by the LnO_xF_{3-2x} formula. As is shown in Fig. 1, the tetragonal phases of Sm, Eu, Gd, Dy, Ho, Er, Tm, and Yb exist as stable mono-phases in the regions of $x=0.75$, $x=0.77$, $0.75<x<0.83$, $0.75<x<0.82$, $0.75<x<0.83$, $0.75<x<0.84$, $x=0.75$, and $x=0.75$ respectively. In the regions of $x<0.75$ and about $x>0.83$, the LnF_3 fluoride and the LnOF rhombohedral oxyfluoride respectively appear as second phases. Therefore, it is resonable to assume that the tetragonal phases have the ideal chemical composition, $LnO_{0.75}F_{1.5}$, that is, $Ln_4O_3F_6(Ln_2O_3\cdot 2LnF_3)$. The results of the chemical analysis of each $Ln_4O_3F_6$ are summarized in Table 3. The X-ray diffraction data of $Sm_4O_3F_6$ and $Er_4O_3F_6$ are shown in Table 4. The second column lists the indices postulated by Zachariasen. The unit cell of the tetragonal oxyfluoride is illustrated in Fig. 2-b in comparison with the unit cell of Zachariasen. The diffraction data of the tetragonal $Ln_4O_3F_6$ are compara-

TABLE 3. COMPOSITION OF $Ln_4O_3F_6$

Ln in $Ln_4O_3F_6$	Observed percentage of metal	Theoretical percentage of metal
Sm	78.50	78.78
Eu	78.45	78.96
Gd	79.36	79.52
Dy	80.01	80.05
Ho	80.26	80.29
Er	80.30	80.52
Tm	80.41	80.89
Yb	81.02	81.04

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7) N. C. Baenziger, J. R. Holden, G. E. Knudsen, and A. I. Popov, *J. Amer. Chem. Soc.*, **76**, 4734 (1954).

8) D. H. Templeton and C. H. Dauben, *ibid.*, **76**, 5237 (1954).

9) K. S. Vorres and Richard Rivriells, Proc. Conf. Rare Earth Res., 4th Phoenix, Ariz., (1954), pp. 521—561 (Pub. 1965).

TABLE 4. DIFFRACTION DATA FOR TETRAGONAL $Sm_4O_3F_6$ AND $Er_4O_3F_6$

hkl[a)]	hkl[b)]	I (obsd)	$Sm_4O_3F_6$ $\sin^2\theta$ (obsd)	$Sm_4O_3F_6$ $\sin^2\theta$ (calcd)	$Er_4O_3F_6$ $\sin^2\theta$ (obsd)	$Er_4O_3F_6$ $\sin^2\theta$ (calcd)
100		vw	0.0189	0.0186	0.0190	0.0194
001	001	w		0.0189	0.0206	0.0205
110	100	vw	0.0370	0.0372	0.0380	0.0389
101		vw		0.0373	0.0400	0.0408
111	101	vs	0.0569	0.0563	0.0595	0.0595
200	110	s	0.0757	0.0747	0.0782	0.0779
002	002	w		0.0757	0.0826	0.0818
201	111	vw	—	0.0936	0.0990	0.0984
112	102	m	0.1134	0.1131	0.1210	0.1211
220	200	s	0.1504	0.1493	0.1564	0.1558
202	112	s		0.1504	0.1604	0.1601
300		w	0.1680	0.1680	0.1777	0.1753
221	201			0.1683		0.1767
003	003	w	0.1707	0.1704	0.1849	0.1845
310	210	w	0.1881	0.1866	0.1977	0.1949
301				0.1890		0.1958
103		vw		0.1887	0.2040	0.2044
311	211	s	0.2065	0.2056	0.2157	0.2153
113	103	m		0.2077	0.2240	0.2239
222	202	m	0.2245	0.2251	0.2380	0.2380
320		vw	—	0.2418	0.2520	0.2522
203	113	m	0.2248	0.2451	0.2630	0.2628
312	212	m	0.2622	0.2628	0.2785	0.2769
400	220	w	0.2978	0.2986	0.3122	0.3116
004	004	w	0.3079	0.3030	0.3293	0.3288
410		vw	0.3189	0.3176	0.3323	0.3322
401	221					
223	203	vw	0.3389	0.3197	0.3409	0.3422
114	104	w		0.3403	0.3683	0.3676
331	301	w	0.3559	0.3549	0.3731	0.3711
313	213	w		0.3571	0.3802	0.3796
420	310	w	0.3737	0.3733	0.3921	0.3895
402	222			0.3744		0.3938
204	114	vvw	—	0.3776	0.4066	0.4066
421	311	vvw	—	0.3922	0.4100	0.4101
332	302	vvw	—	0.4117	0.4342	0.4327
422	312	w	—	0.4492	0.4723	0.4717

a) this work, b) Zachariasen

$Sm_4O_3F_6$ $a=5.643\pm0.003$Å, $c=5.602\pm0.003$Å

$Er_4O_3F_6$ $a=5.524\pm0.001$Å, $c=5.379\pm0.001$Å

tively similar to the data of Zachariasen[1)] for the tetragonal YOF and LaOF with respect to the intensities and line structure, compared after the axis transformation. However, the (110) and (103) planes can not be explained by the unit cell of Zachariasen, as is shown in Table 4. On the other hand, all the diffraction planes can be explained by the unit cell used in this research. According to our results, $Ln_4O_3F_6$ is a tetragonal structure containing 4 molecules in the unit cell with $c/a=1$. Thus, our results differ from those of Zachariasen, who assumed 2 molecules in the unit cell with $c/a=\sqrt{2}$. The lattice parameters and X-ray density are given in Table 5. The lattice parameter of the tetragonal $Gd_4O_3F_6$, $Dy_4O_3F_6$, $Ho_4O_3F_6$, and $Er_4O_3F_6$, all of which have a nonstoichiometric composition range, are plotted as a function of the parameter, x, in Fig. 4 and Fig. 5. The variation in the lattice parameters is plotted in Fig. 6 against the atomic number of the rare earth element. The lattice parameters of the tetragonal $Gd_4O_3F_6$, $Dy_4O_3F_6$, $Ho_4O_3F_6$, and $Er_4O_3F_6$ in the homogeneity range vary in such a way that c increases and a decreases. As is shown in Fig. 6, the tetragonal phases show the well-known lanthanide contraction as a function of the atomic number of the rare earth element.

TABLE 5. LATTICE PARAMETER OF TETRAGONAL RARE EARTH OXYFLUORIDES

Compound	Lattice paremeter in Å		X-Ray density (g/cc)
	a	c	
YO_xF_{3-2x}[a)]	3.910(x=1)	5.431	
	3.930(x=0.7)	5.46	
LaO_xF_{3-2x}[a)]	4.083(x=1)	5.825	
	4.098(x=0.7)	5.840	
$Sm_4O_3F_6$	5.643±0.003	5.602±0.003	7.13
$Eu_4O_3F_6$	5.623±0.002	5.574±0.003	7.28
$Gd_4O_3F_6$	5.595±0.003	5.527±0.003	7.61
$Dy_4O_3F_6$	5.559±0.003	5.456±0.003	8.02
$Ho_4O_3F_6$	5.539±0.002	5.414±0.002	8.23
$Er_4O_3F_6$	5.524±0.001	5.379±0.001	8.43
$Tm_4O_3F_6$	5.513±0.002	5.355±0.002	8.58
$Yb_4O_3F_6$	5.498±0.002	5.323±0.002	8.85

a) Zachariasen, Ref. 1

Cubic Phase (Fluorite-type Structure). In the SmF_3-Sm_2O_3 system, the rhombohedral phase and the tetragonal phase were observed, as is shown in Fig. 1. Some of these specimens were reheated to 1200°C and then quenched to room temperature. The crystal structure of these samples was examined by X-ray analysis; it was thus clarified that lines due to a face-

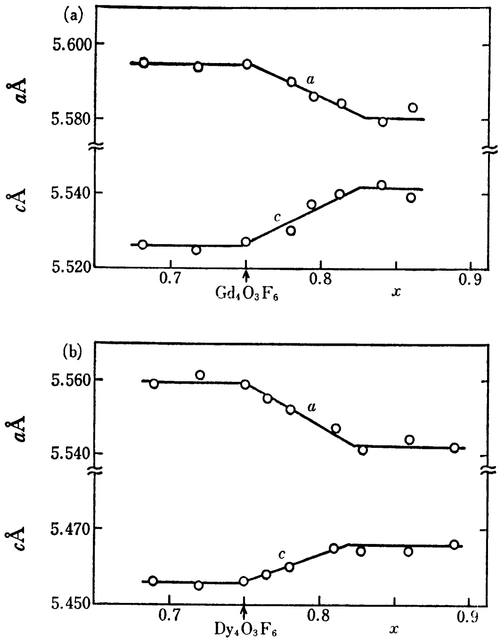

Fig. 4. Lattice parameter of tetragonal oxyfluorides as a function of x in $GdO_x\,F_{3-2x}$ and $DyO_x\,F_{3-2x}$.
(a) gadolinium oxyfluoride (b) dysprosium oxyfluoride

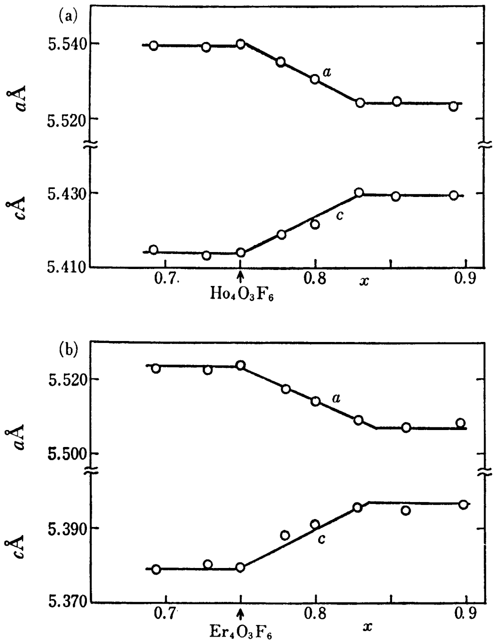

Fig. 5. Lattice parameter of rhombohedral oxyfluorides as a function of x in $HoO_x F_{3-2x}$ and $ErO_x F_{3-2x}$.
(a) holmium oxyfluoride (b) erbium oxyfluoride

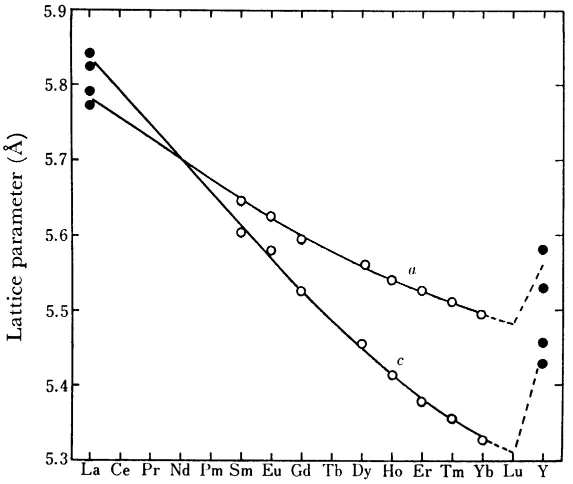

Fig. 6. Lattice parameter of tetragonal oxyfluorides, $Ln_4O_3F_6$, as a function of atomic number of rare earth element.
○ this work, ● Zachariasen, Ref. 1 (The values of a axis are $\sqrt{2}$ times as large as those obtained by Zachariasen.)

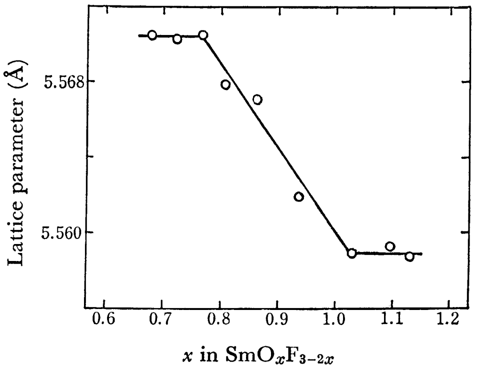

Fig. 7. Variation of the lattice parameter of SmO_xF_{3-2x} with the fluorite type structure.

centered structure exist, and the relative intensities suggested a fluorite-type structure. In specimens containing only the rhombohedral phase ($x=1$), or only the tetragonal phase ($x=0.75$), or both the rhombohedral and tetragonal phases ($0.75<x<1$), only the fluorite-type phase was obtained by quenching. If two-phase specimens contained the rhombohedral oxyfluoride and Sm_2O_3, or the tetragonal oxyfluoride and SmF_3, quenching produced the fluorite-type phase and left the Sm_2O_3 or SmF_3 respectively unchanged. Consequently, it can be considered that a transformation from the rhombohedral and tetragonal phases to the fluorite-type phase may occur. The correlation between the lattice parameter of the fluorite-type SmO_xF_{3-2x} and the parameter, x, is shown in Fig. 7. This curve shows that the lattice parameter decreases linearly with x, *i. e.*, with a decrease in the fluorine content. In all the other systems except SmF_3-Sm_2O_3, the fluorite-type phase was not obtained by quenching. In the $x>1$ region of the SmF_3-Sm_2O_3 system, a strange phenomenon was observed. The Sm_2O_3 used as the starting material had a B-type structure (Sm_2O_3-type, monoclinic), but the Sm_2O_3 found in the quenched products showed a C-type structure (La_2O_3-type, cubic). This means that a transformation of the Sm_2O_3 structure from the B-type to the C-type occurred. According to a previous study,[10] the C-type Sm_2O_3 is stable up to about 950°C and the transition process from the C-type to the B-type is completed within several days at 950°C and within about 1 hr at 1100°C. The transformation had also been found to be irreversible. Therefore, it is conceivable that the C-type Sm_2O_3 obtained in this experiment is stabilized by the presence of small amounts of fluorine.

Discussion

The rare earth oxyfluorides with the rhombohedral-, tetragonal-, and fluorite-type structures were observed in the system of Ln_2O_3-LnF_3. The chemical composition of the rhombohedral structure corresponds to the exact stoichiometric composition, LnOF, and no nonstoichiometric composition range exists in any of the systems. However, two kinds of tetragonal structures could be identified. One is the tetragonal phase, $Ln_4O_3F_6$, with out a nonstoichiometric composition range such as those with Sm, Eu, and Tb. The other type is the tetragonal phase, $Ln_4O_3F_6$ with a comparatively large nonstoichiometric composition range, such as those with Gd, Dy, Ho, and Er. It is very interesting that, in the former type, the rare earth ion is comparatively easy to convert into the divalent ion, but in the latter one this seems to be very difficult.

In the SmF_3-Sm_2O_3 system, the rhombohedral phase, SmOF, was observed at a ratio of 1 : 1, while the tetragonal phase, $Sm_4O_3F_6$, appeared at a ratio of 2 : 1. The fluorite-type phase was observed in the region of SmOF-$Sm_4O_3F_6$ after quenching from a high tempera-

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[10] S. Stephan, "Phase transformation rates of five rare earth sesquioxides(Series)," U. S. Bureau of Mines Report of investigation 6616 (1965).

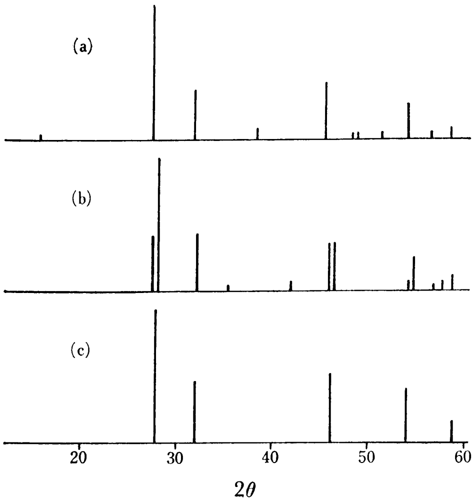

Fig. 8. Typical difraction patterns of samarium oxyfluoride.
(a) Tetragonal, (b) Rhombohedral, (c) Fluorite type

ture. This indicates that both the rhombohedral SmOF and the tetragonal $Sm_4O_3F_6$ are transformed to the cubic phase and form a complete solid solution in the high-temperature range.

Three typical X-ray patterns of the samarium oxyfluorides are illustrated in Fig. 8. The diffraction patterns of the rhombohedral- and tetragonal-type structures are very similar to that of the fluorite type. In view of those results, it is conceivable that the rhombohedral and tetragonal phases are pseudo-cubic.

Zachariasen1) postulated that both the rhombohedral and tetragonal forms have the LaOF composition and result from a complete ordering of the oxygen and fluorine atoms into distinct sites of the unit cell. He also described the tetragonal unit cell as having the axial ratio of $c/a=\sqrt{2}$ and containing two metal atoms. The present results concerning the rhombohedral phase are in agreement with those of Zachariasen. However, it is concluded that the tetragonal phase has the ideal chemical composition, $Ln_4O_3F_6$, and that the unit cell has the axial ratio of $c/a \fallingdotseq 1$ and contains four metal atoms. Zachariasen also mentions that the tetragonal phase has a wide homogeneity range, LaO_xF_{3-2x} $(0.7<x<1.0)$, but that this phase is unstable relative to the rhombohedral phase at $x=1.0$. Therefore, in the system of LaF_3-La_2O_3 examined by Zachariasen, it is considered that the tetragonal phase, $La_4O_3F_6$, has a large homogeneity range reaching up to LaOF $(x=1)$ by chance.

The relation between the rare earth oxyfluorides, LaOF and $Ln_4O_3F_6$, is similar to that between $NaF \cdot YF_3$ and $5NaF \cdot 9YF_3$11) in the system of NaF-YF_3, and to that between the uranium oxides, UO_2 and U_4O_9,12) taking into consideration the fact the fluoride ion is as large as the oxide ion. In the case of the NaF-YF_3 system, two intermediate compounds, $NaF \cdot YF_3$ and $5NaF \cdot 9YF_3$, crystallize from the melt as fluorite-like cubic crystals near the middle of the system, form a continuous series of solid solutions up to the melting temperatre, and are converted to other forms at a low temperature. The $5NaF \cdot 9YF_3$ compound also forms on an ordered phase below 700°C.

As has previously been stated, the fluorite type was observed after quenching only in the SmF_3-Sm_2O_3 system, not in the other Ln_2O_3-LnF_3 systems. However, if more rapid cooling were employed, the fluorite-type structure might appear in all systems.

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11) R. E. Thoma and G. M. Hebert, *Inorg. Chem.*, **2**, 1005 (1963).

12) C. A. Alexander and T. A. Shelvin, Paper No. 14, Presented at the Second Conference on Nuclear Reacter Chemistry, Gatlinburg, Tenn., Oct. 10—12, 1961, TID-7622, p. 139.