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Studies of Rare Earth Oxyfluorides in the High-temperature Region

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The behavior of the rhombohedral LnOF and the tetragonal $Ln_4O_3F_6$ at high temperatures was investigated by differential thermal analysis and the high-temperature X-ray diffraction technique. In the case of the rare earth oxyfluorides, LnOF (Ln=La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y), the high-temperature transition rhombohedral$\rightleftarrows$cubic was observed by means of DTA and a high-temperature X-ray camera. The heat of transformation from rhombohedral to cubic was obtained by means of DTA. The transition temperatures and the heat of transformation, ΔH, shift to higher temperatures and to greater values respectively as the atomic numbers of the rare earth elements increase, although there are some anomalies. One endothermic peak was observed for the rare earth oxyfluorides, $Ln_4O_3F_6$, from Sm to Lu. On the other hand, no peak was observed up to 1300°C for La, Pr, Nd, and Y. The behavior of the peak temperature of DTA against the atomic number for $Ln_4O_3F_6$ is similar to that for LnF_3; this indicates a transformation from an orthorhombic to a hexagonal structure.

In the system of LnF_3–Ln_2O_3, three forms of rare earth oxyfluorides have been reported.[1-9] The relations between these rhombohedral, tetragonal and cubic forms have not, however, been known at all. According to our previous study[10] of the rare earth oxyfluorides (Sm through Lu), the rhombohedral pahses, LnOF, have the stoichiometric composition and the tetragonal phases, $Ln_4O_3F_6$, have the comparatively large nonstoichiometric composition range. The third cubic phases, with a fluorite-type structure, were observed in the SmOF–$Sm_4O_3F_6$ region after quenching from a high temperature, but in the other system the cubic phases were not identified by a similar procedure. The variety of structures reported for the rare earth oxyfluorides suggests that a study of the structures at high temperatures would be fluitful. In particular, based on Zachariasen's structure analysis[3] employing the order-disorder of the anion, it was hoped that the order-to-disorder transition could be observed by means of the high-temperature X-ray technique. In this paper, the behavior of the rhombohedral LnOF and the tetragonal $Ln_4O_3F_6$ at high temperatures was investigated by means of differential thermal analysis and the high-temperature X-ray technique.

Experimental

Materials. Many rare earth oxides[11] (La_2O_3, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_4O_7, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, and Y_2O_3) were separated from a crude rare eath mixture in this laboratory by the ion-exchange method, using the EDTA solution as the solvent. The rare earth oxides obtained by this method were >99.9% pure.

The anhydrous lanthanon trifluorides, LaF_3 through LuF_3, were prepared as has previously been described.[10]

The rare earth metals[12] were prepared by the calcium reduction of LnF_3 according to the following reaction:

$$2LnF_3 + 3Ca = 2Ln + 3CaF_2$$

The metals obtained by this method were >99.5% pure.

Sample Preparation. All the rhombohedral LnOF and tetragonal $Ln_4O_3F_6$ rare earth oxyfluorides, except for Pr and Tb, were prepared as has previously been described.[10] In the cases of Pr and Tb, the oxyfluorides were prepared by the hydrolic heating of the fluorides in an atmosphere with a relatively high humidity, or by the following chemical reactions:

$$3Pr_6O_{11} + 11PrF_3 + 4Pr = 33PrOF \quad (1)$$

$$3Pr_6O_{11} + 22PrF_3 + 4Pr = 11Pr_4O_3F_6 \quad (2)$$

$$3Tb_4O_7 + 7TbF_3 + 2Tb = 21TbOF \quad (3)$$

$$3Tb_4O_7 + 14TbF_3 + 2Tb = 7Tb_4O_3F_6 \quad (4)$$

The mixture of oxide, metal, and fluoride, weighed in a stoichiometric composition, was melted in a platinum boat. The chemical analyses were performed by igniting to the oxide.

High-temperature X-ray Diffraction. High-temperature X-ray diffraction patterns were obtained by means of a Rigaku Denki high-temperature X-ray diffraction camera mounted a X-ray diffractometer. The mounted samples were placed in the camera, which was then evacuated. The pressure at the inlet in the camera was found to be less than 5×10^{-4} mmHg, but either oxidation or hydrolysis occurred when samples were heated above 800—1000°C. Because of this problem, the high-temperature phases of the tetragonal oxyfluorides, $Ln_4O_3F_6$, were not identified.

Differential Thermal Analysis. The DTA apparatus consisted of a platinum-wound furnace, a sample chamber, and a microvolt recorder. The sample holder consisted of a 25-mm-diameter nickel rod, in which two symmetrical, 7.9-mm-diameter, 19.2-mm-deep sample wells were drilled. The rare earth oxyfluoride placed in a platinum sample chamber with the same geometry as the sample wells was

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TABLE 1. THE LATTICE PARAMETER OF THE RHOMBOHEDRAL LnOF AND THE TETRAGONAL LnOF OF Pr, Tb, AND Lu

Ln in LnOF and $Ln_4O_3F_6$	Lattice parameter			
	LnOF		$Ln_4O_3F_6$	
	a in Å	α in degree	a in Å	c in Å
Pr	7.018 ± 0.002	33.05 ± 0.05	5.710 ± 0.004	5.758 ± 0.003
Tb	6.751 ± 0.004	33.09 ± 0.03	5.575 ± 0.003	5.491 ± 0.003
Lu	6.536 ± 0.002	33.05 ± 0.02	5.482 ± 0.002	5.308 ± 0.003

placed in one well, and Al_2O_3 in the other.

The standard conditions for each DTA run were a 950—1000-mg portion of the sample and a heating rate of 2.5°C/min in a vacuum or in an inert gas atmosphere. The Pt-Pt·Rh thermocouples were used for the temperature measurement. The calibration data indicate an error of ±3°C at 600°C.

The DTA apparatus was calibrated for the heat-of-transformation studies by the use of compounds with a known heat of decomposition or transformation in a temperature range not far from that under study. The calibration compounds were $CuSO_4\cdot5H_2O$, SiO_2, and $BaCO_3$. The heat of transformation obtained could be reproduced to within ±7%.

Experimental Results

Sample Preparation. The X-ray diffraction data showed that all of the rhombohedral LnOF and tetragonal $Ln_4O_3F_6$ rare earth oxyfluorides, except for Ce and Pm, from La to Lu had an isostructure with the previously-reported rhombohedral and tetragonal forms[10] respectively. The results of chemical analyses and the lattice parameters for Pr, Tb, and Lu are summarized in Table 1 and Table 2. The preparation of Pr and Tb oxyfluorides by the hydrolysis technique resulted in mixed products of the rhombohedral and tetragonal oxyfluorides. In general, hydrolysis was found to be unsatisfactory since the extent to which the reaction proceeded could not be controlled.

TABLE 2. METAL CONTENT OF LnOF AND $Ln_4O_3F_6$ FOR Pr, Tb, AND Lu

Ln in LnOF and $Ln_4O_3F_6$	LnOF		$Ln_4O_3F_6$	
	obsd%	calcd%	obsd%	calcd%
Pr	79.55	80.10	77.50	77.65
Tb	81.42	81.95	79.24	79.69
Lu	83.31	83.33	81.05	81.20

High-temperature X-ray Diffraction. In the case of the LnOF (Ln=La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) rare earth oxyfluorides, the high-temperature rhombohedral⇄cubic transition was observed by the high-temperature X-ray camera. It was found, from the relative-intensity measurements of the X-ray diffraction, that the high-temperature phase had a fluorite-type structure and that the rhombohedral⇄cubic transition was reversible. The X-ray patterns of LaOF at 25, 450, and 550°C are shown in Fig. 1. The lattice parameters of LaOF and NdOF were determined over the temperature range of 25—700°C. It can be seen from Fig. 2 that the unit cell volume varied continiously with the temperature in the regions of the rhombohedral and cubic forms respectively, and that it increased abruptly at the transition temperatures. The extrapolated values of the volume differences of the two phases at the transition temperature are 0.80 Å^3 and 0.65 Å^3 for LaOF and NdOF respectively.

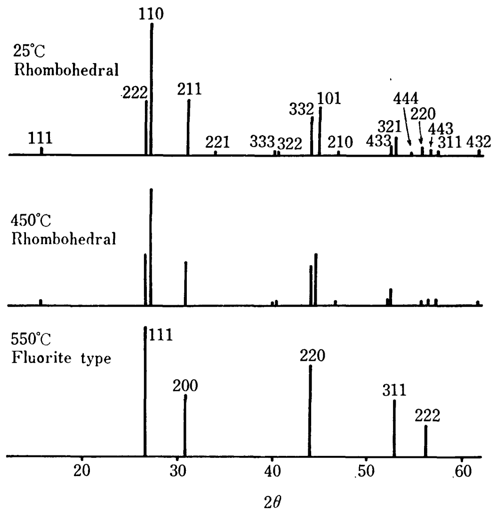

Fig. 1. X-ray patterns of LaOF at 25, 450, and 550°C by high-temperature camera.

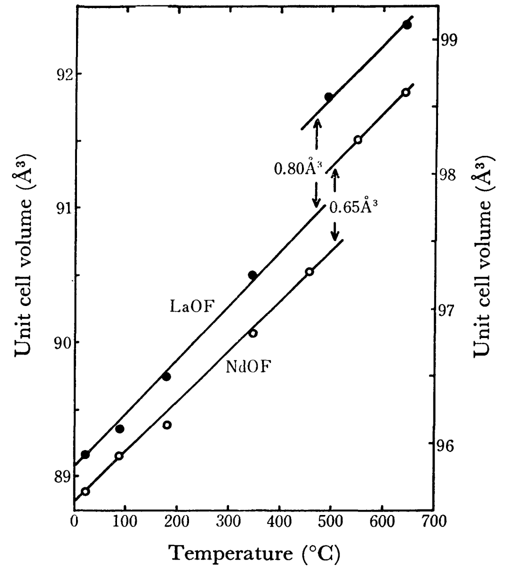

Fig. 2. Thermal expantion of LaOF and NdOF by high-temperature camera. Half cell volume for the fluorite type structure. The scale on the right is NdOF, that on the left for LaOF.

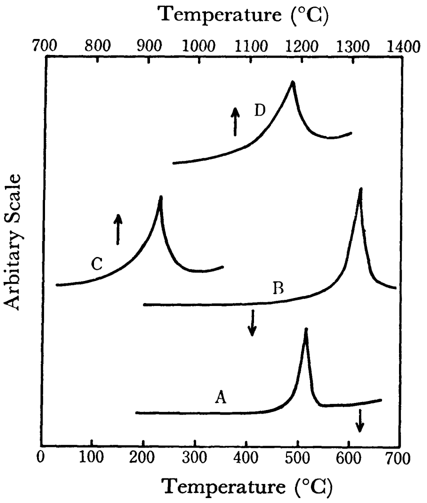

Fig. 3. DTA curves of rare earth oxyfluorides.
A: LaOF B: GdOF C: $Gd_4O_3F_6$ D: $Er_4O_3F_6$

Differential Thermal Analysis. Differential thermal analyses (DTA) were made of both the rhombohedral LnOF and the tetragonal $Ln_4O_3F_6$ of the rare earth oxyfluorides of La through Lu. In the cases of the rhombohedral oxyfluorides, the DTA curves exhibited one endothermic peak up to 1250°C. Since all of the DTA curves were quite similar to each other, only two of them are reproduced in Fig. 3. It can be seen from Fig. 1—3 that the endothermic peak temperatures of DTA correspond to the transition temperatures of rhombohedral⇄cubic. From these results, it can be concluded that all of the LnOF rare earth oxyfluorides transform from the rhombohedral structure to the fluorite-type structure. In Table 3 we list the temperatures of the DTA peaks for the rhombohedral oxyfluorides. The DTA peaks against the atomic numbers are plotted in Fig. 4. As may be shown from Fig. 4, the peak temperatures shift to higher temperature as the atomic numbers increase, that is, as the ionic radii of the rare earth ion decrease, although there are several anomalies.

TABLE 3. DIFFERENTIAL THERMAL ANALYSIS PEAK TEMPERATURE FOR LnOF AND LnOF. ALL AT 2.5°C/min HEATING RATE

Ln in LnOF and $Ln_4O_3F_6$	Peak temperature (°C)	
	LnOF	$Ln_4O_3F_6$
La	505	—
Ce	—	—
Pr	460	—
Nd	515	—
Pm	—	—
Sm	530	553
Eu	495	733
Gd	613	914
Tb	544	892
Dy	579	1049
Ho	590	1098
Er	595	1178
Tm	545	1180
Yb	566	1155
Lu	580	1120
Y	560	—

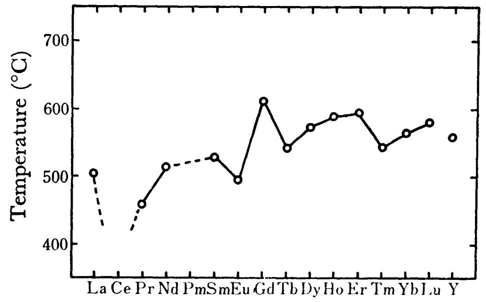

Fig. 4. DTA peak temperature of rare earth oxyfluorides LnOF as a function of atomic number.

The DTA results for the $Ln_4O_3F_6$ oxyfluorides are summarized in Table 3. One endothermic peak was observed for Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, but no peak was observed at all up to 1250°C for La, Pr, Nd, and Y. Two of these DTA curves are reproduced in Fig. 3. The variation in the DTA-peak temperature for the $Ln_4O_3F_6$ oxyfluorides are plotted as a function of the atomic number of the rare earth element in Fig. 5. The efforts to identify the high-temperature phase of the tetragonal oxyfluorides, $Ln_4O_3F_6$, using the high-temperature X-ray technique beyond the DTA peak temperatures were not successful because of the oxidation of samples and the inaccuracy of the diffraction patterns. The high-temperature phases could not be observed by quenching techniques, either.

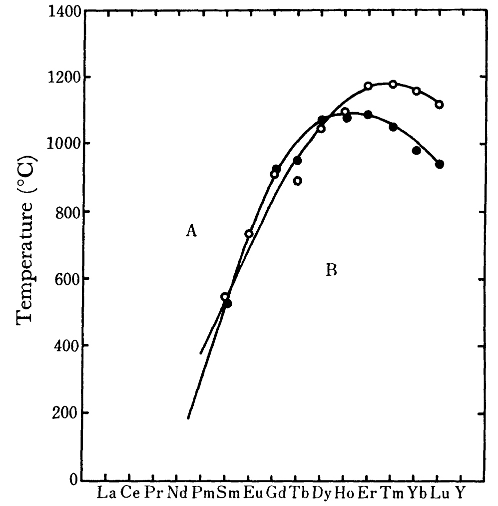

Fig. 5. DTA peak temperature of rare earth oxyfluoride $Ln_4O_3F_6$ as a function of atomic number.
(●: The transition temperature of orthorhombic to hexagonal LnF_3 as a function of atomic number)

The Heat of Transformation from Rhombohedral to Cubic Structure for LnOF. Under specific experimental conditions, DTA can be used to determine the heat of transformation by the integration of the differential curve peak. From the theories of Speil[13] and others[14,15] the area of curve peak is:

$$\text{peak area} = \int_{t_1}^{t_2} \theta dt = \frac{\Delta HM}{g\lambda}$$

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where t_1 and t_2 are the temperature limits of the peak, θ is the differential temperature, ΔH is the heat of transformation, M is the mass of the reactive sample present, λ is the thermal conductivity of sample, and g is a constant dependent on the furnace and sample-holder geometry. In practice, the apparatus is calibrated by studying the reaction of known thermal effects. In this manner, the constants, g and λ, are evaluated. Table 4 gives the heat of transformation from rhombohedral to cubic for LnOF and the values of the ionic radii. The heat of transformation, ΔH, is plotted as a function of the atomic number of the rare earth element in Fig. 6. As is shown by Fig. 6, ΔH shifted to higher values as the atomic number of the rare earth ion increased, although there were several anomalies.

TABLE 4. HEAT OF TRANSFORMATION OF RARE EARTH OXYFLUORIDES LnOF FROM RHOMBOHEDRAL STRUCTURE TO FLUORITE STRUCTURE.

Ln in LnOF	Ln^{3+} radii	ΔH(kcal/mol)
La	1.061	2.65
Ce	1.034	—
Pr	1.013	1.89
Nd	0.995	3.25
Pm	(0.979)	—
Sm	0.964	2.83
Eu	0.950	3.40
Gd	0.938	3.25
Tb	0.923	1.91
Dy	0.908	3.25
Ho	0.894	3.22
Er	0.881	3.71
Tm	0.869	3.53
Yb	0.854	3.60
Lu	0.848	3.70
Y	0.88	2.76

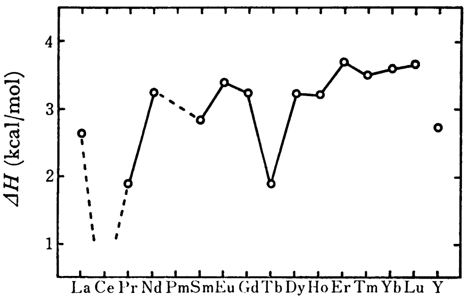

Fig. 6. Heat of transformation of rhombohedral to cubic LnOF as a function of atomic number.

Discussion

All of the rare earth oxyfluorides, LnOF, were observed to be transformed from a rhombohedral to a fluorite-type structure in the temperature region of 450—600°C. It is considered that this transition is due to the order-disorder of the anion: the rhombohedral oxyfluorides,[3] LnOF, result from a complete ordering of the oxygen and fluorine atoms into a distinct site in the unit cell, while the fluorite-type phase results from a statistical distribution of oxygen and fluorine. The transition temperature observed in thermal analyses do not follow the smooth trend so characteristic of lanthanide compounds. However, the phase-transition temperatures in $LnNbO_4$ and $LnTaO_4$ increase as the ionic radii decrease at first and then become relatively constant beyond Gd.[16] The data presented in this paper seem to show a similar phenomenon.

The heat of transformation from a rhombohedral to a fluorite-type structure is 1.8—3.8 kcal/mol. On the other hand, the heats of transformation of cubic to monoclinic Eu_2O_3[17] and of cubic to hexagonal Pr_2O_3[17] are about 4.3 and 1.0 kcal/mol respectively. It can be seen that the values of the heat of transformation from a rhombohedral to a fluorite-type structure are as large as those of the heat of transformation of rare earth sesquioxides, Ln_2O_3. The ΔH of rhombohedral to cubic LnOF shifts to higher values as the atomic number of the rare earth ion increases, although there are some anomalies. This trend is the same as that for the heat of decomposition of rare-earth sulphate and oxysulphate.[18] The ΔH for Pr and Tb is much lower than the other values. A possible explanation of the anomalies for Pr and Tb is that PrOF and TbOF form a solid solution with either oxides or the fluorides. As has previously been reported,[10] all the rhombohedral phases, LnOF, except for Pr and Tb have a stoichiometric composition, and no nonstoichiometric composition range exists in any of the systems. The method of preparing PrOF and TbOF is different from that of other rare earth oxyfluorides. In this method, the stoichiometry of PrOF and TbOF could not be determined by metal analyses alone because the oxides of Pr and Tb have a comparatively large nonstoichiometric composition range at high temperatures,[19] although the oxides of all the rare earths except Pr and Tb have the stoichiometric composition $LnO_{1.500}$.[20] The ions of Pr and Tb are comparatively easy to convert into tetravalent ions relative to other rare earth ions. Judging from this fact, it is possible that the rhombohedral phase for Pr and Tb may be stable for nonstoichiometries, $LnO_{1\pm x}F_{1\pm y}$, and that a small variation in stoichiometry could effect a large change in the transformation of rhombohedral to cubic LnOF.

The efforts to determine the cause of an endothermic peak $Ln_4O_3F_6$ from Sm to Lu were unsuccessful. As is shown in Fig. 5, the variation in the peak temperature of DTA against the atomic number is quite similar to that of the transition temperature of rare earth trifluorides from orthorhombic to hexagonal LnF_3.[21] It is reasonable to consider that the crystal structures are different between the A region and the B region. This point is still open to question, though, and further work is called for.

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