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Study of phase transition and volume thermal expansion in a rare-earth (RE) oxyfluoride system by high-temperature XRD (RE=La, Nd, Sm, Eu and Gd)

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Abstract

Volume thermal expansion behaviour of a number of rare-earth oxyfluorides (REOF) have been studied using high-temperature X-Ray diffractometry (HT-XRD) in the 298–1075 K range in air. The studies revealed an anomalous expansion for each compound associated with phase transition. The phase transition temperature and the coefficient of volume thermal expansion of five compounds in REOF series determined by this method are reported and compared with our earlier results obtained by dilatometry. © 1998 Elsevier Science B.V.

Keywords: Rare-earth oxyfluoride; High-temperature XRD

1. Introduction

Rare-earth oxyfluorides are known to exist over a wide homogeneity range. They also exist in a number of phases namely cubic, tetragonal, orthorhombic and hexagonal (rhombohedral). Recently, detailed phase relation (composition vs. structure) was worked out by us in the $NdO_{1-x}F_{1+2-x}$ system, using XRD, DTA and high- temperature XRD (HT-XRD) [1]. It was found that, in this system, there exist tetragonal phase towards NdF_3 side and rhombohedral phase towards Nd_2O_3 side. The rhombohedral oxyfluoride phase was shown to undergo a transition to cubic modification at high temperatures. It was attributed to an order–disorder phenomenon, involving the anion sub-lattice where the O^{2-} and F^{1-} ions are randomly distributed [2]. All the results were compared with those reported by other authors [3,4]. It was also observed that the tetragonal modification of $NdO_{1-x}F_{1+2x}$ does not show any phase transition. The rhombohedral-to-cubic phase transition in a number of REOF systems was studied, using DSC as described by Petzel et al. [5]. Recently, dilatometry was used by us [6] to investigate the anomalous thermal expansion behaviour in these compounds attributed to rhombohedral-cubic phase transition. The phase-transition temperature in each sample obtained by dilatometry was in close agreement with that obtained by Petzel et al. [5], using DSC. The samples showed an almost identical thermal expansion behaviour. In order to further corroborate our earlier studies on these samples, we extended the investigations on phase transition and volume thermal expansion coefficients using HT-XRD.

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2. Experimental

In order to prepare REOF samples, first corresponding rare-earth trifluorides were prepared by heating RE_2O_3 with excess of ammonium hydrogen fluoride (AHF) at 450°C. The heating with excess of AHF was continued till all RE_2O_3 got converted to REF_3 as confirmed by powder XRD. All the REF_3 products were further dried by heating at 600°C in flowing argon atmosphere. A number of mechanical mixtures of REF_3 and RE_2O_3 (RE=La, Nd, Sm, Eu and Gd) were prepared in 1 : 1 mole ratio and pelletised. Each pellet was heated at 950°C for four days in flowing N_2 atmosphere which was passed through molecular sieves. Powder XRD pattern of each oxyfluoride was recorded from $2\theta=10$–$70°$, using CuK_α radiation on a Philips X-ray diffractometer Model PW 1729. High-temperature X-ray powder studies were carried out using an MRC Model X-86-N3 high-temperature diffractometric attachment described elsewhere [7]. A small amount of the sample ground to ca. 200 mesh was mounted on a Pt–40% Rh stage cum heating element. A Pt/(Pt–13%Rh) thermocouple spot-welded to bottom of the stage was used for temperature measurement. The temperature was controlled by an MRC Model X-8600-5000-2 proportional temperature controller coupled to the sensor. A uniform zone was maintained within ±5 K in the entire temperature range investigated.

3. Results and discussion

It was found that the equimolar mixture of REF_3 and RE_2O_3 in each case yielded a rhombohedral phase of corresponding oxyfluoride as confirmed by comparing the XRD patterns with the reported ones. The typical fits of one of the oxyfluorides in both the modifications are given in Table 1. The rhombohedral modification in hexagonal setting has six molecules per unit cell, whereas the high-temperature cubic modification has four molecules per unit cell. It may be noted that the number of molecules per unit cell becomes two in the rhombohedral lattice. It was observed that the rhombohedral phase showed the presence of three doublets at $2\theta=27°$, 44° and 52° which merged into singlets in the cubic phase [8]. The lattice parameters of various oxyfluorides at different temperatures, as summarised in Table 2(a)–(e), also show a systematic increase as a function of temperature in both, *a* and *c* parameters in the low-temperature rhombohedral phase as well as in *a* parameter in the high-temperature cubic phase. The variation of molecular volume as a function of temperature in each case is shown in Fig. 1(a)–(e). It is observed that the unit-cell volume shows a slight anomalous increase at a temperature corresponding to the phase transition, e.g. the volume of the rhombohedral phase of EuOF, in an hexagonal setting with six molecules in the unit cell ($Z=6$) at room temperature, was found to be

Table 1
Typical fit for EuOF in both, the hexagonal and rhombohedral setting and also for the high-temperature cubic modification

Hexagonal $a_h=3.892\pm0.002$ Å, $c_h=19.36\pm0.02$ Å				Rhombohedral $a_r=6.83\pm0.02$ Å, $\alpha=33.07\pm0.07°$	Cubic [a] $a_c=5.560\pm0.004$ Å	
d_{obs}	%Int	d_{cal}	*hkl*	*hkl*	d_{obs}	*hkl*
3.314	16	3.320	101	100		
3.220	32	3.226	006	222	3.207	111
3.175	100	3.183	102	110		
2.765	48	2.766	104	211	2.780	200
2.546	20	2.542	105	221		
2.137	32	2.138	107	322		
1.971	80	1.965	108	332	1.963	220
1.947	80	1.946	110	$1\bar{1}0$		
1.677	32	1.678	1010	433	1.677	311
1.665	60	1.666	116	321		
1.591	40	1.591	204	220		

[a] At 800 K.

Table 2

Temperature/K	a/Å	c/Å	V/Å^3	V_m	Symmetry
(a) LaOF					
298	4.056(5)	20.21(3)	280.0(6)	47.99	R[a]
419	4.056(6)	20.23(3)	288.2(8)	48.04	R[a]
575	4.069(5)	20.30(4)	291.1(7)	48.52	R[a]
703	4.077(3)	20.39(2)	293.6(5)	48.94	R[a]
823	5.827(7)		197.8(4)	49.45	C[b]
977	5.831(2)		198.3(1)	49.57	C[b]
1077	5.847(4)		199.9(2)	49.99	C[b]
(b) NdOF					
298	3.963(1)	19.77(6)	268.8(1)	44.81	R[a]
427	3.967(2)	19.80(2)	269.8(3)	44.97	R[a]
571	3.972(2)	19.83(2)	270.9(3)	45.14	R[a]
725	3.976(3)	19.86(2)	272.0(4)	45.33	R[a]
823	5.691(3)		184.3(2)	46.08	C[b]
959	5.692(7)		184.4(4)	46.10	C[b]
1075	5.695(8)		184.7(4)	46.17	C[b]
(c) SmOF					
298	3.914(3)	19.46(2)	258.2(3)	43.04	R[a]
423	3.918(2)	19.52(1)	259.5(2)	43.26	R[a]
549	3.923(2)	19.54(1)	260.4(3)	43.41	R[a]
748	3.934(2)	19.54(1)	261.9(3)	43.65	R[a]
811	5.619(5)		177.4(3)	44.36	C[b]
923	5.625(6)		178.0(3)	44.50	C[b]
1075	5.626(6)		178.1(3)	44.53	C[b]
(d) EuOF					
298	3.892(2)	19.36(2)	253.8(3)	42.31	R[a]
425	3.897(2)	19.37(2)	254.7(3)	42.46	R[a]
567	3.903(2)	19.40(2)	255.9(3)	42.66	R[a]
751	3.909(4)	19.42(2)	257.0(5)	42.84	R[a]
805	5.560(4)		171.8(2)	42.96	C[b]
917	5.576(3)		173.4(2)	43.34	C[b]
1077	5.583(3)		174.0(2)	43.50	C[b]
(e) GdOF					
298	3.888(4)	19.25(3)	252.0(5)	42.00	R[a]
427	3.898(4)	19.27(2)	253.5(5)	42.24	R[a]
569	3.900(4)	19.31(3)	254.4(5)	42.40	R[a]
745	3.908(5)	19.34(3)	255.8(6)	42.64	R[a]
823	3.917(5)	19.34(3)	257.1(6)	42.85	R[a]
913	5.580(4)		173.7(2)	43.43	C[b]
993	5.580(4)		173.7(2)	43.43	C[b]
1067	5.584(4)		174.1(2)	43.53	C[b]

[a] Rhombohedral.

[b] Cubic.

253.85 Å^3. This phase was also observed at 750 K. The volume of the cell with (Z=6) at 750 K is 257.03 Å^3 and that of cubic phase with four molecules (Z=4) at 805 K is 171.85 Å^3. The hexagonal-to-cubic transition is, therefore, accompanied with an increase in volume per molecule (V_m) from 42.84 to 43.96 Å^3. The cubic phase could not be retained by quenching to room temperature. The phase-transition temperatures

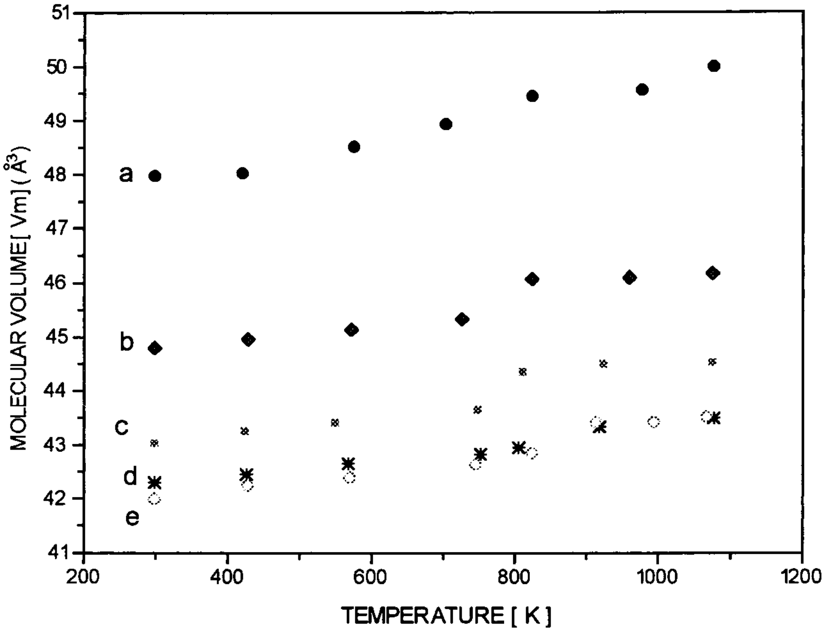

Fig. 1. Plot of molecular volume vs. temperature. (a) LaOF; (b) NdO; (c) SmOF; (d) EuOF; and (e) GdOF.

Table 3
Transition temperature as determined by HT-XRD

S. No.	Compound	Transition temperature [a] (rhombohedral-cubic)/K	Dilatometry [6]	DSC [5]
1	LaOF	703–823	748–783	778
2	NdOF	725–823	773–798	800
3	SmOF	748–811	773–798	803
4	EuOF	701–804	773–798	788
5	GdOF	823–913	873–898	883

[a] The two temperatures in the given range correspond to the highest temperature at which rhombohedral phase and the lowest temperature at which cubic phase was observed. The exact transition temperature should be somewhere in between the respective range.

as obtained by HT-XRD (Table 3) are in agreement with that of our earlier dilatometry results and DSC results of Petzel et al. [5]. However it may be added here that it is difficult to exactly find out the phase-transition temperature by HT-XRD, unlike DSC or DTA where one continuously monitors the heat change or temperature difference as a function of temperature. Table 4 includes the coefficients of volume thermal expansion in the corresponding temperature range. We did not observe any particular trend in thermal expansion coefficients of various rare earths.

REOF with RE=La, Nd, Sm, Eu and Gd exhibited an almost linear relation between cell volume with temperature up to the corresponding phase-transition temperature which was signified by an abrupt increase in volume.

4. Conclusion

The present high-temperature X-ray diffractometric studies on the phase transition of these compounds are found to be in good agreement with the reported DSC,

Table 4
Average volume expansion per molecule

S. No.	Compound	Coefficient of molecular volume thermal expansion[a] (K^{-1})	Temperature range/K
1	LaOF	53.5×10^{-6}	298–1077
2	NdOF	39.1×10^{-6}	298–1075
3	SmOF	44.6×10^{-6}	298–1075
4	EuOF	36.1×10^{-6}	298–1077
5	GdOF	54.4×10^{-6}	298–1067

[a] This term is defined as the change in molecular volume per unit original molecular volume divided by temperature interval.

DTA and dilatometric results. The hexagonal REOF samples undergo a phase transition to cubic modification as revealed by merging of characteristic doublets into singlets above the corresponding phase-transition temperature. The coefficient of volume expansion of all the rare earths are of comparable order; moreover, we did not find any significant correlation of this with the size of rare-earth ions.

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