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Thermodynamics of the rhombohedral–cubic phase transition of ROF with R≡Y, La, Pr, Nd, Sm–Er

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Abstract

The temperatures and enthalpies of the rhombohedral–cubic phase transition of stoichiometric ROF with R≡Y, La, Pr, Nd, Sm–Er, have been determined by differential scanning calorimetry. The temperatures of transition are found in the range 742–880 K in satisfactory agreement with literature data. The enthalpies and entropies of transition of LaOF, PrOF, NdOF and EuOF increase with decreasing cationic radius from 5135±193 to 5504±169 J mol^{-1} and from 6.60±0.25 to 6.908±0.21 J mol^{-1} K^{-1} respectively, and for GdOF, TbOF, DyOF, HoOF, YOF and ErOF from 7085±190 to 7903±187 J mol^{-1} and from 8.02±0.24 to 9.04±0.27 J mol^{-1} K^{-1}. The transition mechanism and relations between the magnitude of the entropy of transition and the defect structure of fluorite-type α-ROF are tentatively discussed.

1. Introduction

Yttrium, lanthanum and the lanthanoid elements form oxide fluorides of the formula type ROF [1]. At ambient conditions of temperature and pressure the oxide fluorides with R≡Y, La–Er and probably Tm are rhombohedral (β-ROF, space group $R\bar{3}m$, weakly distorted fluorite type). YbOF [2] and LuOF are monoclinic (space group $P2_1/c$, baddeleyite type). At elevated temperatures the rhombohedral oxide fluorides undergo a reversible first-order phase transition to cubic α-ROF (space group $Fm\bar{3}m$ or $F\bar{4}3m$). While disordering of the anion sublattice in α-ROF seems to be generally assumed [2, 3], it has to be emphasized that no convincing proof for this assumption exists. Since O^{2-} and F^- are isoelectronic anions of similar size, it appears to be very difficult to obtain experimental evidence for the type of anionic disorder in cubic ROF. The calorimetric determination of accurate data for the entropy of the $\beta \rightarrow \alpha$ transition could therefore be an important step on the way to a solution of this problem. The transition temperatures have been measured by several research groups [3–6], and Niihara and Yajima [4] have determined the enthalpies of transition by quantitative differential thermal analysis. The entropies of transition derived from their results are in the range 9.8–18.5 J mol^{-1} K^{-1}. This range seems to be unusually large for a series of chemically similar, predominantly ionic and presumably stoichiometric compounds, which all undergo the same type of phase transition. Pistorius [7] has measured the transition temperatures of LaOF, NdOF, SmOF and ErOF as a function of pressure and has derived an average constant entropy of transition of approximately 6.4 J mol^{-1} K^{-1} for these oxide fluorides. Since Niihara and Yajima [4] do not give any error limits for their calorimetric results, it is difficult to decide whether the magnitude and the scatter of their enthalpies and of the entropies derived therefrom is a real phenomenon, deserving a detailed theoretical discussion, or is rather the consequence of limited experimental accuracy. Therefore we decided to reinvestigate the thermochemistry of the rhombohedral–cubic phase transition of stoichiometric ROF with R≡Y, La, Pr, Nd, Sm–Er, at ambient pressure by differential scanning calorimetry (DSC).

2. Experimental details

2.1. Preparation and characterization of the rare earth oxide fluorides

The stoichiometric rare earth oxide fluorides were prepared by annealing intimate mixtures of the sesquioxides (stated purity, 99.99%; Auer-Remy) and the anhydrous trifluorides in gas-tight platinum tubes at 1275 K for 5 days and at 1475 K for 2 days. Before use the sesquioxides were annealed at 1300 K for several hours in air in order to destroy the hydroxides and carbonates which usually form during storage at ambient conditions. Pr_2O_3 and Tb_2O_3 were obtained

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by reduction of Pr_6O_{11} and Tb_4O_7 respectively, with highly purified hydrogen at 1100 K; these sesquioxides were stored and handled under dry argon in order to prevent reoxidation. The anhydrous trifluorides were prepared by dissolution of the sesquioxides in hydrochloric acid, precipitation of the hydrated fluorides with hydrofluoric acid, drying at 390 K in air and subsequent dehydration under a gas stream of dry HF–N_2 at 1000 K. DyF_3, HoF_3 and ErF_3 were further purified by distillation in a high vacuum as described elsewhere [8]. The starting materials and the oxide fluorides were characterized by their X-ray powder patterns (Guinier method, Nonius chamber, Cu $K\alpha_1$ radiation, silicon (reference material NBS 640 A) as internal calibration standard). The lattice parameters were calculated using a least-squares computer program. In no case did the powder patterns display any reflections other than those attributable to the compounds in question even after extensive exposure times. The lattice parameters of RF_3 were found in very good agreement with data from the literature [9], and those of ROF, summarized in Table 1, agreed well with the results of Roether [2]. The oxide fluorides were not analysed quantitatively, because we considered the errors of the analytical methods normally applied to determine the fluorine and metal contents of these compounds to be larger than the errors introduced by the weighing of highly pure RF_3 and R_2O_3. Accordingly, the compositions of the oxide fluorides were assumed to be $RO_{1\pm0.0003}F_{1\pm0.0006}$. Because of this small uncertainty we considered the ROF samples as stoichiometric compounds.

TABLE 1. Lattice parameters of rhombohedral ROF ($R\bar{3}m$) in hexagonal setting

ROF	This work			From ref. 2	
	a (pm)[a]	*c* (pm)[b]	*c*/*a*	*a* (pm)	*c* (pm)
LaOF	405.05	2021.15	4.990	405.1	2022
PrOF	398.04	1984.28	4.985	–	–
NdOF	395.51	1971.04	4.983	395.6	1973
SmOF	390.65	1946.21	4.982	390.7	1949
EuOF	388.42	1935.96	4.984	–	–
GdOF	386.71	1927.57	4.984	386.7	1928
TbOF	384.18	1913.34	4.980	–	–
DyOF	381.51	1903.61	4.990	382.0	1905
YOF	379.72	1888.51	4.973	–	–
HoOF	380.14	1893.12	4.980	380.2	1896
ErOF	378.25	1883.25	4.979	378.2	1885

[a] ±0.02 pm.

[b] ±0.25 pm.

2.2. Differential scanning calorimetry measurements: apparatus and procedures

The DSC measurements were performed in a Netzsch apparatus, type DSC 404. The oxide fluoride samples and the reference material (corundum powder) were contained in cylindrical, vacuum-outgassed molybdenum containers with gas-tight lids. Heating and cooling were performed at a rate of 5 K min^{-1} in an atmosphere of dry argon, containing 5% hydrogen and flowing with a rate of 3.5 l h^{-1}. The peak onset temperatures observed on heating and evaluated by appropriate extrapolation procedures were considered as the equilibrium transition temperatures. The peak areas determined by applying linear and sigmoidal baseline interpolation procedures [10] were assumed to be proportional to the amount of heat absorbed or released according to

$$q=\int_{t_1}^{t_2} K\Delta T(t)\,\mathrm{d}t=AK \qquad (1)$$

In eqn. (1) q is the amount of heat, t the time, T the absolute temperature, A the peak area and K the calibration factor of the experimental arrangement. For the temperature calibration of the instrument we measured the phase transition temperatures of the following ICTA standard reference materials: SiO_2 ($T_{tr}=844$ K), K_2SO_4 ($T_{tr}=855$ K) and K_2CrO_4 ($T_{tr}=938$ K). The enthalpy calibration was performed by investigating the phase transitions of CsCl ($T_{tr}=749$ K, $\Delta H_{tr}{}^0=2.9\pm0.03$ kJ mol^{-1}), Li_2SO_4 ($T_{tr}=851$ K, $\Delta H_{tr}{}^0=25.02\pm0.16$ kJ mol^{-1}) and K_2CrO_4 ($T_{tr}=941$ K, $\Delta H_{tr}{}^0=6.79\pm0.10$ kJ mol^{-1}) as recommended in ref. 10. The quality of K_2CrO_4 was p.a. (Merck) and of CsCl and Li_2SO_4 Suprapur® (Merck). The factor K proved to be moderately temperature dependent.

Two specimens of each oxide fluoride differing by weight were first annealed by cycling three times between 1150 and 1450 K and were then run through five heating–cooling cycles within a temperature interval ranging from 100 K below the beginning to 100 K above the end of the transition effect. The average values of the onset temperatures and of the peak areas of cycles 2–5 were considered as representative of the temperature and enthalpy of transition respectively. No drift of the peak onsets and peak areas could be detected on cycling in any case, and the mass change of the molybdenum crucibles never exceeded ±0.4 mg. Considering the results of the calibration procedure and the reproducibility of the measurements on ROF it was concluded that the temperature and enthalpy results were accurate within ±2 K and ±3% respectively.

3. Results and discussion

All DSC signals relating to the $\beta \rightarrow \alpha$ transition had sharp onsets, and their shapes were typical of first-order transitions. Undercooling was 2–8 K for R ≡ La, Y, Nd, Eu, Gd, Ho and Er, and 10–13 K in all other cases. The excellent reproducibility of the measurements is exemplified in Fig. 1 by a plot of the superimposed DSC curves of cycles 2–5 for HoOF. The thermochemical results are summarized in Table 2 together with the appropriate data from the literature. While the transition temperatures agree satisfactorily with the results of other research groups, our enthalpies of transition and the entropies derived therefrom differ significantly from the values of Niihara and Yajima [4]. It is worth noting, however, that our results for LaOF, NdOF and SmOF are in good agreement with the average constant entropy value of 6.4 J mol^{-} K^{-1} derived by Pistorius [7]. The magnitude of the entropies of transition determined in this work is apparently smaller than that of values characteristic of those discontinuous solid state transitions in which phases of very high ionic conductivity (solid electrolytes) are formed [11]. This can be demonstrated by comparing the entropy of transition and the conductivity data of a typical solid electrolyte such as YF_3 with the corresponding properties of LaOF: at 1350 K β-YF_3 transforms to α-YF_3 with $\Delta S_{\mathrm{tr}} = 24.1$ J mol^{-1} K^{-1} [12], and its conductivity σ changes from about 10 to about 170 Ω^{-1} m^{-1} [13], the respective data for LaOF being 5.45 J mol^{-1} K^{-1} and σ increasing from about 10^{-5} to about 10^{-4} Ω^{-1} m^{-1} between 728 and 748 K [14].

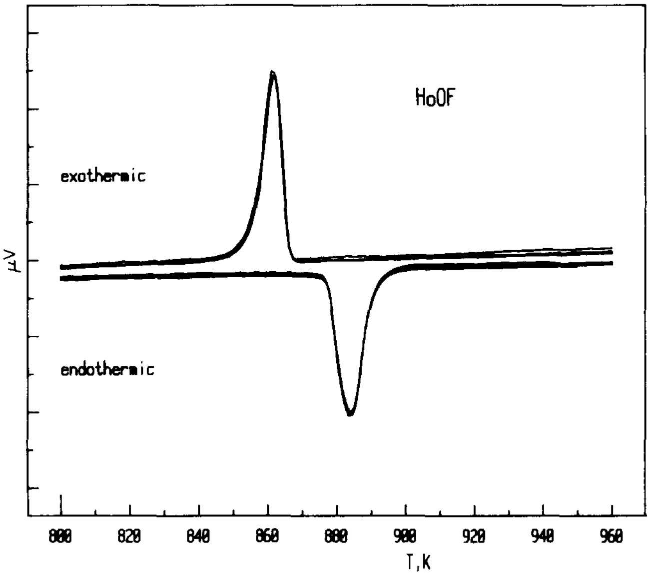

Fig. 1. Superimposed DSC curves of four heating–cooling cycles for the rhombohedral–cubic phase transition of HoOF.

A meaningful discussion of these results should be preceded by an attempt to correlate the thermochemical data with atomic and/or structural properties of ROF. While it is impossible to correlate sensibly the effective crystal radii of R^{3+} or the lattice dimensions β-ROF with the temperatures of the $\beta \rightarrow \alpha$ transition, a relation apparently exists between the cation size and the enthalpy and entropy of transition. Plots of the transitional enthalpies and entropies *vs.* cationic radii for the coordination number 8 [9] in Figs. 2 and 3 reveal a remarkable dichotomy of the transitional characteristics of ROF: the oxide fluorides with R ≡ La–Eu display a weak increase in the enthalpy and entropy of transition with decreasing cationic radius. Between EuOF and GdOF both thermochemical quantities increase significantly (the enthalpy by about 15% and the entropy by about 25%) and continue to increase rapidly with decreasing cationic radius for ROF with R ≡ Gd–Er and Y.

TABLE 2. Thermochemical data of the rhombohedral–cubic phase transition of ROF

ROF	T_{tr} (K)		$\Delta H_{T,\mathrm{tr}}{}^0$ (J mol^{-1})		$\Delta S_{T,\mathrm{tr}}{}^0$ (J mol^{-1} K^{-1})	
	This work[a]	Other work	This work	From ref. 4	This work	Other work
LaOF	778	778 [4]; 767 [3]	5135 ± 193	11880	6.60 ± 0.25	15.27 [4]; 6.40 [7]
PrOF	740	733 [4]	5174 ± 185	7908	6.99 ± 0.25	10.79 [4]
NdOF	800	788 [4]; 790 [3]	4971 ± 188	13598	6.21 ± 0.23	17.26 [4]; 6.40 [7]
SmOF	803	803 [4]; 797 [3]	5246 ± 207	11841	6.53 ± 0.26	14.74 [4]; 6.40 [7]
EuOF	788	768 [4]	5504 ± 169	14226	6.98 ± 0.21	18.52 [4]
GdOF	883	886 [4]; 879 [3]; 877 [7]	7085 ± 190	13598	8.02 ± 0.21	15.38 [4]
TbOF	846	817 [4]; 824 [3]	6751 ± 185	7991	7.98 ± 0.22	9.42 [4]
DyOF	842	852 [4]; 831 [3]; 848 [6]	7102 ± 283	13598	8.43 ± 0.34	15.96 [4]
YOF	845	833 [4]; 844 [3]	7193 ± 166	11548	8.51 ± 0.17	13.86 [4]
HoOF	877	863 [4]; 861 [3]	7565 ± 235	13472	8.62 ± 0.27	15.61 [4]
ErOF	874	868 [4]; 865 [3]	7903 ± 187	15523	9.04 ± 0.21	17.72 [4]; 6.40 [7]

[a] ±2 K.

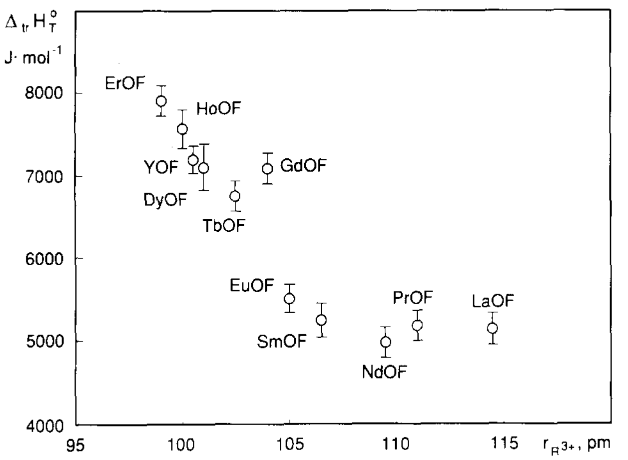

Fig. 2. Enthalpy of the rhombohedral–cubic phase transition of ROF *vs.* cationic radius.

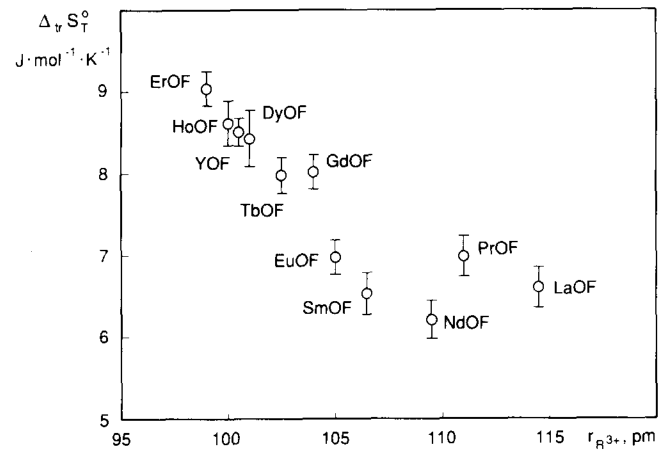

Fig. 3. Entropy of the rhombohedral–cubic phase transition of ROF *vs.* cationic radius.

The discontinuous $\alpha \rightarrow \beta$ transition of ROF is characterized by a very small structural change (both structures are closely related [15]), and also by a small change in formula volume (no more than 1% for LaOF [4] and NdOF [3]; 0.55% for PrOF, as observed in this work). Since both modifications are predominantly ionic, vibrational and electronic contributions to the entropy of transition are probably small and negligible respectively. The truly dominant contribution to the transitional entropy must then be configurational by nature, and should be mainly determined by the degree of disorder in α-ROF. The disordering process can be envisaged by looking at the ordered structure of β-ROF in a direction perpendicular to the hexagonal *c* axis, which on the transition becomes the [111] direction of the parent fluorite structure. According to Mann and Bevan [15], who determined the structure of β-YOF by X-ray powder diffraction, the ordered phase is composed of cation and anion layers in such a way that an R^{3+} layer has adjacent to it on one side two O^{2-} layers, which in case of YOF are separated by 187 pm, and on the other side two F^- layers, separated by 146 pm. On formation of cubic α-ROF, both kinds of anions mix inside the anion layers until each layer contains O^{2-} and F^- in equal proportions. Assuming a stochastic distribution of anions over all regular lattice positions (space group $Fm\bar{3}m$), one calculates an entropy of transition of $2R \ln 2 = 11.53$ J K⁻¹ per mole of ROF. While configuration entropies of this magnitude can be derived for disordering processes of some binary alloy systems [16], the experimental values for the $\beta \rightarrow \alpha$ transition of ROF, although tending to approach this value, are lower and hence suggest a lower degree of randomness than would be expected for the stochastic situation. On the contrary, if the anion sublattice in cubic ROF were ordered (space group $F\bar{4}3m$), one could consider the following limiting possibilities: random arrangement of the ordered unit cells in two different positions, in which case a maximal configurational entropy of 1.44 J K⁻¹ per mole of ROF is expected, and equal orientation of all unit cells, in which case the configurational entropy is zero. Since the observed entropy data are significantly larger than 1.44 J K⁻¹, some type of partial disorder has to be envisaged for cubic α-ROF. One way to imagine partial disorder would be to assume the existence of ordered microdomains ($F\bar{4}3m$) in a disordered matrix ($Fm\bar{3}m$). Another way to introduce partial order into a lattice of space group $Fm\bar{3}m$ would be to reduce the ensemble of microstates of the stochastic anion distribution in a way allowing for an energetically favourable arrangement of two kinds of anions of different charge, although of similar size, around the R^{3+} ion. Since, for instance, microstates with accumulations of eight O^{2-} ions or eight F^- ions around the cation, which are allowed in the stochastic case, are physically quite unfavourable, one could consider only microstates in which four O^{2-} ions and four F^- ions are randomly arranged around a cation. According to the structural model proposed by Mann and Bevan [15] for rhombohedral β-ROF each cation is surrounded by four F^- ions and four O^{2-} ions in an ordered fashion. Anionic disordering can be achieved by a synchronized rotation of squares composed of four anions with a minimal lattice distortion and without violating the condition that four anions of each kind coordinate each cation. If the structure of cubic α-ROF is imagined as being built up of such "random polyhedra" in a statistical arrangement, a maximal configurational entropy of 8.83 J K⁻¹ per mole of ROF is calculated. This value is in fact close to the maximal experimental result, 9.04 J mol⁻¹ K⁻¹, observed for ErOF. Lower configurational entropies of transition have to be expected, if the random polyhedra are arranged in a more or less ordered way. Since the structural differences between the α and β modifications of ROF are very small and the proposed transition process by synchronized rotation of anion squares does not involve the breaking of primary bonds, one is inclined to assume a displacement transition mechanism. The experimental observations that this transition takes place quite rapidly despite the comparatively low temperatures and that undercooling is below 10 K in most cases are indicative of a very small activation energy and hence corroborate the notion of a displacement mechanism. It should be pointed out here that Roether [2] has suggested a transition process by anion diffusion via interstitial positions.

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