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Journal of Alloys and Compounds 224 (1995) 18–21

Journal of ALLOYS AND COMPOUNDS

High-temperature X-ray diffraction study of the rhombohedral–cubic phase transition of ROF with R = Y, La, Pr, Nd, Sm–Er

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Received 27 October 1994; in final form 28 November 1994

Abstract

The rhombohedral–cubic phase transition of ROF with R = Y, La, Nd, Sm–Er and the expansion coefficients of both modifications were studied by the high-temperature Guinier X-ray powder diffraction method. It was found that a constant formula volume increment of 0.37 ± 0.04 Å^3, which is independent of the cationic size, is characteristic of this transition. The formula volumes depend practically linearly on temperature, and the volume expansion coefficients, which are generally larger for the cubic than for the rhombohedral modification, vary irregularly across the R^{3+} series. For the cases of YOF, LaOF, NdOF, SmOF, GdOF and ErOF it could be shown that experimental data for the transitional volume changes, entropies and pressure dependence of the transition temperatures obey the Clausius–Clapeyron equation within the accuracy limits of the data.

Keywords: Rare earth oxide fluorides; Phase transition; Lattice parameters; Ionic radii

1. Introduction

The stoichiometric rare earth oxide fluorides of formula type ROF with R = Y, La, Ce–Er all display a first-order phase transition from a low-temperature β-modification (rhombohedral, space group R$\bar{3}$m) to high temperature α-ROF (cubic, presumably space group Fm$\bar{3}$m or F$\bar{4}$3m). Petzel, Marx and Hormann [1] have recently determined the entropies of transition of most of these ROF by differential scanning calorimetry (DSC). They found a practically constant value of about 6.60 J mol^{-1} K^{-1} for ROF with R = La, Pr, Nd, Eu and Sm, but rapidly increasing values for the heavier rare earth oxide fluorides, including YOF, which eventually reached a maximum transitional entropy of 9.04 J mol^{-1} K^{-1} at ErOF. The pressure dependencies of the transition temperatures of LaOF, SmOF, GdOF and ErOF has been measured by Pistorius [2], and of YOF by Atabaeva and Bendeliani [3], and the results of these studies proved to be very similar in all cases. By applying the Clausius–Clapeyron equation, $\Delta S_{tr} = (dp/dT)\Delta V_{tr}$, and by tentatively assuming the value of ΔV_{tr}, as measured by Shinn and Eick [4] for NdOF, to be equal for all ROF, Pistorius [2] forwarded the conclusion that a transitional entropy of about 6.4 J mol^{-1} K^{-1} should be characteristic of all ROF. While this conclusion is in good accordance with the calorimetric findings of Ref. [1] for LaOF, PrOF, NdOF, SmOF and EuOF, a significant discrepancy exists concerning the values for the heavier ROF with R = Gd–Er and Y. This discrepancy could be explained by calling into question Pistorius' assumption of an equal volume increment of the $\beta \rightarrow \alpha$ transition of all ROF. Shinn and Eick [4], as well as Niihara and Yajima [5], have measured the equilibrium transitional volume increments of many ROF by high-temperature X-ray powder diffraction. Unfortunately the only data given specifically are those for LaOF (0.40 Å^3 [5]), and for NdOF (0.31 Å^3 [4] and 0.35 Å^3 [5] per formula unit). We therefore decided to reinvestigate the expansion accompanying the $\beta \rightarrow \alpha$ transition of ROF with R = Y, La, Pr, Nd, Sm–Er as precisely as possible in order to find out whether and to what extent the volume increments correlate with the cation radii of R^{3+} and consequently with the transitional entropies reported by Petzel et al. [1].

2. Experimental details

2.1. Preparation and characterization of compounds

The stoichiometric rare earth oxide fluorides of composition ROF were prepared by solid state reaction of

SSDI 0925-8388(94)01509-0

RF_3 with R_2O_3 (99.99%, Auer-Remy) as described elsewhere in detail [1]. In the case of LaOF, PrOF and SmOF we actually used the samples which had already been submitted to DSC measurements [1]. The starting materials and the reaction products were characterized by their X-ray powder diffraction patterns (Guinier method, Nonius chamber, $CuK\alpha_1$ with $\lambda = 1.54051$ Å, silicon with $a = 5.4308$ Å (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. The lattice parameters of RF_3 were found to be in excellent agreement with precision data from Ref. [6], and those for ROF agreed well with the data reported in Ref. [1] and also by Roether [7].

2.2. High-temperature X-ray powder diffraction measurements

The high-temperature X-ray powder diffraction measurements were performed with a Huber Guinier chamber, type 632, applying $CuK\alpha_1$ radiation. The samples were contained in sealed, evacuated silica capillaries of 0.5 mm inner diameter. In order to minimize the absorption of radiation by the samples, especially in the case of La–Eu, the empty capillaries were evacuated and flattened prior to use by an appropriate thermal treatment, thereby achieving a sample thickness of ≈ 0.1 mm. No chemical attack of the oxide fluorides on silica, as detectable by careful inspection of the powder patterns, was noticed. The heating of the samples was performed with a loop of Kanthalwire surrounding the capillary in a vertical position. The temperature was measured with a Pt–Pt/Rh thermocouple located approximately 3 mm above the tip of the capillary and connected to a Eurotherm controlling and programming unit. The Guinier patterns were taken discontinuously in steps of 100 K or less. The room temperature θ values of ROF, as determined in a Nonius Guinier chamber with silicon as internal calibration standard, were used as an external reference to calibrate the Guinier patterns obtained in the Huber chamber. The temperature calibration of the system was performed by observing the disappearance of the X-ray reflections of silver (99.99%) at the melting point, 1234 K, and by assuming a linear increase of the difference between the observed and the true temperatures, ranging form zero at room temperature to +157 K at the melting point of silver. The feasibility of this assumption was confirmed by the observation that the phase transitions of the rare earth oxide fluorides occurred in all cases within ±15 K of the transition temperatures given by Petzel et al. [1]. Accordingly we considered the accuracy of our temperature measurements to be ±15 K.

3. Results and discussion

With the exception of PrOF the $\beta \rightarrow \alpha$ transformations occurred rapidly and completely on heating and on cooling in all cases, behaviour which is in agreement with the observations of Ref. [1]. The formula volumes of the rhombohedral as well as the cubic phases were found to depend practically linearly on temperature, in agreement with the findings of Ref. [4] for NdOF and of Ref. [5] for LaOF and NdOF. The results are exemplified by the plot of V vs. T for YOF in Fig. 1 and are summarized in Table 1, which in columns 3–5 contains the formula volumes at selected temperatures, in column 6 the volume increments per formula unit at T_{tr}, and in columns 7 and 8 the volume thermal expansion coefficients α_{rhomb} and α_{cub}, respectively.

The following conclusions can be drawn from these results. First of all, the $\beta \rightarrow \alpha$ phase transition is accompanied by a small but constant volume increase of 0.37 ± 0.04 Å^3, which is apparently independent of the formula volume and hence of the cationic radius. In other words, this phase transition occurs at the temperature where the formula volume difference has reached a critical value of approximately 0.38 Å^3. The volume expansion coefficients α, which are practically independent of temperature, do not vary regularly across the lanthanide series, and a similar irregularity has therefore to be expected with respect to the transition temperatures. This conclusion is in obvious accordance with the well-established unsystematic behaviour of these temperatures [1,4,5]. The experimentally observed critical volume difference also corroborates Pistorius's [2] tentative assumption of a constant volume increment for all ROF undergoing the rhombohedral–cubic phase transition. While it seems to be impossible to explain why the $\beta \rightarrow \alpha$ transition, which is presumably accompanied by a randomization of four O^{2-} and four F^- ions around the cation, occurs at a certain constant

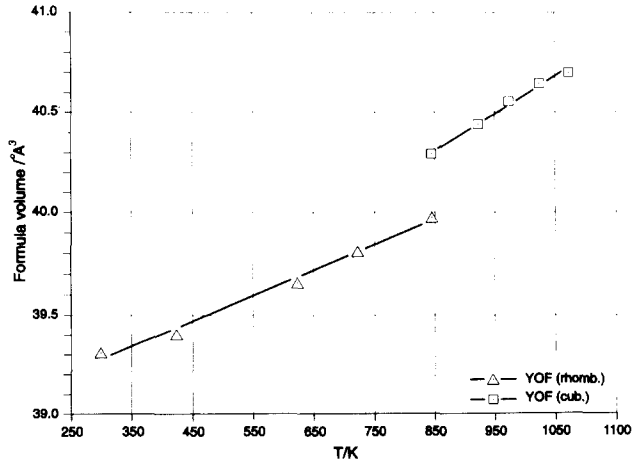

Fig. 1. Formula volume of rhombohedral and cubic YOF as a function of temperature.

Table 1
Volume expansion data for the rhombohedral and cubic modifications of ROF

ROF	T_{tr} (K) [1]	Formula volumes (Å^3) at selected temperatures			ΔV at T_{tr} (Å^3) [a]	α (Å^3 K^{-1})	
		Rhombohedral		Cubic (T_{tr})		Rhombohedral	Cubic (T_{tr})
		298 K	T_{tr}				
LaOF	778	47.84	48.73	49.14	0.41	3.9×10^{-5}	5.7×10^{-5}
PrOF	740	45.36	46.20	46.55	0.35	4.2×10^{-5}	6.5×10^{-5}
NdOF	800	44.48	45.48	45.84	0.36	4.5×10^{-5}	5.5×10^{-5}
SmOF	803	42.83	43.67	44.07	0.40	3.9×10^{-5}	5.6×10^{-5}
EuOF	788	42.10	42.88	43.24	0.36	3.8×10^{-5}	5.0×10^{-5}
GdOF	883	41.60	42.90	43.28	0.38	5.4×10^{-5}	6.5×10^{-5}
TbOF	846	40.73	41.56	41.91	0.35	3.7×10^{-5}	3.5×10^{-5}
DyOF	842	39.92	40.84	41.23	0.39	4.2×10^{-5}	6.7×10^{-5}
HoOF	877	39.45	40.50	40.88	0.38	4.6×10^{-5}	5.2×10^{-5}
ErOF	874	38.86	39.74	40.10	0.36	3.9×10^{-5}	4.2×10^{-5}
YOF	845	39.27	39.96	40.31	0.35	3.2×10^{-5}	4.7×10^{-5}

[a] ±0.04 Å^3

formula volume difference, it is worthwhile to discuss the unit cell dimensions of α-ROF in some detail. In Table 2 the measured lattice parameters of α-ROF at T_{tr} and the extrapolated parameters at 298 K, obtained by means of the experimental expansion coefficients are summarized. Table 2 furthermore contains room temperature parameters estimated on the basis of an average anionic O^{2-}/F^- radius of 1.345 Å for CN 4 (Shannon [8]) in connection with the cationic radii given by Greis and Petzel [6] as well as by Ref. [8]. Although the accuracy of the extrapolated lattice parameters is not better than ±0.005 Å, due to the error limits of the expansion coefficients, the cationic radii from Ref. [6] lead to an average difference of only +0.007 Å between the calculated and the extrapolated parameters while this difference is +0.04 Å when the data of Ref. [8] are used. It should be pointed out that Shannon [8] has actually adopted the R^{3+} radii of Greis and Petzel [6], but has added 0.015 Å to all values for CN 8 in order to improve on the general consistency with experimental interatomic distances and radii–CN plots. However, the results of this work imply that the original R^{3+} radii for CN 8 [6] should be preferred if interionic distances in rare earth fluoride and oxide fluoride systems are concerned.

As pointed out in the introduction, one goal of this work was to find out to what extent a combination of $\Delta V_{T(tr)}$ and (dp/dT) data according to the Clausius–Clapeyron equation could serve to reproduce the calorimetric transitional entropies of [1] and could hence help to explain the interesting trend of the transitional entropies of ROF. In Table 3 the entropies calculated

Table 2
Lattice parameters of cubic ROF

ROF	a at T_{tr} (Å) [a]	a at 293 K (Å)		
		Extrapolated (this work) [b]	Calculated with R^{3+} [6]	Calculated with R^{3+} [8]
LaOF	5.814	5.763	5.750	5.785
PrOF	5.710	5.657	5.672	5.706
NdOF	5.681	5.629	5.633	5.667
SmOF	5.607	5.555	5.563	5.598
EuOF	5.571	5.527	5.533	5.568
GdOF	5.573	5.505	5.503	5.538
TbOF	5.514	5.479	5.473	5.508
DyOF	5.484	5.420	5.443	5.478
HoOF	5.468	5.414	5.415	5.450
ErOF	5.433	5.391	5.390	5.425
YOF	5.443	5.397	5.404	5.459

[a] ±0.002 Å.
[b] ±0.005 Å.

Table 3
Measured entropies of the rhombohedral–cubic phase transition of some ROF vs. entropy values calculated from pressure dependence and volume increment data

ROF	(dp/dT) (Pa K^{-1}) [a]	$\Delta V_{T(tr)}$ (m^3 mol^{-1}) [b]	$\Delta S^0_{T(tr)}$ (J mol^{-1} K^{-1})	
			Calculated from Clausius–Clapeyron equation [c]	Measured [1]
LaOF	3.42×10^{-7}	2.47×10^{-7}	8.4	6.60 ± 0.25
SmOF	3.82×10^{-7}	2.41×10^{-7}	9.2	6.53 ± 0.26
GdOF	2.91×10^{-7}	2.29×10^{-7}	6.7	8.02 ± 0.21
ErOF	3.45×10^{-7}	2.23×10^{-7}	7.7	9.04 ± 0.21
YOF	2.92×10^{-7}	2.11×10^{-7}	6.2	8.51 ± 0.17

[a] From [2] for R = La, Sm, Gd, Er; from [3] for YOF.
[b] From this work; accuracy $\pm0.24\times10^{-7}$ m^3 mol^{-1}.
[c] Accuracy ±0.85 J mol^{-1} K^{-1}.

in this way are compared with the calorimetric data. Despite the considerably limited accuracy of the calculated values, the agreement with the calorimetric data can be considered as fair enough to describe the $\alpha\rightarrow\beta$ transition of ROF as a primarily first-order phenomenon, but does not suffice to explain the dependence of the transitional entropies on cationic size.

Acknowledgements

The authors thank Dr. Ortwin Greis, Technical University of Hamburg-Harburg, for inspiring discussions.

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