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Thermochimica Acta 298 (1997) 165–167

thermochimica acta

Study of phase transition in REOF system by dilatometry (RE = La, Nd, Sm, Gd, Eu and Y)

M.D. Mathews, A.K. Tyagi, P.N. Moorthy*

Applied Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

Received 29 October 1996

Abstract

Bulk thermal expansion behaviour of a number of rare earth oxyfluorides (REOF) has been studied using dilatometry in the temperature range 289–923 K in air. The studies revealed an anomalous expansion for each compound associated with the phase transition. The phase transition temperatures and the coefficients of average linear thermal expansion of the compounds determined by this method are reported. © 1997 Elsevier Science B.V.

Keywords: Dilatometry; Rare earth oxyfluoride

1. Introduction

Homogeneous rare earth oxyfluorides are known to exist over a wide range of compositions. They also exist in a number of crystallographic phases, namely cubic, tetragonal, orthorhombic and rhombohedral. Recently, detailed phase relation (composition vs. structure) has been worked out by us in $NdO_{1-x}F_{1+2x}$ system using XRD, DTA and high temperature XRD [1]. It was found that in this system there was tetragonal phase with NdF_3 rich and rhombohedral phase in Nd_2O_3 rich composition. The rhombohedral oxyfluoride phase was shown to undergo a transition to cubic at high temperature. This was attributed to an order–disorder phenomenon involving the anion sub-lattice. All the results were compared with those reported by other authors [2,3], and it was observed that the tetragonal modification of $NdO_{1-x}F_{1+2x}$ did not show any phase transition. The homogeneity range in tetragonal $NdO_{1-x}F_{1+2x}$ reported by us was wider than that reported by other authors, but this can be attributed to the different heat treatments employed. The rhombohedral to cubic phase transition in a number of REOF systems has also been studied using DSC by Petzel et al. [4]. The role of the rare earth ionic size in determining the homogeneity range has also been investigated [5] in $RE_{1-x}O_{1+2x}$ (RE = La, Nd and Y). Recently, dilatometry was used by us [6] to investigate the anomalous thermal expansion behaviour of K_3REF_6 (RE = Sm – Tb). In the present paper, we report the dilatometric results on rhombohedral-cubic phase transition in REOF, where RE = La, Nd, Sm, Gd, Eu and Y.

2. Experimental

In order to prepare REOF samples, firstly the corresponding rare earth trifluorides were prepared

*Corresponding author. Fax.: 0091 22 556 0760; e-mail: sichem@magnum.barctl.ernet.in.

PII S0040-6031(97)00200-1

by heating RE_2O_3 with excess ammonium hydrogen fluoride (AHF) at 450°C. Heating with excess AHF was continued until all the RE_2O_3 was converted to REF_3 as confirmed by powder XRD. All the REF_3 products were further dried by heating to 600°C in a flowing argon atmosphere. A number of mechanical mixtures of REF_3 and RE_2O_3 (RE = La, Nd, Sm, Gd, Eu and Y) were prepared in 1 : 1 mole ratio and pelletised (diameter 9 mm and height ≈ 6 mm). Each pellet was heated at 950°C for 4 days in flowing N_2 atmosphere which had been passed over molecular sieves. Powder XRD pattern of each oxyfluoride was recorded from $2\theta = 10$ to 70° using CuK_α radiation on a Philips XRD spectrometer Model PW 1729.

Bulk thermal expansion measurements of the compounds were carried out in the temperature range 298–923 K in air at a heating rate of 5 K min^{-1} using a Model LKB 3185 fused quartz push rod dilatometer. Samples in the form of pressed sintered cylindrical pellets were used for the dilatometric measurements.

3. Results and discussion

It was found by comparing the XRD pattern with the reported ones that the equimolar mixture of REF_3 and RE_2O_3 of all the products were in rhombohedral phase of the oxyfluoride. The dilatometry of all the REOF compounds showed similar thermal expansion behaviour in the temperature range of 298–923 K. A typical set of results depicting the variation of percent linear thermal expansion with temperature for YOF is shown in Fig. 1.

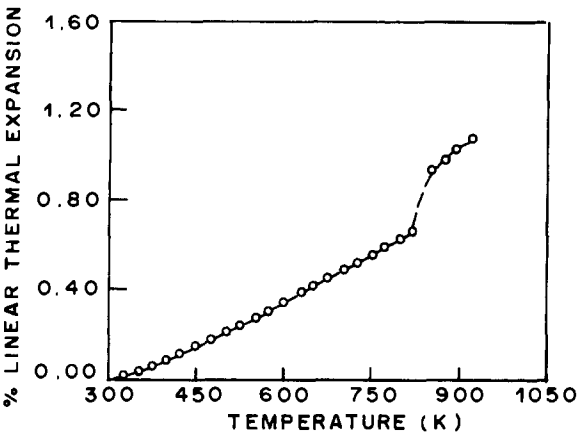

Fig. 1. Percent linear expansion of YOF as a function of temperature.

REOF with RE = Y, La, Nd, Sm, Eu and Gd exhibited a linear relation between expansion with temperature upto 823, 748, 773, 773, 773 and 873 K, respectively. Above these temperatures, in a narrow range of 25 K, an abrupt increase in expansion was observed, indicating anomalous behaviour. Thereafter, all the compounds were found to expand uniformly with increasing temperature upto 923 K. The sharp expansion above a certain temperature for REOF is attributed to the increase in volume associated with the phase transition of the low temperature rhombohedral phase to the high temperature cubic

Table 1
Phase transition temperature and coefficient of average thermal expansion for various REOF compounds

S.No.	Compound	Transition temperature (K)		Coefficient of average linear expansion	
		Present data *	Lit. data (reference)	Temperature range	$\alpha 1 \times 10^6$ K^{-1}
1	YOF	823–848	844 (2)	298–823	12.70
			833 (3)	298–848	17.20
2	LaOF	748–783	778 (4)	298–748	9.70
			767 (2)	298–783	13.04
3	NdOF	773–798	790 (2)	298–773	12.60
			788 (3)	298–798	17.60
4	SmOF	773–798	803 (4)	298–773	8.90
			797 (2)	298–798	12.20
5	EuOF	773–798	788 (4)	298–773	8.86
			768 (3)	298–798	11.57
6	GdOF	873–898	883 (4)	298–873	10.80
			886 (3)	298–898	13.70

* Temperature range indicates over which there is an abrupt increase in the thermal expansion.

phase. The transition temperatures and the values of average linear thermal expansion coefficients ($\alpha 1$) for the temperature ranges from ambient to the beginning as well as completion of the phase transition in these compounds are given in Table 1.

The present dilatometric results on the phase transition temperature of the compounds are in good agreement with the reported DSC and DTA results [2–4]. The increase in $\alpha 1$ associated with the phase transition (Table 1) is attributed to change in crystal symmetry as a result of phase transition. As the symmetry increases the anisotropy decreases and hence the $\alpha 1$ shows an increase. The present results are also in good agreement with our earlier results [1] on $NdO_{1-x}F_{1+2x}$ obtained by high temperature X-ray diffraction. The rhombohedral phase showed the presence of three doublets at $2\theta \approx 27°$, 44° and 52° which merged into singlets in cubic phase [1]. The volume of rhombohedral phase of $NdO_{1-x}F_{1+2x}$ with two molecules in the unit cell ($Z = 2$) at room temperature was found to be 89.97 $(Å)^3$ and that of cubic phase with four molecules ($Z = 4$) at 873 K as 183.85 $(Å)^3$. The rhombohedral to cubic transition is, therefore, accompanied by an increase in volume per molecule from 44.98 $(Å)^3$ to 45.96 $(Å)^3$. The cubic phase could not be retained by quenching to room temperature.

4. Conclusion

The rhombohedral REOF samples undergo a phase transition as revealed by anomalous behaviour in thermal expansion observed in dilatometric studies. The present results are in good agreement with earlier DSC and DTA results.

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