Journal of Thermal Analysis, Vol. 42 (1994) 1075-1079

DERIVATOGRAPHIC STUDY OF THE THERMAL BEHAVIOUR OF 13 RARE EARTH ELEMENT OXIDES

F. Jasim

Department of Chemistry, College of Science, University of Baghdad, Jadriya, Baghdad, Iraq

(Received January 10, 1993; in revised form December 23, 1993)

Abstract

The simultaneous TG-DTG-DTA thermoanalytical curves of 13 rare earth (4f) element oxides, namely, CeO_2, Dy_2O_3, Er_2O_3, Gd_2O_3, HfO_2, Ho_2O_3, Nd_2O_3, Pr_6O_{11}, Sm_2O_3, Tb_4O_7, Tm_2O_3, Yb_2O_3 and Y_2O_3, were recorded with a MOM derivatograph under static air atmosphere over the temperature range from ambient to 1050°C. Only HfO_2, Nd_2O_3, Pr_6O_{11}, Sm_2O_3 and Tb_4O_7 showed appreciable weight losses due to the liberation of small amounts of oxygen. X-ray diffractometry was used to identify the thermal degradation products and their precursors.

Keywords: rare earth element oxides, TG-DTG-DTA, XRD

Introduction

At certain temperatures and pressures, the rare earth element (REE) oxides act as positive-type or negative-type semiconductors, catalysing the degradation of inorganic [1] and organic [2] compounds, i.e. decreasing or increasing their thermal stability through a mechanism of formation of unstable intermediates with the host species. Of course, this behaviour is a function of the non-stoichiometry or defect state of the oxide, or in other words the difference in movement of (+) holes and (–) electrons. Some investigators have found [3–4] that for REE oxides to behave as positive- or negative-type semiconductors there should be a certain REE/O_2 ratio, since the latter determines the nature of the defective structure of the oxide.

As far as the author is aware, no systematic derivatographic study of REE oxides has been carried out. This paper describes such a study, the aim of which was to shed light on their thermal stability and catalytic behaviour.

Experimental

All chemicals were analytical grade reagents (puriss) with a purity of not less than 99.99%, obtained from Fluka AG (Buchs). A MOM derivatograph

0368–4466/94/ $ 4.00

John Wiley & Sons, Limited
Chichester

was used to produce the thermoanalytical curves of the 13 REE oxides (Table 1). For the sake of brevity, thermograms for the thermally stable oxides are not shown since they contain no phase transformation details.

Table 1 Optimised instrumental parameters for REE oxides

Parameters	Settings
Sample weight	100 mg (ground to 200-300 mesh)
Reference materials	α-Al_2O_3
Crucibles	Platinum, MOM No. 3
Atmosphere	Static air
Heating rate	10 deg·min^{-1}
Heating program	Ambient-1050°C
Starting voltage	87 volts
Sensitivities:	
TG	100 mg
DTG	1/5
DTA	1/5

Results and discussion

A careful scrutiny of the thermograms recorded for CeO_2, Dy_2O_3, Er_2O_3, Gd_2O_3, Ho_2O_3, Tm_2O_3, Yb_2O_3 and Y_2O_3 demonstrated their complete thermal stability, without any phase transformation.

Figure 1 depicts the thermoanalytical curves of (a) Pr_6O_{11} and (b) HfO_2. The latter is seen to be thermally stable up to 600°C. Thereafter, a gradual loss in weight is observed in the TG curve. At the end of the heating program (1050°C), this reaches 8 wt%, which is equivalent to the escape of one oxygen atom per mole of HfO_2,

$$HfO_2 \xrightarrow{\Delta} HfO + 1/2O_2$$

The XRD patterns [5] for samples heated up to 1000°C and then cooled prove the presence of HfO_2 alone. This means that beyond 600°C the divalent state, HfO is obtained, which is stable only at high temperature; on cooling to ambient conditions, the tetravalent state is restored by combination with atmospheric oxygen (this is shown by the cooling curve, which is not given here for brevity).

The TG curve (Fig. 1a) indicates that Pr_6O_{11} [6–8] (a dark-brown powder) undergoes a weight loss of 1.6 wt% between 220 and 310°C. This loss is equivalent to one oxygen atom per mole of Pr_6O_{11}:

$$Pr_6O_{11} \underset{\text{cooling}}{\overset{\text{heating}}{\rightleftharpoons}} Pr_6O_{10} + 1/2O_2$$

Beyond 310°C, a meagre degradation continues up to the ceiling temperature of the program. The XRD patterns of the end-products [9] confirm the presence of Pr_6O_{11}. This indicates that, on cooling to room temperature, the unstable intermediate Pr_6O_{10} is reoxidized to Pr_6O_{11}.

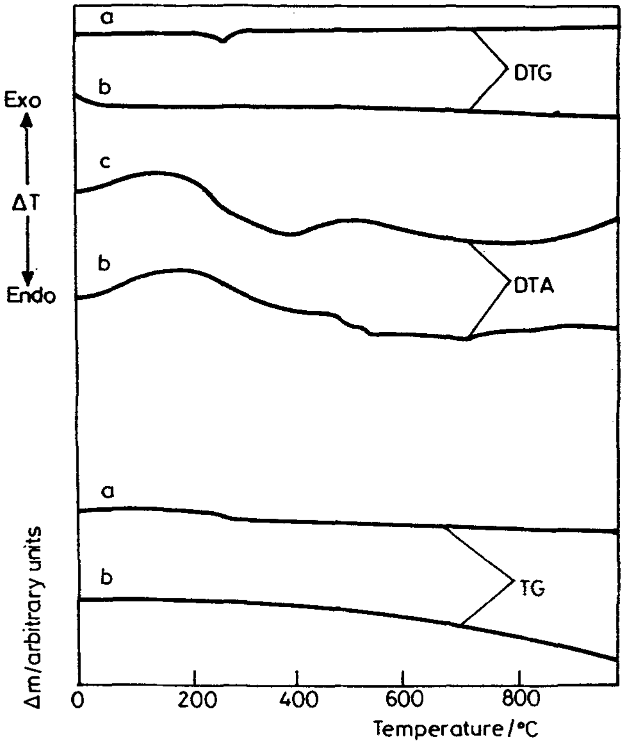

Fig. 1 TG, DTG and DTA curves of : (a) Pr_6O_{11} and (b) HfO_2

This explains why Pr_6O_{11} acts as an *n*-type catalyst semiconductor at high temperature [10].

Sm_2O_3 undergoes a slight degradation in one step (Fig. 2a), characterized by three endotherms, at 250, 420 and 490°C and two DTG endotherms, at 420 and 490°C, corresponding to the loss of one oxygen atom per mole of oxide:

$$Sm_2O_3 \underset{\text{cooling}}{\overset{\text{heating}}{\rightleftharpoons}} 2SmO + 1/2O_2$$

X-ray analysis reveals the presence of strong lines of Sm_2O_3 in the end-products, but very weak lines of SmO. This proves that the intermediate SmO is stable only at high temperature, and is reoxidized by atmospheric oxygen on returning to room temperature.

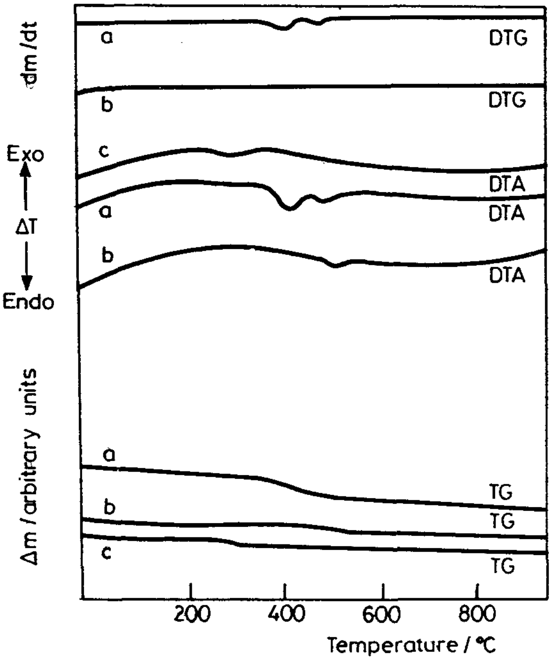

Fig. 2 TG, DTG and DTA curves of: (a) Sm_2O_3 (b) Tb_4O_7 and (c) Nd_2O_3 (DTG is not given for brevity)

Figure 2b depicts the results of thermal analysis of Tb_4O_7. The weight losses relating to the tiny step in the TG curve allow determination of the oxygen lost (a total of 3 wt%) at 505° and 890°C. Calculation on the basis of oxygen atoms lost pointed to the formation of $Tb_2O_3{\cdot}TbO_{1.823}$. The XRD pattern of a samples sintered at 1000°C indicated the presence of strong *d*-lines of Tb_4O_7, but only very weak *d*-lines relating to $Tb_2O_3{\cdot}TbO_{1.823}$. Moreover, the typical dark-brown colour of terbium(III, IV) oxide remained as prior to heating.

In the DTA and TG curves (Fig. 2c) for Nd_2O_3, one endothermic effect and one degradation step (ΔT_{min} = 285°C) were observed; the effect can be assigned to oxygen weight loss. Beyond 320°C, only negligible losses were seen.

It could be concluded that only 5 of the 13 REE oxides investigated show thermal stability at high temperature.

* * *

The author would like to express his thanks to his ex-research students for their help in the experimental work.

References

1 S. Bernal, J. M. Criado, Rev. Inst. Mex. Pet., 8 (1976) 80.
2 A. Burcat and M. Steinberg, J. Inorg. Nucl. Chem., 30 (1980) 35.
3 G. V. Subbarao, S. Ramdas, P. N. Mehrotra and C. N. R. Rao, J. Sol. State Chem. 2 (1970) 377.
4 Y. Wilbert, A. Duquesnoy and F. Marion, C. R. Acad. Sci. Paris, 263 (1966) 1539.
5 ASTM Card 6–318.
6 Per Kofstad, Nonstoichiometry Diffusion and Electrical Conductivity in Binary Metal Oxides, Wiley-Interscience, (1972) p. 283.
7 J. M. Honig, A. F. Cliford and P. A. Faeth, Inorg. Chem., 2 (1963) 791.
8 J. M. Honig, A. A. Cella and J. C. Cornwell, in Rare Earths Research II, ed. K. S. Vorres, Gorden and Breach Science Publishers, Inc. N. Y. (1964).
9 ASTM Cards 24 –1348.
10 I. Jameel, M. Sc. Thesis, College of Science, University of Baghdad (1984).
11 ASTM Cards 13–387.

Zusammenfassung — Mittels eines MOM-Derivatographen wurden in statischer Atmosphäre im Temperaturbereich von Raumtemperatur bis 1050°C die simultanen TG-DTG-DTA thermoanalytischen Kurven von 13 Seltenerdenelementoxiden, namentlich von CeO_2, Dy_2O_3, Er_2O_3, Gd_2O_3, HfO_2, Ho_2O_3, Nd_2O_3, Pr_6O_{11},.Sm_2O_3, Tb_4O_7, Tm_2O_3, Yb_2O_3 und von Y_2O_3 aufgenommen. Lediglich HfO_2, Nd_2O_3, Pr_6O_{11}, Sm_2O_3 und Tb_4O_7 zeigten einen nennenswerten Gewichtsverlust, verursacht durch eine geringe Freisetzung von Sauerstoff. Zur Identifizierung der thermischen Zerfallsprodukte und ihrer Vorstufen wurde die Röntgendiffraktometrie herangezogen.