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THERMAL STABILITY OF RARE EARTH OXYBROMIDES

JORMA HÖLSÄ, MARKKU LESKELÄ and LAURI NIINISTÖ

Department of Chemistry, Helsinki University of Technology, Otaniemi, SF-02150 Espoo 15 (Finland).

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ABSTRACT

The thermal stability of RE oxybromides (RE = La, Pr, Nd, Sm, Gd—Lu and Y) was determined in air and compared with the thermal stability of some RE oxychlorides and oxyfluorides. The stability of the RE oxybromides decreased systematically with increasing atomic number of the RE. The final decomposition product was the oxide, but an intermediate compound, RE_3O_4Br, was found for Pr, Nd, Sm, Gd and Y. TbOBr decomposed through a compound $TbOBr \cdot 3\,Tb_2O_3$. The thermal stability of REOX (RE = La, Gd and Y; X = F, Cl and Br) was found to decrease with increasing atomic number of the RE and halide.

INTRODUCTION

Rare earth oxyhalides, especially the oxybromides, have recently received considerable attention because of their use as luminescent substances [1,2]. No detailed systematic study of their thermal stability in air has been made; however, Mayer and Zolotov [3] studied the thermal decomposition of rare earth bromide hydrates, but paid little attention to the thermal stability of the oxybromides formed during the decomposition. About the same time, Bärnighausen et al. [4] prepared compounds with the formula RE_3O_4Br (RE = Sm, Yb) by heating SmOBr and YbOBr in air.

In studies on rare earth trichlorides, Wendlandt [5,6] found the thermal stability of rare earth oxychlorides to decrease with increase atomic number. Mathur and Bhat [7] made a similar observation in their investigation of rare earth trichloroacetates. They found no intermediate compounds during the decomposition of oxychlorides.

There have been a few reports on the thermal properties of oxyfluorides [8,9], but the oxyiodides seem to have been completely neglected.

EXPERIMENTAL

Preparation of the RE oxyhalides

Rare earth oxyhalides were prepared from RE oxide and the corresponding ammonium halide according to the solid-state reaction [10]

$$RE_2O_3 + 2\,NH_4X \rightarrow 2\,REOX + 2\,NH_3 + H_2O \qquad (1)$$

A small excess of ammonium halide (about 5%) was used to ensure the total conversion of RE oxide to oxyhalide. The ignition time was a few hours and the temperature was 1000°C for the lighter rare earths (including yttrium), and 700°C for the heavier ones (Dy—Lu). The RE oxides used for the synthesis were products of Kemira Oy, Oulu, Finland, with a minimum purity of 99%. Ammonium halides were of analytical grade except for NH_4Br which was a technical product.

The purity of the oxyhalides obtained was checked by X-ray powder diffraction. The samples were found to consist of a single trivalent oxyhalide phase with the exception of cerium and europium; these samples were not included in the thermoanalytical study. PrOBr was greenish, NdOBr was pale violet, ErOBr was pink and HoOBr was yellowish and all the other oxyhalides were white.

Thermal analysis

The thermal decomposition of rare earth oxyhalides in air was studied on a Mettler thermoanalyzer TA-1 allowing simultaneous recording of the TG, DTG and DTA curves. The flow rate of air was 95 $cm^3\ min^{-1}$. The heating rate was 10°C min^{-1}, and for some samples 2°C min^{-1} was also used. Standard platinum crucibles (7 mm diameter and 19 mm depth) were employed and in DTA measurements alumina was used as reference material. The sample weight was 50 mg in all experiments. A few samples were also studied on a Netzsch STA 429 TG, DTG, DTA apparatus under similar experimental conditions.

RESULTS AND DISCUSSION

Thermal decomposition of RE oxybromides

The rare earth oxybromides studied may be divided into three groups according to their thermal decomposition schemes. The first group consists of PrOBr, NdOBr, SmOBr, GdOBr and YOBr, which decompose through an intermediate compound RE_3O_4Br according to the endothermic reactions

$$3\ REOBr + 1/2\ O_2 \rightarrow RE_3O_4Br + Br_2 \quad (2)$$

$$2\ RE_3O_4Br + 1/2\ O_2 \rightarrow 3\ RE_2O_3 + Br_2 \quad (3)$$

The TG, DTG and DTA curves for NdOBr are shown in Fig. 1.

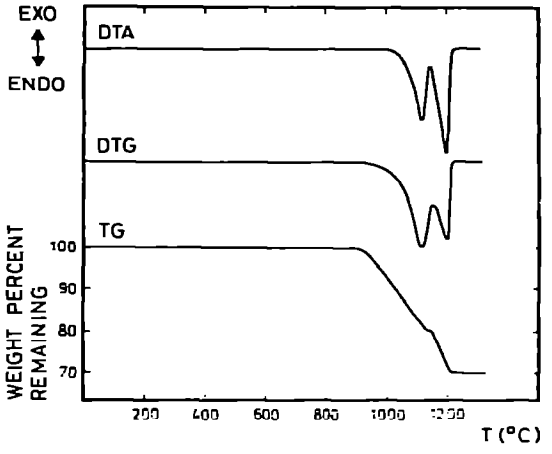
The RE oxybromides of the second group are LaOBr, DyOBr, HoOBr, ErOBr, YbOBr and LuOBr. These decompose in a single step to the oxide without the formation of an intermediate compound

$$2\ REOBr + 1/2\ O_2 \rightarrow RE_2O_3 + Br_2 \quad (4)$$

The thermal decomposition of LaOBr is shown in Fig. 2.

The unique thermal behaviour of TbOBr places it in a third group of its own. The endothermic decomposition of TbOBr involves the formation of an intermediate compound $TbOBr \cdot 3\ Tb_2O_3$ (Fig. 3).

The influence of the heating rate on the decomposition of La, Gd and Y oxybromides was also studied. When the heating rate was slowed from 10°C



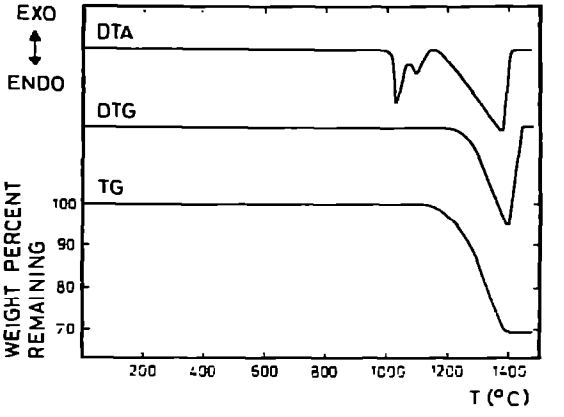


Fig. 1 (left). Thermal decomposition of NdOBr on Netzsch STA 429 apparatus. Heating rate 10°C min^{-1}.

Fig. 2 (right). Thermal decomposition of LaOBr on Netzsch STA 429 apparatus. Heating rate 10°C min^{-1}. Two endothermic peaks in the DTA curve at 1000 and 1100°C with no weight changes are probably due to phase transitions of the oxybromide. This effect cannot be observed in other oxybromides because they begin to decompose at lower temperatures.

min^{-1} to 2°C min^{-1} no change occurred in the decomposition schemes, but the decomposition temperatures decreased by approximately 100°C.

A comparison of the decomposition temperatures of several RE oxybromides measured under similar conditions show a systematic decrease in the temperature with the increasing atomic number of the RE element (cf. Table 1). The formation of RE_3O_4Br occurs, according to the DTG peaks, between 1150 (Pr) and 710°C (Y), but the compound has a stability range of less than 30°C, depending slightly on the heating rate and RE ion. The other intermediate reaction product, TbOBr · 3 Tb_2O_3, is stable over a wide temperature range (cf. Fig. 3).

Thermal decomposition of RE oxychlorides and oxyfluorides

LaOCl begins to lose weight at 1100°C but the reaction is still incomplete

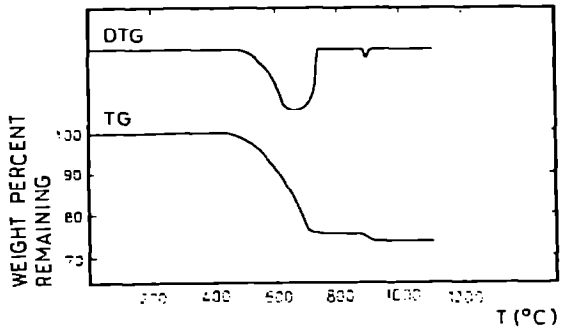


Fig. 3. TG and DTG curves for the decomposition of TbOBr on a Mettler thermoanalyzer. Heating rate 10°C min^{-1}.

TABLE 1

Thermal stability of the rare earth oxybromides (REOBr) measured on a Mettler thermoanalyzer (heating rate 10°C min^{-1})

RE	Temp. range (°C) [a]	DTG peak temp.(°C)
La	770—1350	1330
Pr	670—1235	1150
Nd	720—1180	1070, 1160
Sm	630—1080	940, 1060
Gd	580—1030	820, 960
Tb	470—930	680, 890
Dy	460—760	750
Ho	450—740	720
Er	440—710	700
Tm	430—730	690
Yb	410—700	680
Lu	420—710	700
Y	520—820	710, 790

[a] Temperatures are measured according to ref. 11 from the beginning of the decomposition until the formation of oxide.

at 1600°C, which is the maximum temperature achievable with our apparatus. GdOCl decomposes similarly in a single step but in the lower temperature range of 750—1260°C. The decomposition of YOCl occurs in the narrower temperature range 640—1075°C and proceeds through an as yet unidentified intermediate compound. RE oxyfluorides begin to decompose above 1100°C, but the reaction is not complete at 1600°C. Our data are in agreement with earlier studies [5,6,8].

A comparison of the decomposition temperatures of various La, Gd and Y oxyhalides shows a decrease in the thermal stability with increasing atomic number of RE and halide within each series REOX (RE = La, Gd and Y; X = F, Cl and Br).

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