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THERMOANALYTICAL STUDY ON THE REACTIONS OF SELECTED RARE EARTH OXIDES WITH AMMONIUM HALIDES

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ABSTRACT

A comparative study has been made on the reactions of RE oxides (RE = Y, La, Gd and Lu) with ammonium bromide, and of yttrium oxide with ammonium halides NH_4X (X = F, Cl, Br and I) at different temperatures. Most of the reactions take place in three stages, with formation of two intermediate compounds, $REX_3 \cdot 3\ NH_3$ and $REX_3 \cdot 1.5\ NH_3$. The endothermic reactions begin between 200 and 300°C and the formation of the RE oxyhalide is completed between 340 and 470°C. These temperatures were observed to rise with the increasing atomic number of RE in the series LaOBr—LuOBr, and of halide in the series YOF—YOI.

INTRODUCTION

Several methods of preparation have been suggested for the rare earth oxyhalides [1,2] which are used as phosphors in X-ray intensifying screens [3,4]. Of these methods the reaction of RE oxides with ammonium halides has proved to be the most useful.

This reaction was already known in the 1940's [5,6] but no comparative thermoanalytical study has been made to date. However, there are a few studies concerning the reactions of some individual RE oxides with ammonium fluoride and chloride [7—10]. According to these studies the reaction proceeds in two stages. The first stage involves the formation of an ammonium complex of RE trihalide, $REX_3 \cdot 3\ NH_3$

$$RE_2O_3 + 6\ NH_4X \rightarrow 2\ REX_3 \cdot 3\ NH_3 + 3\ H_2O \quad (1)$$

In the second state the ammonium complex reacts with excess oxide to yield oxyhalide

$$REX_3 \cdot 3\ NH_3 + RE_2O_3 \rightarrow 3\ REOX + 3\ NH_3 \quad (2)$$

The aim of the present study was to compare the reactions of yttrium, lanthanum, gadolinium and lutetium oxides with ammonium bromide, and the reactions of yttrium oxide with different ammonium halides.

EXPERIMENTAL

The minimum purity of the RE oxides (supplied by Kemira Oy, Finland) was 99% and the ammonium halides were of analytical grade. Stoichiometric mixtures of RE oxides and ammonium halides (sample size 250 mg) were heated in an atmosphere of N_2 (flow rate 140 cm^3 min^{-1}) in a MOM Q-derivatograph at a rate of 5°C min^{-1}. The TG, DTG, DTA and *T* curves were recorded simultaneously. Covered platinum crucibles (diameter 9 mm, depth 12 mm) were used for the yttrium oxide and ammonium halide mixtures, and labyrinth crucibles [11] for the RE oxide and ammonium bromide mixtures in order to prevent the vaporization of ammonium halide. α-Al_2O_3 was used as reference material in the DTA measurements.

RESULTS AND DISCUSSION

Reaction of RE oxides with ammonium bromide

The TG curves for the reactions of yttrium, lanthanum, gadolinium and lutetium oxides with ammonium bromide at different temperatures are presented in Fig. 1. As the TG curves indicate, most reactions proceed in three stages. The first stage can be identified as reaction (1), which is accompanied by the loss of water from the reaction mixture. The next two stages involve the release of equal amounts of ammonia, which suggests that reaction (2) takes place in two stages. This reaction scheme is most clearly evident in the reaction of lutetium oxide with ammonium bromide (Fig. 2).

The stability range of the intermediate compound, $LnBr_3 \cdot 3\,NH_3$, is about 50°C for lutetium, but negligible for the other rare earths. The second intermediate phase, corresponding to the formula $LnBr_3 \cdot 1.5\,NH_3$, is even less stable, with the exception of lanthanum which has a stability range of 80°C (Fig. 1). All reactions are endothermic, as can be seen from the DTA curve.

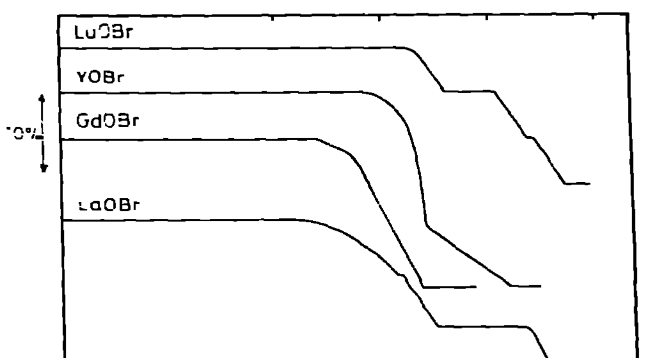

Fig. 1. TG curves for the reactions of Y_2O_3, La_2O_3, Gd_2O_3 and Lu_2O_3 with ammonium bromide.

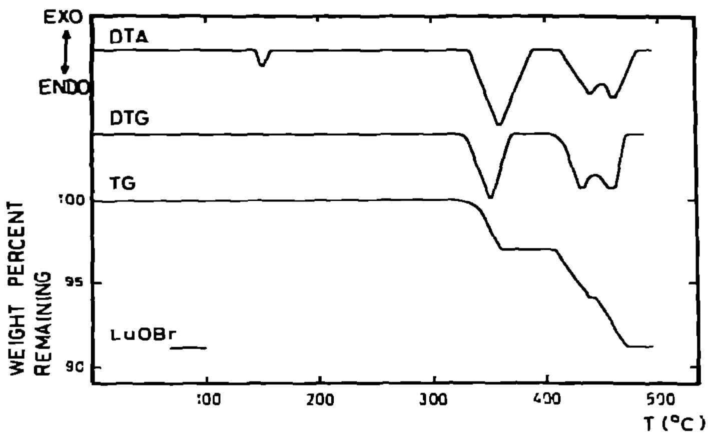

Fig. 2. TG, DTG and DTA curves for the reaction of lutetium oxide with ammonium bromide.

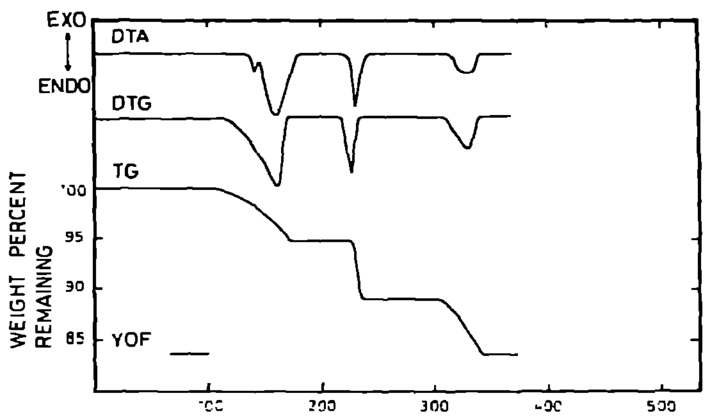

Fig. 3. TG, DTG and DTA curves for the reaction of yttrium oxide with ammonium fluoride.

TABLE 1

Reaction temperatures for the reactions of RE oxides (RE = Y, La, Gd and Lu) with ammonium bromide

RE_2O_3	Reaction (1)		Reaction (2)			
	Range (°C)	DTG peak (°C)	Range (°C)	DTG peak (°C)	Range (°C)	DTG peak (°C)
La_2O_3	210—320	310	320—340	320	430—460	450
Gd_2O_3	220—340	310				
Y_2O_3	270—330	320	330—340	330	340—420	390
Lu_2O_3	300—360	350	410—440	430	440—470	460

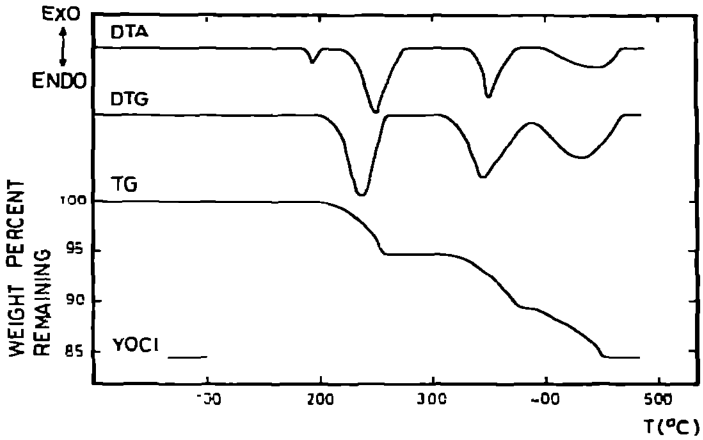

Fig. 4. TG, DTG and DTA curves for the reaction of yttrium oxide with ammonium chloride.

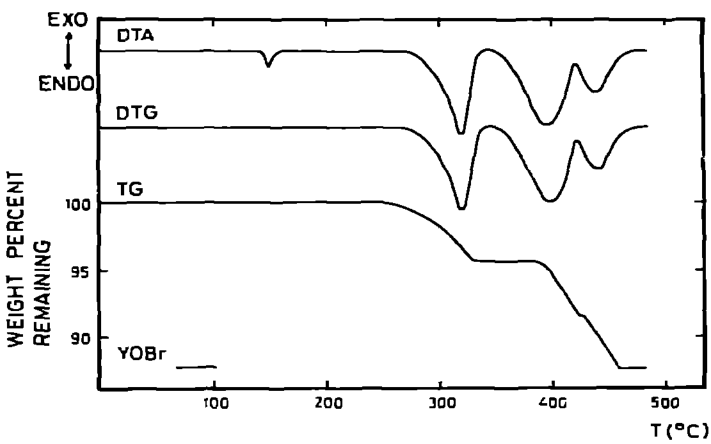

Fig. 5. TG, DTG and DTA curves for the reaction of yttrium oxide with ammonium bromide.

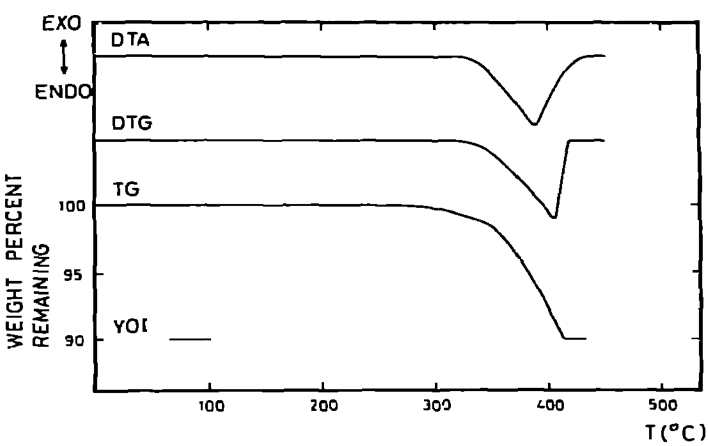

Fig. 6. TG, DTG and DTA curves for the reaction of yttrium oxide with ammonium iodide.

The DTA peak in the temperature range 150—160° C is due to a phase transition of ammonium bromide [12].

The rise in reaction temperatures within the same reaction suggests that the formation of RE oxybromides becomes more difficult with the decreasing ionic radius of RE ion (Table 1). The reactions proceed within a temperature range 120—170° C with the exception of lanthanum, where the higher stability of the ammonium complex causes the temperature range to extend to 250° C.

Reaction of yttrium oxide with ammonium halides

The TG, DTG and DTA curves for the reactions of yttrium oxide with ammonium fluoride, chloride, bromide and iodide are presented in Figs. 3—6. In all except the $Y_2O_3 + 2\,NH_4I$ mixture the reactions take place in three separate stages. The reactions of yttrium oxide with ammonium chloride and bromide proceed in a similar way to the reactions of RE oxides with ammonium bromide. In the reaction of yttrium oxide with ammonium fluoride the first stage appearing in Fig. 3 is the decomposition of NH_4F [12]

$$2\,NH_4F \rightarrow NH_4F \cdot HF + NH_3 \qquad (3)$$

The second and third stages in Fig. 3 correspond to reactions (1) and (2).

By contrast, the reaction of yttrium oxide with ammonium iodide proceeds vigorously in one stage and the YOI formed decomposes almost immediately. The stability range of the intermediate compound, $YX_3 \cdot 3\,NH_3$, is 50° C for the reactions of yttrium oxide with ammonium chloride and bromide.

All reactions are endothermic, as can be seen from the DTA curves in Figs. 3—6. The endothermic reactions with no weight change at 150° C (Figs. 3 and 5) and at 195° C (Fig. 4) are due to phase transitions in NH_4F, NH_4Br and NH_4Cl, respectively. In the reaction of Y_2O_3 with NH_4I no phase transition in NH_4I can be observed.

The rise in reaction temperatures within the same reactions (Table 2) can be explained by the decrease in reactivity of the halides involved. The forma-

TABLE 2

Reaction temperatures for the reactions of yttrium oxide with ammonium halides

NH_4X	Reaction (1)		Reaction (2)			
	Range (°C)	DTG peak (°C)	Range (°C)	DTG peak (°C)	Range (°C)	DTG peak (°C)
NH_4F	220—240	230	300—340	330		
NH_4Cl	200—260	240	300—380	350	380—460	435
NH_4Br	230—330	320	370—420	400	420—460	440
NH_4I	260—420	390				

tion of yttrium oxyhalide seems to become slightly more difficult in the series YOF—YOI.

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