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THERMOANALYTICAL BEHAVIOUR OF EUROPIUM(III) AND ERBIUM(III) OXIDES–ALKALI PERSULFATES BINARY SYSTEMS

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ABSTRACT

Four binary systems, R_2O_3–$M_2S_2O_8$, where R is Eu or Er and M is Na or K, have been studied derivatographically. Four compounds, $Na_2Eu_2(SO_4)_4$, $KEu(SO_4)_2$, $Na_2Er_2(SO_4)_4$ and $KEr(SO_4)_2$, have been prepared by solid state reactions and their entities confirmed by X-ray diffractometry.

INTRODUCTION

The thermal reactions of alkali persulfate–rare earth oxide binary systems were studied using the derivatograph [1–4]. According to the literature cited, europium sesquioxide is thermally stable and acts as an *n*-type semiconductor at 800°C and under a hydrogen gas atmosphere [5]. Erbium sesquioxide is thermally stable at high temperatures [6]. To the best of our knowledge, the high-temperature behaviour of these systems has not been studied. The purpose of this work is to discover the intermediate and final products obtained, their thermal stabilities, and the extent of the catalytic activities of the oxides under the prescribed heating program.

EXPERIMENTAL

All chemicals were of analytical grade. Potassium and sodium persulfates were obtained from Hopkin and Williams and Eu_2O_3 and Er_2O_3 puriss. quality from Fluka AG.

The apparatus and procedure employed were as described elsewhere [7].

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RESULTS AND DISCUSSION

Figure 1 represents the TG and DTA curves for the $Na_2S_2O_8$–Eu_2O_3 system in various molar ratios. It appears from the DTA curve for the 1:6 ratio that the reaction between the oxide and the thermally produced pyrosulfate occurs after the fusion temperature of the latter. For the other molar ratios, it occurs within the fusion temperature of the pyrosulfate, resulting in the disappearance of its fusion endotherm due to thermal neutrality. As is evidenced by the XRD patterns (Fig. 2) and the calculations from the TG curves, the 1:3 Eu_2O_3:$Na_2S_2O_8$ is to be considered as the stoichiometric ratio which is relevant to the reaction

$$Eu_2O_3 + 3\ Na_2S_2O_7 \xrightarrow{\Delta} Na_2Eu_2(SO_4)_4 + 2\ Na_2SO_4$$

Samples sintered at 675°C gave an XRD pattern that confirmed the formation of $Na_2Eu_2(SO_4)_4$ in addition to sodium sulfate. The TG curve indicates that 89% by weight of the produced pyrosulfate has taken part in the stoichiometric reaction. The DTA curve for the 1:3 ratio exhibits a rather sharp exo-peak representing the above stoichiometric reaction. The first endotherm of this curve at 575°C refers to the crystalline solid–solid phase change (Fig. 2) of the double salt; whilst the last endotherm which appears at 745°C corresponds to the melting point temperature of the impure sodium sulfate by-product. The double salt $Na_2Eu_2(SO_4)_4$ is found to be stable up to the end of the heating program (1050°C). This is confirmed by the TG curves and XRD (Figs. 1 and 2).

Eu_2O_3–$K_2S_2O_8$ system

Calculations based on the TG and DTA curves as illustrated in Fig. 3 indicate that 86% $K_2S_2O_7$ has reacted for the ratio 1:3 Eu_2O_3:$K_2S_2O_8$, and therefore the stoichiometric reaction is

$$Eu_2O_3 + 3\ K_2S_2O_7 \xrightarrow{\Delta} 2\ KEu(SO_4)_2 + 2\ K_2SO_4$$

The exothermic reaction does not show up itself as a broad exotherm on the DTA curve because of the thermal neutrality obtained after matching the endotherm of the β- to α-phase transition of $K_2S_2O_7$. Afterwards, a horizontal plateau is seen on the TG curves which ends at 860°C. Samples sintered at 580°C and analysed by X-ray diffraction indicate (Fig. 4) the presence of the double salt, $KEu(SO_4)_2$, as a major constituent of the sample. The sharp endotherm at 860°C refers to the melting point of the double salt. The DTG curve (not shown for space saving) shows that a gradual decomposition of the double salt $KEu(SO_4)_2$ takes place directly after melting and goes up like this till the end of the heating program. The XRD patterns for the final products match with those of $KEu(SO_4)_2$, K_2SO_4 and small amounts of Eu_2O_3.

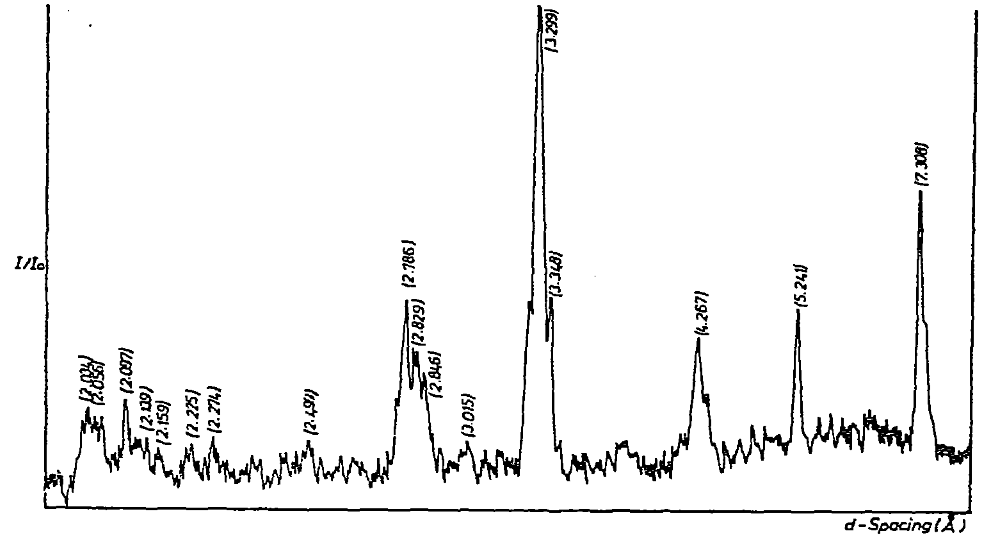

Fig. 1. TG and DTA curves of europium(III) oxide–sodium persulfate mixtures.

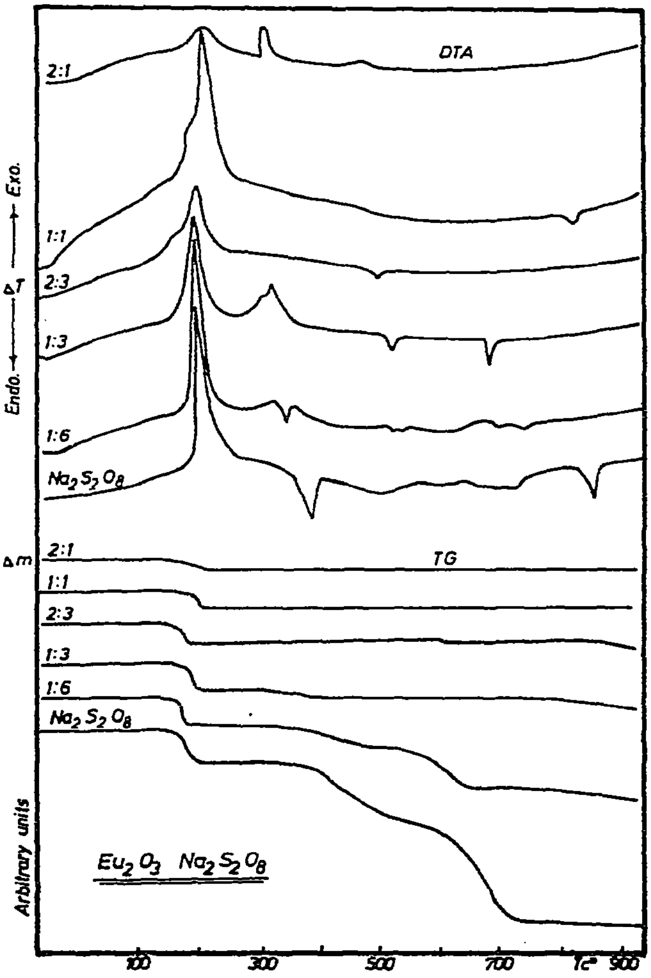

Fig. 2. X-Ray diffraction pattern of 1:3 Eu_2O_3–$Na_2S_2O_8$ mole ratio mixture isolated at 675°C.

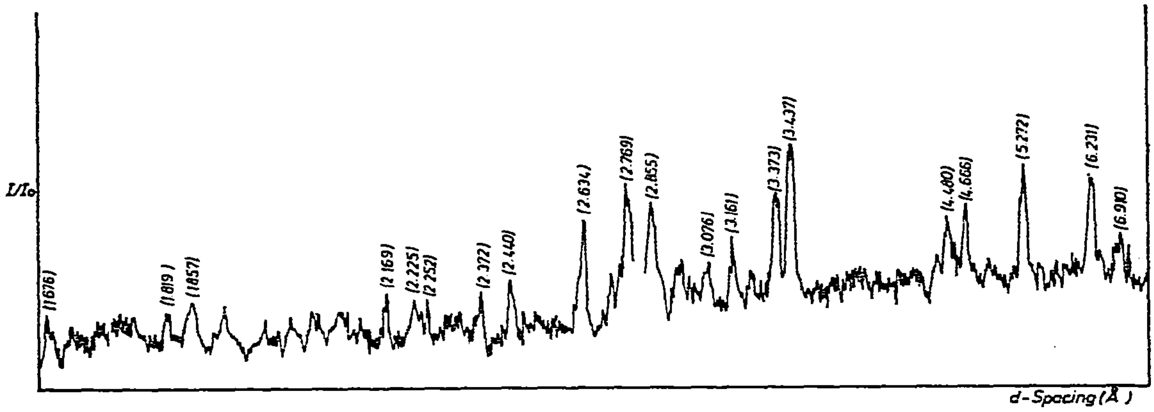

Fig. 3. TG and DTA curves of europium(III) oxide–potassium persulfate mixtures

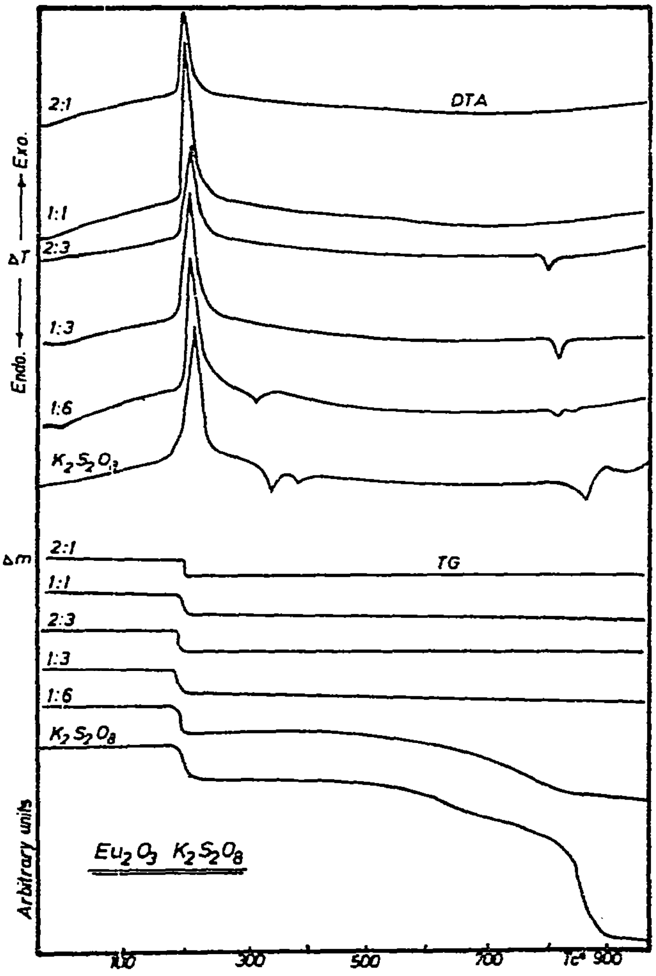

Fig. 4. X-Ray diffraction pattern of 1:3 Eu_2O_3–$K_2S_2O_8$ mole ratio mixture isolated at 580°C.

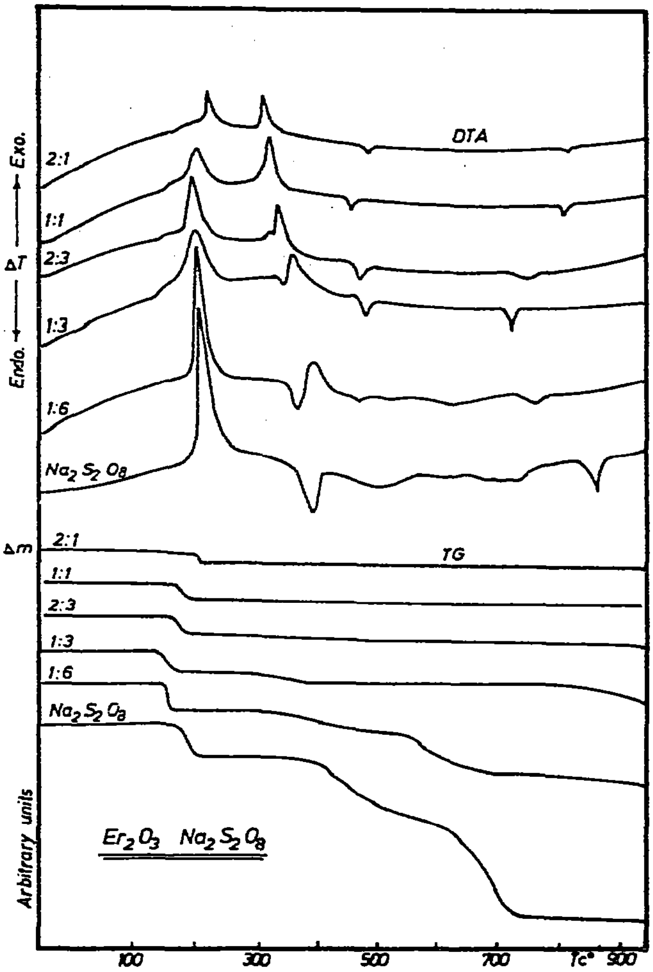

Fig. 5. TG and DTA curves of erbium(III) oxide–sodium persulfate mixtures.

TABLE 1

Milligrams of oxygen lost and temperature ranges of persulfate decomposition and reaction intervals for the 1 : 3 R_2O_3 : $M_2S_2O_7$ systems

System	O_2 lost (mg)		Temp. range for $M_2S_2O_8$ decomp. (°C)		Reaction intervals (°C)	
	Theor.	Pract.	T_i	T_f	T_i	T_f
Eu_2O_3–$Na_2S_2O_8$	9.0	9.8	195	245	360	430
Eu_2O_3–$K_2S_2O_8$	8.2	9.0	180	230		
Er_2O_3–$Na_2S_2O_8$	8.8	9.0	170	235	380	465
Er_2O_3–$K_2S_2O_8$	8.0	8.0	180	218	355	430

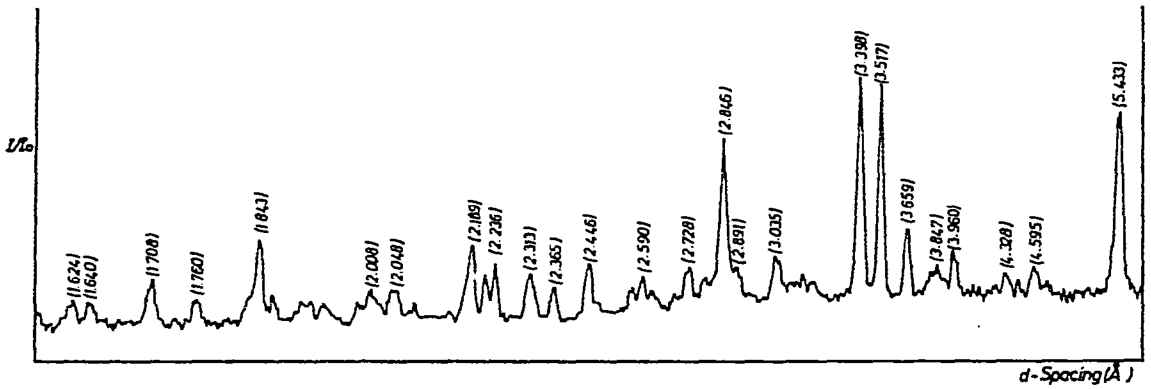

Fig. 6. X-Ray diffraction pattern of 1:3 Er_2O_3–$Na_2S_2O_8$ mole ratio mixture isolated at 640°C.

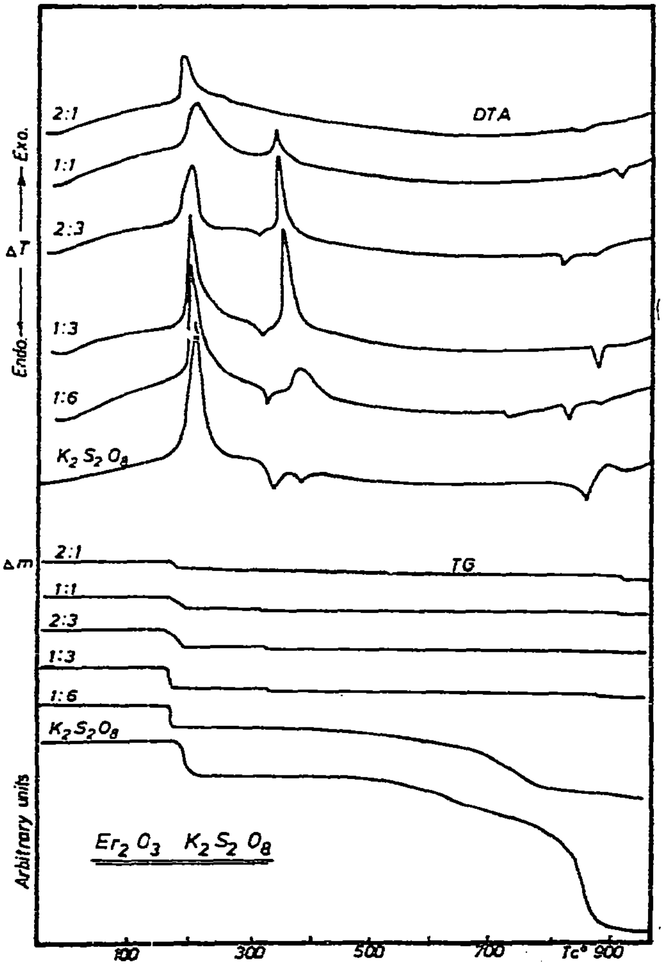

Fig. 7. TG and DTA curves of erbium(III) oxide–potassium persulfate mixtures.

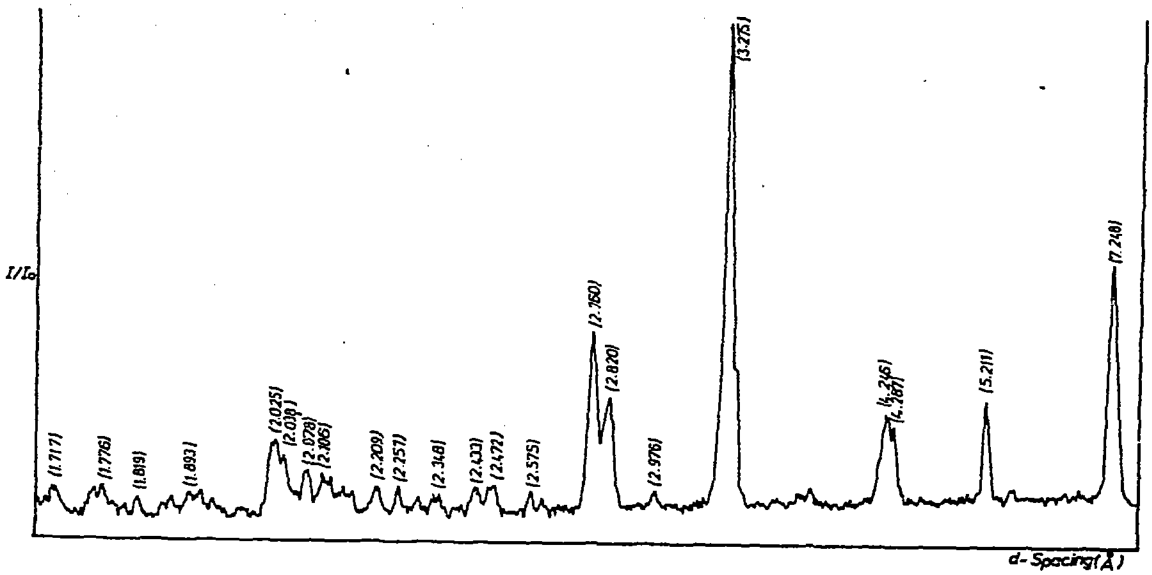

Fig. 8. X-Ray diffraction pattern of 1 : 3 Er_2O_3–$K_2S_2O_8$ mole ratio mixture isolated at 500°C.

$$2\ KEu(SO_4)_2 \xrightarrow{\Delta} Eu_2(SO_4)_3 + K_2SO_4$$

$$Eu_2(SO_4)_3 \xrightarrow{\Delta} Eu_2O_3 + 3\ SO_3$$

An almost similar behaviour was obtained with ratios other than 1 : 3. In the 1 : 6 ratio, two endotherms were noted at 855 and 870°C, which correspond respectively to the decomposition of the $K_2S_2O_7$ and the melting point of the double salt.

Er_2O_3–$Na_2S_2O_8$ System

Figure 5 shows the derivatograms of sodium persulfate mixtures with erbium(III) oxide at $Er_2O_3 : K_2S_2O_8$ mole ratios of 1 : 6, 1 : 3, 2 : 3, 1 : 1 and 2 : 1. The oxide could raise the final decomposition temperature, T_f, of persulfate (Table 1). However, at the 2 : 1 mole ratio, T_f reached its maximum value. The usual sharp endotherms indicating the melting point of Na_2SO_4 were observed on the DTA curves in all molar ratios except those of 1 : 1 and 2 : 1 ratios, where the amounts of the persulfate are decreased. Results obtained from the TG curve of the 1 : 3 ratio advocate that 82% of the available $Na_2S_2O_7$ reacted with the oxide over the 380–465°C temperature interval. X-Ray diffraction analysis of samples isolated at 640°C show sharp lines at 5.43 Å, 2.84 Å and 1.84 Å (Fig. 6). These lines match those available in ASTM cards for the double salt $Na_2Er_2(SO_4)_4 \cdot 2\ H_2O$ [8]. Since Na_2SO_4

is already there as a by-product. the stoichiometric reaction for the system is

$$Er_2O_3 + 3\ Na_2S_2O_7 \xrightarrow{\Delta} Na_2Er_2(SO_4)_4 + 2\ Na_2SO_4.$$

The sharp endotherm formed at 510°C on the DTA curve of the 1:3 ratio represents the crystalline phase change of this double salt; that at 755°C belongs to the melting point of impure Na_2SO_4.

Er_2O_3–$K_2S_2O_8$ system

Calculation based on the TG curve of the 1:3 stoichiometric molar ratio (Fig. 7) shows that 90% of the thermally produced $K_2S_2O_7$ reacted with Er_2O_3. However, the bright lines obtained from X-ray diffraction analysis of the sample isolated at 500°C (Fig. 8) match those of the $KEr(SO_4)_2$ lines available in the ASTM cards. The stoichiometric reaction is

$$Er_2O_3 + 3\ K_2S_2O_7 \xrightarrow{\Delta} 2\ KEr(SO_4)_2 + 2\ K_2SO_4$$

The sharp endotherm formed at 920°C represents the melting point of the new double salt.

It is worth mentioning that this compound was prepared by Degtiarev et al. [9] through reactions in solution.

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