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INVESTIGATIONS OF Ho_2O_3–$X_2S_2O_8$ AND Tm_2O_3–$X_2S_2O_8$ (X = Na, K) BINARY SYSTEMS BY HIGH TEMPERATURE DERIVATOGRAPHY

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ABSTRACT

A range of molar ratios of binary systems consisting of mixtures of Ho_2O_3 and Tm_2O_3 with either sodium or potassium persulfates were examined by derivatography from ambient temperatures to 1050 °C. Holmium(III) oxide was found to accelerate, through its catalytic activity, the persulfate–pyrosulfate transformation reaction. This oxide reacts with sodium pyrosulfate forming a light orange coloured double salt, $Na_2Ho_2(SO_4)_4$, which is thermally stable up to 900 °C. The salt also undergoes a crystalline phase transformation at 520 °C. A similar double salt, $K_2Ho_2(SO_4)_4$, was prepared on reacting Ho_2O_3 with $K_2S_2O_7$. This salt melts at 900 °C and remains thermally stable up to 1000 °C. Thulium(III) oxide has been found to catalytically accelerate the persulfate–pyrosulfate thermal transformation. This reveals the p-type semiconductive nature of Tm_2O_3 at high temperatures. The oxide reacts with either sodium or potassium persulfates to form double salts with formulae such as $Na_2Tm_2(SO_4)_4$ or $K_2Tm_2(SO_4)_4$. Both salts are thermally stable at high temperatures and undergo crystalline-phase transformations. The sodium double salts of holmium and thulium, as well as those of potassium, were found to be isostructural.

INTRODUCTION

The two lanthanide sesquioxides, Ho_2O_3 and Tm_2O_3, are considered to be p-type semiconductive oxides [1] in the presence of oxygen, which catalytically affect thermal reactions and oxidise many organic and inorganic compounds. The two metals form hydrated sulfates [2] which decompose at high temperatures into the anhydrates then oxysulfates of the metals, and finally decompose into the oxide of the metal, SO_2 and O_2 gases. Both metals from double salts. According to Degtiarev et al. [3], holmium forms double salts of the third structure type and thulium of the fourth type. All these salts decompose in the solid state at high temperatures, and their decomposition temperatures lower as their atomic number increases. Jasim and coworkers [4,5] prepared a series of lanthanide double salts by solid-state high temperature reactions, that belong to the metals Sc, Gd, Dy, Yb, Y, Lu, Nd, Tb, Ce, La and Pr, where it was found that the catalytic activity of these

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oxides depends on the nature of the oxides, the type of reaction, and the temperature [6,7]. The aim of these investigations is to substantiate the catalytic activity of both oxides in relation to the thermal behaviour of sodium and potassium persulfates.

EXPERIMENTAL

Binary mixtures of different molecular ratios of Ho_2O_3 and Tm_2O_3 with either $Na_2S_2O_8$ and $K_2S_2O_8$ were carefully ground in an agate mortar for 20 min and dried at 90 °C for at least 3 h. Ho_2O_3 and Tm_2O_3 were obtained from Fluka (Puriss 99.99%), the rest of chemicals were from BDH. α-Al_2O_3 sintered for 3 h at 1300 °C was used as reference. TG, DTA, DTG and T curves were obtained by heating (using a MOM photographic derivatograph) and 200 mg of the binary mixture placed in a No. 3 open platinum crucible.

X-ray diffraction (XRD) patterns of finely divided powdered crystals were obtained using a Philips X-ray diffractometer with Cu$K\alpha$ radiation.

RESULTS AND DISCUSSION

Ho_2O_3–$Na_2S_2O_8$ system

Figure 1 depicts the TG and DTA curves of various molecular ratios of the Ho_2O_3–$Na_2S_2O_8$ system, and Table 1 gives the results obtained from these curves. For the 1 : 6 sample, ~ 54 wt% of the resulting $Na_2S_2O_7$ reacts with the appropriate amounts of Ho_2O_3 forming a double salt of formula $Na_2Ho_2(SO_4)_4$. The unreacted pyrosulfates finally decompose into Na_2SO_4 and SO_3. The exotherm appearing on the DTA curve represents the transformation of $Na_2S_2O_8$ into $Na_2S_2O_7$, and the liberation of O_2 gas [8] between 180 and 210 °C. This is followed by the usual melting endotherm of $Na_2S_2O_7$ at 385 °C. The exotherm at 385–460 °C indicates the formation of a new compound, probably a double salt with formula $Na_2Ho_2(SO_4)_4$. Small endotherms then appear at 490, 660 and 786 °C, indicating, respectively, the crystalline phase change of the compound, decomposition of pyrosulfate, and a eutectic melting endotherm which consists of a mixture of Na_2SO_4 and the double salts.

Data calculated with the aid of the TG curve for the 1 : 3 sample showed that 89 wt% $Na_2S_2O_7$ reacts with the appropriate amounts of the oxide to form the double salt. Since this is the highest reacted percentage, this can therefore be considered as the stoichiometric ratio for the formation of the double salt and therefore the tentative reaction could be written as

$$Ho_2O_3 + 3Na_2S_2O_7 \rightarrow Na_2Ho_2(SO_4)_4 + 2Na_2SO_4$$

TABLE 1

Preparation of standard molar ratios and TG results of the Ho_2O_3–$Na_2S_2O_8$ system

Molar ratio Ho_2O_3–$Na_2S_2O_8$	Sample wt. (mg)	$Na_2S_2O_8$ in sample (mg)	O_2 lost (mg)		SO_3 lost (mg)		Decomp. Temp. (°C)	
			Theor.	Exp.	Theor.	Exp.	T_i	T_f
1:6	199.5	157.771	10.6	10.5	53.0	24.0	180	210
1:3	200.0	130.8	8.8	8.5	43.9	5.0	160	225
2:3	200.0	97.18	6.54	6.0	32.7	3.5	180	220
1:1	200.0	77.30	5.19	5.0	25.97	3.25	160	225
2:1	200.0	47.91	3.22	3.00	16.1	2.00	165	210

The stoichiometry is also supported by the largest exotherm representing the formation of the double salt. Careful scrutiny of the thermogram at this ratio reveals that Ho_2O_3 behaves thermally in a manner similar to some sesquioxides of rare earths such as Er_2O_3, Dy_2O_3, etc. [9], since the compound is

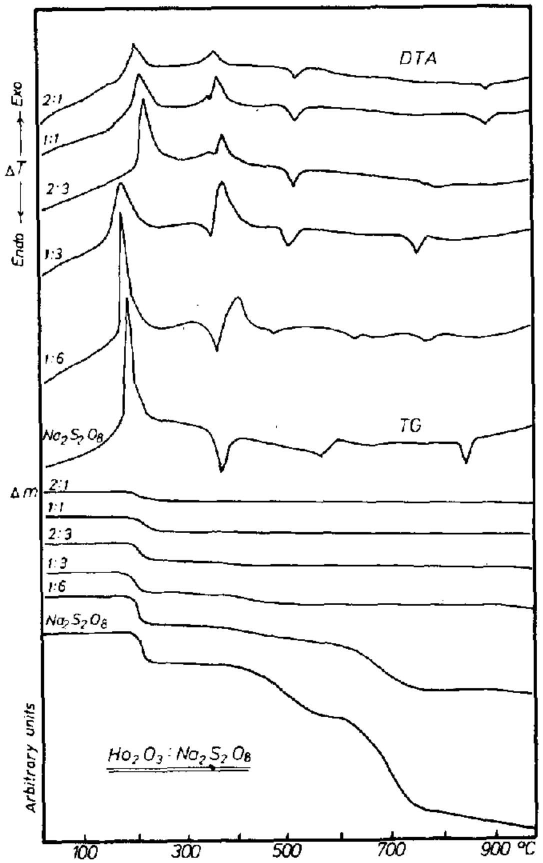

Fig. 1. TG and DTA curves of holmium(III) oxide–sodium persulfate mixtures.

TABLE 2

XRD pattern for the 1:3 sample of the Ho_2O_3–$Na_2S_2O_8$ system sintered at 480 °C

d(Å)	2.81	3.07	3.16	3.42	6.13
I/I_0	100	83	89	79	82

pale orange in colour, stable between 470 and 900 °C, then decomposes slowly

$$Na_2Ho_2(SO_4)_4 \xrightarrow{900\,°C} Ho_2O_3 + Na_2So_4 + SO_3$$

Figure 2 and Table 2 depict the XRD patterns observed for the prepared double salt $Na_2Ho_2(SO_4)_4$ for the 1:3 ratio of $Ho_2O_3:Na_2S_2O_8$ sintered at 480 °C. Here the oxide lowers the initial temperature, T_i, of the decomposition of $Na_2S_2O_8$ by 20 °C by catalysis. The endotherm at 520 °C exhibits the melting of the double salt. This was confirmed by sintering samples at 470 and 480 °C, when the XRD patterns were found to be identical. The phase change at this range of temperatures is typical for almost all double salts of sodium with rare earth metal sulfates [9]. The endothermic peak at 760 °C is the melting endotherm of impure sodium sulfate. It should be noted for samples 2:3, 1:1 and 1:2, when the oxide increases, the amount of the double salt formed decreases. This is also indicated by the duller XRD lines obtained, meanwhile, the bright line of Ho_2O_3 intensifies. The lowering of T_i by 20 and 15 °C for samples 1:1 and 2:1 confirms the catalytic effect of the

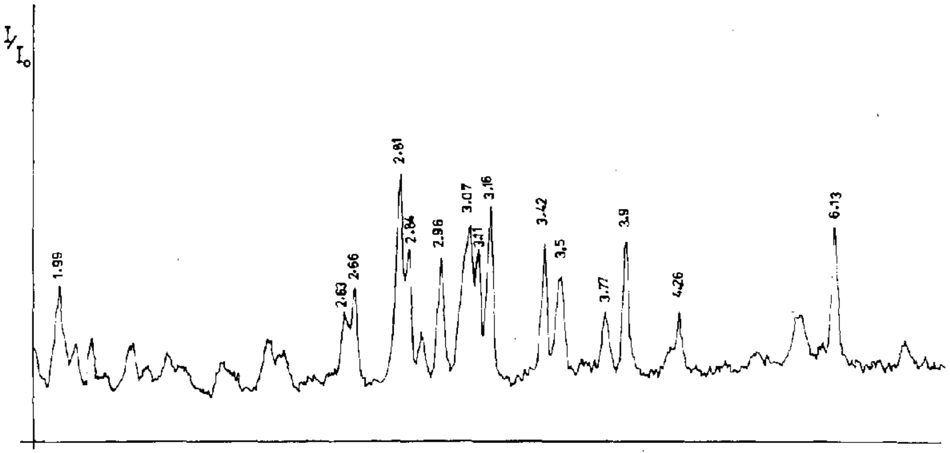

Fig. 2. X-ray diffraction pattern of (1:3) $Ho_2O_3:Na_2S_2O_8$ molar ratio mixture isolated at 480 °C.

TABLE 3

Preparation of standard molar ratios and TG results of the Ho_2O_3–$K_2S_2O_8$ system

Molar ratio Ho_2O_3–$K_2S_2O_8$	Sample wt. (mg)	$K_2S_2O_8$ in sample (mg)	O_2 lost (mg)		SO_3 lost (mg)		Decomp. Temp. (°C)	
			Theor.	Exp.	Theor.	Exp.	T_i	T_f
1:6	199.0	161.4	9.55	8.75	47.76	25.25	160	190
1:3	200.0	136.43	8.08	7.75	40.38	2.50	163	190
2:3	199.5	103.27	6.11	5.00	30.56	3.0	162	190
1:11	200.0	84.41	4.99	4.25	24.98	2.0	156	210
2:1	200.0	52.69	3.12	3.00	15.59	2.5	170	215

oxide. As the oxide increases, a shift in the exothermic peak towards lower temperatures occurs, leading to thermal neutrality of the melting endotherm of $Na_2S_2O_7$. The phase change endotherm at 520°C remains constant for the molar ratios 2:3, 1:1 and 1:2.

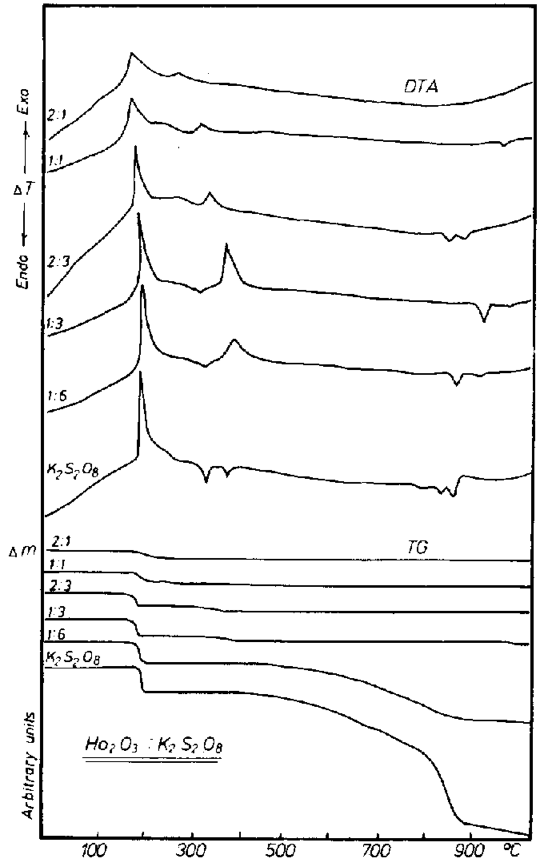

Fig. 3. TG and DTA curves of holmium(III) oxide–potassium persulfate mixtures.

TABLE 4

XRD pattern for the 1 : 3 sample of the Ho_2O_3–$K_2S_2O_8$ system sintered at 420 °C

d (Å)	2.75	2.81	3.26	3.29	7.14
I/I_0	36	24	100	39	43

Ho_2O_3–$K_2S_2O_8$ system

Figure 3 depicts the TG and DTA curves for the various molecular ratio mixtures 1 : 6, 1 : 3, 2 : 3, 1 : 1 and 2 : 1 of $Ho_2O_3 : K_2S_2O_8$. Table 3 summarises the data obtained from theses curves. The DTA curve shows the largest exotherm, comparing all ratios studied at 380° (stoichiometric ratio) of sample 1 : 3, pointing out the occurrence of the only exothermic reaction of the $K_2S_2O_7$ melt and Ho_2O_3. Data deduced from the TG curve for the 1 : 3 sample at 380 °C indicate that 93 wt.% of the melted $K_2S_2O_7$ reacts stoichiometrically with the appropriate amount of Ho_2O_3 forming the pale orange double salt, $K_2Ho_2(SO_4)_4$

$$Ho_2O_3 + 3K_2S_2O_7 \rightarrow K_2Ho_2(SO_4)_4 + 2K_2SO_4$$

This double salt, whose XRD spectrum is given in Fig. 4, was found to be

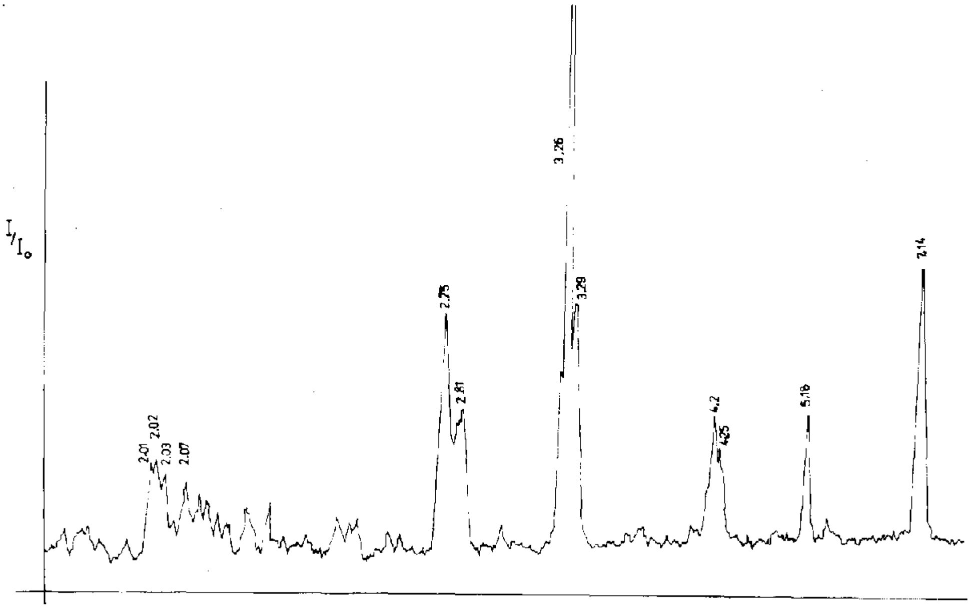

Fig. 4. X-ray diffraction pattern of (1 : 3) $Ho_2O_3 : K_2S_2O_8$ molar ratio mixture isolated at 410 °C.

TABLE 5

Preparation of standard molar ratios and TG results of the Tm_2O_3–$K_2S_2O_8$ system

Molar ratio Tm_2O_3–$Na_2S_2O_8$	Sample wt. (mg)	$Na_2S_2O_8$ in sample (mg)	O_2 lost (mg)		SO_3 lost (mg)		Decomp. Temp. (°C)	
			Theor.	Exp.	Theor.	Exp.	T_i	T_f
1:6	200.0	1757.47	10.58	9.50	52.91	30.50	160	210
1:3	200.0	129.86	8.73	7.75	43.63	5.25	163	210
2:3	200.0	96.14	6.46	6.00	32.30	3.50	182	205
1:1	199.5	76.13	5.20	5.00	25.80	3.00	155	200
2:1	199.0	46.92	3.15	3.00	15.77	4.00	160	210

thermally stable to the end of heating program. Table 4 gives XRD data for the 1 : 3 sample sintered at 420 °C.

Increasing Ho_2O_3 shifts the reaction exotherms of samples 2 : 1, 1 : 1 and 2 : 3 towards lower temperatures, leading to the disappearance of the crystalline phase-change endotherm of $K_2S_2O_7$. In these three ratios the oxide could also lower T_i, by catalysis, for the persulfate-to-pyrosulfate transformation by 20 °C. The two consecutive endotherms appearing above 800 °C for the 1 : 3, 2 : 3 and 1 : 1 samples represent the phase change and melting of $K_2Ho_2(SO_4)_4$, respectively. For the 2 : 1 sample, these endotherms disappear entirely because of the tiny amount of the double salts formed.

Tm_2O_3–$Na_2S_2O_8$ system

Figure 5 shows the TG and DTA curves for the various molar ratios of the system. Table 5 summarises the data deduced from these curves. The TG, DTG and DTA curves of the 1 : 6 sample indicate the liberation of O_2 gas due to the thermal decomposition of $Na_2S_2O_8$. This step is unequally divided catalytically. A small step occurs at 160 °C, and a large one at 180 °C. This division is most likely due to the formation of an unstable intermediate. At 385 °C the melting endotherm of $Na_2S_2O_7$ appears, which is immediately followed by the oxide–pyrosulfate reaction exotherm (385–450 °C). The endotherm at 490 °C belongs to the crystalline phase change of the double salt produced, $Na_2Tm_2(SO_4)_4$. An estimation from the TG curve of the 1 : 3 sample shows that 88 wt% of $Na_2S_2O_7$ reacts with the appropriate amounts of Tm_2O_3 ($T_i - T_f = 380–450$ °C, T_f = final decomposition temperature), and therefore the stoichiometric reaction can be tentatively written as

$$Tm_2O_3 + 3Na_2S_2O_7 \rightarrow Na_2Tm_2(SO_4)_4 + 2Na_2SO_4$$

Its stoichiometry is shown to be the largest of all ratios of the DTG or DTA

TABLE 6

XRD pattern for the 1:3 sample of the Tm_2O_3–$Na_2S_2O_8$ system sintered at 480 °C

d (Å)	2.80	2.82	3.05	3.14	3.88
I/I_0	100	82	83	10014	88

curves. The XRD pattern for samples sintered at 480 °C (a white powder tentatively given the formula $Na_2Tm_2(SO_4)_4$) is shown in Fig. 6, and the d-spacings are given in Table 6. Unfortunately, the ASTM index cards give no indication whatsoever about the presence of this double salt, which may be attributed to the rarity of crystalline compounds of this metal investigated.

The phase change endotherm at about 515 °C is typical of rare earth

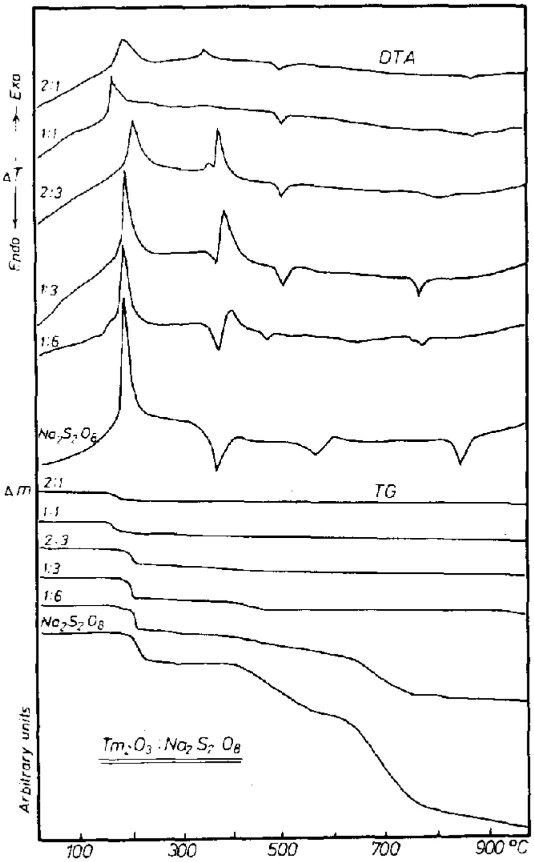

Fig. 5. TG and DTA curves of thulium(III) oxide–sodium persulfate mixtures.

TABLE 7

Preparation of standard molar ratios and TG results of the Tm_2O_3–$K_2S_2O_8$ system

Molar ratio Tm_2O_3–$K_2S_2O_8$	Sample wt. (mg)	$K_2S_2O_8$ in sample (mg)	O_2 lost (mg)		SO_3 lost (mg)		Decomp. temp. (°C)	
			Theor.	Exp.	Theor.	Exp.	T_i	T_f
1:6	200.5	161.96	9.58	8.0	47.93	27.0	154	180
1:3	199.0	134.84	7.90	7.5	39.90	3.0	160	190
2:3	199.5	102.22	6.05	5.0	30.25	4.0	160	190
1:1	199.0	81.98	4.85	4.0	24.26	4.0	178	205
2:1	199.5	51.75	3.06	3.0	15.31	4.0	180	220

sodium double salts, giving another clue towards the formation of the above newly prepared compound. The salt is thermally stable between 470 and 900 °C, thereafter it slowly decomposes [9] according to the equation

$$Na_2Tm_2(SO_4)_4 \xrightarrow{900\,^\circ C} Tm_2O_3 + SO_3 + Na_2SO_4$$

Increasing the quantity of Tm_2O_3 promotes the catalytic activity of the oxide–pyrosulfate reaction. In the 1 : 1 and 1 : 2 samples, the thermal transformation $Na_2S_2O_8$–$Na_2S_2O_7$ takes place at lower temperatures which proves the catalytic activity of the oxide. The disappearance of the melting endotherm of pyrosulfate for the 1 : 1 sample indicates thermal neutrality.

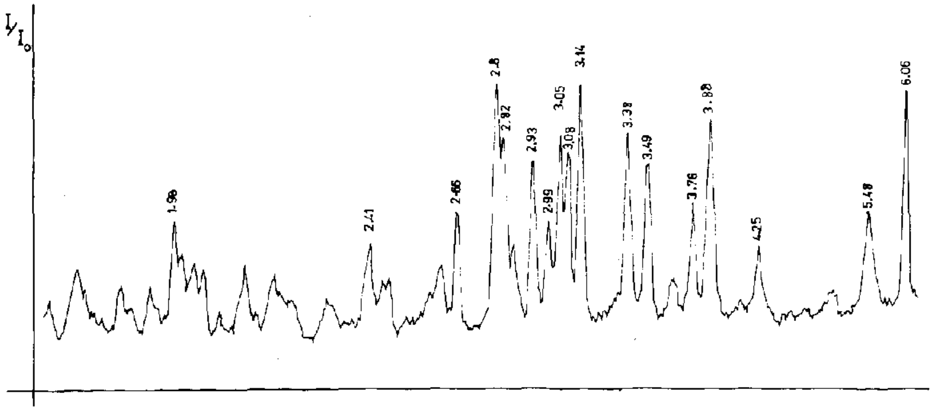

Fig. 6. X-ray diffraction pattern of (1:3) Tm_2O_3:$Na_2S_2O_8$ molar ratio mixture isolated at 480 °C.

TABLE 8

XRD pattern for the 1 : 3 sample of the Tm_2O_3–$K_2S_2O_8$ system sintered at 425 °C

d (Å)	2.75	2.79	3.26	4.21	7.19
I/I_0	45	35	100	32	50

Tm_2O_3–$K_2S_2O_8$ system

Figure 7 describes the TG and DTA curves for the 1 : 6, 1 : 3 and 1 : 2 ratios of $Tm_2O_3 : K_2S_2O_8$. Table 7 summarises the data estimated theoretically and measured experimentally. In the 1 : 6 sample, about 45 wt% of $K_2S_2O_7$ reacts with the appropriate amounts of the oxide. The melting endotherm of $K_2S_2O_7$ (usually appearing at 380 °C) disappears due to the

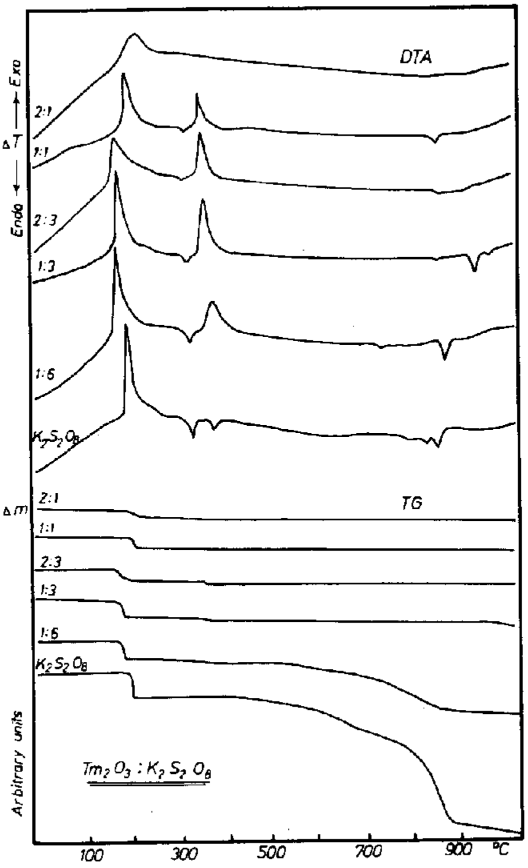

Fig. 7. TG and DTA curves of thulium(III) oxide–potassium persulfate mixtures.

exothermic crystallisation reaction between Tm_2O_3 and $K_2S_2O_7$ within this range of temperatures. The sharp edotherm at 850 °C represents the crystalline-phase change of the newly prepared double salt $K_2Tm_2(SO_4)_4$. The sharp endotherm at 920 °C represents the melting of the double salt. For the 1 : 3 sample, data estimated from the TG and DTA curves at 360 °C indicate that a maximum of 93 wt% of $K_2S_2O_7$ reacts with the appropriate amount of the oxide to form a new double salt according to the stoichiometric equation

$$Tm_2O_3 + 3K_2S_2O_7 \xrightarrow{360\,^{\circ}C} K_2Tm_2(SO_4)_4 + 2K_2SO_4$$

Samples sintered at 360 °C for analysis by X-ray diffractometry gave the XRD spectrum in Fig. 8 and Table 8, respectively. Igal [9] found that metals such as Yb, Er, Dy, etc., which are congeneric to thulium, form double salts such as $KL(SO_4)_2$ (where L = lanthanide) which are crystalline, having characteristic bright *d*-lines and which are isotructural with $K_2Tm_2(SO_4)_4$, which is thermally stable to the end of the heating program. This means that the potassium double salt is thermally more stable than the corresponding double salt of sodium. The oxide did not show any catalytic activity toward lowering the $T_i - T_f$ interval of the $K_2S_2O_8$–$K_2S_2O_7$ transformation. The melting endotherm of the salt can be seen at 920 °C for the 1 : 1 and 1 : 3 samples, but disappears in the 1 : 2 sample.

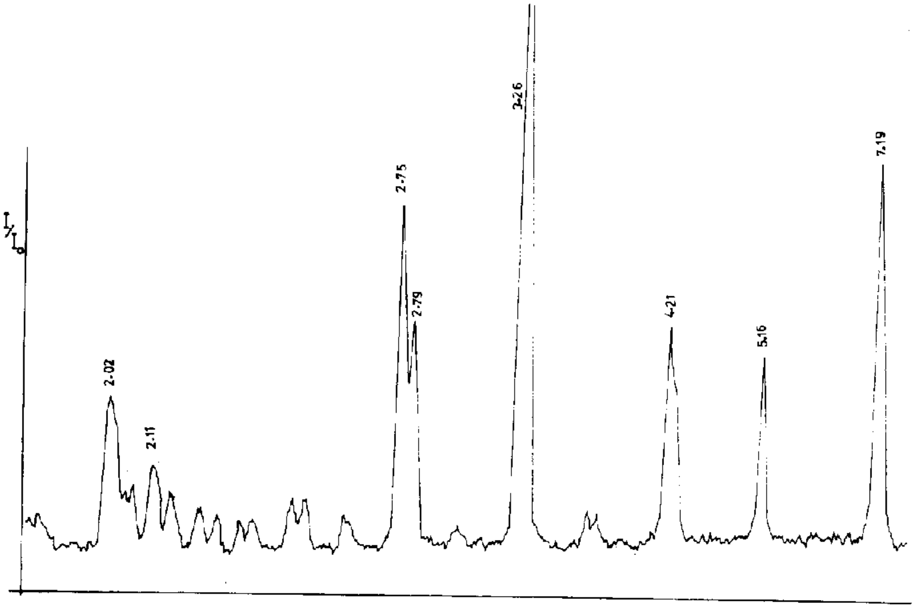

Fig. 8. X-ray diffraction pattern of (1 : 3) $Tm_2O_3 : K_2S_2O_8$ molar ratio mixture isolated at 425 °C.

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