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THERMAL AND X-RAY DIFFRACTION INVESTIGATIONS OF SOME LANTHANUM(III) AND NEODYMIUM(III) OXIDE–ALKALI PERSULFATE BINARY SYSTEMS

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ABSTRACT

Different molar ratios of La_2O_3 or $Nd_2O_3 : Na_2/K_2S_2O_8$ have been prepared, and the results of their TG and DTA investigations, under an atmosphere of static air, are reported. The effects of either La_2O_3 or Nd_2O_3 on the thermal decomposition of the persulfates from ambient to 1050°C, using a derivatograph, have been studied. It has been found that La_2O_3 lowers the initial decomposition temperatures of these alkali persulfates through catalytic activity. Nd_2O_3 shows little or no catalytic effect and therefore it acts as an insulator. Intermediate and final products are identified by X-ray diffraction analysis. The stoichiometric molar ratios of the solid state reactions are $1:3::R_2O_3:M_2S_2O_8$, (R = La or Nd, M = Na or K), which give double salts of formulae: $NaLa(SO_4)_2$, $KLa(SO_4)_2$, $NaNd(SO_4)_2$, and $KNd(SO_4)_2$. No sulfates or oxysulfates of lanthanum or neodymium have been identified.

INTRODUCTION

The effects of some oxides on the thermal decomposition of alkali persulfates were investigated [1–3]. It was found that lanthanides such as Gd_2O_3, Dy_2O_3, Sc_2O_3, CeO_2, and Tb_4O_7 [4–9] behave like *p*-type semiconductors, whereas La_2O_3 was an *n*-type semiconductor at high temperatures [11] due to its structure which has negative vacancies. La_2O_2 is less active than CeO_2, and exists as hexagonal crystals [11], while Nd_2O_3 proved to be the least conducting lanthanide. This paper gives the results of the thermal solid state reactions of La_2O_3 or Nd_2O_3 with $Na_2/K_2/S_2O_8$ as well as the thermal stability of the double salts formed, and accounts for the distinct behavior of these two rare earth sesquioxides towards either persulfates.

EXPERIMENTAL

La_2O_3 and Nd_2O_3 (99.98%) pure were supplied by Fluka AG Buches SG. All other chemicals, equipment, and techniques were as described previously [8].

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RESULTS AND DISCUSSION

The La_2O_3–$Na_2S_2O_8$ system

The curves shown in Fig. 1 indicate that the initial temperature for the thermal decomposition of persulfate is lowered by 10°C for all molar ratios except 2:3, which is lowered by 20°C (Table 1). The lowering is attributed to the catalytic

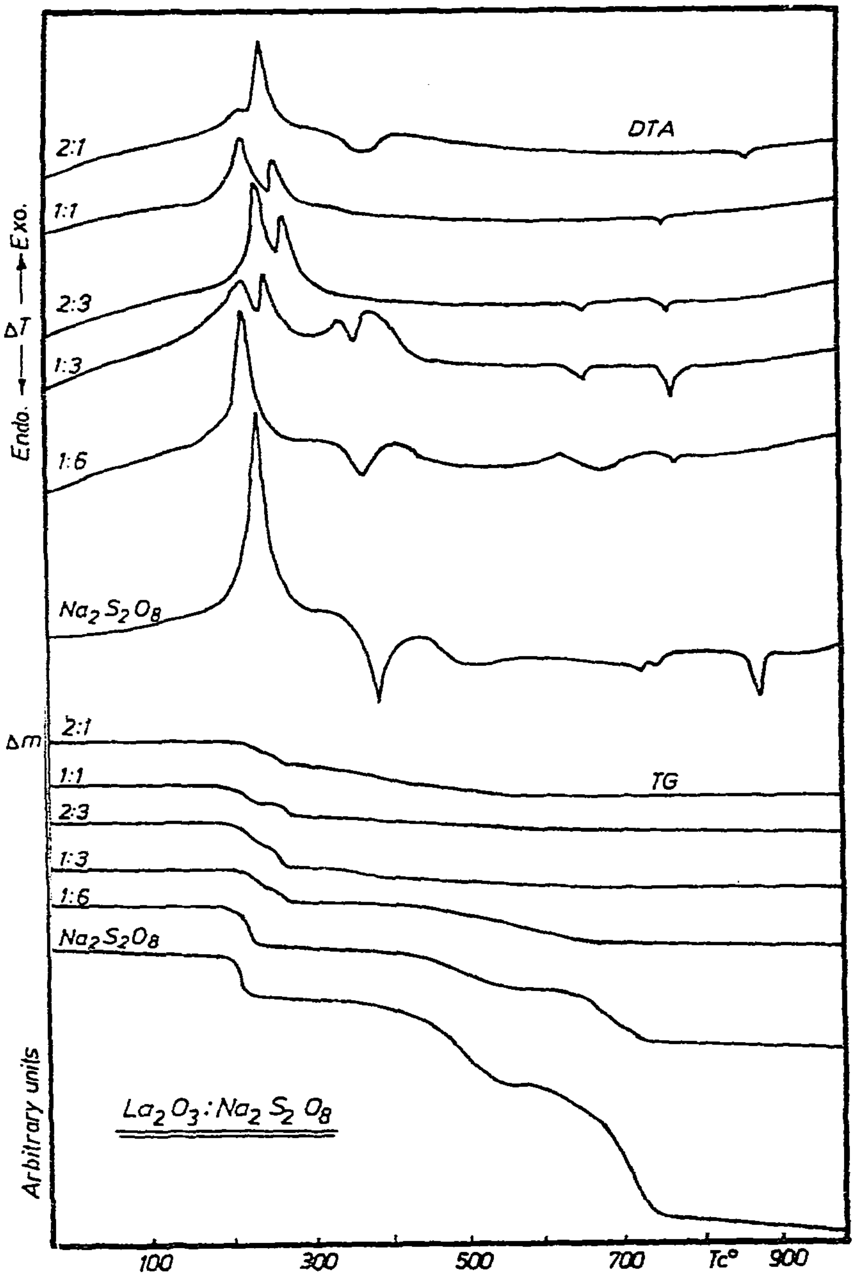

Fig. 1. TG and DTA curves of lanthanum(III) oxide–sodium persulfate mixtures.

TABLE 1

Preparation of various $La_2O_3:Na_2S_2O_8$ ratios and the mass of O_2 evolved

$La_2O_3:Na_2S_2O_8$	O_2 lost (mg)		Decompn. of $Na_2S_2O_8$ to $Na_2S_2O_7$	
	Theor.	Pract.	T_i (°C)	T_f (°C)
0:1	13.40	12.50	190	225
1:6	10.94	11.00	180	220
1:3	9.23	9.50	180	230
2:3	7.02	7.00	170	236
1:1	5.67	6.00	180	210
2:1	3.59	3.00	180	240

activity of the oxide. It is seen from the TG and DTA curves that the decomposition of persulfate occurs in two well-defined stages and especially in the 1:3, 1:1, and 2:3 ratios; this is due to the liberation of atomic oxygen. For the 1:6 ratio it takes place in one step, which is due to insufficient oxide in the system to initiate catalysis. The DTA curves show that the melting point of sodium pyrosulfate is lowered by 25°C because of the catalytic activity of La_2O_3. The reaction between the oxide and the sodium pyrosulfate takes place after the fusion (360–440°) of the latter, giving a double salt, $NaLa(SO_4)_2$. Calculation from the TG curves indicates that the stoichiometric reaction belongs to the ratio $1:3::La_2O_3:Na_2S_2O_8$

$$La_2O_3 + 3\,Na_2S_2O_7 \xrightarrow{\Delta} 2\,NaLa(SO_4)_2 + 2\,Na_2SO_4$$

during which 74% of pyrosulfate reacts with the oxide. The product $NaLa(SO_4)_2$ (Table 3) is thermally stable from 600°C to the end of the heating program. The endotherm at 650°C on the DTA curve refers to the phase change of the compound;

TABLE 2

Preparation of various $La_2O_3:K_2S_2O_8$ ratios and the mass of O_2 evolved

$La_2O_3:K_2S_2O_8$	O_2 lost (mg)		Decompn. of $K_2S_2O_8$ to $K_2S_2O_7$	
	Theor.	Pract.	T_i (°C)	T_f (°C)
0:1	11.89	11.80	180	200
1:6	9.86	10.00	170	210
1:3	8.44	8.00	180	210
2:3	6.56	6.00	180	235
1:1	5.36	5.00	190	220
2:1	3.47	3.00	170	200

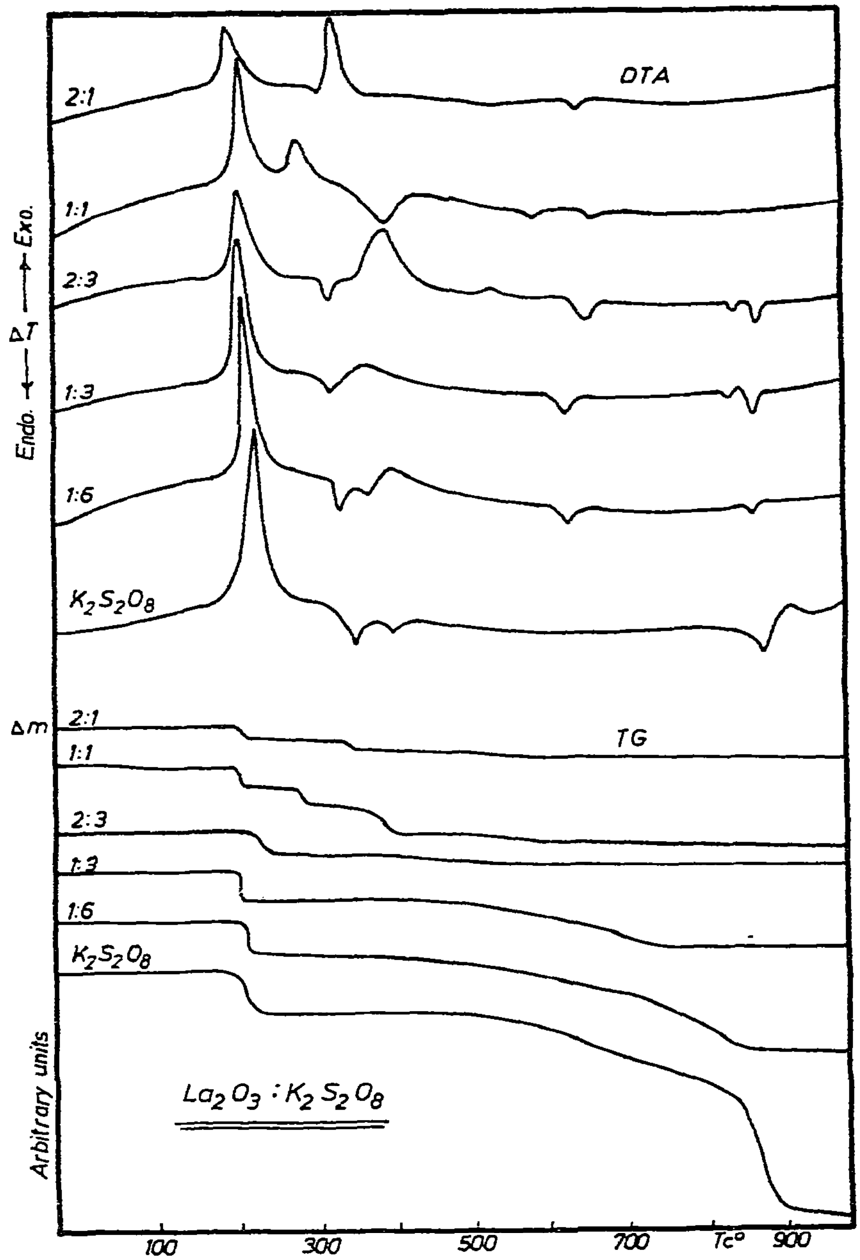

Fig. 2. TG and DTA curves of lanthanum(III) oxide–potassium persulfate mixtures.

TABLE 3

XRD patterns obtained for the 1 : 3 $La_2O_3:Na_2S_2O_8$ system sintered at 1000°C

d (Å)	4.97	4.74	3.53	3.29	3.18	3.06	2.87
I/I_0	66	29	30	100	46	43	52

the endotherm at 755°C is due to the melting point of impure sodium sulfate. The impurity is due to the presence of excess oxide and $NaLa(SO_4)_2$.

The La_2O_3–$K_2S_2O_8$ system

Figure 2 represents the TG and DTA curves for the $La_2O_3:K_2S_2O_8$ molar ratios 1:6, 1:3, 2:3, 1:1, 2:1. The DTA curves show that the decomposition temperature of potassium persulfate is lowered by 10°C for the ratios 1:6 and 2:1 (Table 2) due to the catalytic activity of the oxide, and due to the dilution effect [12] for the 1:1 ratio [12,13]. Calculation showed that $1:3::La_2O_3:K_2S_2O_8$ is the stoichiometric ratio for the reaction

$$La_2O_3 + 3\ K_2S_2O_7 \overset{\triangle}{\rightarrow} 2\ KLa(SO_4)_2 + 2\ K_2SO_4$$

which occurs immediately after β- to α-phase transition of potassium pyrosulfate at 320°C.

The optimum percent for pyrosulfate reacting with the oxide is found to be 67%. The endotherm at 600–640°C indicates that the new compound, $KLa(SO_4)_2$ (Table 4), undergoes a phase change. The two endotherms between 820 and 860°C refer to other phase changes of the compound (Table 4). No melting of the compound has been observed even at the ceiling temperature of the heating program.

The XRD data registered for this compound do not match with those available in ASTM cards and JCPDS current files. The deduction that the formula ought to be as such is based on TG calculations as well as similarities of reaction conditions established for the formation of the $NaLa(SO_4)_2$.

In conclusion, the thermal treatment of alkali persulfate with La_2O_3 can be regarded as an alternative route for the preparation of the double salt by solid state second order reactions, other than those reported by Degtiarev et al. [13] using reactions in solutions.

The Nd_2O_3–$Na_2S_2O_8$ system

Figure 3 illustrates the non-isothermal behavior of the different $Nd_2O_3:Na_2S_2O_8$ molar ratios. It is seen from Table 5 that the decomposition of $Na_2S_2O_8$ occurs at 200°C for the 2:3 and 2:1 molar ratios (compared with 190°C for the pure persulfate), the range T_i–T_f remains constant (40°C) in all other ratios. The DTA curves indicate that the reaction between Nd_2O_3 and $Na_2S_2O_8$ takes place at the

TABLE 4

XRD patterns for the 1:3 $La_2O_3:K_2S_2O_8$ system sintered at 460 and 680°C

d (Å)	4.30	3.13	2.72	2.53	2.15	2.06	1.92
I/I_0	27	100	59	25	30	30	27

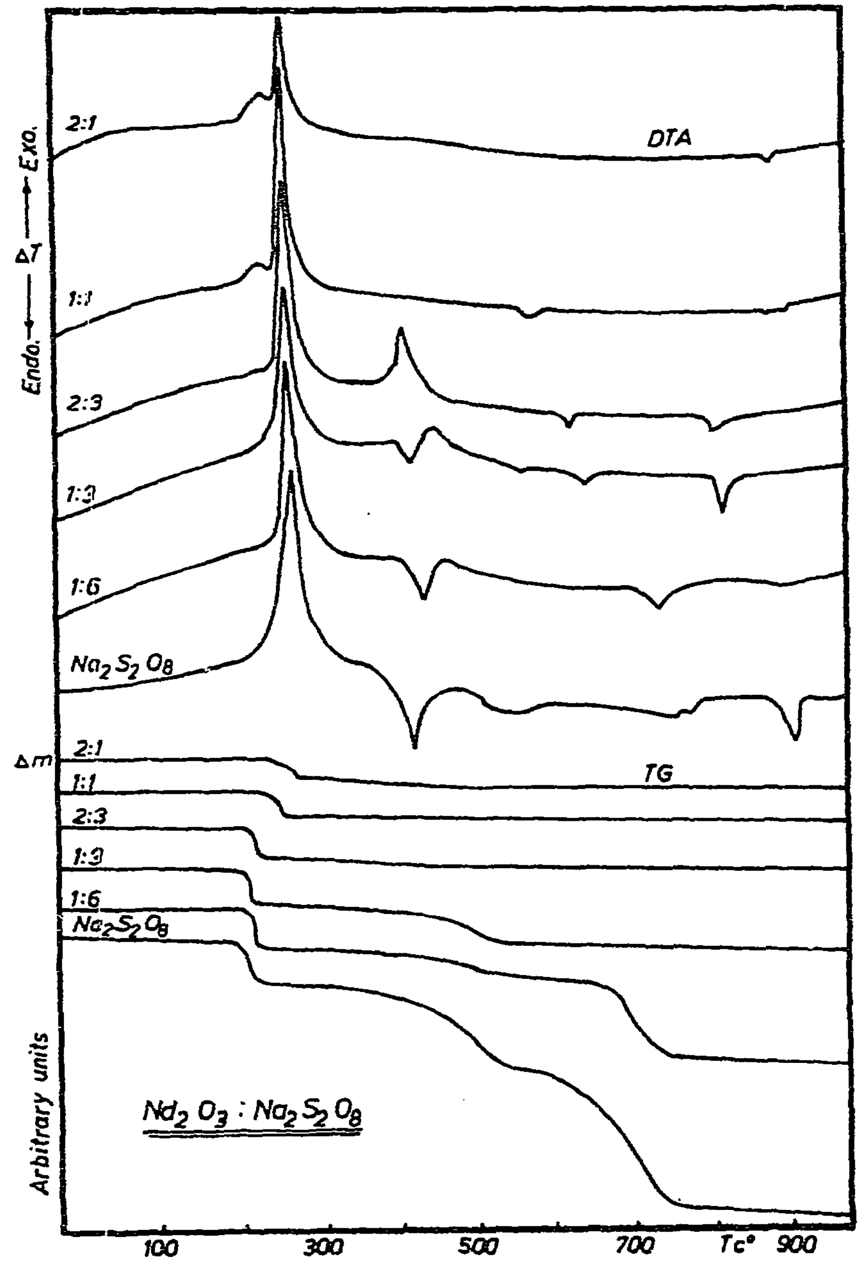

Fig. 3. TG and DTA curves of neodymium(III) oxide–sodium persulfate mixtures.

fusion temperature of the latter, at about 380°C for the ratios 1:6, 1:3, and 2:3. In the case of 1:1 and 2:1 ratios, the DTA curves show thermal neutrality (260–1000°C), due to reaction of excess oxide with pyrosulfate. The compound $NaNd(SO_4)_2$ has been identified as a product of the reaction (Table 6). Calculation from the TG curves indicates that the $1:3::Nd_2O_3:Na_2S_2O_8$ is the stoichiometric ratio and the reaction is

$$Nd_2O_3 + 3\,Na_2S_2O_7 \xrightarrow{\Delta} 2\,NaNd(SO_4)_2 + 2\,Na_2SO_4$$

TABLE 5

The preparation of various $Nd_2O_3:Na_2S_2O_8$ ratios and the effect of the applied heating program

$Nd_2O_3:Na_2S_2O_8$	O_2 lost (mg)		Decompn. of $Na_2S_2O_8$	
	Theor.	Pract.	T_i (°C)	T_f (°C)
0:1	13.40	12.50	190	225
1:6	11.20	11.20	190	230
1:3	9.62	9.20	190	230
2:3	7.48	7.20	200	240
1:1	5.56	6.00	190	230
2:1	3.51	4.00	200	240

TABLE 6

XRD pattern for 1:3::$Nd_2O_3:Na_2S_2O_8$ binary system sintered at 670°C

d (Å)	3.45	2.89	3.41	2.65	5.30	2.82	6.27	1.84
I/I_0	100	92	88	85	77	54	46	23

TABLE 7

d-Spacing and relative intensities of the peaks of some neodymium compounds

	$(NdO)_2SO_4$			$Nd_2(SO_4)_3$			Nd_2O_2S		
d (Å)	3.02	1.77	2.93	3.02	1.71	2.17	3.06	1.97	3.41
I/I_0	100	80	60	100	80	60	100	40	30

in which 80% of the pyrosulfate reacts with the oxide. Samples sintered between 670 and 1000°C for 1:6 and 2:1 ratios do not reveal similar XRD patterns or any other patterns that prove the formation of sulfate or oxysulfate (Table 7). The TG and DTA curves show weight losses of 8 mg for the ratios 1:6 and 1:3 due to the decomposition of excess pyrosulfates. The endotherm at 750–780°C refers to the melting point of impure sodium sulfate, $NaNd(SO_4)_2$. The product is thermally stable over the range 510–1000°C and this is deduced from the TG curve of the stoichiometric molar ratio.

The Nd_2O_3–$K_2S_2O_8$ system

The DTA and TG curves are shown in Fig. 4 where the potassium persulfate decomposes in one stage over the temperature range 180–200°C for the ratios 1:6

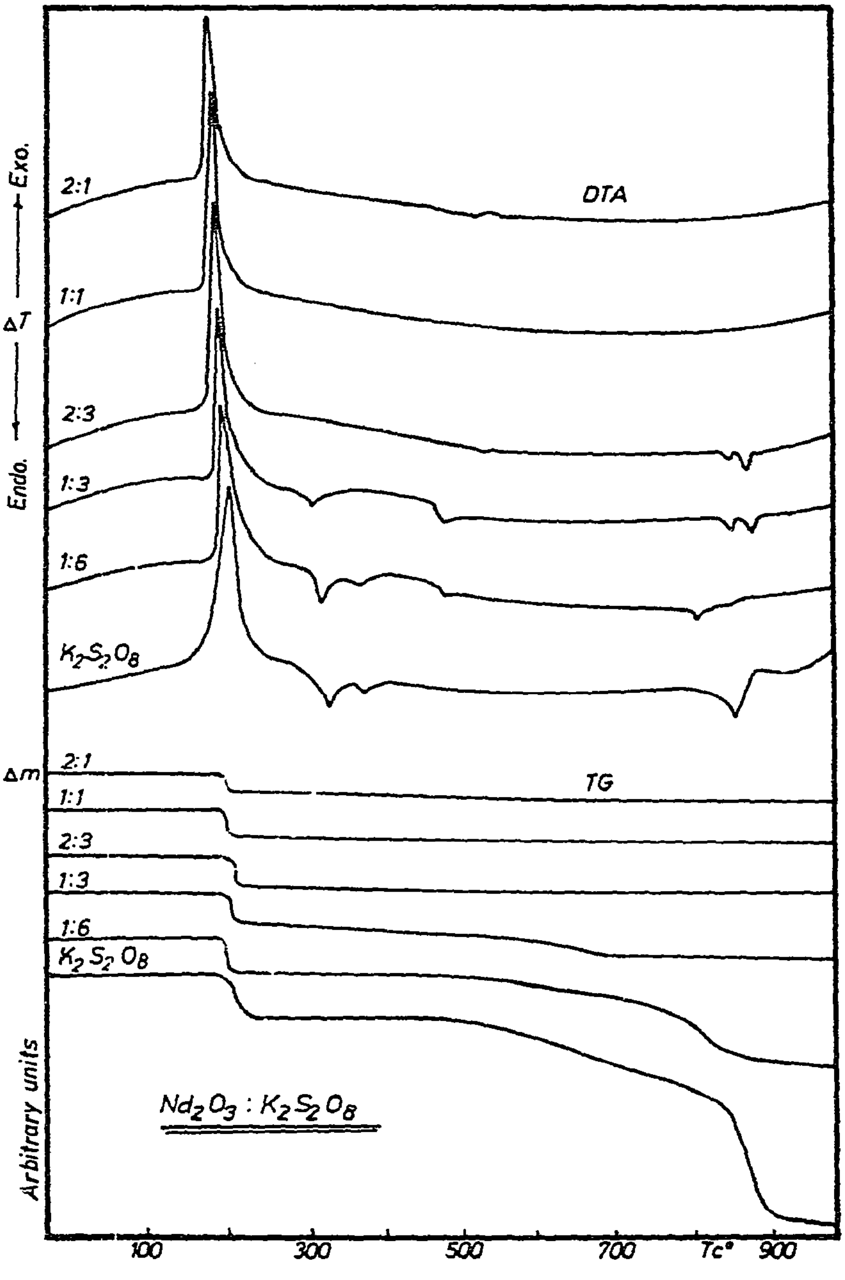

Fig. 4. TG and DTA curves of neodymium(III) oxide–potassium persulfate mixtures.

and 1 : 3. This means that the oxide plays no catalytic role in the thermal decomposition of the persulfate, while it delays its initial temperature by 10°C for the ratios 2 : 1, 1 : 1, 2 : 1, due to the dilution effect of the oxide (Table 8). The reaction for the stoichiometric ratio 1 : 3 : : $Nd_2O_3 : K_2S_2O_8$ can be represented by the equation

$$Nd_2O_3 + 3\,K_2S_2O_7 \xrightarrow{\Delta} 2\,KNd(SO_4)_2 + 2\,K_2SO_4$$

The reaction occurs at 310–340°C, that is at the β- to α-phase transition of

TABLE 8

The preparation of various $Nd_2O_3:K_2S_2O_8$ ratios and the effect of the applied heating program

$Nd_2O_3:K_2S_2O_8$	O_2 lost (mg)		Decompn. of $K_2S_2O_8$	
	Theor.	Pract.	T_i (°C)	T_f (°C)
0:1	11.84	11.80	180	200
1:6	9.80	9.50	180	200
1:3	8.36	8.20	180	200
2:3	6.47	8.00	190	210
1:1	5.27	6.00	195	215
2:1	3.40	5.00	190	210

TABLE 9

XRD pattern for the 1:3::$Nd_2O_3:K_2S_2O_8$ binary system sintered at 1000°C

d (Å)	3.19	3.00	5.94	2.76	3.12	2.89	1.80
I/I_0	100	66	60	37	27	25	20

$K_2S_2O_7$. In the ratios 2:3, 1:1, and 2:1, thermal neutrality is observed. The endotherm at 480°C on the DTA curve belongs to the decomposition of unreacted pyrosulfate. The two endotherms between 820 and 860°C belong to the phase change of the $KNd(SO_4)_2$ formed; the first large one belongs to the double salt alone, whereas the second one is due to formation of a eutectic mixture, $KNd(SO_4)_2 + K_2SO_4$. The optimum percentage of reacting pyrosulfate is 78% for the 1:3 stoichiometric ratio. Samples sintered at 540, 835, and 1000°C, when analyzed by X-ray diffraction (Table 9), gave data that could not be matched with those available in the ASTM cards or JCPDS current files. Nevertheless some authors hinted to the preparation of such compounds via reactions in solutions.

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