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THERMOANALYTICAL BEHAVIOUR OF SOME NIOBIUM(V) AND TANTALUM(V) OXIDE—ALKALI PERSULFATE BINARY SYSTEMS

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ABSTRACT

Four binary systems, R_2O_5—$M_2S_2O_8$, where R is Ta or Nb and M is Na or K, have been studied derivatographically. Three new compounds, $Ta_2O_3(SO_4)_2$, $Nb_2O_3(SO_4)_2$ and $K_{10}Ta_4O_5(SO_4)_{10}$, have been prepared by solid state reactions. Other compounds, e.g. Na_5TaO_5, β-$Nb_2O_4SO_4$, $Na_2Ta_4O_{11}$, $Na_2Nb_8O_{21}$ and $K_2Nb_8O_{21}$, have also been identified during the course of the investigations.

INTRODUCTION

The thermal decomposition of alkali persulfate—metal oxide binary systems was studied derivatographically [1—3]. A crystallographic study by Iyer and Smith [4] was carried out to study newly prepared compounds from thermal double oxide reactions such as Ta_2O_5, Nb_2O_5 and Pa_2O_5 with Na_2O, K_2O and Rb_2O. Maslennikova and Chernyak [5] prepared a set of different hydrated tantalum oxide sulfates, $Ta_2O_3(SO_4)_2 \cdot nH_2O$, by the action of different concentrations of H_2SO_4 on Ta_2O_5 and used DTA and XRD to identify the various products.

In this paper, we describe the results obtained from the thermal studies of four binary systems R_2O_5—$M_2S_2O_8$, where R is Ta or Nb and M is Na or K based on data obtained from TG, DTG, DTA and XRD from the point of view of the chemical reactions, the catalytic effects, the thermal stabilities of the compounds formed and eutectic formation.

EXPERIMENTAL

Mixtures of R_2O_5 and $M_2S_2O_8$ were prepared in the molar ratios 0 : 1, 1 : 5, 1 : 2, 4 : 5, 5 : 5, 8 : 5 and 10 : 5 for each binary system and the TG, DTG and DTA curves were obtained as described previously [6,7]. For the sake of brevity, the DTG curves are not included in this paper. XRD patterns for the intermediate and final products were obtained as previously described [6,7].

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RESULTS AND DISCUSSION

The Ta_2O_5—$Na_2S_2O_8$ system

The DTA curves (Fig. 1) show exothermic peaks at 490° C which represent the reaction between the thermally produced $Na_2S_2O_7$ and Ta_2O_5. The stoichiometric molar ratio is 1 : 2. Samples heated near this temperature have XRD patterns characterized by sharp lines at 7.00, 5.02 and 3.19 Å, which have been found to have no counterparts in either the ASTM cards or JCPDS current files. To identify the compounds formed, chemical methods would be rather misleading owing to the presence of other products, and the problem was therefore tackled from another direction, at least tentatively. It is

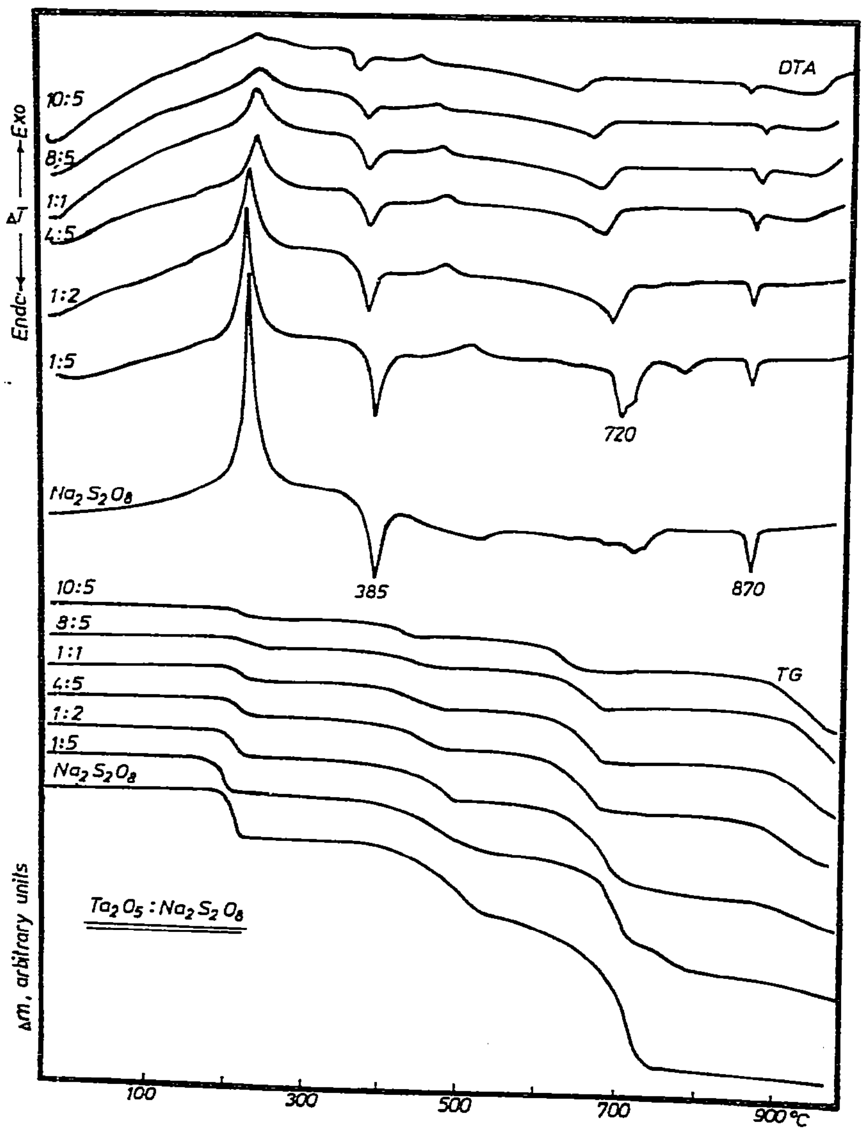

Fig. 1. TG and DTA curves of tantalum(V) oxide—sodium persulfate mixtures.

known that Ta_2O_5 tends to replace one or more of its oxygens by sulfate groups on reacting with sulfate-rich compounds such as pyrosulfates [5], and hence it is probable that anhydrous $Ta_2O_3(SO_4)_2$ is formed by the stoichiometric reaction

$$Ta_2O_5 + 2\,Na_2S_2O_7 \xrightarrow{\Delta} Ta_2O_3(SO_4)_2 + 2\,Na_2SO_4$$

Moreover, the presence of the *d*-lines of Na_2SO_4 (Fig. 2) is indicative of the above reaction. Thereafter, samples with a molar ratio of 1 : 2 heated to about 700°C gave *d*-lines that belong to Ta_2O_5 alone, which means that the $Ta_2O_3(SO_4)_2$ is completely decomposed according to

$$Ta_2O_3(SO_4)_2 \xrightarrow{\Delta} Ta_2O_5 + 2\,SO_3$$

For the 1 : 5 ratio, where the amount of Ta_2O_5 is comparatively small, samples heated between 720 and 760°C produced XRD patterns with bright *d*-lines at 3.11, 2.93 and 2.44 Å which are typical of sodium tantalate, Na_5TaO_5.

$$Ta_2O_5 + 5\,Na_2SO_4 \xrightarrow{\Delta} 2\,Na_5TaO_5 + 5\,SO_3$$

The tantalate immediately decomposes between 780 and 820°C according to

$$2\,Na_5TaO_5 \xrightarrow{\Delta} Ta_2O_5 + 5\,Na_2O$$

Further, the appearance of the melting point endotherms of pure Na_2SO_4 at 875°C (Fig. 1) does not reveal the presence of eutectic mixtures con-

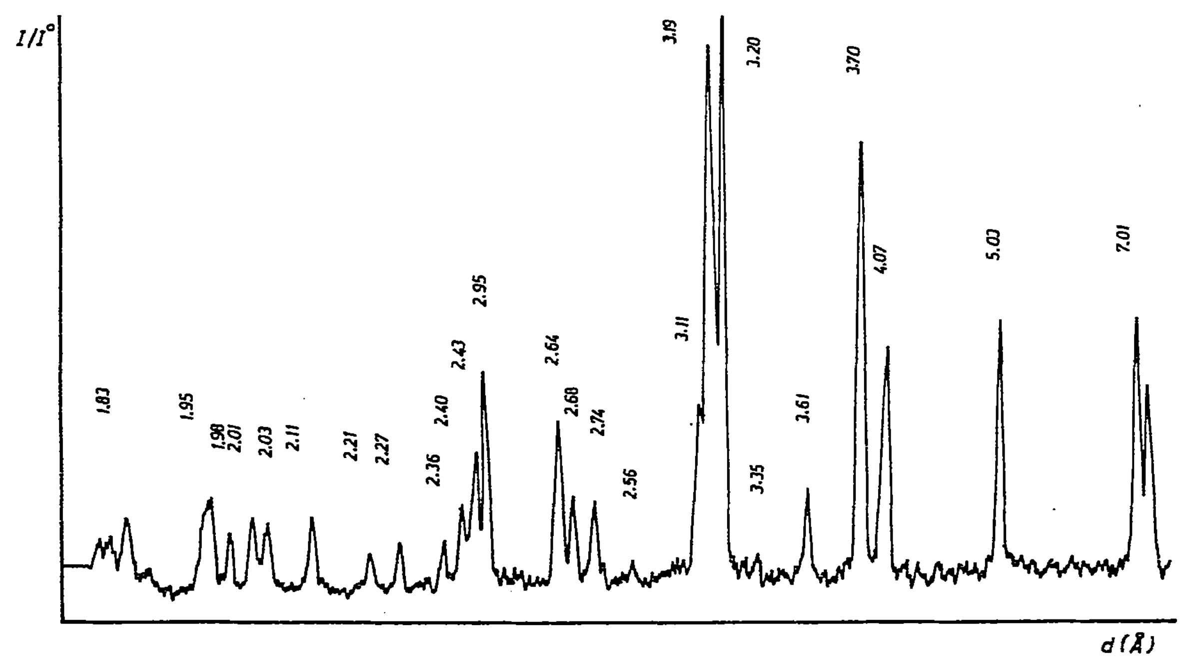

Fig. 2. X-Ray diffraction pattern 1 : 2 molar Ta_2O_5 : $Na_2S_2O_8$ mixture isolated at 520°C.

sisting of $Na_2SO_4 + Ta_2O_5$ (major components) and Na_2O (as a minor component). Afterwards, the two major components react endothermically between 875 and 990°C. The endothermic peak reaches a maximum for a molar ratio of 10 : 5, where samples heated at 1020°C gave bright *d*-lines characteristic of sodium tantalum oxide, $Na_2Ta_4O_{11}$.

$$2\,Ta_2O_5 + Na_2SO_4 \xrightarrow{\Delta} Na_2Ta_4O_{11} + SO_3$$

Alternatively, the compound is written as $Na_2O \cdot 2Ta_2O_5$ and named as sodium ditantalate.

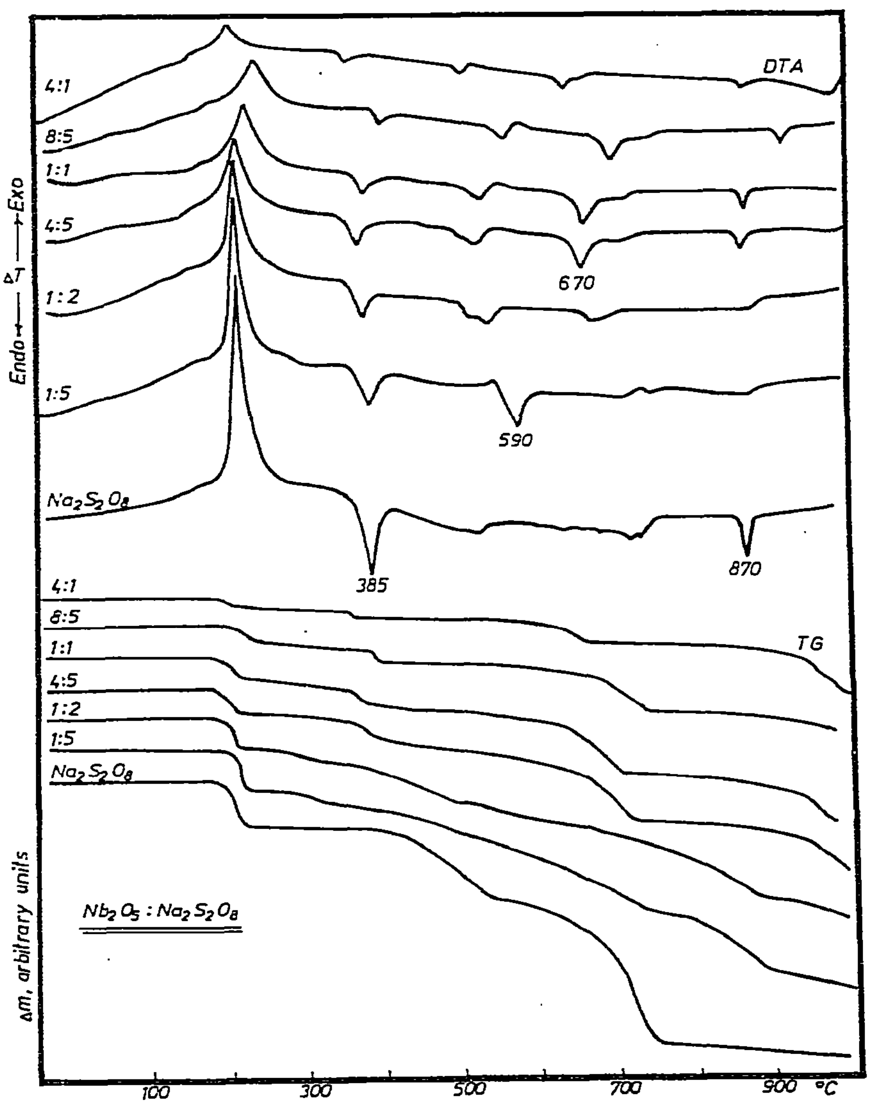

Fig. 3. TG and DTA curves of niobium(V) oxide—sodium persulfate mixtures.

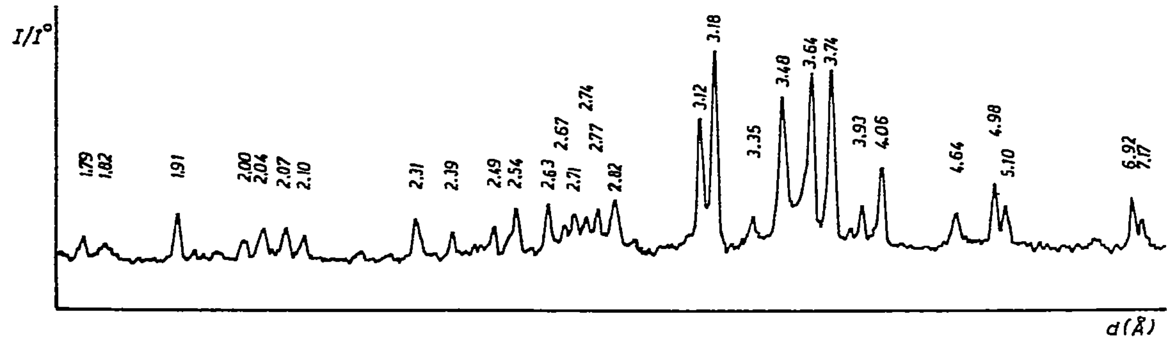

Fig. 4. X-Ray diffraction pattern of 1 : 1 molar Nb_2O_5 : $Na_2S_2O_8$ mixture isolated at 470°C.

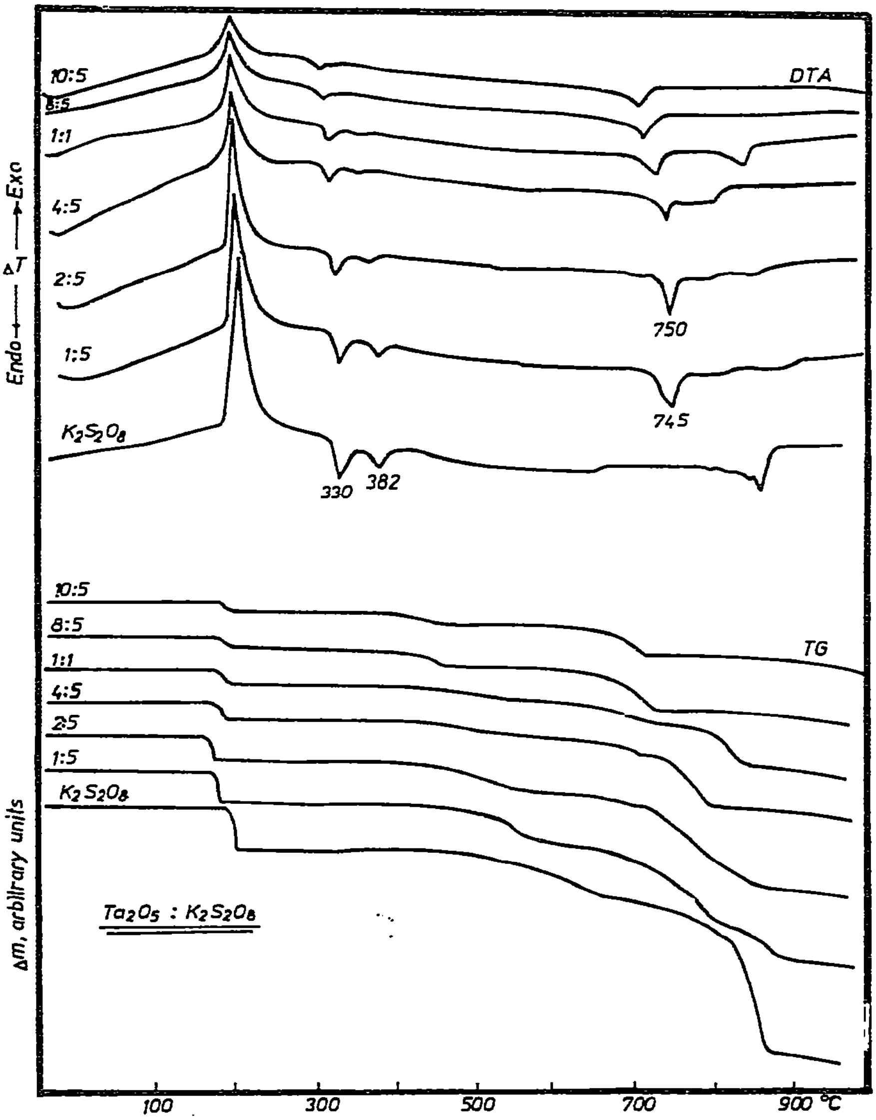

Fig. 5. TG and DTA curves of tantalum(V) oxide—potassium persulfate mixtures.

The Nb_2O_5—$Na_2S_2O_8$ system

Here, the stoichiometric molar ratio (Fig. 3) is 1 : 2, XRD patterns of samples heated at 470°C for this ratio (Fig. 4) could not be matched with data available in ASTM cards and JCPDS current files. However, the main lines in Figs. 2 and 4, are almost identical, probably due to the similarity between the ionic radii of niobium and tantalum leading to the formation of isostructural compounds [9]. Thus the formula $Nb_2O_3(SO_4)_2$ could be proposed to correspond to the *d*-lines obtained according to the stoichiometric equation

$$Nb_2O_5 + 2\,Na_2S_2O_7 \xrightarrow{\Delta} Nb_2O_3(SO_4)_2 + 2\,Na_2SO_4$$

The compound (Fig. 3) melts at 550°C. Samples heated below the endotherm at 550°C were in powder form, whilst after this endotherm, the samples were isolated as solidified melts. Further, $Nb_2O_3(SO_4)_2$ starts decomposition at 670°C according to

$$Nb_2O_3(SO_4)_2 \xrightarrow{\Delta} Nb_2O_5 + 2\,SO_3$$

and the decomposition products were confirmed by X-ray diffractometry. Moreover, it has been found that Nb_2O_5 reacts with molten Na_2SO_4 in a similar manner to Ta_2O_5, which is shown by the endothermic DTA curves (Fig. 3), the reaction reaching a maximum at the 4 : 1 ratio between 870 and 1020°C. XRD patterns of samples heated at 1020°C indicate the presence of sodium tetraniobate, $Na_2Nb_8O_{21}$.

$$4\,Nb_2O_5 + Na_2SO_4 \xrightarrow{\Delta} Na_2Nb_8O_{21} + SO_3$$

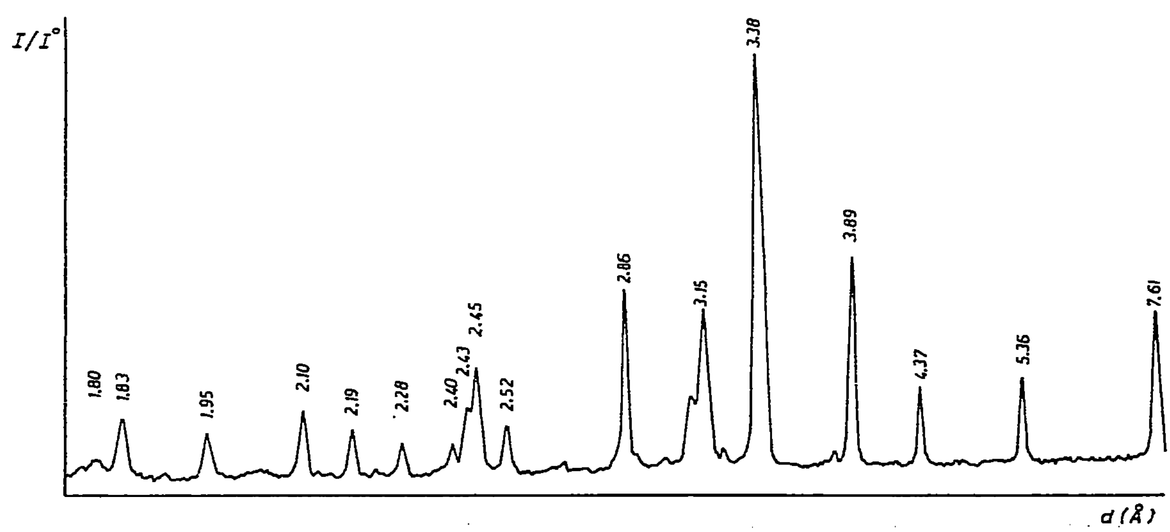

Fig. 6. X-Ray diffraction pattern of 2 : 5 molar Ta_2O_5 : $K_2S_2O_8$ mixture isolated at 740°C.

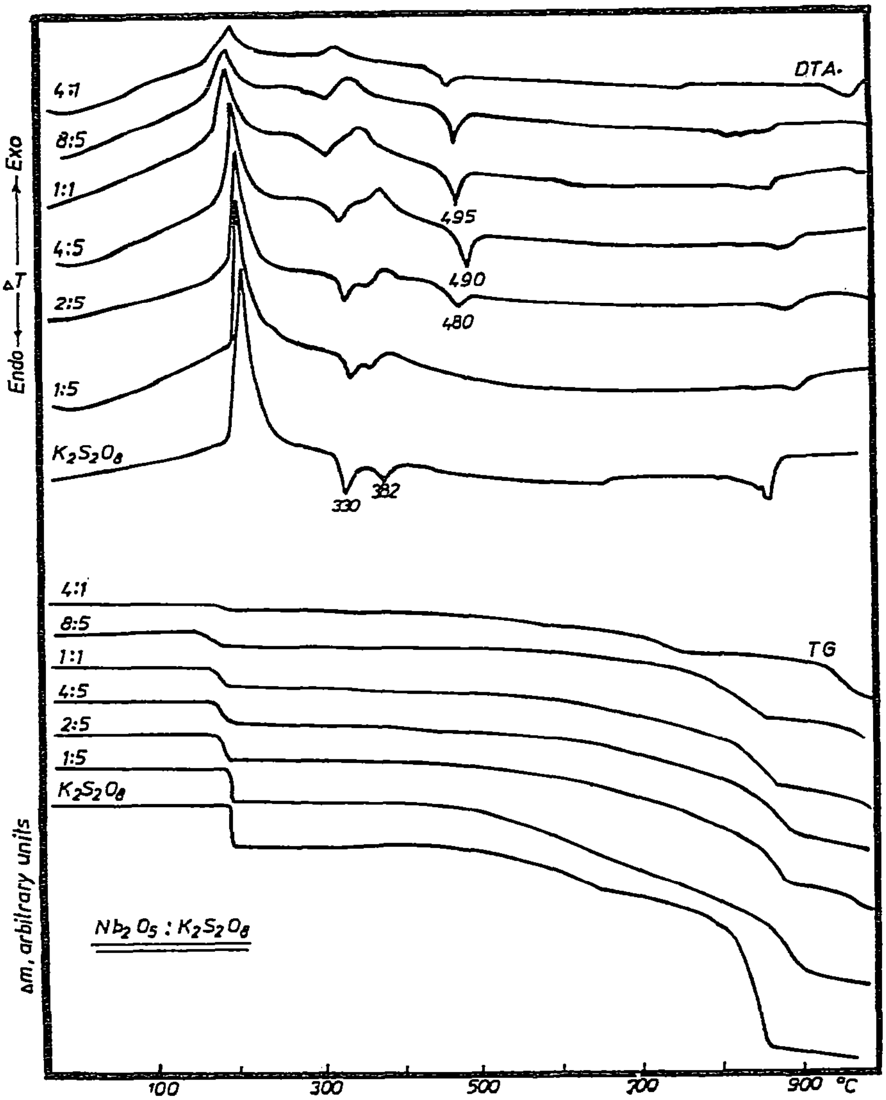

Fig. 7. TG and DTA curves of niobium(V) oxide—potassium persulfate mixtures.

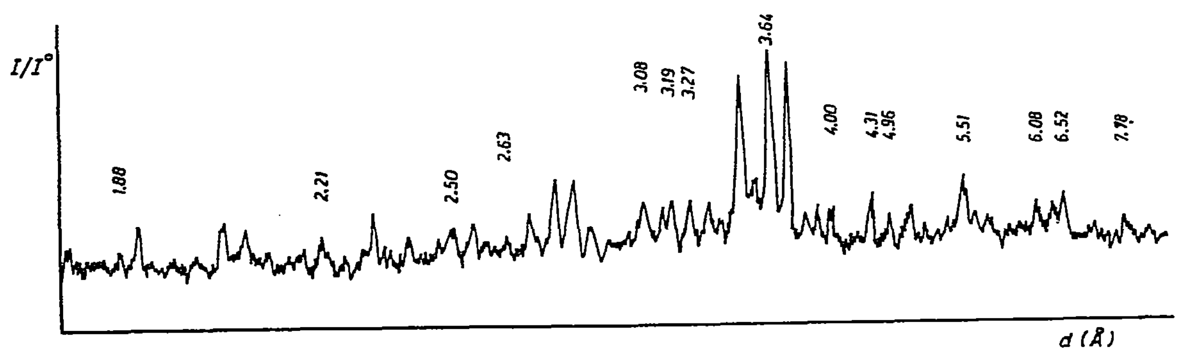

Fig. 8. X-Ray diffraction pattern of 8 : 5 molar Nb_2O_5 : $K_2S_2O_8$ mixture isolated at 450°C.

TABLE 1

Characterization of some compounds of Ta(V) and Nb(V) obtained as a result of investigations of the four systems

Compound formed	Stoichiometric mole ratio	Molecular formula	M.p. (°C)	Formation temp. (°C)	Thermal stability range (°C)	XRD sharp lines (Å)
Anhydrous tantalum oxide disulfate	1 : 2 $Ta_2O_5 : Na_2S_2O_7$	$Ta_2O_3(SO_4)_2$		500	500–700	3.19, 7.0, 5.02
Potassium tantalum oxide sulfate	2 : 5 $Ta_2O_5 : K_2S_2O_7$	$K_{10}Ta_4O_5(SO_4)_{10}$	750	730	730–780	3.38, 2.86, 7.60
Anhydrous niobium oxide disulfate	1 : 2 $Nb_2O_5 : Na_2S_2O_7$	$Nb_2O_3(SO_4)_2$	550	300–400	300–670	3.18, 6.92, 4.98

The Ta_2O_5—$K_2S_2O_8$ system

X-Ray analysis for the 2 : 5 molar ratio samples heated at 750°C (Fig. 5) gives an XRD pattern (Fig. 6) which is isostructural with the known compound potassium niobium(V) oxysulfate, $K_{10}Nb_4O_5(SO_4)_{10}$. Because of the similarity of the two ions [8], Ta^{5+} and Nb^{5+}, it is expected that a compound of similar (isostructural) geometrical character, e.g. $K_{10}Ta_4O_5(SO_4)_{10}$, could be formed in a stoichiometric reaction of the type

$$2\,Ta_2O_5 + 5\,K_2S_2O_7 \xrightarrow{\Delta} K_{10}Ta_4O_5(SO_4)_{10}$$

Experiments have shown that the melting point of this polymer is 750°C, above which it decomposes (Fig. 5). This is confirmed by the sharp *d*-lines for samples heated to 900°C which show the presence of Nb_2O_5 and little K_2SO_4

$$K_{10}Ta_4O_5(SO_4)_{10} \xrightarrow{\Delta} 2\,Ta_2O_5 + 5\,K_2SO_4 + 5\,SO_3$$

The Nb_2O_5—$K_2S_2O_8$ system

Niobium(V) oxide reacts with the thermally produced $K_2S_2O_7$ (Fig. 7) and the reaction is amply evident for the molar ratios 4 : 5, 1 : 1, and 8 : 5. Samples for the 8 : 5 molar ratio heated at 450°C gave noisy X-ray diffraction spectra, (Fig. 8) that belong to β-$Nb_2O_4SO_4$. This compound was predicted by Goroshchenko and Andreeva [9]. The TG and DTA curves indicate that the 1 : 1 ratio is the stoichiometric one, i.e.

$$Nb_2O_5 + K_2S_2O_7 \xrightarrow{\Delta} Nb_2O_4SO_4 + K_2SO_4$$

Unlike Ta_2O_5, Nb_2O_5 also reacts with K_2SO_4 in a molar ratio of 4 : 1, between 910 and 1020°C forming potassium tetraniobate, Nb_8O_{21}, according to the stoichiometric reaction

$$4\,Nb_2O_5 + K_2SO_4 \xrightarrow{\Delta} K_2Nb_8O_{21} + SO_3$$

Data collected from the thermoanalytical investigations for the various binary systems are summarized in Table 1. One of the distinctive features of the table is that Nb_2O_5 forms $Na_2Nb_8O_{21}$, whereas Ta_2O_5 forms $Na_2Ta_4O_{11}$. Also, Nb_2O_5 reacts at high temperatures with K_2SO_4, whereas Ta_2O_5 does not.

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