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A STUDY OF THERMAL BEHAVIOUR OF SODIUM AND ZINC DIPHOSPHATES

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ABSTRACT

Phase transitions in $Na_4P_2O_7$, $Zn_2P_2O_7$ and $Na_2ZnP_2O_7$ in the temperature range 20–800°C have been studied by X-ray diffraction, high-temperature microscopy, electrical conductivity, differential thermal analysis (DTA) and differential scanning calorimetry (DSC). $Na_4P_2O_7$ has five reversible polymorphic transformations at 402.7, 512.0, 518.3, 542.7 and 554.4°C, respectively. $Zn_2P_2O_7$ undergoes one reversible polymorphic transformation at 128.2°C. In the studied temperature range $Na_2ZnP_2O_7$ does not exhibit polymorphism and melts congruently at 779.0°C. The enthalpies of phase transitions have been determined by DSC method.

INTRODUCTION

Phase transitions in $Na_4P_2O_7$, $Zn_2P_2O_7$, $Na_2ZnP_2O_7$ diphosphates cannot be regarded as comprehensively studied. In $Na_4P_2O_7$, besides a transformation within a large endothermal effect at about 400°C, a number of authors [1–9] have noted from one to four transitions in the temperature range of 500–560°C. $Zn_2P_2O_7$ has a reversible polymorphic transformation at 132 ± 8°C [10] but a transformation is also assumed to take place at about 150°C [11], and from the data [12] two endothermal effects are taking place at 344 and 440°C. Also contradictory are the data concerning the melting temperature of $Na_2ZnP_2O_7$ [8,12,13].

EXPERIMENTAL

Sample preparation

$Na_4P_2O_7$ was prepared from a commercial sample $Na_4P_2O_7 \cdot 10H_2O$ (analytically pure) by dehydrating it at 200°C (3 h) and calcining at 600°C (1 h), a part of the product was melted.

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$Zn_2P_2O_7$ was obtained in accordance with the procedure [14] by calcining (at 600°C) NH_4ZnPO_4, precipitating from a solution of ZnO (high purity) in weak HCl with the help of $(NH_4)_2HPO_4$ (analytically pure) solution.

$Na_2ZnP_2O_7$ was synthesized by solid-state reactions between ZnO (high purity) and $NaH_2PO_4 \cdot 2H_2O$ (analytically pure) at 700°C for 35 h.

INSTRUMENTATION

Thermal behaviour of $Na_4P_2O_7$, $Zn_2P_2O_7$, $Na_2ZnP_2O_7$ has been studied by differential thermal analysis (OD-102 derivatograph), high temperature microscopy (NVO-50 microscope, Karl Zeiss Jena), X-ray diffraction (DRON-1.5 diffractometer, Cu$K\alpha$ radiation). The electrical conductivity was measured with an R-568 AC bridge at a frequency of 80 kHz with platinum electrodes under load on the pellets of remelted samples in air. Taking account of the physical parameters of the sample, the reproducibility of the conductivity was 12–15%.

Temperature and enthalpies of phase transitions have been determined with a differential scanning calorimeter DSC III (Setaram) fitted with a Hewlett-Packard 9825 A computer. DSC recordings were made in platinum cells in a flowing argon atmosphere at scanning rates of 1, 5 or 10° min^{-1} and sensitivity ranges of 15 and 35 mJ s^{-1} for samples of mass from 0.025 to 0.250 g. Transition temperatures T_p were defined from the maxima of DSC peaks. The precision of the temperature determination was ± 0.1°C, and the temperature scale uncertainty, ± 1.0°C. Transition enthalpies $\Delta_{tr}H$ have been determined with graphical integration by the Setaram computer program for peaks in DSC curves recorded with a scanning rate of 1° min^{-1}. The enthalpies of transition did not vary by more than ± 4% from run to run on any particular substance. The mean deviations in the T_p and $\Delta_{tr}H$ values are shown in the Results and Discussion section for the various diphosphates.

RESULTS AND DISCUSSION

$Na_4P_2O_7$

From our DTA and high-temperature microscopy data $Na_4P_2O_7$ melts congruently at 988 ± 5°C (the most reliable literature data are 985, 995 and 998°C [1,4,8]).

In all the DSC curves for both the remelted and the calcined unmelted samples a sharp endothermal peak manifests itself at about 400°C and, depending on recording resolution, from four to seven endothermal effects of different intensities take place in the range 500–560°C (Fig. 1a–d; Table 1). In some of the curves an extended endothermal effect may also be noted

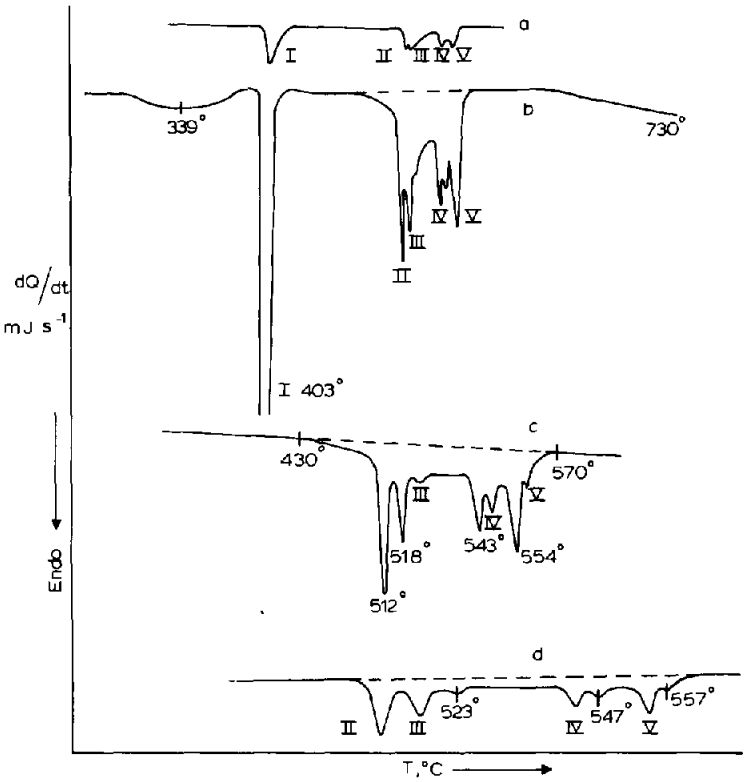

Fig. 1. DSC heating curves of $Na_4P_2O_7$. (a) Unmelted sample. Mass: 0.0255 g; scanning rate: 5° min^{-1}; sensitivity range: 35 mJ s^{-1}; paper rate: 5 mm min^{-1}. (b) Melted sample. Mass: 0.0788 g; scanning rate: 5° min^{-1}; sensitivity range: 15 mJ s^{-1}; paper rate: 5 mm min^{-1}. (c) Melted sample. Mass: 0.2231 g; scanning rate: 1° min^{-1}; sensitivity range: 15 mJ s^{-1}; paper rate: 2.5 mm min^{-1}. (d) Melted sample. Mass: 0.0816 g; scanning rate: 1° min^{-1}; sensitivity range: 15 mJ s^{-1}; paper rate: 5 mm min^{-1}.

TABLE 1

Temperatures and enthalpies of transition for $Na_4P_2O_7$ (the mean deviation is found from 5 runs)

Effect no	Temperature of peak maxima, T_p (°C)			Enthalpies of transition, $\Delta_{tr}H$ (kJ mol^{-1})	
	DTA data [3]	DTA data [5]	Our DSC data	DTA data [5]	Our DSC data
I	392	412	402.7 ± 0.1	10.0	4.27 ± 0.16
II	502	524	512.0 ± 0.1	3.8	The total
III	512	530	518.3 ± 0.1	1.3	$\Delta_{tr}H$(II–V) =
III′	–	–	523	–	8.03 ± 0.08
IV	538	553	542.7 ± 0.1	2.1	
IV′	–	–	547	–	
V	550	562	554.4 ± 0.2	2.9	
V′	–	–	557	–	

at about 340°C (Fig. 1b). In remelted samples the temperature of the effects are 1–2°C lower than in calcined unmelted ones but when the unmelted substance is reheated, the temperature of the effects decreases by 1–2°C.

The four reversible polymorphic transformations in sodium diphosphate in the temperature range 500–560°C were previously found by the DTA method [3,5] and rapid recording was noted to result in the confluence of II–III and IV–V paired effects. This seems to be the cause of a varying number of transitions having been recorded [1,2,4,7,8]. Nor were all the four transformations in this temperature range noted in high-temperature X-ray diffraction studies, so the transition V was not detected in [6] and the transition III in [9].

The DSC curves that we have recorded on samples of a small mass at high scanning rates (Fig. 1a) are identical to the DTA curves in [3,5], namely effects II–V are poorly separated. In high-sensitivity recording of DSC curves, with larger masses of samples and a low scanning rate, we have not succeeded in fully separating the effects either; moreover, three additional small endo effects III′, IV′, V′ (Figs. 1b–d) appeared, whose nature is unclear. The possibility cannot be excluded that the effects are associated with small amounts of impurities. Thus, in the initial $Na_4P_2O_7 \cdot 10H_2O$ sample (analytically pure) the Na_3PO_4 content is 0.3 mass% [15], on dehydration it can rise to 0.5 mass%. According to the data [7], Na_3PO_4 has several transitions with the most intensive endothermal effects at 332 and 515°C; taking into account the fact that the temperature of a number of DTA effects in ref. 7 are somewhat understated in comparison with our DSC data one can assign the 339 and 523°C effects (Fig. 1b–d) to the transformations of Na_3PO_4 impurity. On the other hand, effect III′ (523°C), by its temperature, is close to the α–β transition in $Na_5P_3O_{10}$, and effect IV′ (547°C) to the eutectic in the $NaPO_4$–$Na_4P_2O_7$ system [1,7]. However, allowing for the presence of $NaPO_3$ in the samples studied one should expect the effects of $Na_5P_3O_{10}$ peritectic melting (620°C) and $NaPO_3$ melting (627°C), which are not manifested in the DSC curves (Fig. 1b). Even more uncertain is the nature of effect V′ (557°C).

The curve of temperature of conductivity σ, obtained on a remelted $Na_4P_2O_7$ sample, has five inflections (Fig. 2), apparently associated with changes in the conductivity and activation energy ΔE_0 of conductivity occurring upon the transition from one modification to the other. The temperature of the first inflection is close to that of the transition 1 from the DSC data, the temperature of the second one to the beginning of the broad transition 11 (Fig. 1c). The temperatures of the other inflections are slightly lower than those of the transitions III–V, respectively.

The area under the endo peak 1 between 395 and 425°C corresponds to the enthalpy $\Delta_{tr}H(1) = 4.27 \pm 0.16$ kJ mol^{-1} and the entropy $\Delta_{tr}S(1) = 6.32 \pm 0.24$ J mol^{-1} deg^{-1} (from six runs). Since the varying of thermal exposure conditions in the recording of DSC curves does not lead to the separation of

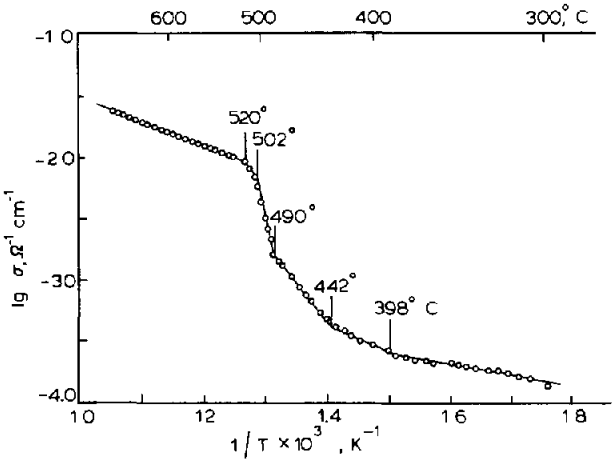

Fig. 2. Temperature dependence of $Na_4P_2O_7$ electrical conductivity.

the effects II–V even in pairs, their enthalpy was assessed as a sum by measuring the total area confined between the DSC curve and the baseline from 450 to 570°C (Fig. 1b–d). From five runs $\Delta_{tr}H(II–V) = 8.03 \pm 0.08$ kJ mol^{-1} and $\Delta_{tr}S(II–V) = 9.98 \pm 0.21$ J mol^{-1} deg^{-1} have been determined. It is remarkable that the $\Delta_{tr}H(II–V)$ value may be lower than the real one probably because of the gradual nature of the transitions II–V and so anomalous enthalpy increases at the early stages of the process are not detected by DSC method. Thus the total transition entropy $\Delta_{tr}S(I–V) = 16.30 \pm 0.45$ J mol^{-1} deg^{-1} obtained in the present study is ten times larger than the configurational entropy $\Delta S = 0.218R = 1.81$ J mol^{-1} deg^{-1} calculated by Leung [6] based on the crystal structures of sodium diphosphate phases.

$Zn_2P_2O_7$

The X-ray pattern of the $Zn_2P_2O_7$ sample obtained is identical to that presented in ref. 10. The melting temperature of $Zn_2P_2O_7$ is 1012 ± 5°C (the literature values are 1015 and 1017°C [8,10]). In accordance with the data [10] but in distinction to refs. 11 and 12 the DSC curves are indicative of only one polymorphic transformation at 128.2 ± 0.1°C (Fig. 3a) with $\Delta_{tr}H = 2.29 \pm 0.04$ kJ mol^{-1} and $\Delta S = 5.71 \pm 0.01$ J mol^{-1} deg^{-1} (from ten runs). It seems that two endothermal effects in [12] at 344 and 440°C are associated, according to the data [16], with $Zn_3(PO_4)_2 \cdot xH_2O$.

$Na_2ZnP_2O_7$

Analysis of the present product for phosphorus content by the quinoline phospho-molybdate method: found, –49.00 mass% of P_2O_5; calcd. for

TABLE 2

X-ray powder diffraction data for $Na_2ZnP_2O_7$

d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
5.71	2	2.86	28	1.98	4
5.24	23	2.72	2	1.86	5
5.15	100	2.56	8	1.76	11
3.73	8	2.43	7	1.71	2
3.45	6	2.39	2	1.63	11
3.13	18	2.32	5	1.56	3
3.08	16	2.20	7		
2.90	8	2.13	2		

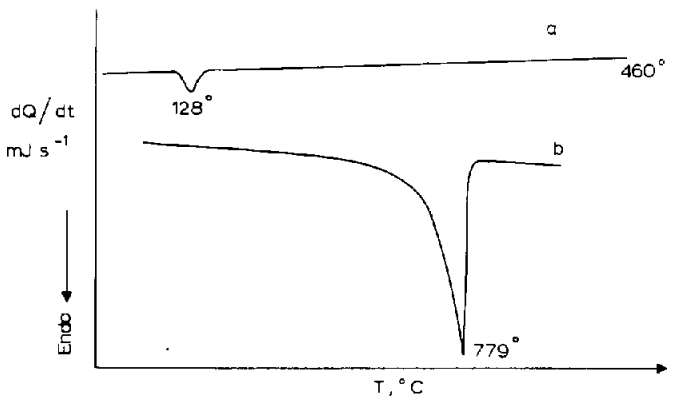

Fig. 3. DSC heating curves of $Zn_2P_2O_7$ (a) and $Na_2ZnP_2O_7$ (b). (a) Sample mass: 0.0278 g; scanning rate: 5° min^{-1}; sensitivity range: 35 mJ s^{-1}; paper rate: 5 mm min^{-1}. (b) Sample mass: 0.0299 g; scanning rate: 1° min^{-1}; sensitivity range: 35 mJ s^{-1}; paper rate: 5 mm min^{-1}.

$Na_2ZnP_2O_7$, −49.71 mass% of P_2O_5. The X-ray pattern of the remelted product is similar to the data of ref. 8, with the exception of the first few diffraction maxima (Table 2).

The melting temperature of $Na_2ZnP_2O_7$ is 779 ± 1.5°C (from five runs) which is in agreement with ref. 13 for the Na_2O–$Zn(PO_3)_2$ system but is lower than the data of ref. 8 (805°C). The compound melts congruently (Fig. 3b). The enthalpy of melting, $\Delta_m H = 58.5 \pm 1.8$ kJ mol^{-1} (from five runs), is close to the calculated value, 60.7 kJ mol^{-1}, obtained [17] on the assumption of a partial dissociation of the compound in the melt. In the temperature range 20–780°C the compound does not exhibit a polymorphism.

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