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DSC STUDY OF POLYMORPHISM OF $Na_4P_2O_7$

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ABSTRACT

The DSC data on the heat capacity and the entropies of sodium diphosphate transformations have shown that the transition of $Na_4P_2O_7$ from low-temperature to high-temperature modification proceeds continuously through intermediate states following the order-disorder mechanism.

INTRODUCTION

The literature data on the number and also temperatures and enthalpies of $Na_4P_2O_7$ polymorphic transformations are contradictory [1-3]. The estimated value of configurational entropy given in [3] for the transition of $Na_4P_2O_7$ from low-temperature orthorhombic [4] to high-temperature hexagonal modification is also doubtful.

MEASURING METHOD

The specimen of $Na_4P_2O_7$ was prepared from a commercial $Na_4P_2O_7 \cdot 10\ H_2O$ (analytically pure) by dehydrating it at 500 K and calcining at 900 K (1 h).

Thermal behaviour of $Na_4P_2O_7$ was studied with a differential scanning calorimeter DSC 111 "SETARAM" combined with "Hewlett-Packard -9825A" computer. DSC recordings were made in platinum cells in a flowing argon atmosphere at scanning rates 1, 2 or 5 K min^{-1} and sensitivity ranges of 15 and 35 mJ sec^{-1} for samples of mass from 0.025 to 0.250 g. The transition enthalpies $\Delta_{tr}H$ were determined by the graphical integration by the computer program for the peaks in DSC heating curves recorded at a scanning rate of 1 K min^{-1} with an error of no more than $\pm 2\%$. The heat capacity C_p was measured in the temperature range from 300-1000 K using the stepwise heating program with a temperature increment of 5 or 6.7 K during each heating.

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RESULTS AND DISCUSSION

According to our DSC data (Figure 1), $Na_4P_2O_7$ has at least five (I-V) reversible transformations at 676, 785, 791, 816 and 828 K. The attempts to separate the effects of II-V transformations were unsuccessful even at high-sensitive recording of the DSC curves and a small scanning rate. The enthalpies and the entropies of transformations (I) and (II-V) are, respectively:
$\Delta_{tr}H(I) = 4.27$ kJ mol^{-1}, $\Delta_{tr}S(I) = 6.32$ J K^{-1} mol^{-1};
$\Delta_{tr}H(II\text{-}V) = 8.03$ kJ mol^{-1}, $\Delta_{tr}S(II\text{-}V) = 9.97$ J K^{-1} mol^{-1}.

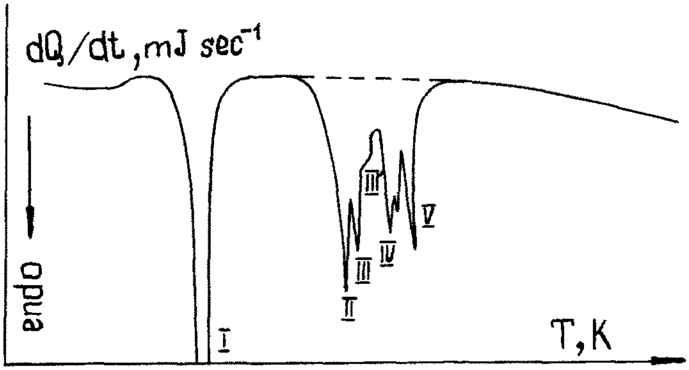

FIGURE 1

DSC heating curve of $Na_4P_2O_7$. Mass: 0.0255 g; scanning rate: 5 K min^{-1}; sensitivity range: 35 mJ sec^{-1}.

Figure 2 illustrates the temperature dependence of $Na_4P_2O_7$ heat capacity within the region of II-V transformations measured by the program of continuous heating at a rate of 1 K min^{-1} and printing $C_p = f(T)$ for each 0.6 K. Just as in the DSC heating curves, the peaks corresponding to II-V transformations are not separated in the C_p-T curve and small peaks III' and IV' appear, whose nature is not quite clear yet.

Figure 3a shows the temperature dependence of $Na_4P_2O_7$ heat capacity in the temperature range from 600 to 1000 K obtained by the program of stepwise heating. Our DSC data on C_p^o agree well with those obtained in [5] with an adiabatic calorimeter for the low-temperature region.

We also present our data on the heat capacity of $Na_4P_2O_7$ in the form of the temperature dependence of the apparent Debye temperature Θ_D calculated according to the equation:

$$C_p = 15\ D(\Theta_D/T)$$

where D is the three-dimensional Debye function for an arbitrarily chosen number of degrees of freedom equal to 15.

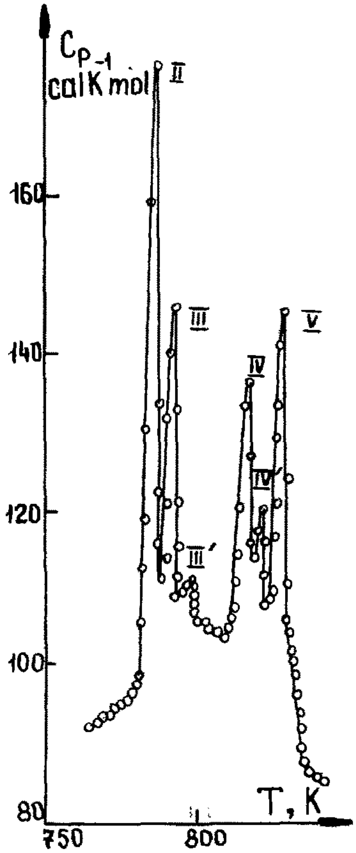

FIGURE 2

Heat capacity of $Na_4P_2O_7$
(continuous heating)

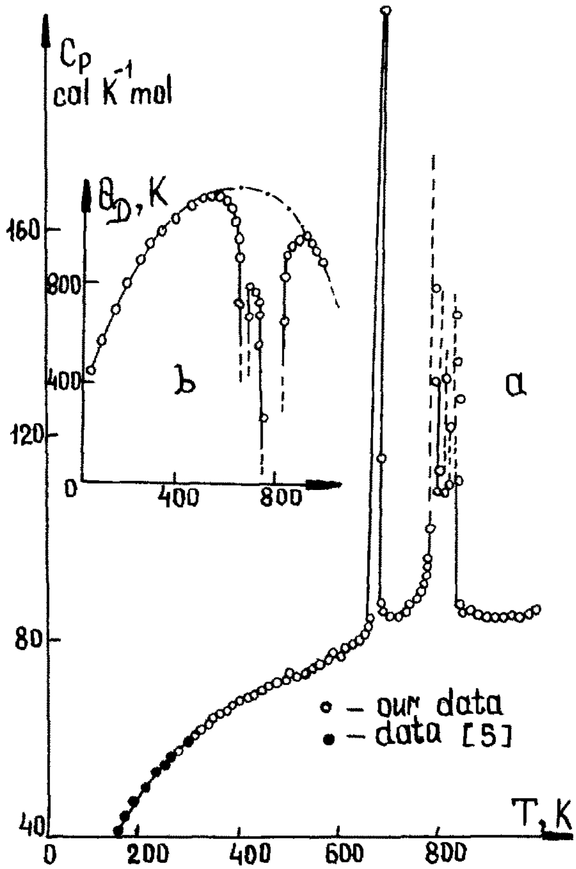

FIGURE 3

(a) Heat capacity of $Na_4P_2O_7$
(stepwise heating)

(b) Apparent Debye temperature of $Na_4P_2O_7$

From the plot $\Theta_D = f(T)$ it follows that an anomalous region covers the range from 520 to 850 K including the transformation I (Figure 3b).

Thus, the transition of $Na_4P_2O_7$ from low-temperature orthorhombic phase to high-temperature hexagonal one proceeds continuously through several stages. The total transition entropy $\Delta_{tr}S(I-V) = 16.30 \pm 0.21$ J K^{-1} $mol^{-1} \approx R \ln 8$ is ten times larger than the configurational entropy $\Delta S = 0.218$ R = 1.81 J K^{-1} mol^{-1} calculated in [3] on the basis of the crystal structures of sodium diphosphate phases. It is to remark that the present $\Delta_{tr}H(I-V)$ and respectively $\Delta_{tr}S(I-V)$ may be lower than the real one because of gradual nature of the transitions I-V and so anomalous enthalpy increases at the early stages of the process are not detected by the DSC method.

CONCLUSION

The heat capacity behaviour shows that low-temperature orthorhombic $Na_4P_2O_7$ changes continuously through intermediate states to high-temperature hexagonal phase. The large value of the total entropy of the transformations I-V indicates that this transition is an orientational order-disorder process. Based on the value $\Delta_{tr}S(I-V) \approx R \ln 8$ the number of equilibrium orientations of diphosphate-ion in the high-temperature disordered phase is eight times more than in the ordered low-temperature one.

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