REACTIVITY OF SODIUM TRIPHOSPHATE CRYSTAL HYDRATES

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Abstract

Kinetics of thermal decomposition of single crystals and polycrystalline samples of $Na_5P_3O_{10} \cdot 6D_2O$ and $Na_5P_3O_{10} \cdot 6H_2O$, interaction of fine-crystalline $Na_5P_3O_{10} \cdot 1.6H_2O$ with humid gaseous ammonia were studied using TLC, XRDA, IRS, TG, DTA, DSK.

Keywords: kinetics, sodium triphosphate crystal hydrates

Introduction

Reactivity of triphosphate compounds in regard to different reactions is not the same, it may vary depending on the type of reaction under investigation, state of division of a solid and other factors [1]. In the present work results of kinetic investigation of two types of reactions were considered: thermal transformations (D-H isotope exchange, D_2O loss, H_2O loss, dehydration localization form on crystal faces, $Na_5P_3O_{10}(II) \rightarrow Na_5P_3O_{10}(I)$ transition etc.) of single crystals and polycrystalline samples of $Na_5P_3O_{10} \cdot 6D_2O$ and $Na_5P_3O_{10} \cdot 6H_2O$ under isothermal and non-isothermal conditions; isothermal interaction of fine-crystalline $Na_3H_2P_3O_{10} \cdot 1.6H_2O$ with humid gaseous ammonia.

Experimental

Single crystals (2.0×0.5×0.1 mm) and polycrystalline samples of $Na_5P_3O_{10} \cdot 6D_2O$ (average crystal size $d = 0.1-0.6$ mm) were synthesized using slow evaporation and other methods of supersaturation of D_2O solutions of low temperature form $Na_5P_3O_{10}(II)$ [2]. Non-deuterated $Na_5P_3O_{10} \cdot 6H_2O$ with crystal sizes close to those of $Na_5P_3O_{10} \cdot 6D_2O$ were synthesized under the same conditions excluding D-reagents. Fine-crystalline $Na_3H_2P_3O_{10} \cdot 1.6H_2O$ was precipitated from acidified $Na_5P_3O_{10} \cdot 6H_2O$ solutions using organic precipitating agents [3].
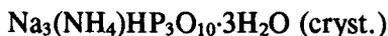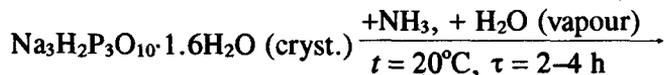
Methods of quantitative thin-layer chromatography (TLC), X-ray diffraction analysis (XRDA) and infrared spectroscopy (IR) were employed to control anion composition, phase composition and D-H isotope exchange degree of samples respectively. When studying ammonization kinetics of fine-crystalline $Na_3H_2P_3O_{10} \cdot 1.6H_2O$ water solutions of NH_4OH (concentration $c = 18\%$ and 24%) were used as a sourse of humid gaseous ammonia [4].
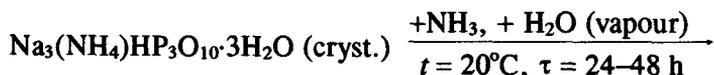
Results and discussion

Microscopic investigation of well-developed (001) facets of partially dehydrated $Na_5P_3O_{10} \cdot 6D_2O$ and $Na_5P_3O_{10} \cdot 6H_2O$ single crystals (mass lose $\Delta m < 2$ mol·D_2O and $\Delta m < 2$ mol·H_2O) shows, that D- and H-hexahydrates do not differ significantly in regard to typical localization form. In both cases the reaction starts on shot crystal edges and advances along b-axis forming characteristic cluster-like dehydration figures. Polycrystalline D- and H- hexahydrates manifest similar behaviour in dehydration kinetic experiments (Fig. 1). The shape of kinetic curves is almost the same excepting more strongly pronounced self-acceleration in case of H-hexahydrate. According to IRS data, $Na_5P_3O_{10} \cdot 6D_2O$ single crystals owing to smaller geometrical surface lose D-isotope more slowly when stored in air than polycrystalline samples.

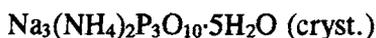The isotope substitution effect becomes noticeable when samples screened into equal size grades are used ($d = 0.1$–0.3 mm): the first endoeffect of initial reversible stage of dehydration is registered on DTA curves at $t = 94°C$ ($Na_5P_3O_{10} \cdot 6D_2O$) and $t = 80°C$ ($Na_5P_3O_{10} \cdot 6H_2O$); following endoeffects of irreversible dehydration stages differs from each other to a smaller degree. H-D isotope substitution influences indirectly the $Na_5P_3O_{10}(II) \rightarrow Na_5P_3O_{10}(I)$ transition which is registered on DSC curves as a single endoeffect ($t = 574°C$, $Na_5P_3O_{10} \cdot 6D_2O$) or splitted endoeffect ($t = 521°C$ and $t = 556°C$, $Na_5P_3O_{10} \cdot 6H_2O$).

Interaction of fine-crystalline $Na_3H_2P_3O_{10} \cdot 1.6H_2O$ with humid gaseous ammonia proceeds in two stages

$$Na_3H_2P_3O_{10} \cdot 1.6H_2O \text{ (cryst.)} \xrightarrow[t = 20°C, \ \tau = 2\text{--}4 \text{ h}]{+NH_3, \ + H_2O \text{ (vapour)}}$$

$$Na_3(NH_4)HP_3O_{10} \cdot 3H_2O \text{ (cryst.)}$$

and

$$Na_3(NH_4)HP_3O_{10} \cdot 3H_2O \text{ (cryst.)} \xrightarrow[t = 20°C, \ \tau = 24\text{--}48 \text{ h}]{+NH_3, \ + H_2O \text{ (vapour)}}$$

$$Na_3(NH_4)_2P_3O_{10} \cdot 5H_2O \text{ (cryst.)}$$

At $t = 7°C$ the interaction time for the first and the second stage is equal to 20–25 h and 80–120 h respectively. Increasing of interaction time is not recommended due beginning of liquefaction of the sample on final stages of ammonization. Keeping of $Na_3(NH_4)_2P_3O_{10} \cdot 5H_2O$ crystal hydrate in dry atmosphere leds to its quantitative conversion into new $Na_3(NH_4)_2P_3O_{10} \cdot 3H_2O$ crystalline phase.
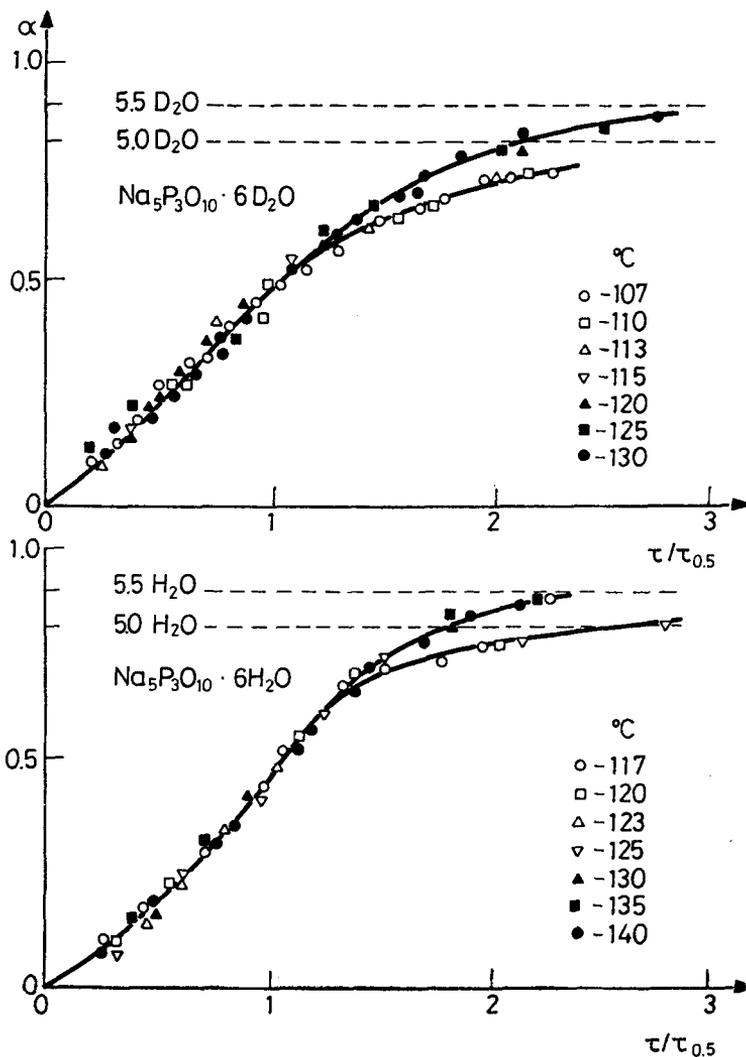
Fig. 1 Kinetics of thermal decomposition of $Na_5P_3O_{10} \cdot 6D_2O$ (a) and $Na_5P_3O_{10} \cdot 6H_2O$ (b)

References

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Zusammenfassung — Mittels TLC, XRDA, IRS, TG, DTA und DSK wurde die Kinetik der thermischen Zersetzung von Einkristallen und polykristallinen Proben von $Na_5P_3O_{10} \cdot 6D_2O$ und $Na_5P_3O_{10} \cdot 6H_2O$ sowie der Wechselwirkung von feinkristallinem $Na_5P_3O_{10} \cdot 1.6H_2O$ mit feuchtem gasförmigem Ammoniak untersucht.