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STUDY OF THERMAL PREPARATION AND STABILITY OF BINARY Mn^{II}–Mg^{II} TETRAMETAPHOSPHATES BY MEANS OF DTA

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ABSTRACT

The method of the synthesis of binary manganese(II)–magnesium(II) tetrametaphosphates is based on the reversibility of passage tetrametaphosphates to higher linear phosphates; it is associated with the thermal stability of the products and it makes possible their preparation in a pure state. The temperature and heat conditions of binary tetrametaphosphate synthesis and their stability were studied using DTA.

INTRODUCTION

Binary manganese(II)–magnesium(II) tetrametaphosphates with cyclic anions have not yet been described in the literature. Recent summarizing papers [1,2] conclude that their existence is not even expected [1].

The procedure suggested by us [3] for preparation of binary manganese–magnesium tetrametaphosphates is based on a two-step thermal synthesis. The first step starts from pure tetrametaphosphates of the two divalent metals which are melted and then abruptly cooled to give a vitreous amorphous product composed of higher linear phosphates of the summary formula $(Mn_{2-x}Mg_x)_{n/4}H_2P_nO_{3n+1}$ [4]. In the second step this product is repeatedly heated to a suitable temperature and recrystallized to give the microcrystalline product $Mn_{2-x}Mg_xP_4O_{12}$.

EXPERIMENTAL

The starting materials, the simple tetraphosphates, $Mn_2P_4O_{12}$ and $Mg_2P_4O_{12}$, were prepared using the thermal method described in ref. 5. In our laboratory this procedure was modified [6] so as to obtain the tetrametaphosphates as pure as possible.

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The required products, the binary manganese(II)–magnesium(II) tetrametaphosphates $\mathrm{Mn}_{2-x}\mathrm{Mg}_x\mathrm{P_4O_{12}}$, were synthesized by a method [3] described in the following scheme

$$x\mathrm{Mg_2P_4O_{12}} + (2-x)\mathrm{Mn_2P_4O_{12}} + \frac{8}{n}\mathrm{H_2O} \xrightarrow[\text{(wet atmosphere)}]{950\text{–}1160\,^\circ\mathrm{C}}$$

$$\rightarrow \frac{8}{n}(\mathrm{Mn}_{2-x}\mathrm{Mg}_x)_{n/4}\mathrm{H_2P}_n\mathrm{O}_{3n+1}(\mathrm{l}) \xrightarrow{1160 \div 25\,^\circ\mathrm{C}}$$

$$\rightarrow \frac{8}{n}(\mathrm{Mn}_{2-x}\mathrm{Mg}_x)_{n/4}\mathrm{H_2P}_n\mathrm{O}_{3n+1}(\text{glass}) \xrightarrow{T\ \text{recrystallization}}$$

$$\rightarrow 2\mathrm{Mn}_{2-x}\mathrm{Mg}_x\mathrm{P_4O_{12}}(\text{crystalline}) + \frac{8}{n}\mathrm{H_2O}$$

The mixtures for syntheses of the binary products were prepared from the starting materials of simple tetrametaphosphates whose ratio was adjusted to make the x value equal to 0.25, 0.5, 0.75, 1.0, 1.25, 1.5 and 1.75. In addition, the same two-step procedure was applied to pure $\mathrm{Mn_2P_4O_{12}}$ ($x=0$) and pure $\mathrm{Mg_2P_4O_{12}}$ ($x=2$). The mixtures were homogenized and then melted on platinum dishes in the electric furnace by heating to 1200 °C. After 30 min, the dishes with melts were removed from the furnace and abruptly cooled by immersion in water. The vitreous products obtained were higher-linear-type phosphates $(\mathrm{Mn}_{2-x}\mathrm{Mg}_x)_{n/4}\mathrm{H_2P}_n\mathrm{O}_{3n+1}$; they were dried at 105 °C and ground in a vibrating pebble mill. The quality of these intermediates was checked by instrumental analytical methods which demonstrated their homogeneity, amorphous character, and the presence of long linear anion chains.

Aliquots of these intermediates were then subjected to DTA (Apparatus Perkin–Elmer DTA 1700/TADS System) in order to find the temperatures of the exothermic processes of thermal recrystallization (Fig. 1). Temperatures of recrystallization correspond to those of formation of the binary manganese–magnesium tetrametaphosphates (Table 1, Fig. 2); therefore, the individual intermediates were then calcined in the electric furnace at temperatures 50 °C higher ($T_{\mathrm{max}} + 50\,^\circ\mathrm{C}$) for 30 min. The sintered blocks of the individual final products obtained in this way were ground in the vibrating pebble mill. The yields of the process (Table 1, Fig. 2) has been determined by analysis [7] of the tetrametaphosphate content in the product.

The final products were analysed by the instrumental methods (chromatography [8], IR spectroscopy [9], using a Perkin–Elmer 684 Infrared Spectrophotometer, X-ray powder diffraction analysis, λ Cu $K\alpha = 0.15418$ nm, HZG-4 GDR and AAS using an Atomspeck made by Hilger and Watts, which confirmed that the composition of the anions corresponded to tetrametaphosphates. The diffractograms were indexed on the basis of the fact that the binary manganese(II)–magnesium(II) tetrametaphosphates are isostructural with $\mathrm{Mn_2P_4O_{12}}$ and $\mathrm{Mg_2P_4O_{12}}$ which crystallize in the monoclinic

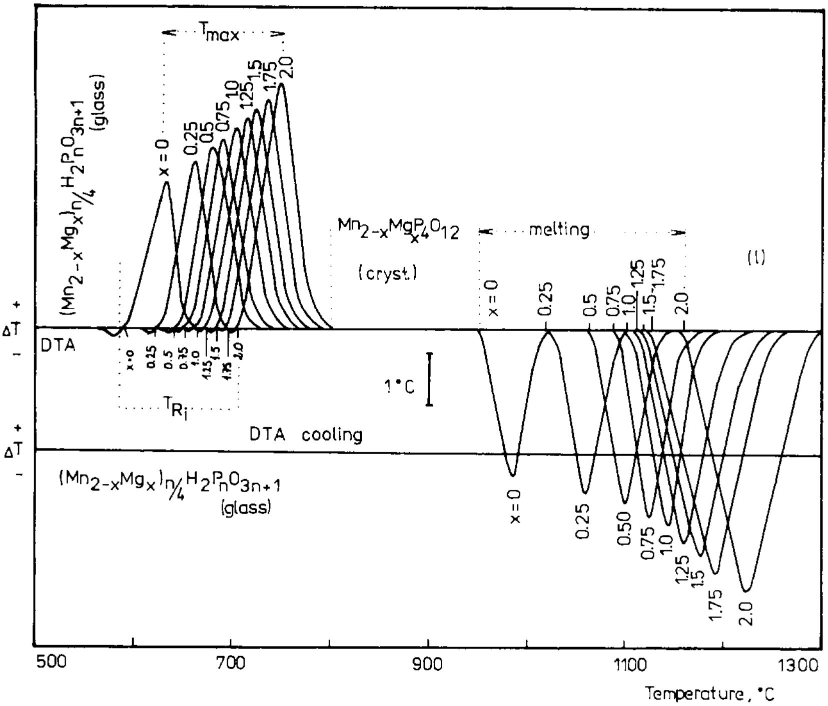

Fig. 1. DTA curves of the vitreous intermediates $(Mn_{2-x}Mg_x)_{n/4}H_2P_nO_{3n+1}$ indicating the formation of the products $Mn_{2-x}Mg_xP_4O_{12}$ (by reaction (1)) and their incongruent melting; see reaction (2).

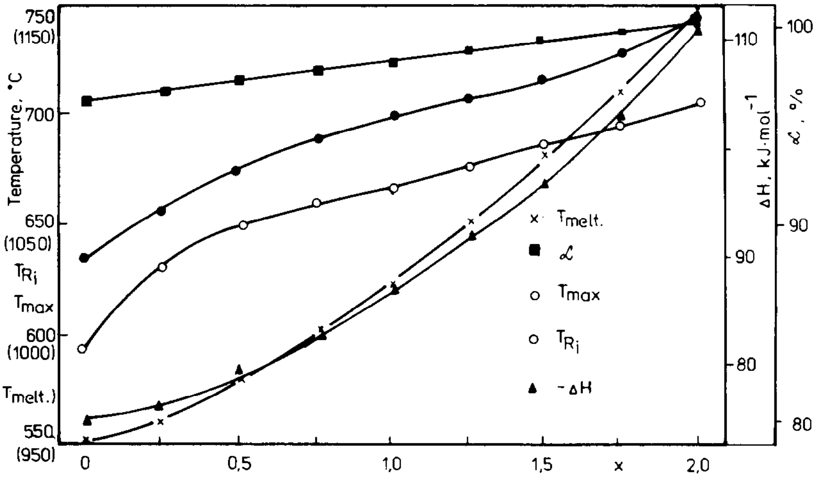

Fig. 2. Values documenting the dependence of the reaction (1) of formation of $Mn_{2-x}Mg_xP_4O_{12}$ on the magnesium content (x): T_{Ri}, the temperatures of the beginning of the reaction (○); T_{max}, the temperatures of the maxima of exothermic effects (●) (see Fig. 1.); ΔH, the heats of the process (▲); α, the yields of the process (■); and T_{melt}, the melting temperatures of the products (×).

TABLE 1

The conditions of formation and thermal stability of $Mn_{2-x}Mg_xP_4O_{12}$

x	0	0.25	0.5	0.75	1.0	1.25	1.5	1.75	2.0
T_{Ri}(°C)	595	631	649	660	668	678	687	695	706
T_{max}(°C)	635	657	675	690	700	707	717	728	745
ΔH (kJ mol^{-1})	74.5	77.3	80.0	84.6	89.7	94.2	97.5	106.3	111.2
Yield (%)	96.6	97.6	98.8	99.2	99.4	99.5	99.6	99.7	99.7
T_{melt}(°C) (~ T_{stab})	950	960	980	1003	1025	1053	1082	1112	1160

system, group $C/2c$ [10]. The least-squares treatment was adopted to calculate the lattice parameters of the elementary monoclinic cell of the binary products. The products were analyzed from the point of view of their thermal stability using DTA (DTA-1700 Perkin–Elmer) and using high temperature microscopy (MHO-2, Zeiss Jena) to estimate their temperatures of melting (Table 1, Fig. 2).

RESULTS AND DISCUSSION

Figure 1 presents the DTA curves whose first sections (up to the temperature of 750 °C) indicate an exothermic process. This process represents the reaction of formation of the binary tetrametaphosphate from the intermediate which is a higher-linear-type phosphate, see eqn. (1), which is connected with recrystallization of the amorphous vitreous phase.

$$(Mn_{2-x}Mg_x)_{n/4}H_2P_nO_{3n+1}(\text{glass}) = \frac{n}{4}Mn_{2-x}Mg_xP_4O_{12}(\text{cryst.}) + H_2O(\text{g}) \tag{1}$$

Both the temperatures and heats of this process, determined in the thermal analysis (Table 1, Fig. 2), indicate that increasing magnesium content is connected with the continuous increase of both the temperature of the beginning (T_{Ri}) and of the maximum of the exothermic effects (T_{max}), as well as with an increase in the heat of the process.

Analysis of the products prepared on a larger scale in electric furnaces at the temperatures $T_{\mathrm{max}} + 50\,°\mathrm{C}$ showed that the yields of this synthesis are high and increase with increasing magnesium content (from 96.6 to 99.7% of the tetrametaphosphate); the molar ratio $P_2O_5/(Mn + Mg)$ determined in the extracted products varies from 0.9995 to 1.0008, and the mutual ratio of the divalent metals, Mn/Mg, corresponds very precisely to the values $(2-x)/x$. The instrumental analyses confirmed that each product represents only a single phase, and that the composition of its anion corresponds to tetrametaphosphate. From these results, it follows that the two-step synthesis described succeeded in producing binary manganese(II)–magnesium(II) tetrametaphosphates of the formula $Mn_{2-x}Mg_xP_4O_{12}$ over the whole range of x from 0 to 2.

The structural parameters of the products a, b and c, and also (to a considerable extent) the angle β slowly but distinctly decrease with increasing magnesium content. Their values lie practically within the intervals limited by the structural parameters of the simple tetrametaphosphates $Mn_2P_4O_{12}$ and $Mg_2P_4O_{12}$ (a is 1.2076–1.1749 nm, b is 0.8484–0.8278 nm, c is 1.0152– – 0.9905 nm and β is 119.32–118.92 deg). Also the volume of the elementary cell of the binary products regularly decreases in the same direction, which is in accordance with the fact that the ionic radius of magnesium is smaller than that of manganese by about one fifth: V is in the range 0.9068–0.8433 nm^3.

As the yields of the synthesis were high, the sections of DTA curves above the recrystallization temperature can be considered to represent the thermal stabilities of the binary tetrametaphosphates. The endothermic effects at these DTA curves document their melting (as confirmed by high temperature microscopy) which is incongruent: the tetrametaphosphates are transformed into higher linear phosphates, see eqn. (2), which is favoured by the presence of at least traces of water vapour in the air atmosphere.

$$Mn_{2-x}Mg_xP_4O_{12}(\text{cryst}) + \frac{4}{n}H_2O(g) = \frac{4}{n}(Mn_{2-x}Mg_x)_{n/4}H_2P_nO_{3n+1}(l) \qquad (2)$$

Hence, with these conditions, the melting temperatures represent the temperatures up to which the binary tetrametaphosphates are stable; with increase in magnesium content, the melting temperatures increase from 950 to 1160 °C (Fig. 2). This demonstrates the high thermostability of the products.

REFERENCES

1 M.I. Kuzmenkov, V.V. Pečkovskij and S.V. Pyevskij, Chimija i technologija metafosfatov, Izd. Univerzitetskoje, Minsk, 1985, pp. 191.
2 L.N. Ščegrov, Fosfaty dvuchvalentnych metalov, Izd. Naukova Dumka, Kiev, 1987, pp. 214.
3 M. Trojan and L. Beneš, Czech. Pat. Appl. 01929-88, 1988.
4 M. Trojan, D. Brandová and Z. Šolc, Thermochim. Acta, 110 (1987) 343; Czech. Pat. 247 449 (1986).
5 E. Thilo and H. Grunze, Z. Anorg. Allg. Chem., 280 (1957) 209.
6 M. Trojan, Czech. Pats. 256 244 (1987) and 257 443 (1988).
7 M. Trojan and D. Brandová, Czech. Pat. 232 090 (1984).
8 D. Brandová and M. Trojan, Chem. Listy, 80 (1986) 499.
9 R.J. Melnikova, V.V. Pečkovskij, E.D. Dzjuba and I.E. Malašonok, Atlas infrakrasnych spektrov fosfatov, Kondensirovannyje fosfaty, Nauka, Moscow, 1985, pp. 235.
10 M. Trojan and L. Beneš, Sci. Papers Inst. Chem. Technol. Pardubice, 49 (1986) 55.