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Double tetrametaphosphates $Mn_{2-x}Mg_xP_4O_{12}$

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The tetrametaphosphates of the type $Mn_{2-x}Mg_xP_4O_{12}$, where $x = 0$ to 2, have been synthesized as new binary compounds, and their existence has been proved. The synthesis is based on a thermal procedure making use of the reversible transformation of tetrametaphosphates to higher linear phosphates. Temperatures and heats of formation of these products have been determined (i.e. formation by thermal recrystallization from higher linear phosphates) along with the yields of this procedure which increase with increasing magnesium content, x. The structure of the binary tetrametaphosphates belongs to the monoclinic system (over the whole range of x); the structural parameters determined slowly decrease with increasing magnesium content. With respect to the proposed application of these products as special inorganic pigments, the following properties have also been determined experimentally: density, thermal stability, colour. With increasing magnesium content the density of these products slowly decreases and the melting temperatures increase; the intensity of pink hue is also changed with changing magnesium or manganese content.

1. Introduction

Binary manganese (II)–magnesium (II) tetrametaphosphates with cyclic anions have not yet been described in the literature. Recent summarizing papers [1, 2] giving, *inter alia*, a number of binary compounds of the condensed phosphate type, even indicate that the existence of these compounds cannot be expected at all [1].

The procedure suggested by us [3] for the preparation of binary manganese–magnesium tetrametaphosphates and documented in the present paper is based on a two-step thermal synthesis. The first step starts from pure tetrametaphosphates of the two divalent metals which are melted in normal air atmosphere and then abruptly cooled to give a vitreous amorphous product composed of higher linear phosphates of the general 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 $Mn_{2-x}Mg_xP_4O_{12}$. In our laboratory these tetrametaphosphates of divalent metals are synthesized [5, 6] and evaluated with respect to their application as special inorganic pigments for high-temperature (ceramic) [7, 8], anticorrosion [9, 10], and luminescence purposes [11, 12]. The aim of the preparation of binary products is to increase the properties required for the above-mentioned applications [13] and, at the same time, to reduce their price [14].

2. Experimental procedure

2.1. Preparation of the starting pure tetrametaphosphates $Mn_2P_4O_{12}$ and $Mg_2P_4O_{12}$

The simple starting tetraphosphates were prepared on the basis of the thermal method described by Thilo and Grunze [15]. In our laboratory this procedure was modified [16] in order to obtain tetrametaphosphates as pure as possible. This result was achieved first of all by the use of increased water vapour pressure in the calcination area and by precise determination of the temperatures of the individual Reactions 1 to 3 by the methods of thermal analysis at quasi-isobaric and quasi-isothermal conditions [17]. Table I gives the temperatures of the individual Reactions 1 to 3 under conditions of water vapour pressure approaching 100 kPa in the calcination area.

$$M^{II}CO_3 + 2H_3PO_4 \overset{T_1}{=\!=} M(H_2PO_4)_2 + H_2O + CO_2 \quad (1)$$

$$M(H_2PO_4)_2 \overset{T_2}{=\!=} MH_2P_2O_7 + H_2O \quad (2)$$

$$2MH_2P_2O_7 \overset{T_3}{=\!=} M_2P_4O_{12} + 2H_2O \quad (3)$$

The carbonates of the individual metals used and phosphoric acid were of p.a. purity grade (the acid concentration was 40 wt % H_3PO_4); their mixtures corresponding to the left-hand side of Equation 1 were calcinated separately in an electric muffle furnace (L 112.2 VEB Frankenhausen, East Germany). The rate of temperature increase was 2° C min^{-1}, the temperatures T_1 to T_3 being maintained for 60 min each. The carrier of the calcinated mixture consisted of six platinum crucibles in a labyrinth arrangement, which ensured the water vapour pressure of about 100 kPa in the calcination area. Thereafter the tetrametaphosphates were purified by extraction with 0.3 M HCl to

TABLE I The temperatures (° C) of the individual reactions in the synthesis of $Mn_2P_4O_{12}$ and $Mg_2P_4O_{12}$ ($pH_2O_{(g)} \sim 100$ kPa)

	T_1	T_2	T_3
Mn	120	205	310
Mg	120–150	170–230	395

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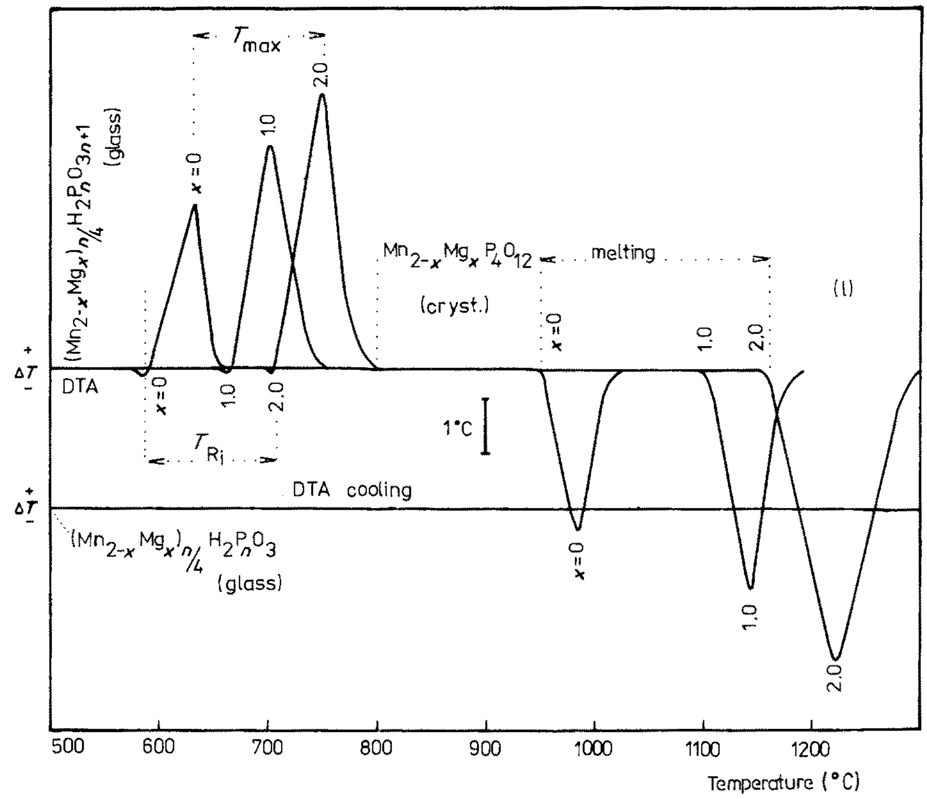

Figure 1 The DTA curves of the intermediates (for example $X = 0, 1, 2$) $(\mathrm{Mn_{2-x}Mg_x})_{n/4} \cdot \mathrm{H_2P_nO_{3n+1}}$ indicating the formation of the products $\mathrm{Mn_{2-x}Mg_xP_4O_{12}}$ (by Reaction 5) and their incongruent melting Reaction 6.

remove all the side products [18]. The quality of the product was confirmed by instrumental analytical methods (chromatography [19, 20] with a TLC II set from Kavalier Sázava, Czechoslovakia, infrared spectroscopy [21] with a Perkin Elmer 684 Infrared Spectrophotometer, X-ray diffraction analysis [22, 23] with a HZG-4 GDR, differential thermal analysis [24] with a DTA 1700 apparatus with DSC Mode, Perkin Elmer).

2.2. Preparation of $\mathrm{Mn_{2-x}Mg_xP_4O_{12}}$

The required products, namely the binary manganese (II)-magnesium (II) tetrametaphosphates, were synthesized by the two-step method which, in our laboratory, proved useful earlier for the purpose of introducing admixtures into the structure of tetrametaphosphates [25] and synthesis of luminescent materials [12]. This method is described in the following scheme

$$\begin{aligned}&(2-x)\mathrm{Mn_2P_4O_{12(cryst.)}} + x\,\mathrm{Mg_2P_4O_{12(cryst.)}}\\&\quad + 8/n\mathrm{H_2O}\\&\xrightarrow[\text{(air-wet atmosphere)}]{\text{melting (950–1160° C)}} 8/n\,(\mathrm{Mn_{2-x}Mg_x})_{n/4}\mathrm{H_2P_nO_{3n+1}}\ (\ell)\\&\xrightarrow[\text{(solidification)}]{\text{1160 to 25° C}} 8/n\,(\mathrm{Mn_{2-x}Mg_x})_{n/4}\mathrm{H_2P_nO_{3n+1}}\ \text{(glass)}\\&\xrightarrow{T\text{ recrystallization}} 2\mathrm{Mn_{2-x}Mg_xP_4O_{12(cryst.)}} + 8/n\mathrm{H_2O}\end{aligned} \quad (4)$$

The mixtures for the synthesis of the binary products were prepared from the simple starting tetrametaphosphates whose ratio was adjusted to give an 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 also applied to the pure $\mathrm{Mn_2P_4O_{12}}$ ($x = 0$) and pure $\mathrm{Mg_2P_4O_{12}}$ ($x = 2$). The mixtures were homogenized in an agate mortar and then melted in platinum dishes in an electric furnace L 112.2 by heating to 1200° C, i.e. above the melting temperature of the higher-melting starting tetrametaphosphate ($\mathrm{Mg_2P_4O_{12}}$: 1160° C). After 30 min, the dishes with melts were removed from the furnace and abruptly cooled by immersion in water. The vitreous products obtained of the type of higher linear phosphates $(\mathrm{Mn_{2-x}Mg_x})_{n/4}\mathrm{H_2P_nO_{3n+1}}$ were dried at 105° C and ground in a vibrating pebble mill. The quality of these intermediates was checked by instrumental analytical methods which proved their homogeneity, amorphous character, and long linear chains of the anions [19–23]; the sample aliquots were treated with 0.3 M HCl and dissolved completely therein, which confirmed that the intermediates did not contain any residual starting tetrametaphosphates [26]. Other aliquots of these intermediates were then subjected to DTA (Fig. 1) in order to find the temperatures of the exothermic processes of

TABLE II The conditions of formation of $\mathrm{Mn_{2-x}Mg_xP_4O_{12}}$

	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
$-\Delta H$(kJ mol^{-1})	74.5	77.3	80.0	84.6	89.7	94.2	97.5	106.3	111.2
Yields (α (%))	96.6	97.6	98.8	99.2	99.4	99.5	99.6	99.7	99.7

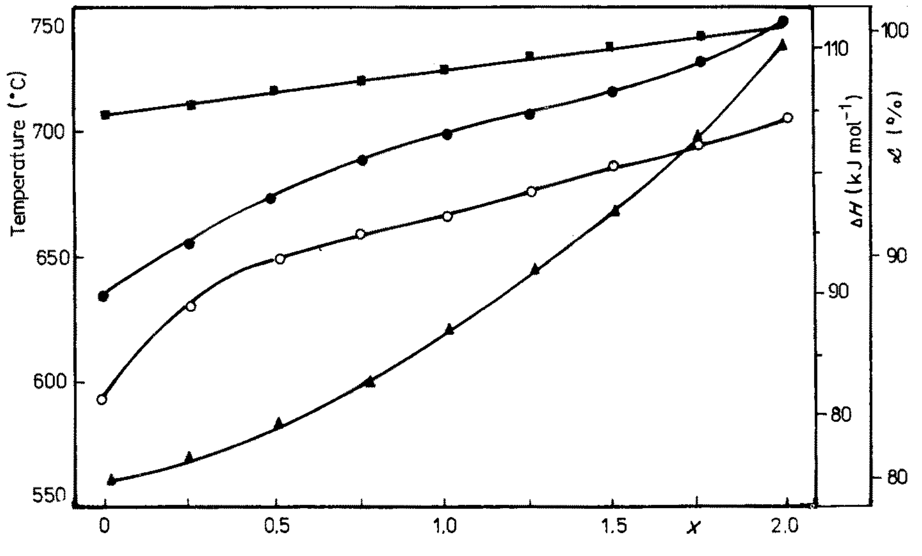

Figure 2 Values documenting Reaction 5 for the dependence of the formation of $Mn_{2-x}Mg_xP_4O_{12}$ on the magnesium content (x). T_{Ri}, the temperatures of the beginning of the reaction (○); T_{max} the temperatures of the exothermic effects maxima (Fig. 1) (●); ΔH heats of the process (▲); and α, the yields of the process (■).

thermal recrystallization. These temperatures correspond to those of formation of the binary manganese–magnesium tetrametaphosphates (Table II, Fig. 2); therefore, the individual intermediates were then calcined in an electric furnace L 112.2 at temperatures 50° C higher (T_{max} + 50° C) for 30 min. The sintered blocks of the individual final products obtained in this way were ground in the vibrating pebble mill, weighed (mass m_1), and extracted with a hundred-fold amount of 0.3 M HCl for 2 h; the solid was separated by filtration, dried at 105° C, and weighed (m_2). As the tetrametaphosphates of divalent metals resist extraction in dilute HCl [18], X-ray diffraction analysis (see Section 3.1.) was used to confirm the presence of only one phase (binary tetrametaphosphates) in each final product; the ratio m_2/m_1 can be used to determine the yield of the recrystallization (Table II, Fig. 2).

2.3. Evaluation of products

2.3.1. *The quality test*

The final products were analysed by the instrumental analytical methods [19–21] which confirmed the composition of their anions corresponding to tetrametaphosphates. The sample aliquots of the individual products were dissolved by boiling in 15% HCl (for several days) and analysed by means of atomic absorption spectrometry [27] to determine the ratios P_2O_5/(Mn + Mg) and Mn/Mg.

2.3.2. *Determination of structural parameters*

X-ray powder diffractograms of the samples were obtained using a vertical X-ray diffractometer HZG-4B (VEB Freiberger Präzisionsmechanik, East Germany), equipped with a goniometer of 25 cm diameter and a proportional detector. Cu$K\alpha$ radiation was used with the elimination of $K\beta$ radiation by a nickel filter; in the range 2θ = 10 to 35° the interplanar spacing was calculated using Cu$K\alpha$ radiation (λ = 0.154 178 nm) and in the range 2θ = 35 to 90° Cu$K\alpha_1$ radiation (λ = 0.154 051 nm) was used. Powdered silicon (a = 0.543 055 nm) served as an external standard. The lattice parameters were computed using the least-squares technique to inrease the accuracy, the minimized quantity being $(2\theta_{exp} = 2\theta_{calc})^2$.

The diffractograms were indexed on the basis of the fact that the binary manganese (II)–magnesium (II) tetrametaphosphates are isostructural with $Mn_2P_4O_{12}$ and $Mg_2P_4O_{12}$ which crystallize in the monoclinic system, C/2c group [22, 23]. The least-squares treatment was adopted to calculate the lattice parameters of the elementary monoclinic cell of the binary products (Table III); their dependences on the amount of magnesium in the products are presented in Fig. 3.

2.3.3. *Estimation of some physical properties*

The products were analysed by the pycnometrical method [28] to estimate their density and by the DTA method (DTA-1700 with DSC Mode, Perkin Elmer [29]) along with high-temperature microscopy (MHO-2, Zeiss Jena) to estimate their temperatures of melting (the values found are given in Table IV, and their dependence on the manganese content in the products

TABLE III The structural parameters of $Mn_{2-x}Mg_xP_4O_{12}$

x	a (nm)	b (nm)	c (nm)	β (deg)	V (mm³)	Δ*
0	1.2076(4)	0.8484(3)	1.0152(3)	119.32(2)	0.9068	0.009
0.25	1.2029(3)	0.8461(2)	1.0112(2)	119.17(2)	0.8987	0.008
0.5	1.1990(3)	0.8450(3)	1.0057(3)	119.10(2)	0.8903	0.008
0.75	1.1942(4)	0.8419(3)	1.0013(3)	118.97(2)	0.8808	0.009
1.0	1.1904(5)	0.8408(4)	0.9967(4)	118.92(2)	0.8732	0.009
1.25	1.1867(6)	0.8375(5)	0.9944(5)	118.89(3)	0.8652	0.012
1.5	1.1828(6)	0.8343(5)	0.9929(5)	118.88(3)	0.8579	0.011
1.75	1.1787(7)	0.8311(5)	0.9912(5)	118.87(3)	0.8504	0.013
2.0	1.1749(5)	0.8278(4)	0.9905(4)	118.92(2)	0.8433	0.009

*$\Delta = 1/N\ \Sigma_1^N \mid 2\theta_{exp} - 2\theta_{calc} \mid$, where $2\theta_{exp}$ is the experimental diffraction angle, $2\theta_{calc}$ is the angle calculated from lattice parameters and N is the number of investigated diffraction lines

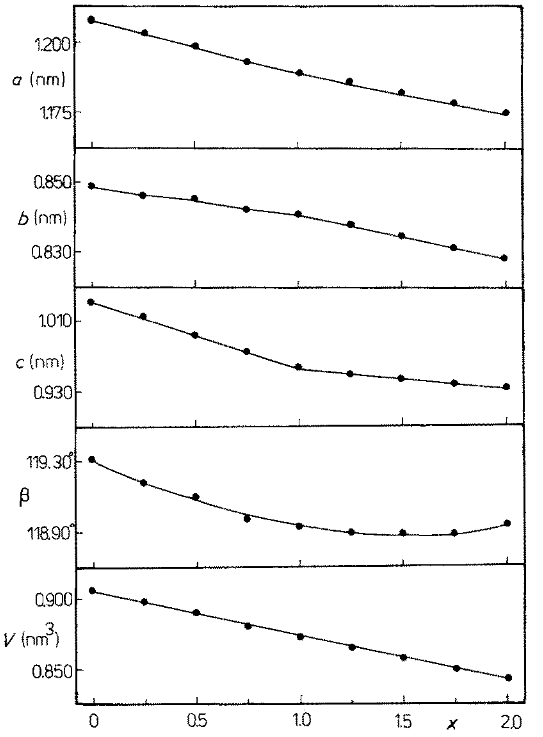

Figure 3 The structural parameters *a*, *b*, *c* and *β* and the volume *V* of the elementary unit cell of $Mn_{2-x}Mg_xP_4O_{12}$.

is presented in Fig. 4). The reflectance factor of the products in the visible light region was measured by means of a Specol 10 apparatus (Zeiss Jena) equipped with the respective 45/0 adaptor (Fig. 5).

3. Results and discussion

Fig. 1 shows the DTA curves whose first sections (up to the temperature of 750° C) indicate an exothermic process. This process represents the formation reaction of the binary tetrametaphosphate from the intermediate of the higher linear phosphate type (Reaction 5) which is connected with the recrystallization of the amorphous vitreous phase.

$$(Mn_{2-x}Mg_x)_{n/4}H_2P_nO_{3n+1}\text{ (glass)}$$
$$= n/4\ Mn_{2-x}Mg_xP_4O_{12(\text{cryst.})} + H_2O(g) \qquad (5)$$

Both the temperatures and heats of this process determined under the conditions of thermal analysis (Table II, Fig. 2) indicate that increasing magnesium content is connected with a continuous increase in both the temperature of the beginning (T_{Ri}; in the interval of 595 to 706° C) and the temperature of the maximum ($T_{\max}$; 635 to 745° C) of the exothermic effects as well as the heat of the process (-74.5 to $111.2\,\mathrm{kJ\,mol^{-1}}$).

The analysis of the products prepared on a larger scale in electric furnaces at temperatures $T_{\max} + 50°\mathrm{C}$ 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 analytical methods confirmed that each product represents only a single phase, and composition of its anion corresponds to tetrametaphosphate. From this it follows that the two-step synthesis described succeeded in producing products of the binary manganese (II)-magnesium (II) tetrametaphosphate type of the formula $Mn_{2-x}Mg_xP_4O_{12}$; this conclusion applies to the whole range of $x = 0$ to 2.

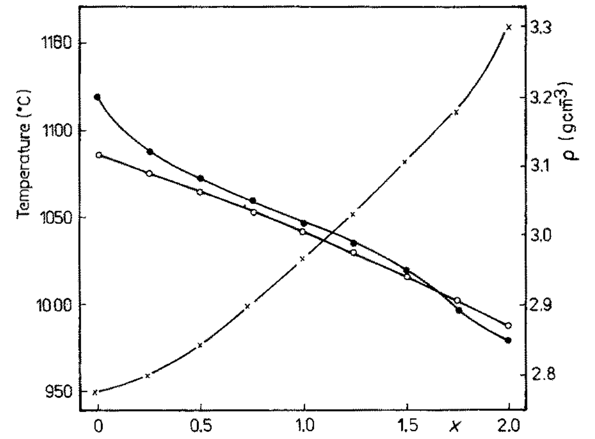

Figure 4 The dependence of melting temperatures (x) and experimental (●) and calculated (○) densities of the products $Mn_{2-x}Mg_xP_4O_{12}$ on *x*.

The structural parameters of the products (Table III, Fig. 3a, b, c) and (to a considerable extent) also the angle slowly but distinctly decrease with increasing proportion of magnesium. Their values practically lie in the intervals limited by the structural parameters of the pure simple tetrametaphosphates $Mn_2P_4O_{12}$ and $Mg_2P_4O_{12}$. Also the volume of the elementary cell of the binary products quite 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.

Some physical properties of the products determined with respect to their potential application as pigments are summarized in Table II. As the yields of this synthesis were high, the section of DTA curves above the recrystallization temperature can be considered to determine 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

TABLE IV Melting temperatures and densities 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_{melting} (° C)	950	960	980	1003	1025	1053	1082	1112	1160
ϱ_{exp} ($\mathrm{g\,cm^{-3}}$)	3.20	3.12	3.08	3.05	3.02	2.99	2.95	2.89	2.85
ϱ_{calc} ($\mathrm{g\,cm^{-3}}$)	3.116	3.090	3.062	3.038	3.006	2.975	2.941	2.907	2.871

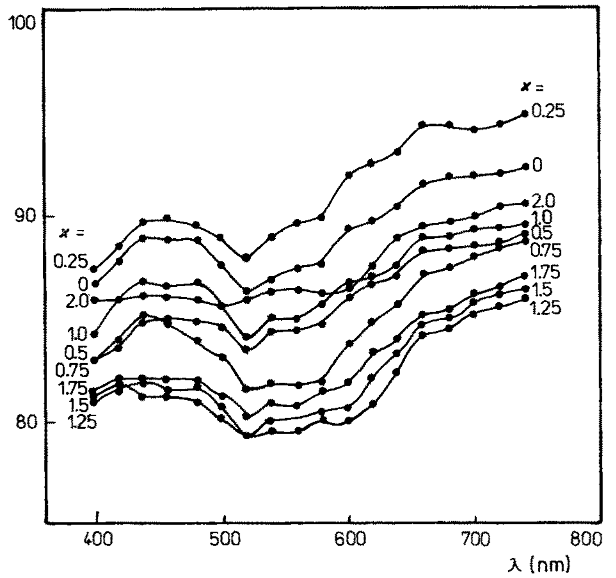

Figure 5 The colour hues of the products $Mn_{2-x}Mg_xP_4O_{12}$ expressed by their reflectance factor curves.

into higher linear phosphates (Reaction 6) which is favoured by the presence of at least traces of water vapour in the air atmosphere [24].

$$Mn_{2-x}Mg_xP_4O_{12(\mathrm{cryst.})} + 4/nH_2O_{(g)} = 4/n\,(Mn_{2-x}Mg_x)_{n/4}H_2P_nO_{3n+1}\ (\ell) \qquad (6)$$

Hence, under these conditions the melting temperatures represent the temperatures up to which the binary tetrametaphosphates are stable; they increase with magnesium content from 950 up to 1160° C (Fig. 4). This fact indicates the high thermostability of the products, which extends the range of their applicants to high-temperature purposes.

The density of the binary products also continuously changes with the magnesium content; however, as expected, in this case the density values decrease with increasing x, the experimental values (ϱ_{exp}) being in accordance with the density values calculated (ϱ_{calc}) from the X-ray diffraction analysis (Fig. 4).

The colour hue of the binary manganese (II)–magnesium (II) tetrametaphosphates is light pink to white, the intensity of pink hue being decreased with increasing magnesium content in the product (Fig. 5).

References

1. M. I. KUZMENKOV, V. V. PEČKOVSKIJ and S. V. PLIŠEVSKIJ, "Chimija i technologija metafosfatov" (Izd. Universitetskoje, Minsk, 1985).
2. L. N. ŠČEGROV, "Fosfaty dvuchvalentnych metalov" (Izd. Naukova Dumka, Kiev, 1987).
3. M. TROJAN and L. BENEŠ, Czech. Pat. 263 979 (1989).
4. M. TROJAN, Proceedings 10th International Conference on Phosphorus Chemistry, edited by R. Appel, Bonn 1986 (D-10) p. 234.
5. M. TROJAN, D. BRANDOVÁ and Z. ŠOLC, Thermochim. Acta **110** (1987) 343.
6. M. TROJAN and Z. ŠOLC, *J. Thermal. Anal.* **32** (1987) 1707.
7. M. TROJAN and I. SVOBODOVÁ, Czech. Pat. 243 367 (1985).
8. M. TROJAN, *Dyes and Pigments* **8** (1987) 129.
9. *Idem*, Czech. Pat. 247 844 (1986), 248 540 (1986), 253 098 (1987) and 253 192 (1987).
10. M. TROJAN and D. BRANDOVÁ, *Chem. Listy* **81** (1987) 799.
11. M. KAPLANOVÁ, M. TROJAN, D. BRANDOVÁ and J. NAVRÁTIL, *J. Luminiscence* **29** (1984) 199.
12. M. TROJAN and M. KAPLANOVÁ, Czech. Pat. 253 027 (1987).
13. M. TROJAN, D. BRANDOVÁ and P. MAZAN, Proceedings of the Conference 4 ESTAC '87, edited by M. Ludwig, Jena 1987, p. C25.
14. M. TROJAN, D. BRANDOVÁ, P. MAZAN, F. PAULIK and J. PAULIK, *ibid.* p. C51.
15. E. THILO and H. GRUNZE, *Z. Anorg. Allg. Chem.* **280** (1957) 209.
16. M. TROJAN, Czech. Pat. 256 244 (1987) and 257 443 (1988).
17. D. BRANDOVÁ and M. TROJAN, *J. Thermal Anal.* **30** (1985) 159.
18. M. TROJAN and D. BRANDOVÁ, Czech. Pat. 232 090 (1984).
19. J. P. EBEL, *Bull. Soc. Chem. Fr.* **10** (1953) 991.
20. D. BRANDOVÁ and M. TROJAN, *Chem. Listy* **80** (1986) 499.
21. R. J. MELNIKOVA, V. V. PEČKOVSKIJ, E. D. DZJUBA and I. E. MALAŠONOK, "Atlas infrakrasnych spektrov fosfatov" (Kondensirovannyje fosfaty, Nauka, Moscow, 1985).
22. M. BEGIEU-BECHER, M. CONDRAND and M. PERROUX, *J. Solid. State Chem.* **19** (1976) 359.
23. M. TROJAN and L. BENEŠ, *Sci. Papers Inst. Chem. Technol. Pardubice* **49** (1986) 55.
24. M. TROJAN and D. BRANDOVÁ, *Thermochim. Acta* **88** (1985) 415.
25. M. TROJAN, Czech. Pat. 247 449 (1986)
26. *Idem, Chem. Listy* **80** (1986) 541.
27. J. ZÝKA, "Analytická příručka", Vol. 2 (SNTL-ALFA, Praha, 1980).
28. L. ŠAŠEK, "Laboratorní metody voboru silikátů" (SNTL-ALFA, Praka, 1981).
29. J. MÁLEK and J. KLIKORKA, *J. Thermal Anal.* **32** (1987) 1883.

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