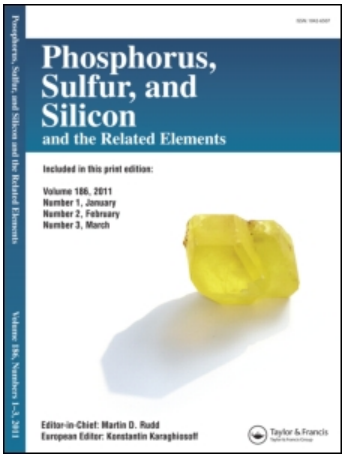

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A STUDY OF THE HIGH-TEMPERATURE BINARY CYCLO-TETRAPHOSPHATES SYNTHESIS AND THERMAL STABILITY OF THE $Cd_{2-x}Ca_xP_4O_{12}$

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A STUDY OF THE HIGH-TEMPERATURE SYNTHESIS AND THERMAL STABILITY OF THE BINARY CYCLO-TETRAPHOSPHATES $Cd_{2-x}Ca_xP_4O_{12}$

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The cyclo-tetraphosphates (tetrametaphosphates) of the type $Cd_{2-x}Ca_xP_4O_{12}$, where $x \in (0; 0.7\rangle$, have been synthetized as new binary compounds. The synthesis is based on a thermal procedure making use of the reversible transformation of cyclo-tetraphosphates to higher linear phosphates. This is the method used in our work place for synthesis of special pigments of binary cyclo-tetraphosphates, especially some bivalent metals combined with calcium. It is necessary in view of the fact of possible presence of ecologically inconvenient cadmium ions in starting phosphoric acid to know the conditions of probable original of cadmium(II)–calcium(II) binary cyclo-tetraphosphates. Temperatures and heats of formation off these products are increasing with the value x (the calcium content). The structure of the binary cyclo-tetraphosphates belongs to the monoclinic system; the structural parameters determined usually increase with increasing calcium content. In view of the fact that those products will have remained as nonsoluble (ecologically practically harmless) impurities in the mentioned special pigments, some of their properties were determined, having relation to their using as pigments: density, thermal stability and colour.

Key words: cadmium(II)–calcium(II) binary cyclo-tetraphosphates; preparation; identification; structural parameters; thermostability; physical properties.

INTRODUCTION

The cyclo-tetraphosphates of some divalent metals, are prepared in our laboratory and examined for potential applications as special inorganic pigments.[1,2] The purposes involved comprise the high-temperature applications (e.g. in ceramics[3,4]), anticorrosion[5,6] purposes and luminescence.[7,8] It appears economically advantageous to replace a part of cation (divalent metal) by some cheaper divalent element which, in addition, could improve, in some cases, special pigment properties, too. Such a suitable element, in our opinion, is calcium, which itself, however, does not give the cyclo-tetraphosphate.[9] Therefore, the binary cadmium–calcium tetraphosphates with cyclic anions have not been described in literature so far. Even the newest reviews,[10–12] which inter alia mention a number of binary compounds of the type of condensed phosphates, refuse to accept their existence.

Therefore, we examined the possibility of thermal preparation of binary Cd(II) and Ca(II) cyclo-tetraphosphates by the procedure developed in our laboratory for other purposes.[13] The anhydrous products were prepared by calcination of the starting mixtures of Cd(II) and Ca(II) carbonates and phosphoric acid (the molar

ratio $Me(II)/P_2O_5 = 1$) at the conditions of enhanced water vapour pressure.[14,15] The mixture of these products were then heated above the melting temperature of $Ca(PO_3)_2$ and by remelting transformed into higher polyphosphates. Their abrupt cooling gave homogeneous phosphate glasses of the formula $(Cd_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1}$ which were then reheated to a relatively narrow temperature interval to be recrystallized to the compound of cyclo-tetraphosphate type.

Phosphoric acid, frequently containing ecologically and hygienically inconvenient cadmium ions, is the starting raw material for the synthesis of cyclo-tetraphosphates of single bivalent metals (which are base for the synthesis of binary cyclo-tetraphosphates). Admission of cadmium ions into the binary phosphate compounds (by high-temperature preparation of above mentioned special pigments[1-8] would have been in a way a solution for their elimination). Products of the $Cd_{2-x}Ca_xP_4O_{12}$ type would have remained in this way as chemically and thermally stable (nonsoluble problems in the special pigments.

The revealing of existence of the new compounds—the binary cadmium(II)–calcium(II) cyclo-tetraphosphates—as well as the way of their thermal preparation documented in this present communication are dealt with in Czechoslovak patents;[16,17] similar situation is encountered also with the synthesis of the products mentioned at lower temperatures.[18]

EXPERIMENTAL

Preparation of the starting phosphates $Cd_2P_4O_{12}$ and $Ca(PO_3)_2$. The starting phosphates were prepared on the basis of the thermal method (1)–(4) described in Reference 9. In our laboratory this procedure was modified so as to obtain the phosphates as pure as possible[14,15,19,20] (Table I).

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

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

$$2CdH_2P_2O_7 \overset{T_3}{=} Cd_2P_4O_{12} + 2H_2O \quad (3)$$

$$CaH_2P_2O_7 \overset{T_4}{=} Ca(PO_3)_2 + H_2O \quad (4)$$

The applied carbonates of the individual metals and phosphoric acid were of p.a. purity grade (the acid concentration was 60% 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 GDR). The rate of temperature increase was 2°C min^{-1}, the temperatures T_1 to T_4 being maintained 60 min each. The final calcination was made always at 500°C for 3 hours. 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 cyclo-tetraphosphates were purified by extraction.[21]

TABLE I

The temperatures (°C) of the individual reactions in the synthesis of $Cd_2P_4O_{12}$ and $Ca(PO_3)_2$ ($pH_2O_{(g)} \sim 100$ kPa)

	T_1	T_2	T_3	T_4
$Cd_2P_4O_{12}$	120–175	175–190	380–390	—
$Ca(PO_3)_2$	170–200	200–240	—	400

Preparation of $Cd_{2-x}Ca_xP_4O_{12}$. The following scheme describes our procedure of synthesis of $Cd_{2-x}Ca_xP_4O_{12}$ (5):

$$(1-x/2)Cd_2P_4O_{12} + xCa(PO_3)_2 + 4/nH_2O \xrightarrow[\text{(air-wet-atmosphere)}]{970°C} 4/n(Cd_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1(l)}$$

$$\xrightarrow[\text{solidification}]{970-25°C} 4/n(Cd_{2-x}Ca_n)_{n/4}H_2P_nO_{3n+1(glass)}$$

$$\xrightarrow{T\ \text{recrystallization}} Cd_{2-x}Ca_xP_4O_{12(cryst.)} + 4/nH_2O \qquad (5)$$

The mixtures for syntheses of the binary products were prepared from the starting simple cyclo-tetraphosphates whose ratio was adjusted to make the x value equal to 0.2, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0. In addition, the same two-step procedure was also applied to the pure $Cd_2P_4O_{12}$ ($x = 0$) and pure $Ca(PO_3)_2$. The mixtures were homogenized in an agate mortar and then melted on platinum dishes in the electric furnace L 112.2 by heating to 970°C, i.e. above the melting temperature of the higher-melting starting phosphate ($Ca(PO_3)_2$: 920°C). After 30 min, the dishes with melts were removed from the furnace and abruptly cooled by immersion in water. The obtained virtreous products of the type of higher linear phosphates $(Cd_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1}$ were dried at 105°C and ground in a vibrating pebble mill. Other aliquots of these intermediates were then subject to DTA (Figure 1) in order to find the temperatures of the exothermic processes of thermal recrystalliztion. These temperatures correspond to those of formation of the binary cadmium–calcium cyclo-tetraphosphates (Table II, Figure 2); therefore, the individual intermediates were then calcinated in the electric furnace L 112.2 at temperatures by 20°C higher (T_{max} + 20°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 (α) were determined by the special extraction analytical method.[21]

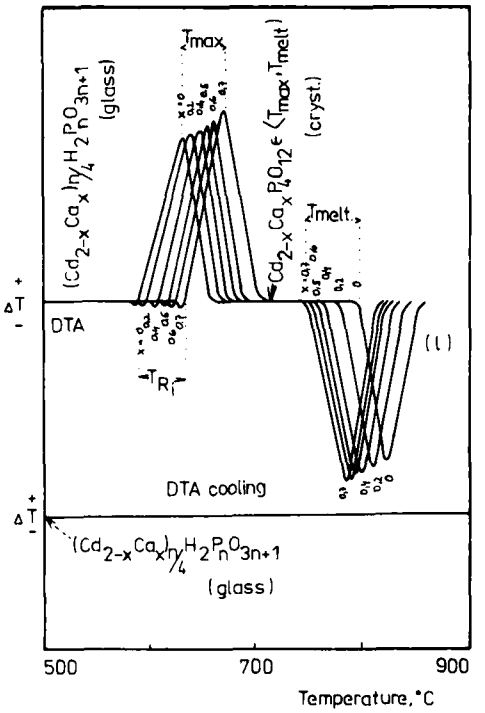

FIGURE 1 The DTA curves of the vitreous intermediates $(Cd_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1}$ indicating the formation of the products $Cd_{2-x}Ca_xP_4O_{12}$ (by the reaction (6)) and their incongruent melting (7). (Sample weight: 15 mg, temperature increase: 20°C min^{-1}, Pt crucible (open), atmosphere: air).

TABLE II

The conditions of formation of $Cd_{2-x}Ca_xP_4O_{12}$

x	0	0.2	0.4	0.5	0.6	0.7
T_{Ri}(°C)	592	597	609	618	626	632
T_{max}(°C)	629	633	642	652	658	660
$-\Delta H$(J g^{-1})	135	144	155	159	164	168
yields (α; %)	87.6	89.8	92.3	93.5	94.4	95.1

Evaluation of Quality of the Starting Phosphates, Intermediates, and Products. The evaluation was carried out by the method chromatography,[22,23] IR spectroscopy,[24] X-ray diffraction analysis[25,26] and atomic absorption spectroscopy.

Determination of Structural Parameters of $Cd_{2-x}Ca_xP_4O_{12}$. The products were studied by means of X-ray powder diffraction ($\lambda Cu_{K\alpha} = 0.154178$).[26] The diffractograms were indexed under the presumption that the binary cyclo-tetraphosphates are isostructural with $Cd_2P_4O_{12}$;[25] the lattice parameters of the monoclinical elementary cell (C2c group) were calculated by the squares treatment.

Estimation of Some Physical Properties. The final products were also evaluated by the pycnometrical method to estimate their density and by the DTA method[27] along with high-temperature microscopy to estimate their temperatures of melting and the measured reflectance factor in the visible light region.

RESULTS AND DISCUSSION

Figure 1 represents the DTA curves of the virtreous intermediates $(Cd_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1}$ for $x = 0$, 0.2, 0.4, 0.5, 0.6 and 0.7. Their first sections indicate an exothermic process. This process represents the reaction of formation of the cyclo-tetraphosphate which is connected with initial softening and subsequent recrystallization of the amorphous virtreous phase (6).

$$(Cd_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1(glass)} = n/4Cd_{2-x}Ca_xP_4O_{12(cryst)} + H_2O_{(g)} \qquad (6)$$

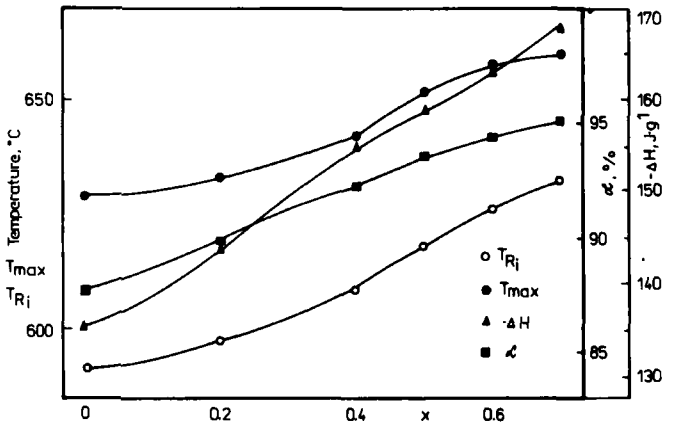

FIGURE 2 The values documenting the reaction (6) of formation of $Cd_{2-x}Ca_xP_4O_{12}$ in the dependence on the calcium content (x); T_{Ri}—the temperatures of the beginning of the reaction (○), T_{max}—the temperatures of the maxima of exothermic effects (Figure 1) (●), $-\Delta H$—the heats of the process (▲), α—the yields of the process (■).

Both the temperatures and heats of this process determined under the conditions of thermal analysis (Table II, Figure 2) indicate that increasing calcium content is connected with continuous increase of both the temperature of the beginning and the temperature of the maximum of the exothermic effects and the heat of the process.

The analysis of the products prepared at larger scale in electric furnaces at the temperature $T_{max} + 20°C$ showed that the yields of this synthesis are high (increase with increasing calcium content). The molar ratio $P_2O_5/(Cd + Ca)$ determined in the extracted products varies from 0.9990 to 1.0009, and the mutual ratio of the divalent metals, Cd/Ca, 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 cyclo-tetraphosphate. Therefore it follows that the two-step synthesis described succeeded in giving the products of the type of binary cadmium(II)–calcium(II) cyclo-tetraphosphates of the formula $Cd_{2-x}Ca_xP_4O_{12}$. However, the X-ray diffraction analysis showed that no binary products are formed within the whole range of x (Table III).

The dependence of the lattice parameters and volume of the elementary cell on the proportion of the Ca(II) component in the product are given in Figure 3. It is obvious that the volume of the elementary cell of the binary cyclo-tetraphosphate is increased with the Ca(II) content, which agrees with the fact its radius is greater than that of Cd(II). At the values $x = 0.7$ (molar ratio of Cd/Ca = 1.86) in the product, there appears a break in the dependences of the elementary cell volume and lattice parameters on the Ca(II) content. At higher Ca(II) proportions in the product, the values of the quantities mentioned are practically no longer changed. The diffractograms then exhibit lines of a further phase. The results thus indicate that it is possible to prepare binary Cd(II)–Ca(II) cyclo-tetraphosphates with the molar ratio of $Ca/Cd \leq 0.54$. Hence, the existence of this type of product containing a higher calcium content than that corresponding to the ratio given cannot be expected. (This fact is obviously connected with the non-existence of pure calcium(II) cyclo-tetraphosphate as already stressed in the Introduction).

TABLE III

The structural parameters of $Cd_{2-x}Ca_xP_4O_{12}$

x	a (nm)	b (nm)	c (nm)	β^0	V (nm^3)	Δ^*	Number of phases	
0	1.2328 (4)	0.8639 (3)	1.0368 (3)	119.33 (2)	0.9645	0.008	one	$Cd_{2-x}Ca_xP_4O_{12}$
0.2	1.2353 (6)	0.8670 (4)	1.0399 (4)	119.37 (3)	0.9714	0.013	one	
0.4	1.2396 (5)	0.8691 (4)	1.0407 (6)	119.40 (2)	0.9768	0.011	one	
0.5	1.2410 (5)	0.8698 (4)	1.0422 (6)	119.39 (3)	0.9802	0.011	one	
0.6	1.2425 (4)	0.8711 (3)	1.0427 (4)	119.43 (2)	0.9829	0.008	one	
0.7	1.2457 (5)	0.8732 (4)	1.0443 (4)	119.45 (2)	0.9891	0.010	one	
0.8	1.2459 (5)	0.8728 (4)	1.0452 (4)	119.46 (2)	0.9896	0.010	more than one	mixtures
0.9	1.2460 (6)	0.8730 (4)	1.0451 (4)	119.43 (3)	0.9891	0.013		
1.0	1.2457 (5)	0.8730 (3)	1.0446 (3)	119.47 (2)	0.9891	0.008		

* $\Delta = 1/N \sum_1^N |2\theta_{exp} - 2\theta_{calc}|$, 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.

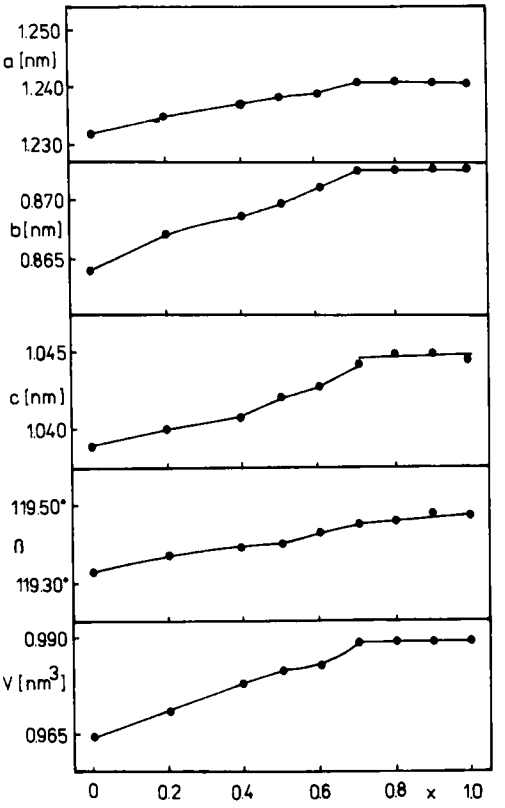

FIGURE 3 The structural parameters a, b, c and β and the volume V of the elementary unit cell of $Cd_{2-x}Ca_xP_4O_{12}$.

Some physical properties of the products determined with respect to their potential application as pigments are summarized in Table IV.

As the yields of this synthesis were high, the sections of DTA curves above the recrystallization temperature can be considered to determine the thermal stabilities of the binary cyclo-tetraphosphates. The endothermic effects at these DTA curves document their melting (as it was confirmed by means of high-temperature microscopy) which is incongruent: the cyclo-tetraphosphates are transformed into higher linear phosphates (7), which is favoured by the presence of at least traces of water vapour in the air atmosphere.

$$Cd_{2-x}Ca_xP_4O_{12(cryst)} + 4/nH_2O_{(g)} = 4/n(Cd_{2-x}Ca_x)_{n/4}P_nO_{3n+1(l)} \qquad (7)$$

TABLE IV

Temperatures melting and densities of $Cd_{2-x}Ca_xP_4O_{12}$

x	0	0.2	0.4	0.5	0.6	0.7
T melting (°C)	800	780	763	757	753	750
ρ_{exp} (g cm^{-3})	3.85	3.65	3.52	3.46	3.39	3.30
ρ_{calc} (g cm^{-3})	3.723	3.598	3.467	3.431	3.360	3.291

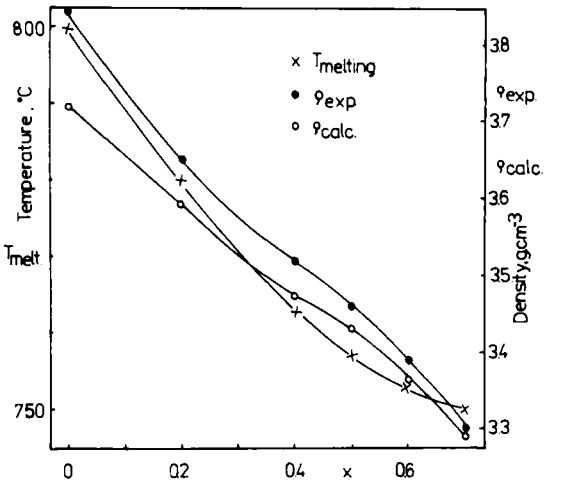

FIGURE 4 The dependence of melting temperatures (×) and experimental (●) and calculated densities (○) of the products $Cd_{2-x}Ca_xP_4O_{12}$ on the calcium content (x).

Hence, at these conditions the melting temperatures represent the temperatures up to which the binary cyclo-tetraphosphates are stable; with the calcium content they decrease from 800 up to 750°C (Figure 4). This fact documents good thermostability of the products, which extends the range of their applications to high-temperature purposes.

Also the density of the binary products continuously changes with the calcium content, however, according to expectation, in this case the density values decrease with increasing x (which again agrees with the lower density found for $Ca(PO_3)_2$ as compared with that found for the pure $Cd_2P_4O_{12}$), the experimental values (ρ_{exp}) being in accordance with the density values calculated (ρ_{calc}) on the basis of the X-ray diffraction analysis (Figure 4). The binary cadmium(II)–calcium(II) cyclo-tetraphosphates were colourless (white) (Figure 5).

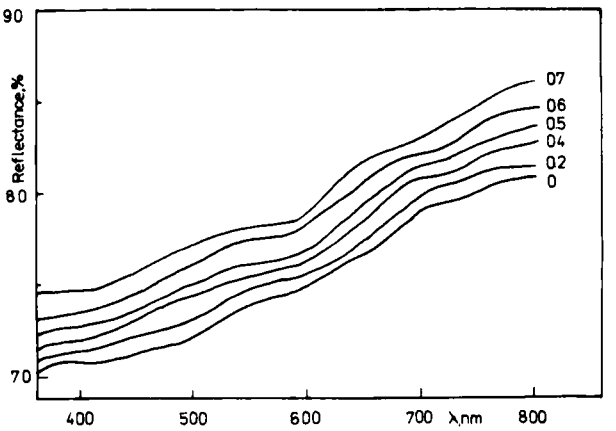

FIGURE 5 The reflectance of products $Cd_{2-x}Ca_xP_4O_{12}$.

CONCLUSION

Our communication shows that it is possible to prepare binary cadmium(II)–calcium(II) cyclo-tetraphosphates $Cd_{2-x}Ca_xP_4O_{12}$, where $x \in (0; 0.7\rangle$. (However, the existence of this type of product with the Ca/Cd mol. ratio above 0.54 cannot be expected). The colourless (white) products crystallize in the monoclinic system, C/2c group. Their structural parameters have the values: $a = 1.2328$ to 1.2457 nm, $b = 0.8639$ to 0.8732, $c = 1.0368$ to 1.0443 nm, $\beta = 119.33°$ to 119.45° (the volume of elementary cell increases from 0.9645 nm^3 to 0.9891 nm^3 with increasing proportion of calcium in the product). The melting temperatures and densities decrease with increasing calcium content (the respective intervals are 800–750°C and 3.85–3.30 g cm^{-3}).

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