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The binary Cd(II)-Zn(II) cyclo-tetraphosphates

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Abstract

The cyclo-tetraphosphates of the type $Cd_{2-x}Zn_xP_4O_{12}$ have been synthesized. 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 laboratory for synthesis of special pigments of binary cyclo-tetraphosphates, especially of some bivalent metals combined with zinc. The compounds prepared have been evaluated from the standpoint of their structure, colour hue, density and thermal stability. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The cyclo-tetraphosphates of some divalent metals have been prepared in our laboratory and examined for potential applications as special inorganic pigments. It appears economically advantageous to replace partially cations (divalent metal) by some cheaper divalent element [1,2] which could also improve special pigment properties. In our opinion is zinc the suitable element which does give the cyclo-tetraphosphates. Therefore, we examined the possibility of thermal preparation of Cd(II)-Zn(II) tetraphosphates with cyclic anions by the procedure developed in our laboratory for other purposes. The anhydrous products by the procedure were prepared by calcination of the starting mixtures of Cd(II) and Zn(II) carbonates and phosphoric acid at the conditions of enhanced water vapour pressure.

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 the basis for synthesis of binary cyclo-tetraphosphates). In view of the possible presence of cadmium ions in starting phosphoric acid it is necessary to know the conditions of synthesis of cadmium(II)-zinc(II) binary cyclo-tetraphosphates. Incorporation of cadmium ions into the binary phosphates (by high-temperature preparation of above mentioned special pigments [3–5]) would have been in a way the solution for their elimination. Products of the $Cd_{2-x}Zn_xP_4O_{12}$ type could remain in this way as chemically and thermally stable in the special pigments.

2. Experimental

The preparation of $Cd_{2-x}Zn_xP_4O_{12}$ is based on a two-step thermal process. The first step starts with the

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pure cyclo-tetraphosphates of the two divalent metals: mixtures of both are melted in air atmosphere and then abruptly cooled to give a vitreous product composed of higher linear phosphates $(Cd_{2-x}Zn_x)_{n/4}H_2P_nO_{3n+1}$. In the second step this product is repeatedly heated to a suitable temperature and recrystallized to give microcrystalline $Cd_{2-x}Zn_xP_4O_{12}$.

The starting simple cyclo-tetraphosphates were prepared by thermal method [6]. In our laboratory this procedure was modified to obtain the cyclo-tetraphosphates as pure as possible (schemes 1, 2 and 3) where $M^{II} = Cd$ (Zn).

$$M^{II}CO_3 + 2\ H_3PO_4 \rightarrow M(H_2PO_4)_2 + H_2O + CO_2 \quad 125°C\ (115°C) \tag{1}$$

$$M(H_2PO_4)_2 \rightarrow MH_2P_2O_7 + H_2O \quad 215°C\ (260°C) \tag{2}$$

$$MH_2P_2O_7 \rightarrow \tfrac{1}{2}M_2P_4O_{12} + H_2O \quad 400°C\ (325°C) \tag{3}$$

The synthesis of the binary cyclo-tetraphosphates is described by the following schemes:

$$(1-x/2)\ Cd_2P_4O_{12}(\text{cryst.}) + x/2\ Zn_2P_4O_{12}(\text{cryst.}) + 4/nH_2O \rightarrow 4/n(Cd_{2-x}Zn_x)_{n/4}H_2P_nO_{3n+1}(l) \quad \text{melting} \tag{4}$$

$$4/n(Cd_{2-x}Zn_x)_{n/4}H_2P_nO_{3n+1}(l) \rightarrow 4/n(Cd_{2-x}Zn_x)_{n/4}H_2P_nO_{3n+1}(\text{glass}) \quad \text{solidification} \tag{5}$$

$$4/n(Cd_{2-x}Zn_x)_{n/4}H_2P_nO_{3n+1}(\text{glass}) \rightarrow Cd_{2-x}Zn_xP_4O_{12}(\text{cryst.}) + 4/nH_2O \quad \text{recrystallization} \tag{6}$$

The values of x were equal to 0, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75 and 2.0. The mixtures were melted on platinum dishes in an electric furnace by heating to 880°C, i.e. above the melting temperature of both cyclo-tetraphosphates [7] ($Cd_2P_4O_{12}$, 800°C; $Zn_2P_4O_{12}$, 810°C). After 30 min, the dishes with the melts were removed from the furnace and abruptly cooled by immersing in water. Vitreous products $(Cd_{2-x}Zn_x)_{n/4}H_2P_nO_{3n+1}$ were obtained and dried at 105°C and then ground in a vibrating pebble mill. Aliquots of these intermediates were then subjected to DTA in order to find the temperatures (T_{Ri}, T_{max}) and heats (ΔH) of the exothermic process of thermal recrystallization (T_{Ri} is the temperature of the beginning of the reaction of formation of $Cd_{2-x}Zn_xP_4O_{12}$, and T_{max} is the maximum temperature of the exothermic effects). The individual intermediates were then calcinated in the electric furnace at temperatures 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 (α) of the process were determined by a special extraction analytical method.

The cyclo-tetraphosphates, vitreous amorphous intermediates and final products were analyzed by X-ray diffraction [8]. Structural parameters of the products were determined by means of X-ray powder diffraction (Cu Kα, $\lambda = 0.154178$ nm, HZG-4B apparatus Germany). The diffractograms were indexed under the assumption that the mixed cyclo-tetraphosphates are isostructural with $Cd_2P_4O_{12}$ and $Zn_2P_4O_{12}$. The lattice parameters of the monoclinic unit cell (C2c group) were calculated by the least square method.

The final products were also investigated by the pycnometric method to estimate their densities. The optical properties were evaluated with regard to their colour hues by measurements of spectral reflectance in the visible region of light (colour coordinates L^*, a^*, b^* of the colour system $CIEL^*a^*b^*$ introduced in 1976) using a MiniScan (HunterLab, USA).

3. Results and discussion

The methods of thermal analysis facilitate detection and explanation of processes that accompany melting of cyclo-tetraphosphates and their recrystallization. Available papers dealing with their preparation do not give sufficiently precise data on the calcination temperatures necessary for the condensation reactions.

An exothermic process was indicated by means of the DTA method. This process represents the formation of the binary cyclo-tetraphosphate from intermediate higher linear phosphates and is connected with recrystallization of the amorphous vitreous phase (6).

The temperatures (T_{Ri}, T_{max}) and the heats (ΔH) of this process determined are tabulated in Table 1. The

Table 1
The conditions of formation of $Cd_{2-x}Zn_xP_4O_{12}$

x	T_{Ri} (°C)	T_{max} (°C)	$-\Delta H$ (J g^{-1})	Yield α (%)
0	592	629	135	87.6
0.25	586	621	136	88.1
0.50	580	615	138	88.5
0.75	574	609	140	88.9
1.00	569	601	142	89.1
1.25	562	595	144	89.8
1.50	556	588	146	90.1
1.75	550	581	148	90.4
2.00	545	573	149	90.5

temperatures (T_{Ri}, T_{max}) and the heats (ΔH) of this process decrease with increasing zinc content. The yields (α) are high and increase with increasing zinc content. The molar ratio $P_2O_5/(Cd + Zn)$ in the extracted (0.3 M HCl) product varies from 0.99886 to 1.0009, and the molar ratio Cd/Zn corresponds very closely to the values $(2 - x)/x$. Each product is a single-phase material with a cyclo-tetraphosphate anion. Hence, the products are of the type of the binary cadmium(II)-zinc(II) cyclo-tetraphosphates of formula $Cd_{2-x}Zn_xP_4O_{12}$. This conclusion applies to the whole range of x (Table 2).

The lattice parameters of the products (Table 2) a, b and V (the volume of the elementary unit cell) are slowly but distinctively decreasing with increasing proportion of zinc. The lattice parameter c decreases from 1.0388(3) nm ($x = 0$) to 0.9886(5) nm ($x = 1$) with the increasing content of zinc in the product. At higher content of zinc the parameter c changes only slightly. The values of angle β decrease from 119.33(2)° to 118.46(3)° in the range $x \in (0,1)$. At higher content of zinc the values of angle β slightly increase from 118.48(3)° ($x = 1.25$) to 118.83(3)° ($x = 2.0$). The values practically lie in the intervals limited by the structural parameters of the pure cyclo-tetraphosphates $Cd_2P_4O_{12}$ [9] and $Zn_2P_4O_{12}$. The volume of the elementary cell of the binary products decreases quite regularly in the same direction as a and b in accordance with the fact that the ionic radius of zinc [$r(Zn^{2+}) = 0.075$ nm] is smaller than that of cadmium [$r(Cd^{2+}) = 0.095$ nm].

Some physical properties of the products determined with respect to their potential application as special pigments are summarized in Table 3. As the yields of this synthesis were high, the intervals of DTA curves above the recrystallization and melting temperature can be considered to indicate the thermal stabilities of the binary cyclo-tetraphosphates. The endothermic effects on the DTA curves document the melting (which was confirmed by means of high-temperature microscopy) which is incongruent. The cyclo-tetraphosphates are transformed into higher linear phosphates, which is favoured by the presence of at least traces of water vapour in the air atmosphere.

Hence, at these conditions the melting temperatures represent the temperatures up to which the binary cyclo-tetraphosphates are stable. The temperatures increase with the zinc content from 800°C to 810°C. This fact documents high thermal stability of the products that extends the range of their applications to high-temperature purposes.

The densities of the binary cadmium(II)-zinc(II) cyclo-tetraphosphates continuously decrease with

Table 2
Structural parameters of $Cd_{2-x}Zn_xP_4O_{12}$

x	a (nm)	b (nm)	c (nm)	β (degrees)	V (nm^3)	Δ^a
0	1.2328(4)	0.8639(3)	1.0388(3)	119.33(2)	0.9645	0.008
0.25	1.2240(6)	0.8605(6)	1.0285(6)	119.12(4)	0.9465	0.011
0.50	1.2161(9)	0.8568(9)	1.0179(9)	118.92(7)	0.9283	0.021
0.75	1.2080(7)	0.8517(5)	1.0083(2)	118.69(5)	0.9101	0.015
1.00	1.1994(4)	0.8570(5)	0.9886(5)	118.46(3)	0.8934	0.011
1.25	1.1965(4)	0.8535(5)	0.9880(5)	118.48(3)	0.8870	0.011
1.50	1.1930(4)	0.8503(5)	0.9875(5)	118.52(3)	0.8801	0.010
1.75	1.1860(4)	0.8406(4)	0.9893(4)	118.67(3)	0.8650	0.010
2.00	1.1788(5)	0.8305(4)	0.9910(4)	118.83(3)	0.8492	0.011

[a] $\Delta 2\upsilon = N^{-1}(2\upsilon_{exp} - 2\upsilon_{calc})$, where $2\upsilon_{exp}$ is the experimental diffraction angle, $2\upsilon_{calc}$ is the angle calculated from lattice parameters and N is the number of investigated diffraction lines.

Table 3
Melting temperatures and densities of $Cd_{2-x}Zn_xP_4O_{12}$

x	T_{melting} (°C)	$\rho_{\mathrm{exp.}}$ (g cm^{-3})	$\rho_{\mathrm{calc.}}$ (g cm^{-3})
0	800	3.85	3.723
0.25	800	3.81	3.710
0.50	802	3.76	3.700
0.75	804	3.71	3.686
1.00	806	3.69	3.670
1.25	808	3.63	3.610
1.50	808	3.57	3.548
1.75	809	3.53	3.520
2.00	810	3.50	3.493

increasing x. The experimental values ($\rho_{\mathrm{exp.}}$) are in accordance with the density values calculated ($\rho_{\mathrm{calc.}}$) on the basis of the X-ray diffraction analysis.

The binary cadmium(II)-zinc(II) cyclo-tetraphosphates were colourless, which is advantageous for their application as special anticorrosive pigments of high thermal stability. The coatings containing these anticorrosive pigments may be easily coloured to the desired hue by means of cheaper classical pigments.

4. Conclusion

This paper has shown that it is possible to prepare the binary cadmium(II)-zinc(II) cyclo-tetraphosphates $Cd_{2-x}Zn_xP_4O_{12}$. The colourless products crystallize in the monoclinic system, space group C2c, the lattice parameters continuously change with the zinc content. The synthesis is based on a thermal procedure making use of the reversible transformation of cyclo-tetraphosphates to higher linear phosphates.

The aim was to obtain high yields of a cyclo-tetraphosphate, which constitutes the insoluble portion of the calcinate. The method would then provide binding of the problematic cadmium ions that are often present in phosphoric acid, when it is used in the preparation of cyclo-tetraphosphates of bivalent metals serving as special inorganic pigments [10]. The formation of the binary cadmium(II)-zinc(II) cyclo-tetraphosphates from the cadmium ions that are often present in starting phosphoric compounds used in the technological preparation, would represent an important, hygienic method of binding them to insoluble, less harmful cadmium compounds.

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