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SYNTHESIS OF BINARY CYCLO-TETRAPHOSPHATES BY THERMAL DECOMPOSITION OF POLYPHOSPHATE GLASSES

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Binary cyclo-tetraphosphates $Me^{II}_{2-x}M^{II}_xP_4O_{12}$ were synthetized via the thermal decomposition and recrystallization of polyphosphate glasses, i.e. binary higher linear phosphates $(Me^{II}_{2-x}M^{II}_x)_{n/4}H_2P_nO_{3n+1}$. The syntheses of c-$Zn_{2-x}Mg_xP_4O_{12}$ and c-$Zn_{2-x}Ca_xP_4O_{12}$ are presented as examples.

Binary tetraphosphates (containing Ca or Mg) with cyclic anions have not yet been described in the literature. The possibility of the existence of c-tetraphosphate compounds with calcium as cation has not previously been acknowledged [1, 2]. The method of synthesis we have developed, based on the reversible transition of higher linear phosphates to cyclo-tetraphosphates (by means of thermal decomposition combined with recrystallization [3]), gave a possibility for the formation of these substances and of showing them to be new inorganic compounds [4].

Experimental

The method suggested for the preparation of binary cyclo-tetraphosphates is based on a two-step thermal synthesis. The first step starts from a mixture of the pure cyclo-tetraphosphates of the two divalent metals or $Ca(PO_3)_2$, which is melted in normal air atmosphere and then abruptly cooled to give a vitreous amorphous product composed of higher linear phosphates with the overall formula $(Zn_{2-x}M^{II}_x)_{n/4}H_2P_nO_{3n+1}$ (M^{II} = Mg, Ca). Aliquots of these intermediates are next subjected to DTA (Perkin-Elmer DTA 1700/TADS system) (determination of T_{Ri}, T_m, ΔH and T_{melt}) and are then calcined in an electric furnace at a temperature 20° higher than

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T_m for 30 min. In this second step, the vitreous intermediates decompose and recrystallize to give the microcrystalline product c-$Zn_{2-x}M_xP_4O_{12}$. The yields of the process (α) are determined by a special extraction method [5]. (The same two-step procedure was also applied to the pure c-$Zn_2P_4O_{12}$, c-$Mg_2P_4O_{12}$ and $Ca(PO_3)_2$.) The starting phosphates, intermediates (higher linear phosphates) and final products obtained were analyzed by instrumental analytical methods (chromatography, IR-spectroscopy, X-ray powder diffraction analysis, AAS and electron and high-temperature microscopy). The diffractograms ($\lambda Cu_{K\alpha}$ = 0.15418 nm) were indexed on the basis of the fact that the binary products c-$Zn_{2-x}Mg_x$-P_4O_{12} and c-$Zn_{2-x}Ca_xP_4O_{12}$ are isostructural with c-$Zn_2P_4O_{12}$ and c-$Mg_2P_4O_{12}$, respectively [6].

Results and discussion

The first sections in the DTA curves (Fig. 1) indicate an exothermic process. This process is the reaction of formation of the binary tetrametaphosphate from the intermediate higher linear phosphates (1), which is connected with decomposition and recrystallization of the amorphous vitreous phase (T_{Ri}, T_m and ΔH are given in Table 1 and Fig. 2).

Table 1 Conditions of formation and melting of c-$Zn_{2-x}M^{II}_xP_4O_{12}$

x Zn−Mg (Zn−Ca)	0	0.25	0.5	0.75	1.0	1.5	2.0
T_{Ri}, °C	545	563	577	592	607	648	706
	(545)	(558)	(573)	(590)	(610)		
T_m, °C	573	600	618	635	654	693	745
	(573)	(586)	(602)	(620)	(639)		
$-\Delta H$, J/g	149	157	170	185	202	242	305
	(149)	(155)	(163)	(172)	(182)		
yield, α, %	90.5	95.6	97.0	98.2	98.5	99.4	99.7
	(90.5)	(93.2)	(94.8)	(95.6)	(96.0)		
T_{melt}, °C	810	820	845	875	905	990	1160
	(810)	(770)	(748)	(735)	(730)		

$$(Zn_{2-x}M^{II}_x)_{n/4}H_2P_nO_{3n+1(glass)} = n/4\ c\text{-}Zn_{2-x}M^{II}_xP_4O_{12(cryst.)} + H_2O_{(g)} \quad (1)$$

Analysis of the products prepared in the electric furnace at a temperature of $T_m + 20°$ showed that the yields of these syntheses are high: α = 90.5-99.7% (for the Zn-Mg product) and 90.5-96.0% (Zn-Ca) (Table 1 and Fig. 2); the

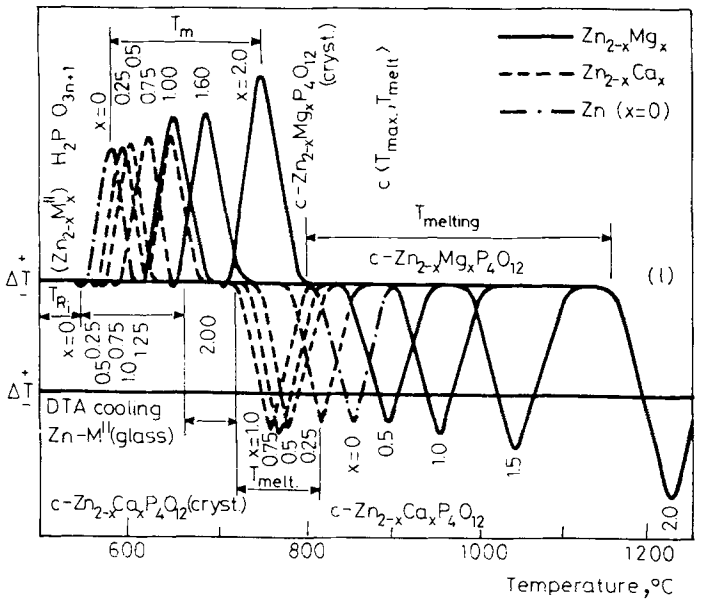

Fig. 1 The DTA curves indicate the formation and melting of c-$Zn_{2-x}M_xP_4O_{12}$ (M = Mg, Ca) Sample weight 15 mg, heating rate 20 deg/min^{-1}, Pt crucible, open, atmosphere air

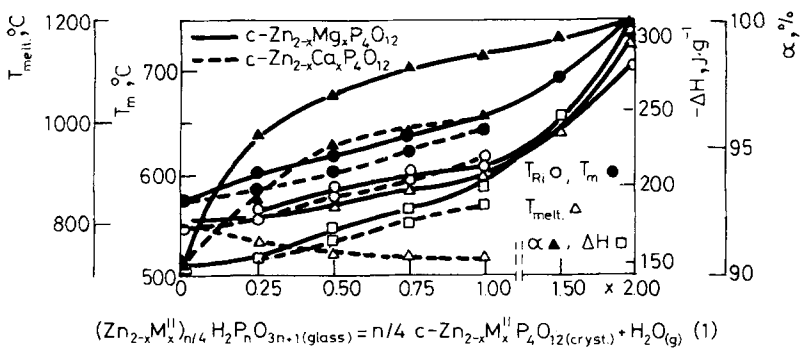

Fig. 2 Data documenting the formation and melting of c-$Zn_{2-x}M_x$-P_4O_{12}

molar ratio $P_2O_5/(Zn+M^{II})$ determined on the extracted product is 0.9990-1.0008 (Zn-Mg) or 0.9974-1.0025 (Zn-Ca), and the molar ratio $Zn/M^{II} = 1$. The instrumental analytical methods confirmed that each product comprises

only a single phase, in the interval $x \in <0; 2>$ (Zn-Mg) or $x \in <0; 1>$ (Zn-Ca) and the composition of the anion corresponds to cyclo-tetraphosphate. The structural parameters of the products lie between the parameters corresponding to the cyclo-tetraphosphates with $x = 0$ and 2 (Zn-Mg) or $x = 0$ and 1 (Zn-Ca) [4]. As the yields of these syntheses were high, the section of the DTA curve above the recrystallization temperature can be considered to determine the thermal stabilities of the binary tetrametaphosphates. The endothermic effects in these DTA curves document the melting, which is incongruent (Table 1 and Fig. 2): the tetrametaphosphate is transformed reversibly into higher linear phosphates (2), this being favoured by the presence of at least traces of water vapour in the air atmosphere:

$$c\text{-}Zn_{2-x}M_xP_4O_{12(cryst.)} + 4/n\ H_2O_{(g)} = 4/n\ (Zn_{2-x}M_x)_{n/4}{-}H_2P_nO_{3n+1(l)} \qquad (2)$$

The high termal stability of the c-$Zn_{2-x}M_xP_4O_{12}$ products extends the range of their applications as special pigments [7].

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Zusammenfassung — Mittels thermischer Zersetzung und Rekristallisierung von Polyphosphatgläsern, d.h. von binärem höherem, linearem Phosphat der Formel $Me^{II}_{2-x}M^{II}_x)_{n/4}H_2P_nO_{3n+1}$ wurden in unserem Laboratorium die binären Cyclotetraphosphate $Me^{II}_{2-x}M^{II}_xP_4O_{12}$ synthetisiert. Als Beispiel wird die Synthese von c-$Zn_{2-x}Mg_xP_4O_{12}$ und c-$Zn_{2-x}Ca_xP_4O_{12}$ beschrieben.