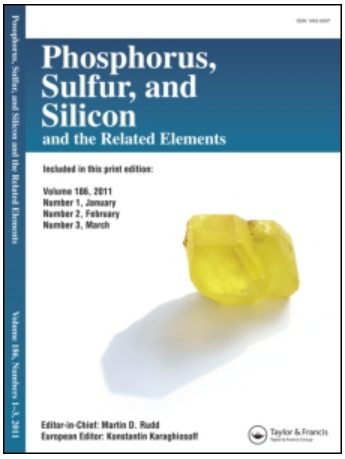

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Binary Cyclo-Tetraphosphates as New Special Pigments

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To cite this Article Trojan, M. , Brandová, D. and Mazan, P.(1990) 'Binary Cyclo-Tetraphosphates as New Special Pigments', Phosphorus, Sulfur, and Silicon and the Related Elements, 51: 1, 117 — 120
To link to this Article: DOI: 10.1080/10426509008040695
URL: http://dx.doi.org/10.1080/10426509008040695

Phosphorus, Sulfur, and Silicon, 1990, Vols. 51/52, pp. 117–120
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BINARY CYCLO-TETRAPHOSPHATES AS NEW SPECIAL PIGMENTS

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Abstract The binary cyclo-tetraphosphates $Me_{2-x}^{II}M_x^{II}P_4O_{12}$ as new inorganic compounds (M^{II}=Zn, Mn,Co; M^{II}=Ca,Mg) have been prepared in our laboratory. The products were tested as special pigments (for anti-corrosion, ceramic, luminescence purposes and as pearlescent pigments).

INTRODUCTION

Binary tetraphosphates (containing Ca or Mg) with cyclic anions have not yet been described in literature. The recent summarizing papers[1-4] giving, inter alia, a number of binary compounds of the condensed phosphate type even allow to make the conclusion that the existence of these compounds cannot be expected at all.[2]

EXPERIMENTAL

First the products were synthesized as pure substances, which is based on the preparation of glass semiproducts of binary higher linear phosphate type. These products were thermally recrystallized to the cyclo-tetraphophates (see scheme I).

$$(1-x/2)Me_2^{II}P_4O_{12(cryst.)} + x/2\underset{(xCa(PO_3)_2)}{Mg_2P_4O_{12(cryst.)}} + 4/nH_2O \longrightarrow$$

$$\xrightarrow[\text{(wet air atmosphere)}]{T_{melt.}} 4/n(Me_{2-x}M_x)_{n/4}H_2P_2O_{3n+1(l)} \longrightarrow$$

$$\xrightarrow[(\text{solidification})]{T_{melt.}\div 25^{o}C} 4/n(Me_{2-x}M_{x})_{n/4}H_2P_nO_{3n+1}(glass) \longrightarrow$$

$$\xrightarrow[(\text{recryst.})]{T_{recr.}} Me_{2-x}M_xP_4O_{12}(cryst.) + 4/nH_2O \qquad (I)$$

After evaluation of the products by analytical and physico-chemical methods, experiments were carried out with the aim of their possible synthesis by more frasible low-temperature processes, based on dehydration of a suitable starting mixture (see scheme II).

$$2Me^{II}_{1-x/2}M^{II}_{x/2}(H_2PO_4)_2\cdot yH_2O \xrightarrow[-2yH_2O]{T_D(\text{dehydrat.})} 2Me_{1-x/2}M_{x/2}H_2PO_4$$

$$\xrightarrow[-2H_2O]{T_{CR-1}(1.\text{condensed reaction})} 2M_{1-x/2}M_{x/2}H_2P_2O_7 \xrightarrow[-2H_2O]{T_{CR-2}(2.\text{condensed reaction})} \qquad (II)$$

$$(1-z)Me_{2-x}M_xP_4O_{12}+z(2-x)Me_2P_4O_{12}+zxMg_2P_4O_{12}(2zxCa(PO_3)_2)$$

RESULTS AND DISCUSSION

It seems that in the case of binary cyclo-tetraphosphates containing calcium it is possible to prepare the requested product only within a closed range of x (where $x \in (0; 1\rangle$) whereas binary products with magnesium exist in the whole range x, i.e. $x \in (0;2)$). As an example there are further given the results concerning the two products - $Mn_{2-x}Ca_xP_4O_{12}$ and $Co_{2-x}Mg_xP_4O_{12}$. The first one seems to be advantageous by its anticorrosive properties[5] and the second one has an intensive colour and thermal stability.[6] The values of quantities showing the conditions of synthesis of both products by the first (high-temperature) way[7] and their thermal stability are summarized in Fig.1. Fig. 2 gives the values of structural parameters of both the type of products. In the case of the product with calcium there is a well noticeable limitation of area of existence of the requested binary product ($x \leqslant 1$). The course of

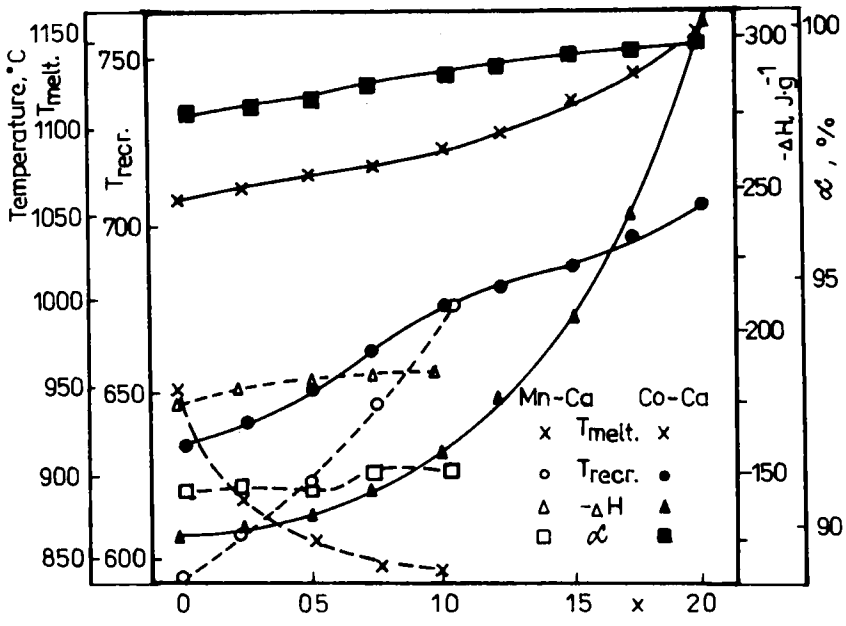

FIGURE 1 The values documenting the reaction of formation and stability of $Mn_{2-x}Ca_xP_4O_{12}$ and $Co_{2-x}Mg_xP_4O_{12}$ Temperatures of the recrystallization ($T_{recr.}$), heats (ΔH) and yields (α) of the process, melting.temp.-$T_{melt.}$

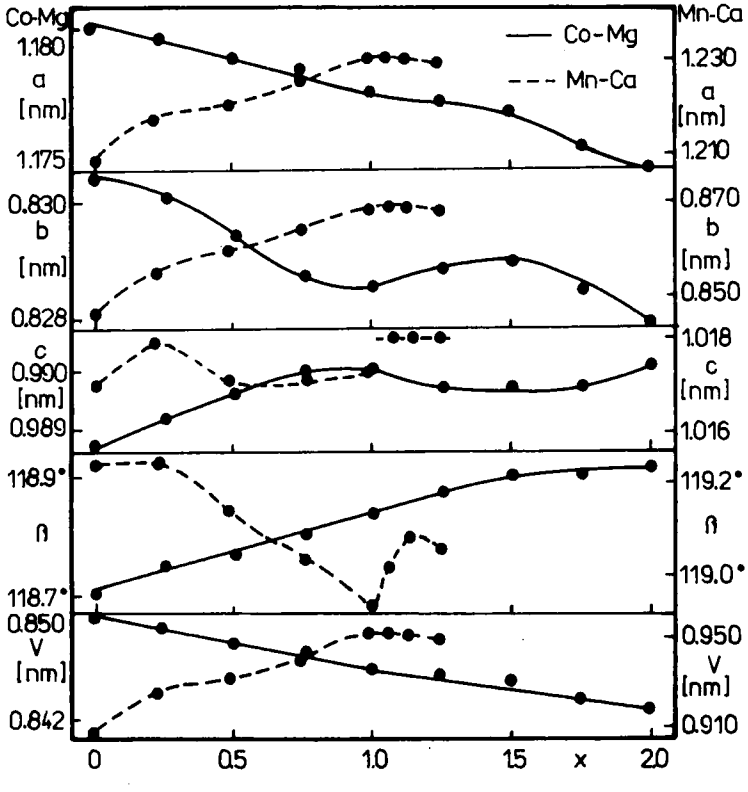

FIGURE 2 The structural parameters a, b, c, and V (volume of the elementary unit cell) of Mn-Ca and Co-Mg binary cyclo-tetraphosphates

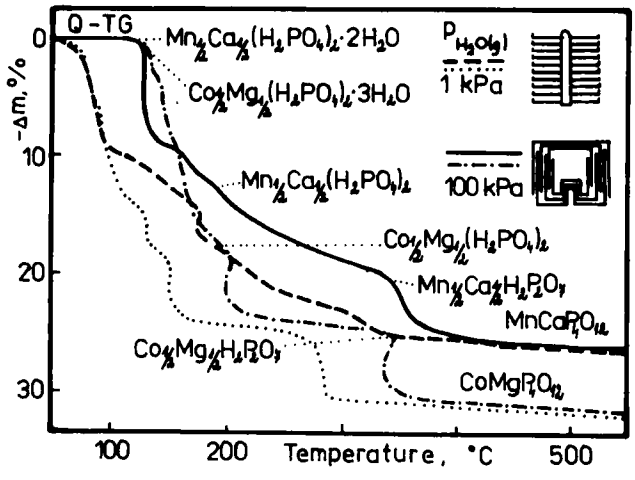

FIGURE 3

Thermogravimetric curves at quasi-isothermal-isobaric conditions of the starting phosphates (decomposition rate 0.2 mg.min^{-1}).

thermal analysis of suitable starting mixtures (binary dihydrogenphosphate, where x=1) under quasi-isothermal-isobaric conditions is shown in Fig.3. The solid curves in the figure show the weight decreases of the starting sample (and therefore the thermal course of dehydration and condensation reactions) under conditions, where the tension of water vapour in the space of the calcinated sample is near to the outer atmospheric pressure (100 kPa). Under these conditions (and in addition to them sufficient by slow increase of temperature and keeping the requested pauses at the temperature of the individual processes and with application of the nuclei of the requested product) it is possible to prepare such products which contain more than 90% $MnCaP_4O_{12}$ and $CoMgP_4O_{12}$[8].

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