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THE THERMAL ANALYSIS OF BINARY Zn(II)–Sr(II) CYCLO-TETRAPHOSPHATES

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Abstract

Binary Zn(II)–Sr(II) cyclo-tetraphosphates have been synthesised 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. With respect to the proposed application of these products as special inorganic pigments some properties (thermal stability, structural parameters, anti-corrosion activity) have been determined.

Keywords: anticorrosive pigments, condensed phosphates, cyclo-tetraphosphates

Introduction

Binary (mixed) cyclo-tetraphosphates of the c-$Zn_{2-x}Sr_xP_4O_{12}$ type have been prepared in our laboratory as new thermally stable anticorrosive pigments [1]. From the point of view of application the combination of the Zn and Sr cations in these compounds appears very advantageous. The content of strontium was selected so that the molar ratio Sr/Zn was 0.3/2.0. The synthesis of products with higher content of strontium is problematic. Their synthesis is based on two types of thermal methods.

Experimental

Two methods of preparation of condensed phosphates can be used for their synthesis. The first one consists in high-temperature calcination. This procedure is based on a two-step thermal synthesis. The first step, starting from the cyclo-tetraphosphates of the two bivalent metals, involves their melting in air atmosphere and then abruptly cooling to give a vitreous amorphous product [2] composed of higher linear phosphates. In the second step this product is repeatedly heated to a suitable temperature and recrystallized to give a microcrystalline product. On the basis of this method new high-temperature pigments have been prepared.

The second method of preparation, which is called as middle temperature synthesis, is based on the thermal dehydration of useful compound or a mixture of dihydrogenphosphates [3]. The main aim is to find such compounds that can be used as special thermostable pigments with anticorrosion-inhibition properties.

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The first method (high-temperature) was used to test possibility of synthesis and determination of binary metaphosphate systems. Then we tested the second method of synthesis. Realisation of this method is easier (the high temperatures are not used, corrosive melt of phosphates does not appear during synthesis). The products obtained by the second method are then tested for pigment's application, especially, anticorrosion-inhibition properties.

Mixtures of pure c-$Zn_2P_4O_{12}$ and $(Sr(PO_3)_2)_n$ melted in normal air atmosphere and then abruptly cooled to give vitreous amorphous products (polyphosphate glasses):

$$(1–x/2)Zn_2P_4O_{12}+x/2(Sr(PO_3)_2)_n+4/nH_2O \rightarrow 4/n(Zn_{2–x}Sr_x)_{n/4}H_2P_nO_{3n+1}(glass)$$

Table 1 Lattice parameters of binary products (monoclinic system C2c)

Formula	a_o/nm	b_o/nm	c_o/nm	β/°	V/nm^3
$Zn_{1.7}Sr_{0.3}P_4O_{12}$	1.1798	0.8319	0.9925	118.761	0.8513
$Zn_{1.8}Sr_{0.2}P_4O_{12}$	1.1791	0.8312	0.9917	118.787	0.8505
$Zn_{1.9}Sr_{0.1}P_4O_{12}$	1.1785	0.8308	0.9913	118.801	0.8499
$Zn_2P_4O_{12}$	1.1778	0.8305	0.9911	118.831	0.8492

Table 2 Conditions of formation of binary products using high-temperature methods and their melting points

Formula	$T_{recryst.}$/°C	$T_{melt.}$/°C	Yield/%
$Zn_{1.7}Sr_{0.3}P_4O_{12}$	514–582	755–760	93.6
$Zn_{1.8}Sr_{0.2}P_4O_{12}$	510–568	765–770	93.1
$Zn_{1.9}Sr_{0.1}P_4O_{12}$	505–560	780–785	92.2
$Zn_2P_4O_{12}$	545–573	810	90.5

Aliquots of these intermediates were next subjected to DTA (Perkin Elmer DTA 1700/TADS System) for determination of $T_{recryst.}$ and T_{melt} (Table 2) and calcinated in an electrical resistance furnace at a temperature 50°C higher than $T_{recryst.}$ for 30 min (in platinum mortar). The polyphosphate glasses decomposed and recrystallised:

$$(Zn_{2–x}Sr_x)_{n/4}H_2P_nO_{3n+1}(glass) \rightarrow n/4c\text{-}Zn_{2–x}Sr_xP_4O_{12}(cryst.)+H_2O(g)$$

Microcrystalline products obtained in this way were analysed by IAM methods and the diffractograms (X-ray CuK_α=0.15418 nm) were indexed on the basis of the fact that the products are isostructural with c-$Zn_2P_4O_{12}$ [4].

The values x (or molar ratio Sr/Zn) which allows existence of binary Zn(II)–Sr(II) cyclo-tetraphosphates were determined. These cyclo-tetraphosphates were prepared by middle-temperature synthesis. The synthesis of the cyclo-tetraphosphates can be described by the following scheme:

$$(2–x)ZnO+xSrO+4H_3PO_4 \rightarrow 2Zn_{(1–x/2)}Sr_{x/2}(H_2PO_4)_2+2H_2O\ (T_1)$$
$$2Zn_{(1–x/2)}Sr_{x/2}(H_2PO_4)_2 \rightarrow 2Zn_{(1–x/2)}Sr_{x/2}H_2P_2O_7+H_2O\ (T_2)$$
$$2Zn_{(1–x/2)}Sr_{x/2}H_2P_2O_7 \rightarrow c\text{-}Zn_{2–x}Sr_xP_4O_{12}(cryst.)+H_2O\ (T_3)$$

Results

The high-temperature synthesis shows that binary product c-$Zn_{2-x}Sr_xP_4O_{12}$ can be prepared only in the region where $x \leq 0.3$. At higher content of strontium the binary product does not appear but the mixture of products is formed. This is probably caused by large ionic radius of strontium that does not allow substitution of zinc ions into the structure of cyclo-tetraphosphate, because the bivalent zinc ion has a smaller radius than the bivalent strontium ion. Lattice parameters of binary cyclo-tetraphosphates are demonstrated in Table 1.

The yields of the final products (where $x \leq 0.3$) prepared by middle-temperature synthesis are sufficiently high (94.3–95.6%). The thermal analysis has been used for study of middle-temperature synthesis of the binary cyclo-tetraphosphates. The thermoanalytical curves indicating formation of c-$Zn_{1.7}Sr_{0.3}P_4O_{12}$ are demonstrated in Fig. 1.

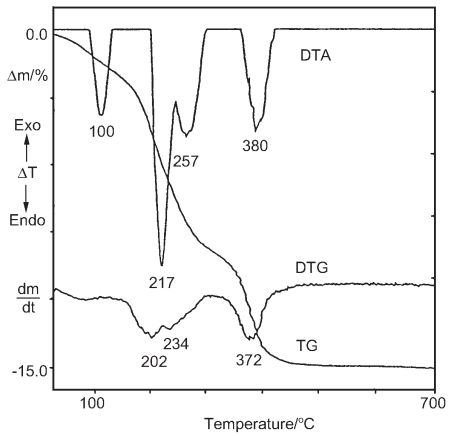

Fig. 1 Thermoanalytical curves of the middle-temperature synthesis of the binary product $Zn_{1.7}Sr_{0.3}P_4O_{12}$, Apparatus derivatograph-C, heating rate 5°C min^{-1}, initial mass: 100.45 mg, standard α-Al_2O_3, atmosphere air, platinum crucible with cover

The thermal analysis provided the first information about the temperature region of formation of this type of compounds. The temperature regions of particular processes are demonstrated in Fig. 1. The position of endothermic effects (axis of temperature) corresponds to temperatures mentioned in the second scheme.

From the results of thermal analysis it follows that process of formation of dihydrogenphosphate (T_2) is represented by two endothermic effects on the DTA curve. The TG curve shows the decrease of mass that accompanies this formation. From the DTA curve it follows that this process has two steps. The analyses of intermediates are also in agreement with the results of thermal analysis and show that intermediates are composed of mixtures of diphosphates Zn(II) and Sr(II). The pure

product of the binary character is formed during the third step (T_3). The product described by formula c-$Zn_{1.7}Sr_{0.3}P_4O_{12}$ had a yield of 95.6%.

Conclusions

The main attention was focused on the synthesis of the binary cyclo-tetraphosphates c-$Zn_{1.7}Sr_{0.3}P_4O_{12}$. Their application and anticorrosion-inhibition properties are followed [5].

Some of these compounds are shown as new hopeful environmentally safe anticorrosive pigments, mainly c-$Zn_{1.7}Sr_{0.3}P_4O_{12}$. The binary products containing strontium seem to be interesting as to their anticorrosion properties. These pigments are environmentally friendly and therefore very progressive too.

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