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THERMAL SYNTHESIS OF MIXED Zn(II)–Ca(II)–Co(II) CYCLO-TETRAPHOSPHATES

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Abstract

Cyclo-tetraphosphates of the type $Zn_{2-x-y}Ca_xCo_yP_4O_{12}$ were synthesized by thermal decomposition and recrystallization of polyphosphate glasses, i.e. mixed higher linear phosphates.

Keywords: cyclo-tetraphosphates, thermal synthesis

Introduction

Mixed cyclo-tetraphosphates have been synthesized in our laboratory as new thermally stable anticorrosive pigments. From the aspect of application, the combination of the cations Zn–Ca–Co in these compounds appears very advantageous [1]. The Ca content was selected so that the molar ratio Ca/(Zn+Co) lay in the interval from 3/7 to 2/3 (the synthesis of products with higher Ca content is problematic [2]), while the content of Co was kept low, with the molar ratio Co/(Zn+Ca) between 1/19 and 3/17 (because of the cost of cobalt compounds).

Experimental

Mixtures of pure $Zn_2P_4O_{12}$, $Co_2P_4O_{12}$ and $(Ca(PO_3)_2)_n$ were melted in normal air atmosphere and were then abruptly cooled to give vitreous amorphous products (polyphosphate glasses) with the overall formula $(Zn_{2-x-y}Ca_xCo_y)_{n/4}H_2P_nO_{3n+1}$. Aliquots of these intermediates were next subjected to DTA (Perkin Elmer DTA 1700/TADS system for determination of T_{Ri}, T_m, ΔH and T_{melt} (Fig. 1, Table 1)) and then calcined in an electric furnace at a temperature 20 deg higher than T_m for 30 min. The polyphosphate glasses decomposed and recrystallized to give the microcrystalline products $Zn_{2-x-y}Ca_xCo_yP_4O_{12}$ ($x = 0.6$–0.8, $y = 0.1$–0.3).

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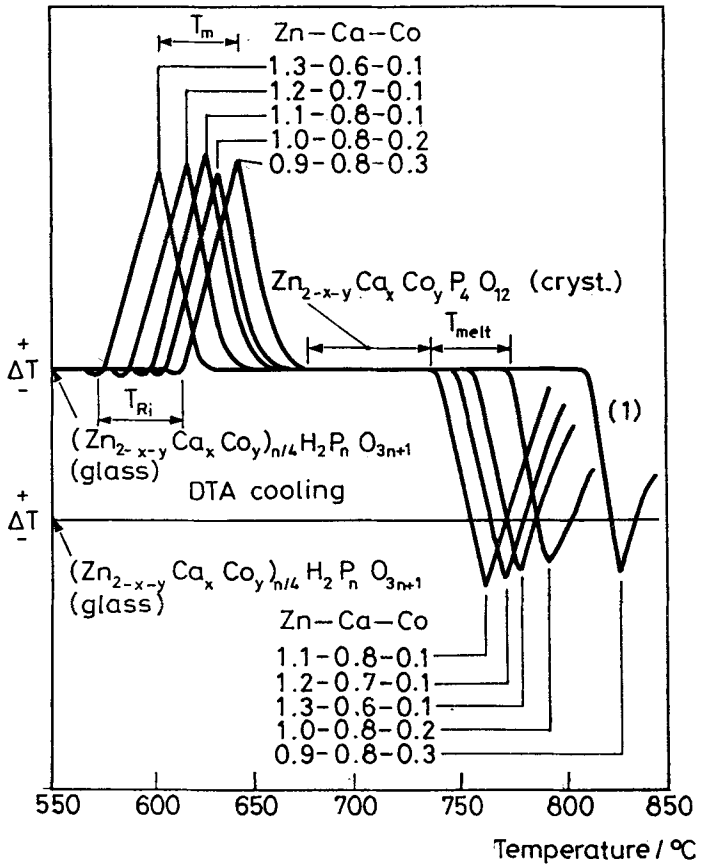

Fig. 1 DTA curves indicating the formation (1) and melting (2) of $Zn_{2-x-y}Ca_xCo_yP_4O_{12}$ Apparatus: Perkin Elmer DTA 1700/TADS system; sample mass: 15 mg; heating rate: 20 deg·min^{-1}; atmosphere: air

The intermediates and products obtained were analyzed by IAM methods, and the diffractograms (X-ray λCuK_α = 0.15418 nm) were indexed on the basis of the fact that the mixed products are isostructural with $Zn_2P_4O_{12}$, $Co_2P_4O_{12}$ and $ZnCaP_4O_{12}$ [3].

Results and discussion

The conditions of formation of the mixed products (1) (exothermic process in the DTA curves (Fig. 1) are given in Table 1:

$$(Zn_{2-x-y}Ca_xCo_y)_{n/4}H_2P_nO_{3n+1(glass)} =$$

$$^{n}/_{4}\ Zn_{2-x-y}Ca_xCo_yP_4O_{12(cryst.)} + H_2O_{(g)} \quad (1)$$

Analysis of the products prepared in the electric furnace showed that the yields in these syntheses are high (Table 1). The IAM methods confirmed that each product comprises only a single phase in the selected intervals x and y, and the composition of the anion corresponds to cyclo-tetraphosphate. The structural parameters of the products are given in Table 2.

Table 1 Conditions of formation and melting of $Zn_{2-x-y}Ca_xCo_yP_4O_{12}$

	T_{Ri}/ °C	T_m/ °C	$-\Delta H$/ J·g^{-1}	α/ %	T_{melt}/ °C
$Zn_{1.3}Ca_{0.6}Co_{0.1}$	575	602	167	95.2	755
$Zn_{1.2}Ca_{0.7}Co_{0.1}$	588	616	172	95.5	747
$Zn_{1.1}Ca_{0.8}Co_{0.1}$	597	625	178	95.9	738
$Zn_{1.0}Ca_{0.8}Co_{0.2}$	605	632	173	96.3	773
$Zn_{0.9}Ca_{0.8}Co_{0.3}$	614	639	166	96.9	810

Table 2 Structural parameters of $Zn_{2-x-y}Ca_xCo_yP_4O_{12}$

	a/ nm	b/ nm	c/ nm	β^o	V/ nm^3
$Zn_{1.3}Ca_{0.6}Co_{0.1}$	1.2061	0.8638	0.9863	118.52	0.9029
$Zn_{1.2}Ca_{0.7}Co_{0.1}$	1.2058	0.8634	0.9864	118.54	0.9021
$Zn_{1.1}Ca_{0.8}Co_{0.1}$	1.2064	0.8645	0.9853	118.44	0.9036
$Zn_{1.0}Ca_{0.8}Co_{0.2}$	1.2068	0.8628	0.9863	118.37	0.9036
$Zn_{0.9}Ca_{0.8}Co_{0.3}$	1.2045	0.8614	0.9870	118.39	0.9009

As the yields in the syntheses were high, the second section of the DTA curves (Fig. 1) can be considered to determine the thermal stabilities of the mixed products. The endothermic effects document the melting, which is incongruent (passes according to Eq. (1), but in the opposite direction (2)). This is favoured by the presence of even traces of water vapour in the air atmosphere:

$$^{n}/_{4}\ Zn_{2-x-y}Ca_xCo_yP_4O_{12(cryst.)} + H_2O_{(g)} = (Zn_{2-x-y}Ca_xCo_y)_{^{n}/_{4}}H_2P_nO_{3n+1(glass)} \quad (2)$$

References

1 M. Trojan and P. Kalenda, Proc. XII. ICPC 92', Toulouse 1992, p.100.
2 M. Trojan, Dyes and Pigments, 13 (1990) 1.
3 M. Trojan and L. Beneš, J. Mater. Sci., 24 (1989) 3745.

Zusammenfassung — Mittels thermischer Zersetzung und Rekristallisierung von Polyphosphatgläsern, z.B. von gemischten höheren linearen Phosphaten, wurden Cyclotetraphosphate vom Typ $Zn_{2-x-y}Ca_xCo_yP_4O_{12}$ synthetisiert.