Journal of Thermal Analysis, Vol. 54 (1998) 71-77

PHASE ANALYSIS AND CRYSTALLOGRAPHIC PROPERTIES OF THE PHOSPHATE SYSTEMS $MO–ZrO_2–P_2O_5$ (M=Mg, Ca, Sr or Ba)

V. I. Petkov and A. I. Orlova

Department of Chemistry, Nizhny Novgorod State University, Gagarin Av. 23
603600 Nizhny Novgorod, Russia

Abstract

Phase formation in the systems $MO–ZrO_2–P_2O_5$ (M=Mg, Ca, Sr or Ba) with various ratios of M to Zr cations and within the temperature interval from 20 to 1200°C was investigated by means of DTA, TG, XRD and IR spectroscopy. The orthophosphate phases $M_{0.5x}Zr_{2.25-0.25x}(PO_4)_3$ with x=0–1, 3 and 7 were synthesized. Concentration and temperature limits of phase existence were found for phosphates belonging in the $NaZr_2(PO_4)_3$ structural family. They exist within the regions with M to Zr ratios of $0 \leq x \leq 1$ (with the exception of the Mg phases) and in the temperature interval from room temperature to 900–1700°C.

Keywords: complex phosphates, NZP structure, phase formation

Introduction

The valuable physicochemical properties of crystalline phosphates with the $NaZr_2(PO_4)_3$ (NZP) structure, such as thermal, radiation and hydrolytic stability, resistivity in aggressive media, and low thermal conductivity, are determined by their structural peculiarities [1–3]. Some phosphates with such a structure and having special compositions are characterized by ultralow thermal expansion, high ionic conductivity and catalytic activity [4].

The basis of this structure is a mixed anionic framework of $\{[Zr_2(PO_4)_3]^-\}_{3\infty}$, consisting of individual Zr octahedra and single P tetrahedra [1]. Sodium cations are situated in some of the cavities of the anionic framework that are open for occupation, and play the role of compensators of negative charge.

In the case of substances analogous to sodium-zirconium phosphates, the framework cavities may be empty, or partly or completely occupied by other cations with different oxidation states and sizes. Extremely wide variations of cation composition with the conservation of crystallographic characteristics close to those of NZP are guaranteed by correlated rotations of the tetrahedra and octahedra.

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Until recently, only few of the compounds theoretically predicted to have the NZP structure had been synthesized. Their preparation often demands very difficult experimental work and depends upon the synthetic methods available. The shortage of data on the chemical mechanisms of formation of complex orthophosphates of zirconium and other elements, including compounds with the NZP structure, hampers the choice of the best synthetic method and its optimization, and leads to the formation of waste phases besides the desired reaction products.

We earlier reported the results of our investigations on the synthesis and phase formation of orthophosphate systems containing zirconium and alkali metal elements M^{I}_2O–ZrO_2–P_2O_5 [1].

The present work relates to the phase formation in the systems of the alkaline earth elements, MO–ZrO_2–P_2O_5, where *M*=Mg, Ca, Sr or Ba, at various ratios of *M* and Zr cations and within a wide temperature interval (20–1200°C). It was also desirable to establish the concentration and temperature regions of existence of phases with the NZP structure within $M_{0.5x}Zr_{2.25-0.25x}(PO_4)_3$, and to study the influence of the method of synthesis and thermal treatment on the formation of monophase zirconium and alkaline earth element orthophosphates with the NZP structure.

Experimental

For the systems MO–ZrO_2–P_2O_5 studied, many compositions were prepared, with general formula $M_{0.5x}Zr_{2.25-0.25x}P_3O_{12}$, with x=0, 0.5, 1, 2, 3, 4, 5, 6, 7 and 9. They included all phase existence regions of the proposed orthophosphate phases, such as $Zr_{0.25}Zr_2(PO_4)_3$=$Zr_3(PO_4)_4$, x=0; $M_{0.5}Zr_2(PO_4)_3$, x=1; $M_{1.5}Zr_{1.5}(PO_4)_3$, x=3; $M_{3.5}Zr_{0.5}(PO_4)_3$, x=7; and $M_{4.5}(PO_4)_3$=$M_3(PO_4)_3$, x=9. We used synthetic methods based upon reactions taking place in aqueous solutions (sol-gel, hydrothermal methods) and in the solid state [2]. In all cases, we used reagent grade $M(NO_3)_2$, H_3PO_4, $NH_4H_2PO_4$, $ZrOCl_2 \cdot 8H_2O$, $ZrO(NO_3)_2 \cdot 2H_2O$, amorphous ZrO_2, and zirconium *iso*-propylate $Zr(OPr\text{-}i)_4 \cdot i\text{-}PrOH$.

The set of synthetic methods chosen gave us an opportunity to extend the thermal region of formation of compounds with desirable compositions, and to reveal the influence of solvent and temperature upon the structures of the phases formed. The phosphates prepared were studied by DTA, TG, XRD and IR spectroscopy. The same methods were used to investigate the chemical mechanisms of the processes at different stages of synthesis by controlling the starting reagents, the intermediate phases, and the final products in the samples.

Simultaneous DTA-TG measurements were performed with a Q-1500D derivatograph. The sample mass was ~0.5 g. Samples were heated in the temperature interval from 20 to 1000°C under static air, at a heating rate of 10°C min^{-1}, using platinum crucibles. Al_2O_3 was used as standard.

X-ray powder diffractograms were recorded with a DRON-407 diffractometer, using CuK_α radiation at room temperature. X-ray diffraction data on the phases formed during annealing of the samples investigated were conpared with data on the phases contained both in the card index PDF JCPDS and in the original works.

IR spectra were recorded on a Specord M-80 spectrophotometer between 400 and 1400 cm^{-1}. Samples were prepared by using the KBr disc techniquc. Thc vibrations were assigned by using standard characteristic intervals for group vibrations and literature data.

Results and discussion

By means of various synthetic methods, phosphates of alkaline earth elements and zirconium, $M_{0.5x}Zr_{2.25-0.25x}P_3O_{12}$, where $x_{min}=0$ and $x_{max}=9$, were prepared both as individual and as mixed phases of various compositions. To perform more detailed studies of the phase-forming processes that occur in the synthetic methods, we preferred the sol-gel procedure. This ensured the formation of highly fine powder mixtures with uniformly distributed ingredients and the best reproducibility of the results.

By using DTA and TG curves of the gels investigated, we determined the most characteristic temperatures at which the different physicochemical conversions took place. Next, new gel portions were heated up to chosen temperatures and XRD and IR spectroscopic analyses were then performed on the annealing products obtained.

The samples were subsequently subjected to isothermal annealing at 600, 800, 900, 1000 and 1150°C. The duration of heat exposure was 24 h for each temperature. At the end of each annealing stage, part of the sample was fast-hardened with air and analysed. The remaining part was subjected to further heating, and this procedure was repeated at each step of the annealing.

The processes that took place in the course of gel heat treatment within the temperature and time intervals were characterized by partial chemical interaction of the contacting phases and differed in the temperature region of their occurrence.

The results of phase investigations of the products obtained in the course of step-like isothermal heating of the samples from the systems $MO–ZrO_2–P_2O_5$ are shown in Tables 1–4.

The existence of orthophosphate substances such as $Zr_3(PO_4)_4$, $M_{0.5}Zr_2(PO_4)_3$, $M_{1.5}Zr_{1.5}(PO_4)_3$, $M_{3.5}Zr_{0.5}(PO_4)_3$ and $M_3(PO_4)_2$ was found for all systems involving alkaline earth elements. The ratios M to Zr changed monotonously; they were members of the series $M_{0.5x}Zr_{2.25-0.25x}(PO_4)_3$.

Table 1 Phase composition of the system $Mg_{0.5x}Zr_{2.25-0.25x}P_3O_{12}$ at different annealing temperatures

Stoichiometry/ x	Heat treatment/ °C	Phase composition
0.5	900	$Mg_{0.5}Zr_2(PO_4)_3+ZrP_2O_7+\alpha\text{-}Zr_2P_2O_9$
1	800	$Mg_{0.5}Zr_2(PO_4)_3$
	900	$Mg_{0.5}Zr_2(PO_4)_3+ZrP_2O_7+\alpha\text{-}Zr_2P_2O_9+Mg_2P_2O_7+ZrO_2$
3	800	$Mg_{0.5}Zr_2(PO_4)_3+ZrP_2O_7+Mg_3(PO_4)_2$
	1100	$Mg_{0.5}Zr_2(PO_4)_3+Mg_3(PO_4)_2+ZrP_2O_7+Mg_2P_2O_7+ZrO_2$
7	800	$Mg_3(PO_4)_2+ZrP_2O_7+Mg_{0.5}Zr_2(PO_4)_3$
	1100	$Mg_3(PO_4)_2+\alpha\text{-}Zr_2P_2O_9+Mg_{0.5}Zr_2(PO_4)_3+Mg_2P_2O_7+ZrO_2$

Table 2 Phase composition of the system $Ca_{0.5x}Zr_{2.25-0.25x}P_3O_{12}$ at different annealing temperatures

Stoichoimetry/ x	Heat treatment/ °C	Phase composition
0.5	800	$Ca_{0.25}Zr_{2.125}(PO_4)_3$
	900	$Ca_{0.25}Zr_{2.125}(PO_4)_3+Ca_{0.5}Zr_2(PO_4)_3+ZrP_2O_7+\alpha\text{-}Zr_2P_2O_9$
	1000	$Ca_{0.5}Zr_2(PO_4)_3+ZrP_2O_7+\alpha\text{-}Zr_2P_2O_9+\beta\text{-}Zr_2P_2O_9$
	1150	$Ca_{0.5}Zr_2(PO_4)_3+ZrP_2O_7+\beta\text{-}Zr_2P_2O_9+\alpha\text{-}Zr_2P_2O_9$
1	800	$Ca_{0.5}Zr_2(PO_4)_3$
	1150	$Ca_{0.5}Zr_2(PO_4)_3$
3	800	$Ca_{0.5}Zr_2(PO_4)_3+Ca_3(PO_4)_2$
	900	$Ca_{0.5}Zr_2(PO_4)_3+Ca_3(PO_4)_2$
	1000	$Ca_{0.5}Zr_2(PO_4)_3+Ca_{1.5}Zr_{1.5}(PO_4)_3+Ca_3(PO_4)_2$
	1150	$Ca_{1.5}Zr_{1.5}(PO_4)_3$
4	900	$Ca_{0.5}Zr_2(PO_4)_3+Ca_3(PO_4)_2$
	1150	$Ca_{1.5}Zr_{1.5}(PO_4)_3+Ca_{0.5}Zr_2(PO_4)_3+Ca_3(PO_4)_2$
6	900	$Ca_3(PO_4)_2+Ca_{0.5}Zr_2(PO_4)_3$
	1000	$Ca_3(PO_4)_2+Ca_{1.5}Zr_{1.5}(PO_4)_3+Ca_{0.5}Zr_2(PO_4)_3$
	1150	$Ca_3(PO_4)_2+Ca_{1.5}Zr_{1.5}(PO_4)_3$
7	900	$Ca_3(PO_4)_2+Ca_{0.5}Zr_2(PO_4)_3$
	1000	$Ca_3(PO_4)_2+Ca_{1.5}Zr_{1.5}(PO_4)_3$
	1150	$Ca_3(PO_4)_2+Ca_{1.5}Zr_{1.5}(PO_4)_3$

Table 3 Phase composition of the system $Sr_{0.5x}Zr_{2.25-0.25x}P_3O_{12}$ at different annealing temperatures

Stoichiometry/ x	Heat treatment/ °C	Phase composition
0.5	800	$Sr_{0.25}Zr_{2.125}(PO_4)_3$
	900	$Sr_{0.25}Zr_{2.125}(PO_4)_3+Sr_{0.5}Zr_2(PO_4)_3+ZrP_2O_7+\alpha\text{-}Zr_2P_2O_9$
	1000	$Sr_{0.5}Zr_2(PO_4)_3+ZrP_2O_7+\alpha\text{-}Zr_2P_2O_9+\beta\text{-}Zr_2P_2O_9$
	1150	$Sr_{0.5}Zr_2(PO_4)_3+ZrP_2O_7+\beta\text{-}Zr_2P_2O_9+\alpha\text{-}Zr_2P_2O_9$
1	800	$Sr_{0.5}Zr_2(PO_4)_3$
	1150	$Sr_{0.5}Zr_2(PO_4)_3$
2	800	$Sr_{0.5}Zr_2(PO_4)_3+ZrP_2O_7+Sr_3(PO_4)_2+ZrO_2$
	900	$Sr_{0.5}Zr_2(PO_4)_3+ZrP_2O_7+Sr_3(PO_4)_2+ZrO_2$
	1000	$Sr_{0.5}Zr_2(PO_4)_3+Sr_{1.5}Zr_{1.5}(PO_4)_3+ZrP_2O_7+Sr_3(PO_4)_2+ZrO_2$
	1150	$Sr_{0.5}Zr_2(PO_4)_3+Sr_{1.5}Zr_{1.5}(PO_4)_3$
3	800	$Sr_{0.5}Zr_2(PO_4)_3+ZrP_2O_7+Sr_3(PO_4)_2+ZrO_2$
	900	$Sr_{0.5}Zr_2(PO_4)_3+ZrP_2O_7+Sr_3(PO_4)_2+ZrO_2+Sr_{1.5}Zr_{1.5}(PO_4)_3$
	1000	$Sr_{1.5}Zr_{1.5}(PO_4)_3+ZrP_2O_7+Sr_{0.5}Zr_2(PO_4)_3+Sr_3(PO_4)_2+ZrO_2$
	1150	$Sr_{1.5}Zr_{1.5}(PO_4)_3$
7	800	$Sr_3(PO_4)_2+ZrP_2O_7+ZrO_2+Sr_{3.5}Zr_{0.5}(PO_4)_3$
	1150	$Sr_{3.5}Zr_{0.5}(PO_4)_3$

Zirconium monophosphate, $Zr_3(PO_4)_4$ (x=0), is a general member. It is isostructural with NZP [1]. Above 900°C, zirconium monophosphate decomposes slowly to a mixture of zirconium di- and oxydiphosphate.

Crystallization of the compositions $M_{0.5}Zr_2(PO_4)_3$ (x=1) prepared by means of the sol-gel method proceeds within the temperature interval 730–800°C. This is evident from the DTA and XRD data. The hydrothermal synthetic method led to the formation of crystalline phases (with the exception of $Mg_{0.5}Zr_2(PO_4)_3$) at 200°C.

The cell parameters of $M_{0.5}Zr_2(PO_4)_3$ (M=Ca, Sr or Ba) phases structurally analogous to NZP are shown in Table 5. The phosphates are stable up to a temperature not less than 1700°C.

Monoclinic $Mg_{0.5}Zr_2(PO_4)_3$ is the only double magnesium and zirconium orthophosphate in the $MgO–ZrO_2–P_2O_5$ system and is stable up to 900°C (Table 1).

Solid solutions formed by the isostructural phosphates $Zr_3(PO_4)_4$ and $M_{0.5}Zr_2(PO_4)_3$ were found in the series of phosphates with calcium, strontium and barium at $0 \leq x \leq 1$. They belong to the NZP structural type. The solid solutions decompose at temperatures up to 900°C (Tables 2–4).

Table 4 Phase composition of the system $Ba_{0.5x}Zr_{2.25-0.25x}P_3O_{12}$ at different annealing temperatures

Stoichiometry/ x	Heat treatment/ °C	Phase composition
0.5	800	$Ba_{0.25}Zr_{2.125}(PO_4)_3$
	900	$Ba_{0.25}Zr_{2.125}(PO_4)_3$+$Ba_{0.5}Zr_2(PO_4)_3$+$ZrP_2O_7$+α-$Zr_2P_2O_9$
	1000	$Ba_{0.5}Zr_2(PO_4)_3$+ZrP_2O_7+α-$Zr_2P_2O_9$+β-$Zr_2P_2O_9$
1	800	$Ba_{0.5}Zr_2(PO_4)_3$
	1150	$Ba_{0.5}Zr_2(PO_4)_3$
2	800	$Ba_{0.5}Zr_2(PO_4)_3$+ZrP_2O_7+$Ba_3(PO_4)_2$+ZrO_2
	1000	$Ba_{0.5}Zr_2(PO_4)_3$+$Ba_{1.5}Zr_{1.5}(PO_4)_3$+$Ba_3(PO_4)_2$+ZrP_2O_7+ZrO_2
	1150	$Ba_{0.5}Zr_2(PO_4)_3$+$Ba_{1.5}Zr_{1.5}(PO_4)_3$
3	800	ZrP_2O_7+$Ba_3(PO_4)_2$+ZrO_2
	900	$Ba_{1.5}Zr_{1.5}(PO_4)_3$+ZrP_2O_7+$Ba_3(PO_4)_2$+ZrO_2
	1000	$Ba_{1.5}Zr_{1.5}(PO_4)_3$
5	800	$Ba_3(PO_4)_2$+ZrP_2O_7+ZrO_2
	900	$Ba_3(PO_4)_2$+ZrP_2O_7+ZrO_2+$Ba_{3.5}Zr_{0.5}(PO_4)_3$
	1000	$Ba_{1.5}Zr_{1.5}(PO_4)_3$+$Ba_{3.5}Zr_{0.5}(PO_4)_3$+$Ba_3(PO_4)_2$+ZrP_2O_7+ZrO_2
	1150	$Ba_{1.5}Zr_{1.5}(PO_4)_3$+$Ba_{3.5}Zr_{0.5}(PO_4)_3$+ZrO_2
7	800	$Ba_3(PO_4)_2$+ZrP_2O_7+ZrO_2+$Ba_{3.5}Zr_{0.5}(PO_4)_3$
	1150	$Ba_{3.5}Zr_{0.5}(PO_4)_3$

The chemical mechanism of phase formation is different for monoclinic $M_{1.5}Zr_{1.5}(PO_4)_3$ phosphates. Thus, $Ca_{1.5}Zr_{1.5}(PO_4)_3$ is formed in sol-gel processes after the crystallization of $Ca_{0.5}Zr_2(PO_4)_3$ and calcium monophosphate and their subsequent interaction at temperatures above 1000°C (Table 2). $Sr_{1.5}Zr_{1.5}(PO_4)_3$ and $Ba_{1.5}Zr_{1.5}(PO_4)_3$ are formed from the corresponding $M_{0.5}Zr_2(PO_4)_3$, $M_3(PO_4)_2$ and ZrO_2 at temperatures of 900–1150°C (Tables 3 and 4).

As concerns phosphate phases richer in alkaline earth elements, it was established that $M_{3.5}Zr_{0.5}(PO_4)_3$ phases with *M*=Sr or Ba are formed (Tables 3 and 4). They crystallize in the cubic crystallographic system.

Table 5 Cell parameters of the $M_{0.5}Zr_2(PO_4)_3$ phases (*M*=Ca, Sr or Ba), space group $R\bar{3}c$, *Z*=3

Phosphate	*a*/nm	*c*/nm
$Ca_{0.5}Zr_2(PO_4)_3$	0.880(2)	2.272(2)
$Sr_{0.5}Zr_2(PO_4)_3$	0.873(2)	2.332(0)
$Ba_{0.5}Zr_2(PO_4)_3$	0.867(8)	2.404(7)

Conclusions

The phase formation of orthophosphates in the systems $MO–ZrO_2–P_2O_5$ (M=Mg, Ca, Sr or Ba) has been studied in a wide range of cation ratios of M and Zr. An analysis of the data gave us an opportunity to find the concentration and temperature limits of the region of existence of the NZP structural phase. The concentration range for existence of the NZP structure in the systems $M_{0.5x}Zr_{2.25-0.25x}(PO_4)_3$, where M=Ca, Sr and Ba, is limited to $Zr_3(PO_4)_4$ and $M_{0.5}Zr_2(PO_4)_3$, which corresponds to the change of x from 0 to 1 in the formula.

The NZP structure may be formed at 200°C (under hydrothermal conditions) and persists on cooling down to room temperature and on increase of the temperature up to that of phosphate decomposition. The decomposition temperature depends upon the composition. The highest thermal stability above 1700°C was that of $M_{0.5}Zr_2(PO_4)_3$ phases (x=1). The decomposition temperature of $Zr_3(PO_4)_4$ (x=0) is lowest, at 900°C.

The phase formation regularities stated give a possibility to choose optimal conditions for the preparation of orthophosphate phases of desired composition, including phases with the NZP structure.

* * *

This research was supported by the Russian Foundation for Basic Research, Grant No. 98-03-32571a.

References

1 V. I. Petkov, A. I. Orlova and O. V. Egorkova, Russ. J. Struct. Chem., 37 (1996) 1104.
2 A. I. Orlova, V. I. Petkov and O. V. Egorkova, Radiochemistry, 38 (1996) 15.
3 Dean-Mo Lin, J. Mat. Sci. Lett., 13 (1994) 129.
4 D. K. Agraval, C.-Y. Huang and H. A. McKinstry, Inter. J. Thermophys., 12 (1991) 697.