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Crystal chemistry of complex orthophosphates with framework structure containing group IV d-transition metals and sodium

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Abstract

The phosphates $Na_5M(PO_4)_3$ (M = Ti, Zr, Hf) of NZP type structure were synthesized by solid-state procedure and precipitating methods. Their thermal behavior and heat capacity were studied in the range 7–650 K. Solid-to-solid phase transitions were observed for the phosphates $Na_5Zr(PO_4)_3$ (406.9 K) and $Na_5Hf(PO_4)_3$ (516.5 K). The crystal structure of a novel phosphate, $Na_5Hf(PO_4)_3$, at 298.15 K was refined by the Rietveld method. The basis of the structure is the framework built up of corner-sharing NaO_6- and HfO_6-octahedra (with ordered distribution of Na and Hf fragments) and PO_4-tetrahedra. Cavities in the framework are occupied mainly by Na^+ cations and small part of Hf^{4+} cations. Structure and phase formation data on the phosphates of alkali and group IV d-transition metals are generalized.

Keywords: NZP phosphates; Sodium; Group IVB metals; Crystal structure; Heat capacity

1. Introduction

Phosphates of the $NaZr_2(PO_4)_3$ (NZP) type structure are of interest as constructional and functional ceramics due to their stability to the extreme environmental conditions (high temperature and pressure, aggressive media, radiation), near-zero thermal expansion, high ionic conductivity, and catalytic activity [1]. The basis of their structure is three-dimensional framework $\{[L_2(PO_4)_3]^{p-}\}_{3\infty}$ (L is octahedral cation) which may include from 0 to 4 cations in its cavities [2].

It is known that double phosphates $AM_2(PO_4)_3$ (A = Li, Na, K, Rb, Cs; M = Ti, Zr, Hf) have NZP type structure, some of them also have other polymorphs [3]. The phosphates containing different alkali elements in the framework cavities $A_{1-x}A_x'M_2(PO_4)_3$ have been described by our group [4,5]. With systematic investigation of NZP substances, it was of interest to study the phosphates in which framework positions L are occupied by both alkali metal and group IV d-transition metal.

Herein, synthesis, crystal structure, thermal behavior and generalization of structure and phase formation data on sodium-containing phosphates $Na_5M(PO_4)_3$ (M = Ti, Zr, Hf) are reported.

2. Experimental

2.1. Synthesis

The compounds $Na_5M(PO_4)_3$ (M = Ti, Hf) were synthesized by powder technique. All used reactants were provided by REACHEM. Mixtures of NaCl (99.8%), TiO_2 (99.9%) or HfO_2 (99.9%), and $NH_4H_2PO_4$ (99.5%) in the stoichiometric proportions were heated in unconfined air access at 473 K for 10–12 h, 873 and 1023 K for 24 h. Compound $Na_5Zr(PO_4)_3$ was synthesized by precipitating method. Starting reagents, NaCl, $ZrOCl_2 \cdot 8H_2O$ (98%) and $NH_4H_2PO_4$ were previously dissolved in distilled water. The zirconium concentration in the solution taken for synthesis was confirmed gravimetrically [6]. During synthesis, the solution of $NH_4H_2PO_4$ taken in accordance with the stoichiometry of

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the phosphate was dropped into the solution containing NaCl and $ZrOCl_2$ under stirring. The mixture was dried at 353 K and thermally treated at 873 and 1073 K with 24 h plateaus at each step. All the thermal treatment stages were alternated with careful grinding.

2.2. Scanning electron microscopy and composition analysis

The obtained samples were colorless crystalline powders. Their homogeneity was confirmed by scanning electron microscopy on a CamScan MV-2300 device with a Link INCA ENERGY 200C energy-dispersion detector. The presence of the elements, Na, Ti (Zr or Hf), and P, was verified. The chemical composition of the samples was determined by chemical analysis. Known masses of the samples were dissolved in the HF aqueous solution. The sodium mass contents were determined by atomic absorption method on a Perkin–Elmer 603 device. The zirconium (titanium, hafnium) mass contents were determined gravimetrically [6]. The phosphorus mass contents were determined colorimetrically on an SF-46 spectrophotometer according to the method employing solutions of ammonia vanadate and ammonia molybdate [7]. The results of analyses prove that the stoichiometry of the samples, $Na_{4.99(4)}Ti_{1.00(3)}P_{3.01(3)}O_{12}$, $Na_{4.84(7)}Zr_{0.99(3)}P_{3.04(4)}O_{12}$, $Na_{4.97(3)}Hf_{1.01(2)}P_{3.00(3)}O_{12}$, is close to theoretical.

2.3. X-ray powder diffraction and Rietveld refinement

Phase purity of the phosphates $Na_5M(PO_4)_3$ (M = Ti, Zr, Hf) was established by powder X-ray diffraction (XRD) on a STOE STADI MP powder diffractometer equipped with a scanning position sensitive detector and curved Ge(111) primary monochromator using Cu Kα1 radiation (λ = 1.54056 Å). XRD patterns of the compounds were indicated in the space group *R*32. Unit-cell parameters of the compounds were determined at room temperature from the corresponding diffraction patterns indexed within range 10–50° in 2θ (Table 1).

XRD data for the structure refinement of the novel phosphate $Na_5Hf(PO_4)_3$ were collected in the angular range 8–117° in 2θ with a step size of 0.02° and a counting time of 600 s for each step. The structure refinement was carried out by a Rietveld analysis [8] using the program WYRIET, Version 3.3 [9]. The shape of the reflections was modeled with a Pearson VII function. Ionic scattering curves were used for all elements.

For the initial fractional coordinates we used those of $Na_5Ti(PO_4)_3$ ([10], model I) and $Na_5Zr(PO_4)_3$ ([11], model II). In both models octahedrally coordinated framework positions (6c) are ordered occupied by Na^+ and M^{4+} (Ti^{4+} or Zr^{4+}) cations. The models differ by centering or off-centering of M^{4+} in their framework positions: they occupy one type of position in $Na_5Ti(PO_4)_3$ structure and distributed between two closely situated framework positions in $Na_5Zr(PO_4)_3$ structure. In both models framework cavities are occupied by Na^+ (with a small part of Zr^{4+} cations in $Na_5Zr(PO_4)_3$ structure). There are also differences in Na^+ distribution in the cavities of these compounds. On carrying out structure investigations, Na^+ and Hf^{4+} site occupancies were refined.

The experimental conditions and results of refinements in both models are presented in Table 2, the final fractional coordinates and isotropic atomic displacement parameters are listed in Tables 3 and 4, and the selected interatomic distances in Tables 5 and 6. As a result, in both refined models we have obtained satisfactory values of all *R* factors. Calculated in both models bond lengths and angles in structure-forming polyhedra were within a typical range in other phosphates of NZP structure [11,12]. Obtained for all atoms *B* parameters are positive and reasonable. So, the results of structural refinement do not allow choosing one of these models. An example for a Rietveld plot for model II is shown in Fig. 1. It is seen that the observed and calculated profiles are in good agreement.

2.4. Heat capacity measurements

The thermal behavior and heat capacity of the samples $Na_5M(PO_4)_3$ (M = Ti, Zr, Hf) in the ranges 7–350 K and 330–650 K were measured with a BCT-3 low-temperature adiabatic vacuum calorimeter [13] and an automated dynamic calorimeter (ADCTTB) [14], respectively. The apparatus and the measurement procedure allowed us to obtain the $C^0_{p,m}$

Table 1
The unit-cell parameters of the phosphates $Na_5M(PO_4)_3$ (space group *R*32)

M	r^{4+}_M, Å	Unit-cell parameters		
		a, Å	*c*, Å	*V*, Å^3
Ti	0.61	9.064(4)	21.70(4)	1544
Zr	0.72	9.162(9)	22.27(2)	1619
Hf	0.71	9.15591(7)	22.2521(3)	1615.490

Table 2
Conditions of XRD experiment and results of Rietveld refinement of $Na_5Hf(PO_4)_3$ structure

	I	II
Starting model	$Na_5Ti(PO_4)_3$	$Na_5Zr(PO_4)_3$
Space group, *Z*	*R*32, 6	
2θ, °	8.00–117.10	
2θ step width, °	0.02	
Reflection number	325	
Variables	46	54
a, Å	9.15600(6)	9.15591(7)
c, Å	22.2514(2)	22.2521(3)
V, Å^3	1615.470(13)	1615.490(12)
R_{wp}, %	5.77	6.09
R_P, %	4.55	4.66
R_B, %	1.47	1.46
R_F, %	1.36	1.51
R_{exp}, %	4.28	4.28
S	1.35	1.42