Synthesis and Hydrothermal Study of (Na,K)$M_2(PO_4)_3$ (M = Ti, Zr, Hf) Solid Solutions

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Abstract

(Na,K)$M_2(PO_4)_3$ (M = Ti, Zr, Hf) continuous solid solutions were synthesized by sol-gel and solid-state methods. Cation-exchange reactions in the $NaM_2(PO_4)_3$–$KM_2(PO_4)_3$–NaCl–KCl–H_2O systems were studied at T = 723 – 973 K and p = 100 – 200 MPa. The concentration dependences of unit cell parameters of the studied phosphates were found. The sodium/potassium distribution coefficients in the phosphate-fluid systems were functions of the solid solution compositions, that is, the systems behave nonideally. The excess volumes and excess Gibbs functions of solid solutions mixing were fitted to third-order polynomials and described in terms of the Margules model. From the comparison of the results obtained Ti-, Zr-, and Hf-systems, we made the conclusion that the titanium phosphates show greater nonideality than zirconium and hafnium phosphates and lower thermodynamic stability to decomposition to double phosphates at high pressures and temperatures.

Introduction

The crystalline compounds of the $NaZr_2(PO_4)_3$ (NZP) type structure are known as ceramics exhibiting high thermal stability, resistance to thermal shock, radiation damage and action of aggressive media. So these substances are proposed in industrial applications, particularly as hosts for immobilizing radioactive waste [1, 2].

It is known [3] that the double phosphates $AM_2(PO_4)_3$ (A = Li, Na, K, Rb, Cs; M = Ti, Zr, Hf) may crystallize in the NZP type structure with the framework built up of corner-sharing MO_6 octahedra and PO_4 tetrahedra, alkali metals cations are distributed in the cavities situated in the ribbons of octahedra and tetrahedra, parallel to the c axis (Fig. 1). Study of NZP solid solutions with mixed alkali metals is of interest for the understanding of isovalent isomorphism features in framework structures and in connection with the perspective of phosphate immobilization of spent alkali chloride melts wastes in pyroelectrochemical nuclear fuel processing technologies [4].

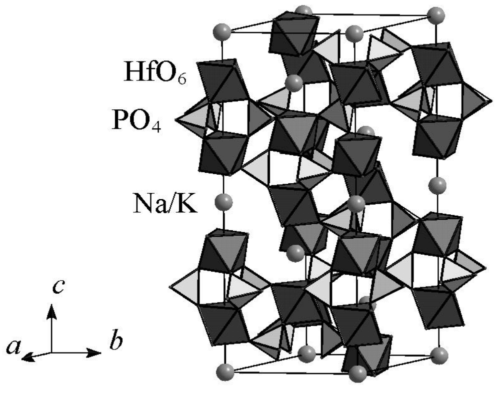

Fig. 1. The structure of $NaZr_2(PO_4)_3$ (space group $R\bar{3}c$)

In deep storages, immobilized wastes are exposed to temperature elevation (363-523 K), because of the heat generated by radioactive decay inside the waste, and lithostatic pressure (up to 10 MPa) [5]. Therefore, to estimate the stability of the obtained NZP solid solutions, one needs to study their behavior in severe p-T settings and in interaction with the fluid (a high-temperature salt solution) of the Earth's crust.

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In this work, we have studied cation-exchange reactions in the $NaM_2(PO_4)_3$–$KM_2(PO_4)_3$–NaCl–KCl–H_2O (M = Ti, Zr, Hf) systems at T = 723 – 973 K and p = 100 – 200 MPa, have calculated the excess functions of mixing for (Na,K)$M_2(PO_4)_3$ solid solutions and have founded the concentration dependences of their unit cell parameters.

Experimental

The starting solid samples of the compositions $Na_{1-x}K_xM_2(PO_4)_3$ ($0 \le x \le 1$) were synthesized using the sol-gel and solid state methods from the reagent-grade NaCl, KCl, $TiOCl_3$, $ZrOCl_2$, HfO_2, $NH_4H_2PO_4$ solutions or powders. During sol-gel synthesis the stoichiometric amounts of aqueous solutions of alkali chlorides and titanium (zirconium) oxychloride were combined under continuous stirring at room temperature. Then, ammonium dihydrogen phosphate solution was added under stirring in accordance with the phosphate stoichiometry. The mixtures were dried at 353 K and thermally treated at 873, 1073, and 1273 K for at least 24 h at each stage. During solid-state synthesis the fine mixtures of the stoichiometric amounts of solid alkali chlorides, hafnia and ammonium dihydrogen phosphate were dried at 473 K for 10-16 h, then thermally processed in unconfirmed air access at 873, 1073, 1273 and 1473 K for at least 24 h at each stage. All thermal stages were alternated with careful grinding.

For the ion-exchange hydrothermal syntheses and investigation of the cation-exchange reactions, we used the synthesized solid phosphates, liquid NaCl and KCl aqueous solutions (in various proportions). The phosphate-fluid systems were treated at T = 723 K and p = 100 MPa; T = 823 K and p = 150 MPa; T = 923 or 973 K and p = 200 MPa. The homogeneity of the water-salt solutions under the p-T parameters used in this work was verified previously [6]. The experiments were carried out in platinum ampoules inside reactors of high-pressure hydrothermal setups equipped with external heaters and a cold seal. Each ampoule was charged with 50-100 mg of double or triple phosphate and 100-300 ml of the solution. The ampoules were weighed before and after experiment to verify their air-tightness. The temperature oscillations were within 5 K, the pressure oscillations were not more than 5 MPa. The homogeneity of the final solid products served as the equilibrium-acquisition criterion. After the experiments were over, contents of the ampoules were washed out with hot distilled water. The solid products were filtered from the solution, washed with water on a filter, and dried at 363 K.

The phase composition of the solid products of sol-gel, solid-state syntheses and hydrothermal experiments was determined using powder X-ray diffraction (a Shimadzu XRD-6000 diffractometer, filtered CuKα-radiation). The unit cell parameters of the phosphates in the hexagonal axes were determined from indexed X-ray diffraction patterns in the 2θ range from 10 to 50 degrees and refined by the least-squares fits.

The chemical composition and homogeneity of the samples were monitored using a CamScan MV-2300 (VEGA TS 5130MM) scanning electron microscope (YAG secondary and scattered electron detectors) and an energy-dispersive X-ray microanalyzer equipped with a Link INCA Energy 200C semiconductor Si(Li) detector. The uncertainty in compositions was within 2.5 mass %.

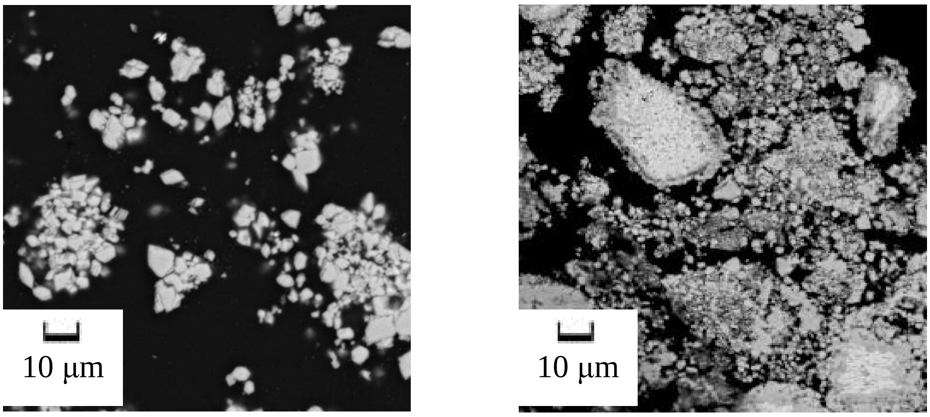
The sodium and potassium in the filtrate were determined by atomic absorption on an AAS-1 instrument. The uncertainty of determination was not more than 2 mass %.

Results and discussion

Synthesis of solid solutions and their X-ray characterization

Starting crystalline samples of double and triple phosphates $Na_{1-x}K_xM_2(PO_4)_3$ ($0 \le x \le 1$) were obtained by sol-gel and solid-state methods at 1073-1373 K. X-ray microanalysis showed that these samples were homogeneous, and their compositions corresponded to theoretical x. Synthesis by hydrothermal cation-exchange reactions leaded to obtaining of solid homogeneous products (Fig. 2a), their elemental compositions were determined from the X-ray microanalysis data. Note, that insufficient (to allow the equilibrium) duration of hydrothermal experiments may lead to obtaining nonhomogeneous products (Fig. 2b). However, since the homogeneity of the final products was the equilibrium-acquisition criterion, we included into the calculations only the experiments that yielded single-phase phosphates.

X-ray diffraction showed that NZP continuous solid solutions $Na_{1-x}K_xM_2(PO_4)_3$ (M = Ti, Zr, Hf; $0 \le x \le 1$) were obtained in all of the studied systems. The products of all syntheses were structural analogues, their X-ray diffraction patterns were indexed basing on the known structural analogues (space group $R\bar{3}c$): $NaM_2(PO_4)_3$ and $KM_2(PO_4)_3$ [3].



a b

Fig. 2. Microphotographs of the products of hydrothermal experiments in the (Na,K)$Ti_2(PO_4)_3$ system: homogeneous solid solution (a) and solid solution with TiO_2 rim (b)

For example, the unit cell parameters of the titanium phosphates are shown in Fig. 3. In all studied systems the increase of *c* and *V* unit cell parameters and decrease of *a* parameter with the increase of larger (potassium) cation content in the phosphate was observed. Such dependences are typically for NZP phosphates with one cation in the framework cavities per formula unit.

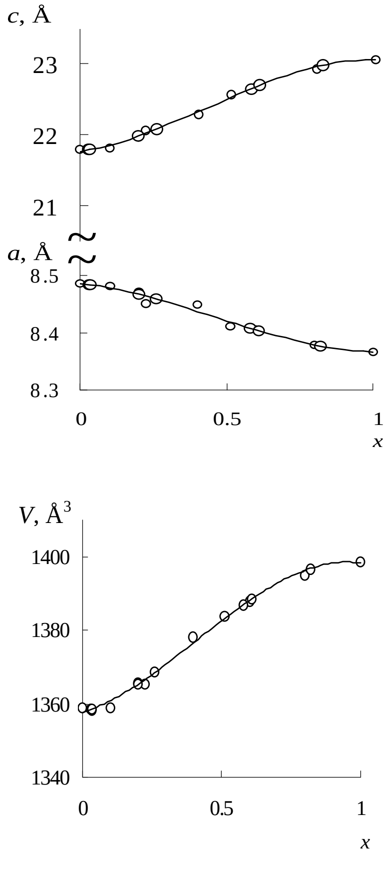


Fig. 3. The unit cell parameters of the phosphates $Na_{1-x}K_xTi_2(PO_4)_3$

The unit cell volumes versus compositions of the solid solutions $Na_{1-x}K_xM_2(PO_4)_3$ are described by third-order polynomials $V(Å^3) = f(x)$:

V=1357.5+24.6x+85.0x^2–69.0x^3 for Ti-phosphates,

V=1527.9+44.9x+58.9x^2–58.8x^3 for Zr-phosphates,

V=1505.0+42.9x+62.2x^2–59.0x^3 for Hf-phosphates.

The given equations describe the unit cell volumes of the phosphates with uncertainty of not more than 0.9 $Å^3$.

Thermodynamic data processing

The ion-exchange reactions:

$$NaM_2(PO_4)_3(cr) + xKCl(fl) \rightleftarrows Na_{1-x}K_xM_2(PO_4)_3(cr) + xNaCl(fl)$$

were studied. The experimental cation distribution data evident that the solid phases were enriched in potassium in wider compositional ranges compared with fluids. However, the increase of temperature leaded to change of alkali metals distribution isotherm to the enrichment in potassium of fluid.

The sodium/potassium distribution coefficients K_d in the phosphate-fluid systems were calculated from the experimental data using equation: $K_d = x[1-x_{fl}]/[(1-x)x_{fl}]$. The distribution coefficients in the studied systems were functions of the solid solution compositions, that is, the systems behaved nonideally. For example, logarithmic distribution coefficients for the titanium phosphates are shown in Fig. 4.

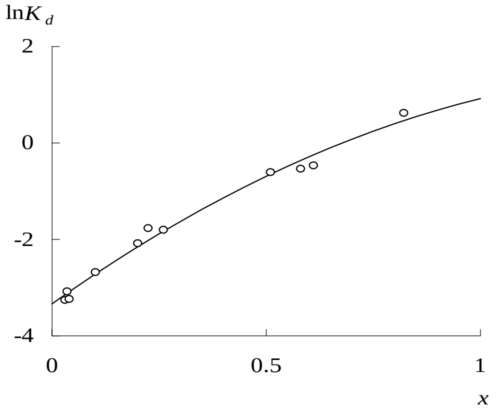


Fig. 4. Sodium/potassium distribution coefficients in the system $NaTi(PO_4)_3 - KTi_2(PO_4)_3 - NaCl - KCl - H_2O$ vs. the solid solution composition x (T = 973 K and p = 200 MPa)

To quantify the nonideality of the solid solutions, we calculated their excess functions of mixing which are the differences between the functions of real and ideal solid solutions. The excess volumes of mixing were calculated from the unit cell parameters of phosphates:

$$V^E_{mix}(Na_{1-x}K_xM_2(PO_4)_3) = V(Na_{1-x}K_xM_2(PO_4)_3) - (1-x)V(NaM_2(PO_4)_3) - xV(KM_2(PO_4)_3).$$

The dependences of the excess volumes of the studied solid solutions mixing are described by third-order polynomials (Fig. 5). The obtained dependences of the excess functions of mixing correspond to the subregular solid solutions model (the Margules model) [7]. Within this model the excess volumes of mixing (V^E, cm^3/mol) are described by the equation:

$$V^E = x(1-x)[xW_1 + (1-x)W_2],$$

where W_1 and W_2 are the Margules parameters given in Table. The uncertainty of the approximations was not more than 0.2 cm^3/mol. It is seen that concentration dependences of excess volumes of mixing for zirconium and hafnium solid solutions are close and differ from such dependence for titanium compounds which is characterized by significant region of negative values of function. This difference may be explained by the influence of the framework cation radius on the structural formation of solid solutions. The NZP structure is more characteristic for the phosphates with middle-size framework cations Zr^{4+} (0.72 Å) and Hf^{4+} (0.71 Å). The incorporation of small cation Ti^{4+} (0.61 Å) into the framework sites lead to decrease of stability of NZP type of structure that may be reason of significant deviation of solid solutions behavior from ideal.

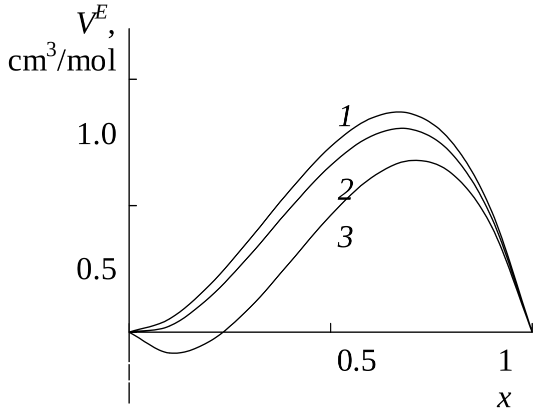


Fig. 5. The excess volume of mixing vs. concentration for $Na_{1-x}K_xM_2(PO_4)_3$ solid solutions: M = Ti (*3*), Zr (*1*), Hf (*2*)

Table

The Margules parameters for the excess volumes of mixing of $Na_{1-x}K_xM_2(PO_4)_3$

M	W_1, cm^3/mol	W_2, cm^3/mol
Ti	5.31	–1.61
Zr	5.88	0.01
Hf	5.60	–0.32

To calculate the excess Gibbs function of mixing for the studied solid solutions, we used the procedure described in [8] and the equation:

$$G^E_{mix}(Na_{1-x}K_xTi_2(PO_4)_3) = xG^E_1 + (1-x)G^E_2,$$

where

$$G^E_1 = -RT\int_0^{(1-x)}(1-x)d\ln K_d,\quad G^E_2 = RT\int_0^x x d\ln K_d,$$

R – universal gas constant.

In the calculations, we assumed that the high-temperature water-salt fluid is ideal, it is right for $NaCl - KCl - H_2O$ solutions with concentrations of 0.5 – 2 mol/l [9, 10].

The excess Gibbs functions of mixing are also may be described in Margules model. Since the Gibbs energy of mixing for ideal binary solid solutions is found from the equation $\Delta_{mix}G = -T\cdot\Delta_{mix}S^{conf} = RT[(x\ln x + (1-x)\ln(1-x)]$, the Gibbs energy of mixing for subregular solid solutions $\Delta_{mix}G = G^E + \Delta_{mix}G$ were calculated.

From the comparison of the results obtained for the (Na,K)$M_2(PO_4)_3$ (M = Ti, Zr, Hf) systems, it is seen (Fig. 6) that the titanium phosphates show greater nonideality than zirconium and hafnium phosphates and lower thermodynamic stability to decomposition to double phosphates at high pressures and temperatures.

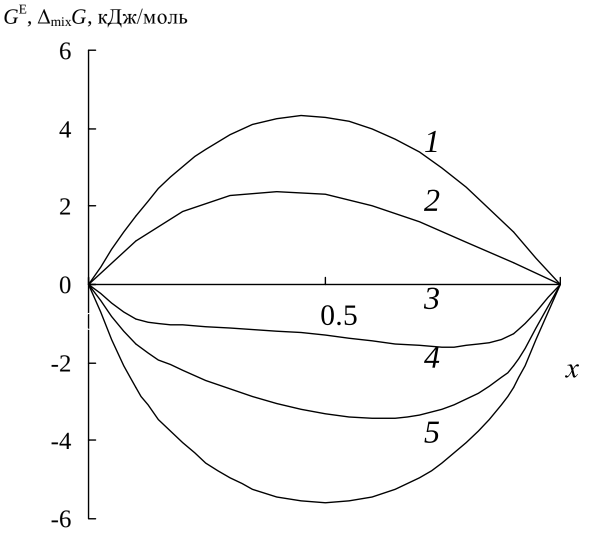


Fig. 6. Excess Gibbs energy and Gibbs energy of mixing vs. concentration for $Na_{1-x}K_xTi_2(PO_4)_3$ (*1*, *3*) and $Na_{1x}K_xZr_2(PO_4)_3$ (*2*, *4*) solid solutions, Gibbs function of mixing for ideal binary solid solutions (*5*)

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