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Utilization of the NZP matrixes of the kosnarite structure for immobilization of technogenic wastes

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The NZP materials, whose prototype is $\text{NaZr}_2(\text{PO}_4)_3$ (space group $R\bar{3}c$, $a = 8.815 \text{ \AA}$, $c = 22.746 \text{ \AA}$, $V = 1530.5 \text{ \AA}^3$, $Z = 6$) [1] of the kosnarite structure ($\text{KZr}_2(\text{PO}_4)_3$, $a = 8.687 \text{ \AA}$, $c = 23.877 \text{ \AA}$, $V = 1560.4 \text{ \AA}^3$, $Z = 6$) [2], are able to concentrate in the crystal structure diverse components of toxic wastes. Crystal chemical formula of the NZP phosphates is $(\text{M1})(\text{M2})_3\{[\text{L}_2(\text{PO}_4)_3]^{p-}\}_{3\infty}$, where M1 and M2 are non-equivalent cationic sites in the network cavities, L is octahedral cationic site in the network. The network and the cavities can be occupied by 1 to 5-valent ions. Cations of similar type can occupy different sites in the structure, while similar sites can be occupied by ions of different size and valency. 3-5-valent ions of radiuses 0.6-0.8 \AA prefer the L-site. Larger 1-2-valent ions occupy M1 and M2 sites. Owing to substitution of cations of dif-

ferent valency in the L-site (e.g. +1, +4), the network can be composed by small cations and larger (of radius about 1 \AA) cations simultaneously.

The study presents results of synthesis and investigation of stability fields of the NZP structure for cadmium and mercury-bearing systems $\text{Na}_{1-x+4m}\text{B}_{0.5x}\text{Zr}_{2-m}(\text{PO}_4)_3$, where $\text{B} = \text{Cd}, \text{Hg}$; $m = 0$ ($0 \leq x \leq 1$), $m = 0.5$ ($0 \leq x \leq 3$), $m = 1$ ($0 \leq x \leq 5$). A source for the toxic cadmium and mercury-bearing compounds is industry of ore concentration, polymer production, galvanic industry, etc.

New binary and ternary Cd- and Hg-bearing zirconium phosphates are synthesized using of the sol-gel technology and are studied with powder XRD, including the high-temperature XRD, thermal analysis, and IR spectroscopy.

X-ray diagrams for uni-phase NZP samples of similar space group ($R\bar{3}c$, $R\bar{3}$, or $R32$) are determined by similar indexes, but show differences in the position and relative intensities of the reflexes of similar index. There is insignificant change of interplanar distances in complex zirconium and sodium-cadmium and zirconium and sodium-mercury phosphates. The dependence of the unit-cell parameters of cadmium-bearing phosphates on composition is shown in Figure 1.

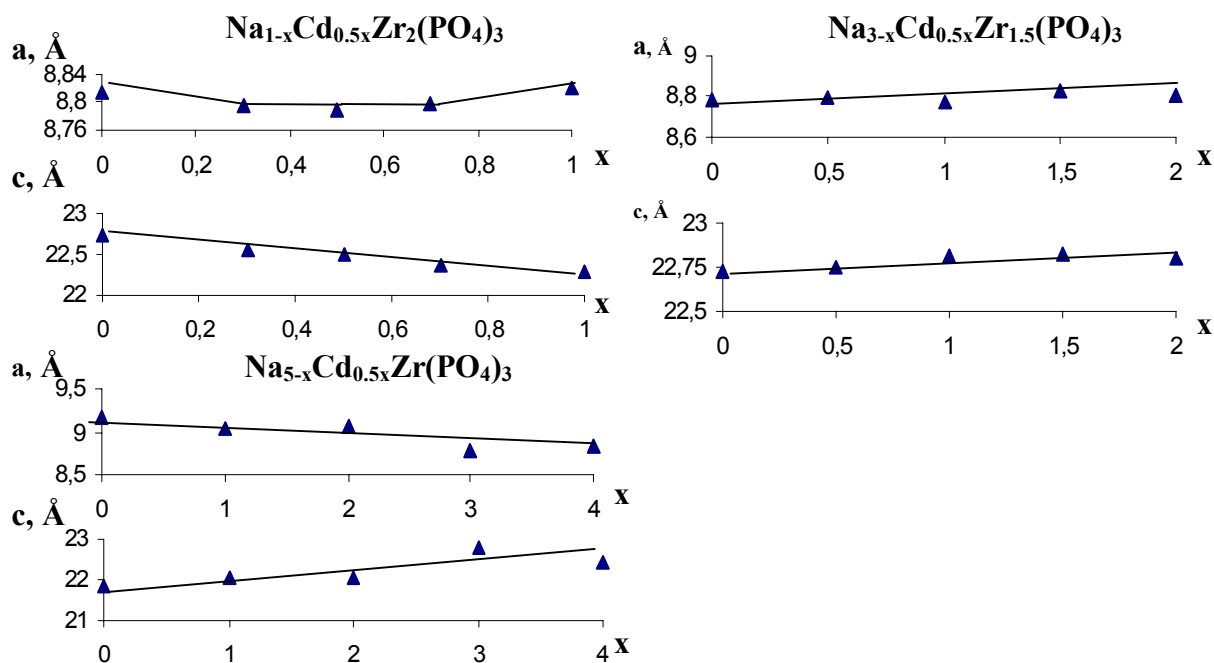


Fig.1. Compositional dependence of unit-cell parameters of Cd-bearing phosphates.

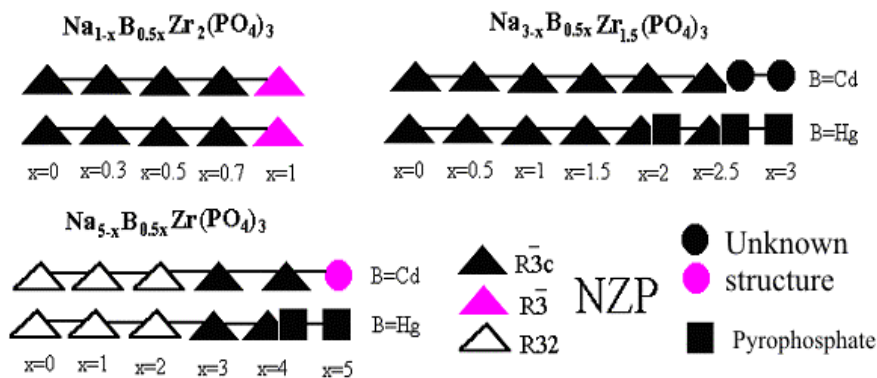


Fig.2. Coexistence of structural types of Cd and Hg phosphates.

Table 1. Thermal expansion coefficients ($T = 25\text{-}600^{\circ}\text{C}$) for zirconium and cadmium phosphates.

| Chemical formula | $\alpha_a \times 10^6 / ^{\circ}\text{C}$ | $\alpha_c \times 10^6 / ^{\circ}\text{C}$ | $\alpha_{cp} \times 10^6 / ^{\circ}\text{C}$ |
|---|---|---|--|
| $\text{Cd}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ | -3.50 | 10.20 | 1.1 |
| $\text{Na}_{0.1}\text{Cd}_{0.45}\text{Zr}_2(\text{PO}_4)_3$ | -5.21 | 13.41 | 1.0 |
| $\text{Na}_{0.3}\text{Cd}_{0.35}\text{Zr}_2(\text{PO}_4)_3$ | -2.82 | 6.44 | 0.3 |
| $\text{Na}_{0.5}\text{Cd}_{0.25}\text{Zr}_2(\text{PO}_4)_3$ | -0.70 | 6.27 | 1.6 |
| $\text{Na}_{0.7}\text{Cd}_{0.15}\text{Zr}_2(\text{PO}_4)_3$ | -2.18 | 6.27 | 0.6 |
| $\text{NaZr}_2(\text{PO}_4)_3$ | -5.50 | 22.30 | 3.8 |
| $\text{NaCd}_2\text{Zr}(\text{PO}_4)_3$ | -2.42 | 15.04 | 3.4 |
| $\text{Na}_2\text{Cd}_{1.5}\text{Zr}(\text{PO}_4)_3$ | -1.40 | 17.40 | 4.9 |
| $\text{Na}_3\text{CdZr}(\text{PO}_4)_3$ | 7.04 | 13.90 | 9.3 |
| $\text{Na}_4\text{Cd}_{0.5}\text{Zr}(\text{PO}_4)_3$ | 7.53 | 16.70 | 10.6 |

Figure 2 shows fields of coexistence of different structural types. All systems are characterized by the NZP structure. This structure is characteristic for the systems $\text{Na}_{1-x}\text{B}_{0.5x}\text{Zr}_2(\text{PO}_4)_3$ ($B = \text{Cd}, \text{Hg}, m = 0$) in the whole compositional range. The systems with lower zirconium content ($m = 0.5, 1$) form limited solid solutions.

Thermal expansion of complex zirconium and cadmium phosphates is studied within the temperature interval $25\text{-}600^{\circ}\text{C}$ (Table). An anisotropy of the thermal expansion is found for most NZP phosphates. Phosphates of the $\text{Na}_{1-x}\text{Cd}_{0.5x}\text{Zr}_2(\text{PO}_4)_3$ system show thermal expansion close to zero.

Heating of Cd-bearing phosphates up to 1000°C does not result in phase and chemical modifications. Hg-bearing compounds are stable up to 800°C .

Thus, monophasic NZP phosphates with the kosnarite structure are able to chemically immobilize the toxic Cd- and Hg-bearing wastes of high concentration (up to 40 % of the NZP matrix mass).

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References:

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