

Synthesis, Characterization and Thermodynamic Properties of the Phosphates $\text{NaM}_2(\text{PO}_4)_3$ and $\text{Na}_5\text{M}(\text{PO}_4)_3$ (M = Ti, Zr, Hf)
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Crystalline phosphates of the $\text{NaZr}_2(\text{PO}_4)_3$ (NZP) type structure form a large family of substances attracting wide research interest due to their stability to high temperatures and pressures, aggressive media and thermal shock resistance. In the present work we synthesized the NZP phosphates $\text{NaM}_2(\text{PO}_4)_3$ and $\text{Na}_5\text{M}(\text{PO}_4)_3$ (M = Ti, Zr, Hf), studied their structure, thermal behavior and thermodynamic properties. The crystalline phosphates were prepared by sol-gel and solid-state methods. Their phase purity and chemical compositions were checked by X-ray diffractometry, electron microprobe and chemical analysis, IR spectroscopy. It was shown from the DTA measurements (298-1273 K) that the phosphates $\text{Na}_5\text{Zr}(\text{PO}_4)_3$ and $\text{Na}_5\text{Hf}(\text{PO}_4)_3$ undergo reversible phase transitions at 407 K and 509 K respectively, the compound $\text{Na}_5\text{Ti}(\text{PO}_4)_3$ melts with decomposition at 1083 K. The heat capacity of the samples was measured in the range 7-650 K. The heat capacity of $\text{NaM}_2(\text{PO}_4)_3$ and $\text{Na}_5\text{Ti}(\text{PO}_4)_3$ increases monotonically over the entire temperature range studied. For the phosphates studied thermodynamic functions $H^0(T)-H^0(0)$, $S^0(T)$, $G^0(T)-H^0(0)$ in the range 0-650 K were calculated, the standard entropies of their formation at 298.15 K and thermodynamic characteristics of the phase transitions were determined. The standard enthalpies of formation of Zr-phosphates at 298.15 K were obtained using hydrofluoric acid solution microcalorimetry. From the values of the standard enthalpies and entropies of phosphates formation, the Gibbs functions of their formation and the logarithmic values of formation reaction constants were found. To analyze the conditions for the formation of some NZP-substances, the standard thermodynamic functions for the reactions of their solid-state synthesis were calculated. Derived temperatures of synthesis at standard pressure are not high: 430 K for $\text{NaZr}_2(\text{PO}_4)_3$ and 570 K for $\text{Na}_5\text{Zr}(\text{PO}_4)_3$. For this reason, ceramic technology is one of the commonly used methods for obtaining such compounds.

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