Synthesis, Characterization and Thermodynamic Properties of the Phosphates NaM_2(PO_4)_3 and Na_5M(PO_4)_3 (M = Ti, Zr, Hf)

- IACT Doctorate Award Presentation -

V.I. Pet'kov, E.A. Asabina, A.V. Markin and N.N. Smirnova

Department of Chemistry, Nizhni Novgorod State University, Nizhniy Novgorod, Russia
petkov@uic.nnov.ru

Crystalline phosphates of the NaZr_2(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 NaM_2(PO_4)_3 and Na_5M(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 Na_5Zr(PO_4)_3 and Na_5Hf(PO_4)_3 undergo reversible phase transitions at 407 K and 509 K respectively, the compound Na_5Ti(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 NaM_2(PO_4)_3 and Na_5Ti(PO_4)_3 increases monotonically over the entire temperature range studied. For the phosphates studied thermodynamic functions H^θ(T)-H^θ(0), S^θ(T), G^θ(T)-H^θ(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 NaZr_2(PO_4)_3 and 570 K for Na_5Zr(PO_4)_3. For this reason, ceramic technology is one of the commonly used methods for obtaining such compounds.

This work was supported by the Russian Foundation for Basic Research (Project No. 05-03-32127).