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CONSTITUTION AND THERMODYNAMIC PROPERTIES OF PHOSPHATES OF GROUP IV ELEMENTS (Si, Ge, Ti, Zr, Hf)

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The regularities of phase formation in the systems $\text{MO}_2 - \text{P}_2\text{O}_5$ ($\text{M} = \text{Si, Ge, Ti, Zr, Hf}$) are established and the phase diagrams for them are constructed. In the systems $\text{MO}_2 - \text{P}_2\text{O}_5$ ($\text{M} = \text{Si, Ge}$) the following compounds are obtained: $\text{M}_5\text{O}(\text{PO}_4)_6$ and MP_2O_7 (for Si - cubic, tetragonal and two monoclinic modifications; for Ge - cubic and monoclinic modifications). At low temperatures (up to 500°C) the hexagonal forms $\text{SiP}_2\text{O}_7 \cdot 0,8 \text{ H}_2\text{O}$ and $\text{GeP}_2\text{O}_7 \cdot 1,6 \text{ H}_2\text{O}$ are stable. Two phases are determined in the $\text{TiO}_2 - \text{P}_2\text{O}_5$ system: the phase of the variable composition based on $5\text{TiO}_2 \cdot 3\text{P}_2\text{O}_5$ with 40,2 to 54,2 mass % P_2O_5 , and another phase TiP_2O_7 (cubic and water-stabilized pseudo-hexagonal $\text{TiP}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$). Four compounds are found in the systems $\text{MO}_2 - \text{P}_2\text{O}_5$ ($\text{M} = \text{Zr, Hf}$): $(\text{MO})_2\text{P}_2\text{O}_7$ (β - and α -forms for Zr and β -form for Hf), $\text{M}_3(\text{PO}_4)_4$, MP_2O_7 and $\text{M}(\text{PO}_3)_4$. The crystal-chemical analogy is considered between silicium and germanium phosphates, and accordingly between those of zirconium and hafnium. The isolation of titanium phosphates is discussed. The crystallographic, refractometric and thermal characteristics of the compounds and their forms are given as well as the values of electrical and thermal conductivities for cubic modifications of MP_2O_7 . High-temperature mass spectrometry was used to determine the vapour composition and partial pressures as well as the activities of the components and Gibbs free energy in the system $\text{GeO}_2 - \text{P}_2\text{O}_5$ at $1000\text{--}1200^\circ\text{C}$. negative deviations from the ideal are obtained and compared with the results of investigation of the phase diagram for the $\text{GeO}_2 - \text{P}_2\text{O}_5$ system.