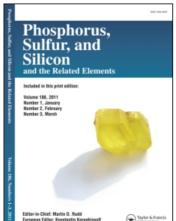
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## Phosphorus, Sulfur, and Silicon and the Related Elements

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## Constitution and Thermodynamic Properties of Phosphates of Group IV Elements (Si, Ge, Ti, Zr, Hf)

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

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The regularities of phase formation in the systems  ${
m MO}_2$  - $P_2O_5$  (M = Si, Ge, Ti, Zr, Hf) are established and the phase diagrams for them are constructed. In the systems MO, - $P_2O_5$  (M = Si, Ge) the following compounds are obtained:  ${\rm M_5O(PO_4)_6}$  and  ${\rm MP_2O_7}$  (for Si - cubic, tetragonal and two monoclinic modifications; for Ge - cubic and monoclinic modifications). At low temperatures (up to 500°C) the hexagonal forms  $SiP_2O_7 \cdot O_1 \cdot O_2 \cdot O_3 \cdot O_4 \cdot O_4 \cdot O_5 \cdot O_5 \cdot O_7 \cdot$ Two phases are determined in the  $TiO_2 - P_2O_5$  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  $P_2O_7$  (cubic and water-stabilized pseudohexagonal TiP<sub>2</sub>O<sub>7</sub>·3H<sub>2</sub>O). Four compounds are found in the systems  $MO_2 - P_2O_5$  (M = Zr, Hf): (MO)  $_{2}P_{2}O_{7}$  ( $\beta$ - and  $\alpha$ -forms for Zr and  $\beta$ -form for Hf),  $M_3(PO_4)_4$ ,  $MP_2O_7$  and  $M(PO_3)_4$ . 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<sub>2</sub>O<sub>7</sub>. High-temperature mass spectrometry was used to determined the vapour composition and partial pressures as well as the activities of the components and Gibbs free energy in the system GeO<sub>2</sub> - P<sub>2</sub>O<sub>5</sub> at 1000-1200 C. negative deviations from the ideal are obtained and compared with the results of investigation of the phase diagram for the  $GeO_2 - P_2O_5$  system.