PHASE EQUILIBRIA AND CHEMICAL PROCESSES IN SYSTEMS ZnO-SiO_2-NiO AND ZnO-SiO_2-MnO

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This paper examines chemical interactions and phase equilibria in the ternary systems ZnO-SiO_2-NiO and ZnO-SiO_2-MnO. This information is necessary for selecting optimal conditions for the synthesis of functional materials based on willemite Zn_2SiO_4 (green phosphor Zn_2SiO_4:Mn, cool blue pigment $Zn_{2-2x}Ni_{2-2x}SiO_4$) and olivine Ni_2SiO_4. Solid-phase reactions between three reactants begin at the interfaces of only two at a time. In the ZnO-SiO_2-NiO and ZnO-SiO_2-MnO systems synthesized in air, the first pair of oxides to react are metal oxides, forming solid solutions of $Ni_{1-x}Zn_xO$ (rock salt structure) and $Zn_{1-x}Mn_xMn_2O_4$ (spinel structure), respectively. With further increase in annealing time, the proportion of the dopant ion in the solid solutions increases. Upon heating to 900 °C, zinc and silicon oxides begin to react in both systems, forming willemite Zn_2SiO_4, which gradually becomes enriched with dopant metal ions to form the solid solution $Zn_{2-2x}M_{2-2x}SiO_4$ (M = Ni or Mn).

At higher temperatures, the reaction of $Ni_{1-x}Zn_xO$ and SiO_2 in the ZnO-SiO_2-NiO system results in the formation of a phase with the olivine structure $Ni_{2-2x}Zn_{2-2x}SiO_4$. Phase equilibria in the system are determined by the quasi-binary equilibrium of the boundary compositions of the $Zn_{1.8}Ni_{0.2}SiO_4$ and $Ni_{1.5}Zn_{0.5}SiO_4$ solid solutions and the conodes connecting these compositions with the $Ni_{0.83}Zn_{0.17}O$ solid solution, as well as the conode connecting the boundary composition of the $Ni_{1.6}Zn_{0.4}O$ solid solution with Zn_2SiO_4.

In the ZnO-SiO_2-MnO system, no phases with an olivine structure were detected. In the temperature range of 800-1250 °C, the sequential appearance of intermediate phases $ZnMnO_3$, $ZnMn_2O_4$, and $MnSiO_3$ was detected. Phase equilibria were established for temperatures of 800 °C and 1250 °C. It is shown that the phase relationships in the $MnOx$–ZnO–SiO_2 system are determined by changes in the charge states of manganese ions with increasing temperature, leading to phase transformations of manganese oxide $MnO \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$. Triangulation of the Mn_2O_3–ZnO–SiO_2 system at 800°C is determined by the conode $ZnMn_2O_4$–Zn_2SiO_4 and decomposes the system into elementary triangles ZnO–Zn_2SiO_4–$ZnMn_2O_4$, Zn_2SiO_4–$ZnMn_2O_4$–SiO_2, and $ZnMn_2O_4$–SiO_2–Mn_2O_3. The triangulation of the ternary system MnO–ZnO–SiO_2 is determined by the elementary triangle $Zn_{1.6}Mn_{0.4}SiO_4$–ZnO–$MnSiO_3$.

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