STABILITY FIELD OF ENTHALPICALLY STABILIZED COMPOUNDS OF VARIABLE COMPOSITION WITH PYROCHLORE STRUCTURE IN THE Bi_2O_3–Fe_2O_3–WO_3–(H_2O) SYSTEM

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When using the hydrothermal synthesis method, the stabilization of the crystalline phase occurs at low temperatures (100 – 200 °C), which means that it is primarily due to the enthalpic contribution to the change in Gibbs energy ($\Delta G = \Delta H - T\Delta S$), while the influence of the entropic term is minimized.

Compounds of variable composition with pyrochlore structure in the Bi_2O_3–Fe_2O_3–WO_3 system, obtained under hydrothermal conditions ($T = 90 - 200$ °C, $P \leq 7$ MPa), are enthalpically stabilized phases [1], since they are unstable at temperatures above ~725 °C [2]. The study of these compounds is of particular interest because their properties may reveal features that are not typical of compounds in which the entropy factor plays a significant role in the change in Gibbs free energy.

In this work, the concentration limits of the stability field of $(Bi_zVac_{2-z})(Fe_{2-y}W_y)O_6O'_{\delta}$ compounds (where Vac is a cation vacancy) with pyrochlore structure ($T = 200$ °C and $P \sim 7$ MPa: $0.60 \leq z \leq 1.35$; $1.32 \leq y \leq 1.96$; $\delta \sim 1$) were determined and it was shown that they are several times higher than those for pyrochlore phases obtained in most other oxide systems using the solid-phase synthesis method.

1. Fedorov P.P., Almyasheva O.V., Alexandrov A.A., Proydakova V.Yu., Korotkova N.A., Baranovskaya V.B., Gusarov V.V. Low-temperature phase formation in the ZrO_2–In_2O_3 system // Mendeleev Commun. 2025. Vol. 35. P. 376–378. https://doi.org/10.71267/mencom.7642

2. Lomakin M.S., Proskurina O.V., Levin A.A., Kozlov S.S., Semenov V.G., Kozlov V.S., Koroleva A.V., Zhizhin E.V., Shevaleevskiy O.I. Pyrochlore phase in the Bi_2O_3–Na_2O–Fe_2O_3–WO_3–(H_2O) system: crystal structure and energy band diagram depending on chemical composition // Ceram. Int. 2025. Vol. 51. P. 43488–43510. https://doi.org/10.1016/j.ceramint.2025.06.323

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