PECULIARITIES OF PHASE EQUILIBRIA IN OXIDE SYSTEMS BASED ON RARE EARTH, ALKALINE EARTH AND 3d (Fe, Co) METALS

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The results of a systematic study of phase equilibria in the oxide systems ½ Ln_2O_3 – MO – TO_x (Ln – rare earth elements; M – Ca, Sr, Ba; T = Fe, Co) at 1100°C in air are presented in the form of phase diagrams. It is shown that for M = Ca, Sr, the general appearance of the phase diagrams of systems containing iron and cobalt is similar, while for M = Ba, they differ significantly. The similarity of the diagrams of the first group implies the formation of solid solutions with the perovskite structure $(Ln_{1-x}M_x)TO_{3-\delta}$ and related representatives of the Ruddlesden-Popper type $(Ln_{1-x}M_x)_{n+1}T_nO_{3n+1-\delta}$ homologous series for practically all systems. The similarity of the diagrams, however, does not mean they are completely identical. As a rule, the homogeneity ranges of solid solutions in Sr-containing systems are much wider than in similar Ca-containing systems, and the set of Ruddlesden-Popper phases is larger in Fe-containing systems than in similar Co-containing systems.

A characteristic feature of Ba-containing systems, which distinguishes them from Ca- and Sr-containing analogues, is the formation of layered structures due to the increasing difference in the sizes of rare earth element and barium ions.

However, in Co-containing systems, the formation of a double perovskite phase $LnBaCo_2O_{6-\delta}$ is observed in air, whereas in similar Fe-containing analogous the formation of a triple-layered $LnBa_2Fe_3O_{8+w}$ (Ln = Dy, Ho, Y) or even a more complex quintuple perovskite structure $Ln_{2-\varepsilon}Ba_{3+\varepsilon}Fe_5O_{13+w}$ (Ln =Sm, Eu) is revealed. Fe-based double perovskites $LnBaFe_2O_{5+w}$ can also be obtained, but under much more severe reducing conditions ($Po_2 \approx 10^{-15}$ atm). It should be noted that the above-mentioned single-phase triple-layered 123-type ferrites exhibit significant nonstoichiometry in the metallic sublattices in air conditions, for example, $Y_{1.05}Ba_{1.92}Fe_{3.03}O_{8+w}$ or $Dy_{1.05}Ba_{1.95}Fe_3O_{8+w}$.

Another specific feature of phase relations in Ba-containing systems is the possibility of partial replacement of iron by a rare earth element in barium ferrite with the formation of cubic perovskite solid solutions $BaFe_{1-y}Ln_yO_{3-\delta}$ even for relatively large Pr. A similar substitution was also found in barium cobaltite $BaCo_{1-y}Ln_yO_{3-\delta}$, but for smaller rare earth elements (Ln = Sm, Y).

This work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation (project № FEUZ-2026-0011)