INTERACTION OF CERIA WITH REAR EARTH OXIDES

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Study of phase equilibria in the series of the systems CeO_2-Ln_2O_3 (Ln = La, Sm, Eu, Gd, Er, Dy, Yb) is considered essentially important to create new materials based on rare-earth oxides (REO). The solid solutions based on CeO_2 demonstrate high ionic conductivity, 4-5 times higher than the conductivity of yttria-stabilized ZrO_2, low activation energy for total conductivity, high catalytic activity of methane oxidation at temperatures lower than 800 °C. Applications of ceria in electrolites and anodes are perspective in solid oxide solid cells and other electrochemical devises. The weakness of all known solid solutions based on CeO_2 (rather narrow homogeneity field and low mechanical strength for electrolites) one can overcome by means of complex dopping of CeO_2 with REO.

In the present work, phase equilibria and physico-chemical poperties of the phases formed in the binary systems CeO_2-Ln_2O_3 have been studied first at temperatures of 1500 and 1100 °C in air and in the whole concentration range.

In the system CeO_2-La_2O_3, two types of solid solutions have been revealed at 1500 and 1100 °C: cubic of fluorite type F-CeO_2 and hexagonal A-modification of lanthana, which are separated by two phase field (A+F). It has been found that the solubility of La_2O_3 in F-modification of CeO_2 achieves 49 mol. % at 1500, 1100 °C. The lattice parameter increases from a=0.5409 nm in pure CeO_2 to a=0.5590 nm (at 1500 °C) and a=0.5587 nm (at 1100 °C) in the sample containing 50 mol. % La_2O_3. The solubility of CeO_2 in hexagonal A-modification of lanthana achieves 25 mol. % CeO_2 at 1500 °C and ~ 15 mol. % CeO_2 at 1100 °C.

In the CeO_2-Sm_2O_3 system, three types of solid solutions are formed: cubic structures F-CeO_2 and C-Sm_2O_3, monoclinic modification B-Sm_2O_3, which are separated by two phase fields (F+C) and (C+B). The solubility of Sm_2O_3 in F-CeO_2 achieves 25 mol. % at 1500 °C. The lattice parameter has been found increased from a=0.5409 nm in pure CeO_2 to a=0.5446 nm in the sample, containing 30 mol. % Sm_2O_3. The solubility of CeO_2 in B-Sm_2O_3 is at the level of 3 mol. % CeO_2 at1500 °C and the lattice parameters of B solid solutions vary from a=1.3925, b=0.3632, c=0.8680 nm, γ=90.42 in pure Sm_2O_3 to a=1.3018, b=0.3578, c=0.9437 nm, γ=88.5 in boundary solid solution, respecively. The lattice parameters of C phase vary from a = 1.0904 nm in the composition 60 mol. % CeO_2-40 mol. % Sm_2O_3 to a = 1.0912 nm in the solid soluftion composed of 30 mol. % CeO_2-70 mol. % Sm_2O_3. When temperature decresed to 1100 °C, the homogeneity field of the F-CeO_2 and B-Sm_2O_3 solid solutions narrowed.

In the system CeO_2-Gd_2O_3, the solubility of Gd_2O_3 in F-CeO_2 achieves 15 mol. %. The lattice parameter increases from a=0.5409 nm in pure CeO_2 to a=0.5420 nm in the sample containing 15 mol. % Gd_2O_3. The solubility of CeO_2 in B-Gd_2O_3 is not higher than 2 mol. % CeO_2 at 1500 °C. The lattice parameters of B phase vary from a=1.4061, b=0.3566, c=0.8760 nm, γ=100.1 for pure Gd_2O_3 to a=1.4380, b=0.3572, c=0.8783 nm, γ=86.9 for boundary solid solution. The lattice paameters of C-phase vary from a = 1.0783 nm in the composition 15 mol. % CeO_2-85 mol. % Gd_2O_3 to a = 1.0804 nm in the solid solution containing 35 mol. % CeO_2 and 65 mol. % Gd_2O_3.

The system CeO_2-Er_2O_3 may be specified by two types of solid solutions at 1500 and 1100 °C: F-CeO_2 and C-Er_2O_3, which are commonly separated by the two-phase field (C+F). The solubility of Er_2O_3 in F-CeO_2 achieves 30 mol. % at 1500 ºC and 25 mol. % at1100 °C. The lattice parameters decrease from a=0.5409 nm in pure CeO_2 to a=0.5369 nm at 1500 °C and a=0.5376 nm at 1100°C in boundary solid solutions. The solubility of CeO_2 in cubic C-Er_2O_3 was found at the level of 45 mol. % CeO_2 at 1500 °C and ~5 mol. % CeO_2 at 1100 °C. The lattice parameter vary from a = 1,0531 nm in pure Er_2O_3 to a=1.0639 nm at 1500 °C and a = 1,0543 nm at 1100 °C in boundary solid solution.

The boundary solubility of lanthanide oxides in ceria has been revealed to decrease with ion radius of Ln^{3+} decrease.

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