Oral Contributions

[MS28 - 05] Interstitial oxide ion conduction in $(Ln_{2-x}Zrx)Zr_2O_{7+\delta}$ (Ln= Nd, Sm) A.V. Shlyakhtina[1], D.A. Belov[1,2], A.V. Knotko[2], M. Avdeev[3], I.V. Kolbanev[1], A.N. Streletskii[1], L.G. Shcherbakova[1]

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We have studied the structure and transport properties of $(Ln_{2-x}Zr_x)Zr_2O_{7+x/2}$ (Ln= Nd, Sm; x=0; 0.2; 0.32; 0.39; 0.48; 0.67; 0.78; 0.96; 1.14; 1.27) solid solutions, which lie in the ZrO_2-$Ln_2Zr_2O_7$ (Ln= Nd, Sm) isomorphous miscibility range (33.3, 29, 26.6, 25.3, 23.5, 20, 18, 15, 12, 10 mol% Ln_2O_3) in the Nd_2O_3-ZrO_2 (NdZrO) and Sm_2O_3-ZrO_2 (SmZrO) systems. Major attention has been focused on the structure and properties of pyrochlore-like $(Ln_{2x}Zr_x)Zr_2O_{7+x/2}$ (Ln=Nd, Sm) solid solutions with x = 0–0.78, which are thought to be potential interstitial oxide ion conductors. The crystal structure of the solid solutions has been investigated by X-ray and neutron diffraction techniques using Rietveld refinement, and their microstructure has been examined by SEM. The excess oxygen content of the $(Ln_{2-x}Zr_x)Zr_2O_{7+x/2}$ (Ln= Nd, Sm; x= 0.2;0.32) pyrochlore-like solid solutions has been determined by thermal analysis and mass spectrometry in a reducing atmosphere (H_2/Ar-He). The transport properties of the solid solutions in the two systems have been studied by impedance spectroscopy in air.

$(Nd_{2-x}Zr_x)Zr_2O_{7+x/2}$ (x=0; 0.2; 0.32; 0.39; 0.48; 0.67; 0.78; 0.96; 1.14; 1.27) solid solutions undergo an order–disorder (pyrochlore–defect fluorite) structural phase transition, accompanied by a gradual reduction in the intensity of major pyrochlore superstructure peaks with decreasing Nd2O3 concentration in the range 33.3 to 18 mol%, so that there are no such peaks for the fluorite-like solid solutions containing 10, 12 and 15 mol% Nd_2O_3. X-ray diffraction Rietveld refinement results for the NdZrO system demonstrate the formation of two types of pyrochlore-like solid solutions, differing in the degree of cation disorder (fraction of antistructure pairs under 5% (P1) and up to ~50% (P2)). In contrast to NdZrO, the SmZrO system most likely contains a two-phase (fluorite + pyrochlore) region for the $(Sm_{2-x}Zr_x)Zr_2O_{7+x/2}$ ($0.96 \le x < 0.48$) solid solutions, containing 15–23.5 mol% Sm_2O_3. The interstitial oxide ion conductivity of the $(Sm_{2x}Zr_x)Zr_2O_{7+x/2}$ ($0.2 \le x \le 0.48$) pyrochlore-like solid solutions, $3 \cdot 10^{-3}$ S/cm at 750 °C, is comparable to the vacancy-mediated conductivity of undoped $Sm_2Zr_2O_7$. The$(Nd_{2-x}Zr_x)Zr_2O_{7+x/2}$ (x= 0.2; 0.32;0.38; 0.48, 0.67; 0.78) pyrochlore-like solid solutions have almost the same conductivity, ~$(1.2–4) \cdot 10^{-3}$ S/cm at 750 °C, which is two orders of magnitude higher than that of the ordered pyrochlore Nd2Zr2O7. All of the $(Sm_{2-x}Zr_x)Zr_2O_{7+x/2}$ ($0.2 \le x \le 0.48$) pyrochlorelike solid solutions are similar in structure to $(Nd_{2x}Zr_x)Zr_2O_{7+x/2}$ with a low degree of substitution (within x = 0.2) (P1) and contain a relatively small percentage of antistructure pairs (within 6.9%).

Keywords: REE zirconates, oxygen interstitials, oxygen vacancy, fluorite, pyrochlore.