Phase stability and ion-electron transport in strontium ferrites SrFO3-x, Sr3Fe2O7-x and Sr4Fe6O13-x

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Abstract

The study of electrical conductivity, Seebeck coefficient and oxygen nonstoichiometry in perovskite-related strontium ferrites SrFeO3-x, Sr3Fe2O7-x and Sr4Fe6O13- $xisperformedatoxygenpartialpressuresfrom10^{-19}$ to 0.5 atm in the temperature range 750-950. The partial ionic and p- and n-type electronic conductivities are determined based on the analysis of total conductivity variations with the oxygen pressure in the vicinity of electron-hole equilibrium point. The electron transport is analyzed using the oxygen nonstoichiometry and Seebeck coefficient data. The parameters of ionic and electronic conduction are discussed in terms of specific structure of the ferrite phases. The high concentration and isotropic mobility of oxygen vacancies are characteristics of SrFO3-x, providing high ion conductivity (0.2 S/cm at 900C). Decreasing oxygen pressure at temperatures below 870 results in structural transformation from perovskite to brownmillerite polymorph accompanied by a decrease of ionic and electronic transport. The phase Sr3Fe2O7-x with a Ruddlesden-Popper structure is formed by the perovskite layers alternated by rock-salt sheets. Such an arrangement prevents three-dimensional transport of ions and electrons (ion conductivity at 900C is about 0.06 S/cm) but ensures higher thermodynamic stability. The vacancy ordering results in formation of double layers of square pyramids Sr3Fe2O6 (x=1), which weakly affect electronic conduction and, on the contrary to the tetrahedral layers in brownmillerite, have a smaller negative influence on the ionic transport. The crystal lattice of intergrowth ferrite Sr4Fe6O13-x consists of alternating perovskite-type layers and slabs of pentacoordinated iron polyhedra. In accordance with structural data obtained by X-ray and neutron diffraction, the perovskite layers in this oxide are complete with oxygen ions while the ion transport occurs in the slabs of pentacoordinated iron ions by vacancy (at x¿0) or interstitial (at x¡0) mechanism. The level of ion conductivity in intergrowth ferrite is rather low, $itdoesnotexceed10^{-3}$ S/cm at 900C.