Thermal Behaviour of PrCo$_{1-x}$Fe$_x$O$_3$ Probed by X-Ray Synchrotron Powder Diffraction and Impedance Spectroscopy Measurements

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Crystal structure and transport properties of the mixed praseodymium cobaltites-ferrites PrCo$_{1-x}$Fe$_x$O$_3$ have been studied in the temperature range of 298–1173 K by a combination of in-situ X-ray synchrotron powder diffraction and temperature dependent impedance spectroscopy measurements.

Series of micro- and nanocrystalline powders of PrCo$_{1-x}$Fe$_x$O$_3$ were obtained by solid-state reactions technique in air at 1473 K and via low-temperature sol-gel citrate route at 973 K, respectively. At the ambient conditions both series of the samples adopt orthorhombic perovskite structure isotypic with GdFeO$_3$. Concentration dependence of the unit cell dimensions of PrCo$_{1-x}$Fe$_x$O$_3$ proves a formation of continuous solid solution, peculiarity of which is the lattice parameters crossover and appearance of dimensionally cubic structure at $x = 0.4$ [1]. In-situ high temperature powder diffraction examination of PrCo$_{1-x}$Fe$_x$O$_3$ series revealed considerable anomalies in the lattice expansion which are especially pronounced for the cobalt-reach specimens. These anomalies, which are reflected in a sigmoidal dependence of the unit cell dimensions and in the considerable increasing of the thermal expansion coefficients, are obviously associated with transitions of Co$^{3+}$ ions from low spin to the higher spin states and the coupled metal-insulator transitions, occurred in in rare earth cobaltites at the elevated temperatures. Observed deviations in the lattice expansion in the PrCo$_{1-x}$Fe$_x$O$_3$ series become less pronounced with the decreasing cobalt content, but they are clearly detectable even in the iron-richest PrCo$_{0.1}$Fe$_{0.9}$O$_3$ specimen. Indeed, the temperature-dependent impedance measurements clearly prove the change of conductivity type from dielectric to the metallic behaviour in the mixed cobaltite-ferrites PrCo$_{1-x}$Fe$_x$O$_3$ at the elevated temperatures (Figure). The temperature of insulator-metal transition in PrCo$_{1-x}$Fe$_x$O$_3$ series increases from 723 K for $x = 0.4$ to 1100 K for $x = 0.8$ (Figure), which is in a good agreement with the results obtained from the analysis of thermal expansion data. Activation energy of electrical conductivity in the PrCo$_{1-x}$Fe$_x$O$_3$ series derived from the Arrhenius plots increases systematically with increasing Fe content from 0.56 eV for $x = 0.4$ to 0.93 eV for $x = 0.8$ samples, being in good agreement with the literature data for the parent PrCoO$_3$ and PrFeO$_3$ compounds (Figure, inset).

**Figure.** Temperature dependencies of the electrical conductivity of the PrCo$_{1-x}$Fe$_x$O$_3$ samples and concentration dependence of activation energy in the PrCo$_{1-x}$Fe$_x$O$_3$ series (inset).


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