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High-temperature defect thermodynamics of nickel substituted double-perovskite cobaltite $PrBaCo_{2-x}Ni_xO_{6-\delta}$ ($x = 0.2$)

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Abstract

The double perovskite praseodymium cobaltites $PrBaCo_{2-x}Ni_xO_{6-\delta}$, where $0.1 \leq x \leq 0.3$, were obtained by combustion of organo-metallic precursors and shown to have a tetragonal structure with the crystalline lattice parameters $a = 3.91$ and $c = 7.63$ Å consistent with electron compensation $2Co^{3+} = Ni^{2+} + Co^{4+}$ of Ni^{2+} impurity centers. The oxygen content $(6 - \delta)$ vs. $\log(p_{O_2})$ dependencies were measured by a coulometric titration technique for $x = 0.2$ at 650 – 950 °C and oxygen pressure variations within 10^{-10} – 0.6 atm. The reductive decomposition of the cobaltite is found to take place at $\delta = 1.13$. The experimental data were utilized in order to derive partial thermodynamic functions of oxygen that govern defect equilibration. The oxygen partial enthalpy $\Delta\bar{H}_O$ and entropy $\Delta\bar{S}_O$ are found to exhibit strong changes near $(6 - \delta) = 5$. The observed behavior is explained in frameworks of the defect formation model, which involves reactions of charge disproportionation of Co^{3+} cations, oxygen exchange with the gas phase and oxygen disordering over O2 and O3 structural positions.

1. Introduction

The double perovskite cobaltites $RBaCo_2O_{6-\delta}$, where R is a rare-earth metal or yttrium, are distinguished among other complex oxides owing to their capability to withstand large variations [1-3] of oxygen non-stoichiometry (δ) at changes of the ambient temperature (T) and oxygen partial pressure (p_{O_2}) while keeping high levels of both contributions, electron and oxygen ion, to conductivity [4–7] on the background of fast oxygen exchange with the gas phase [8–10]. These properties significantly impact operation characteristics of SOFC cathodes [11–13] and thin film oxygen sensors [14] as well as oxygen separating ceramics [15, 16]. However, the applicability of the cobaltites is heavily hampered because of their large expansion at heating [12, 13]. In attempts to mitigate this highly undesirable drawback, authors [17] have studied partial replacement of

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