OXYGEN NONSTOICHIOMETRY AND THERMODYNAMIC QUANTITIES OF PEROVSKITE-TYPE $La_{1-x}Sr_xFeO_{3-\delta}$ (x=0.2, 0.5, 0.8)

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Key Words: Defect chemistry, Thermodynamic properties, Theoretical approaches, Oxide-ion conductors, Mixed conductors

In this work, the defect structure analysis of $La_{1-x}Sr_xFeO_{3-\delta}$ (x=0.2, 0.5, 0.8) was presented. Thermogravimetric measurements were performed to determine the change in oxygen nonstoichiometry ($\Delta\delta$) with oxygen partial pressure (pO_2) in $10^{-19} \leq (pO_2/\text{atm}) \leq 0.21$ and temperature in $750 \leq (T/℃) \leq 900$ range. $La_{1-x}Sr_xFeO_{3-\delta}$ showed a clear electronic stoichiometric point around $\delta \approx 3-x/2$. The relative partial molar enthalpy ($h_o-h_o^o$) and entropy ($s_o-s_o^o$) of oxygen were calculated from δ-pO_2-T relation by using Gibbs-Helmholtz equation. The negative sign of $h_o-h_o^o$ and $s_o-s_o^o$ indicated that the incorporation of oxygen was an exothermic process and showed that the experimentally observed variations in $h_o-h_o^o$ and $s_o-s_o^o$ with δ matched well with the statistical thermodynamic model proposed by Mizusaki[1]. The defect diagram analysis showed that in n-type regime Fe^{2+} concentration varied with $(pO_2)^{-1/4}$ whereas in p-type regime Fe^{4+} concentration varied with $(pO_2)^{1/4}$.

Reference

[1] J. Mizusaki et al. J. Solid State Chem. 67 (1987) 1-8.