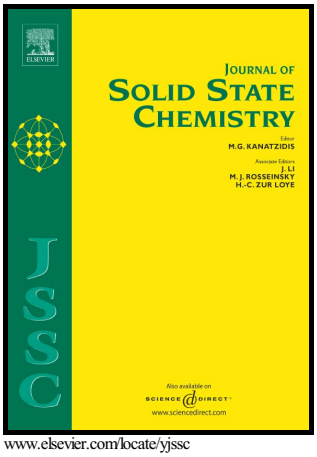

www.elsevier.com/locate/yjssc

Thermodynamic analysis of defect equilibration in double perovskites based on $PrBaCo_2O_{6-\delta}$ cobaltite

B.V. Politov, A.Yu. Suntsov, I.A. Leonidov, M.V. Patrakeev, V.L. Kozhevnikov

PII: S0022-4596(17)30056-7
DOI: http://dx.doi.org/10.1016/j.jssc.2017.02.021
Reference: YJSSC19697

To appear in: *Journal of Solid State Chemistry*

Received date: 26 January 2017
Revised date: 17 February 2017
Accepted date: 18 February 2017

Cite this article as: B.V. Politov, A.Yu. Suntsov, I.A. Leonidov, M.V. Patrakeev and V.L. Kozhevnikov, Thermodynamic analysis of defect equilibration ir double perovskites based on $PrBaCo_2O_{6-\delta}$ cobaltite, *Journal of Solid Stat Chemistry,* http://dx.doi.org/10.1016/j.jssc.2017.02.021

Thermodynamic analysis of defect equilibration in double perovskites based on $PrBaCo_2O_{6-\delta}$ cobaltite

B.V.Politov, A.Yu.Suntsov*, I.A.Leonidov, M.V.Patrakeev, V.L.Kozhevnikov

Institute of Solid State Chemistry, Pervomaiskaya str.91, Yekaterinburg, 620990, Russia

*Corresponding author. Tel: c; Fax: +7-343-3744495; suntsov@ihim.uran.ru

Abstract

The double perovskite praseodymium cobaltite lightly doped with yttrium $Pr_{0.9}Y_{0.1}BaCo_2O_{6-\delta}$ (PYBCO) was obtained by combustion of organo-metallic precursors and shown to have a tetragonal structure with the crystalline lattice parameters $a = b = 3.903$ and $c = 7.621$ Å. The PYBCO composition occurs remarkably stable as show coulometric titration measurements of oxygen content $(6-\delta)$ in the oxygen pressure range $10^{-13} - 0.21$ atm and at temperatures variations within 650 – 950 °C. The experimental data were utilized in order to derive partial thermodynamic functions of oxygen that govern equilibration of defects in PYBCO. The oxygen partial enthalpy $\Delta\bar{H}_O(\delta)$ and entropy $\Delta\bar{S}_O(\delta)$ both experience strong changes near $(6-\delta) = 5$. The observed behavior of $\Delta\bar{H}_O(\delta)$ and $\Delta\bar{S}_O(\delta)$ 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. The verification of the suggested approach is carried out by comparison with independently obtained thermochemical data.

Keywords: cobaltites; double perovskites; partial molar quantities; thermodynamic analysis; defect equilibrium

Graphical abstract caption: The oxygen content dependent variations of oxygen partial molar entropy and enthalpy in $Pr_{0.9}Y_{0.1}BaCo_2O_{6-\delta}$.