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Effects of A-site composition and oxygen nonstoichiometry on the thermodynamic stability of compounds in the Ba–Sr–Co–Fe–O system

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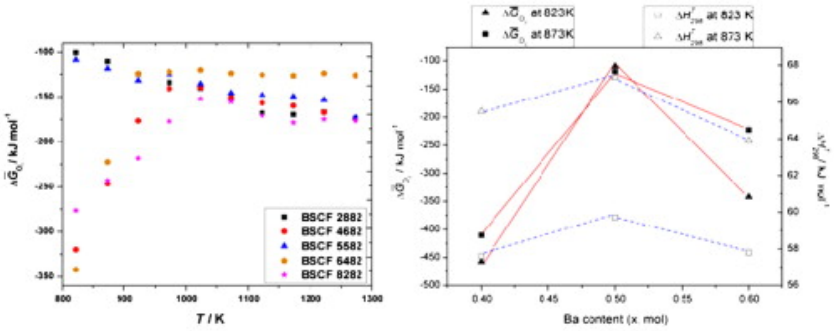
Abstract

The thermodynamic stability of the perovskite-type oxides in the $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) system was investigated with varying Ba:Sr ratios (x=0.2, 0.4, 0.5, 0.6, 0.8) and correlated with the charge compensation mechanism and the change in the oxygen stoichiometry of the materials. Thermodynamic properties represented by the relative partial molar free energies, enthalpies and entropies of oxygen dissolution in the perovskite phase, as well as the equilibrium partial pressures of oxygen have been obtained in the temperature range of 823–1273 K using solid electrolyte electrochemical cells (EMF) method. The influence of the oxygen stoichiometry change on the thermodynamic properties was examined using a coulometric titration technique coupled with EMF measurements. The temperature dependence of enthalpy increment (H_T–H_{298}) in the temperature range of 700–900 K was measured by drop calorimetry. The energetic parameters allow for the correlation of the structural and electrical stability with the defect structures.

Graphical abstract

Partial molar energy of oxygen dissolution ($\Delta\overline{G}_{O_2}$) (EMF measurements) and enthalpy increment (H_T–H_{298}) (drop calorimetry data) of perovskite materials with the composition $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ as a function of temperature and Barium content.



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Highlights

► We report relevant data for thermodynamic stability of $Ba_xSr_{1-x}Co_{1-y}Fe_yO_{3-\delta}$ compounds. ► Temperature of structural transformations is evidenced as a function of Ba content. ► Correlation between thermodynamic, electrical and structural data is investigated. ► The results are discussed based on the properties-defect structure relationship.

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Keywords

Perovskites; Thermodynamic properties; SOFC cathodes; Oxygen nonstoichiometry; Coulometric titration; Oxygen vacancies

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2021, International Journal of Hydrogen Energy

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>
> …Its oxygen vacancies can be intrinsically formed when calcined at high temperature, offering high oxygen storage capability (OSC) and, therefore, high reducibility. A and B site in the perovskite compounds can be substituted to improve its specific properties i.e. electronic conductivity, oxygen mobility and oxygen exchange rate [26–28]. La1-xSrxO3 (LSO) perovskite family was widely researched due it its thermal stability and oxygen storage capacity [29–31].…

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Synthesis and characterization of Nanocrystalline Ba<inf>0·6</inf>Sr<inf>0·4</inf>Co<inf>0·8</inf>Fe<inf>0·2</inf>O<inf>3</inf> for application as an efficient anode in solid oxide electrolyser cell

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Characterisation of La<inf>0.6</inf>Sr<inf>0.4</inf>Co<inf>0.2</inf>Fe<inf>0.8</inf>O<inf>3-δ</inf> – Ba<inf>0.5</inf>Sr<inf>0.5</inf>Co<inf>0.8</inf>Fe<inf>0.2</inf>O<inf>3-δ</inf> composite as cathode for solid oxide fuel cells

2017, Electrochimica Acta

> *Citation Excerpt :*
>
> …Below 900 °C, BSCF undergoes a phase transition from cubic to hexagonal structure with a lower catalytic activity. According to the literature dealing with BSCF structural changes [19–21], phase transitions are affected by the lattice distortion [22,23], due to the valence changes of B-site cations [24], and also depend on the doping contents of A-site cations [25], since these structural transformations occur by the partial decomposition into Ba-rich and Sr-rich phases [26,27]. In addition, BSCF in contact with CO2 containing atmosphere is prone to form carbonates, even when the CO2 content is lower that 1% [28,29].…

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Thermodynamic properties of the Ba<inf>0.75</inf>Sr<inf>0.25</inf>TiO<inf>3</inf>nanopowders obtained by hydrothermal synthesis

2017, Journal of Alloys and Compounds

> *Citation Excerpt :*
>
> …Previous reports on the substituted perovskites indicate that the mismatch at the A-site creates strain on grain boundaries which affect not only the electrical, but also the thermodynamic properties of the ABO3 perovskites [21]. Besides, the role of charge ordering in explaining the transport properties of the variable valence transition metals perovskites was emphasized [22,23]. Investigating the influence of different compositional variables on the thermodynamic properties of some multiferroic materials, Tanasescu et al. [22,24] pointed out that the remarkable behavior of the substituted samples could be explained not only qualitatively by the structural changes upon doping, but also by the fact that the thermodynamic properties are extremely sensitive to the chemical defects in oxygen sites.…

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