Materials Letters 235 (2019) 107–110

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Thermodynamic quantities and defect formation in solid solution $La_{0.49}Sr_{0.5-x}Ba_xFeO_{3-\delta}$

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ARTICLE INFO

Article history:
Received 13 September 2018
Received in revised form 26 September 2018
Accepted 30 September 2018
Available online 2 October 2018

Keywords:
Perovskite
Ba-substituted ferrites $La_{0.49}Sr_{0.5}FeO_{3-\delta}$
Oxygen nonstoichiometry
Thermodynamic quantities
Defect equilibrium

ABSTRACT

The key factors determining the applicability of mixed-conducting oxides in energy-related technologies refer to the stability to reduction and the level of oxygen ionic and electronic transport, both determined by partial molar enthalpy and entropy of oxygen in the oxide. Therefore, any information about the thermodynamic properties of the oxide has an important predictive value.

The chemical potential of oxygen in $La_{0.49}Sr_{0.5-x}Ba_xFeO_{3-\delta}$ relative to the standard state in the gas phase, $\Delta\mu_O$, was calculated using experimental data on oxygen content in oxides depending on the partial pressure of oxygen, p_{O_2}, and temperature. The partial molar enthalpy, ΔH_O, and partial molar entropy, ΔS_O, of oxygen were determined as functions of $(3-\delta)$ from $\Delta\mu_O$ data using the Gibbs-Helmholtz equation. The previously proposed defect equilibrium model assuming the presence of unavailable oxygen vacancies in barium-containing oxides was successfully verified. Thermodynamic quantities ΔH_O and ΔS_O, obtained by statistical thermodynamic calculation based on this model were found to be in a reasonable agreement with those obtained with the Gibbs-Helmholtz equation. The performed calculations allowed enhancing the accuracy of the defect equilibrium model parameters.

1. Introduction

Perovskite-type oxides with ion and electron conductivity are considered as promising materials for use as electrodes of solid oxide fuel cells and oxygen transport membranes for partial oxidation of methane to synthesis gas [1–3]. Heterovalent cation substitution is widely used to adjust the charge carrier concentration and transport properties of such oxides [4,5]. Isovalent substitution may also influence the oxygen content and transport properties of oxides due to cation size difference [6]. These effects are, however, insufficiently studied.

Sr- and Ba-doped lanthanum ferrites are suitable materials to study the cation size effects on the oxygen thermodynamics due to considerable difference in the ionic radii of Ba^{2+} ($R_{CN12} = 1.61$ Å) and Sr^{2+} ($R_{CN12} = 1.44$ Å) [7]. The A-site cation size difference was found to influence the transport and thermodynamic characteristics of ferrites [8,9]. In our prior work, experimental data on oxygen content in $La_{0.49}Sr_{0.5-x}Ba_xFeO_{3-\delta}$ depending on temperature and oxygen partial pressure were satisfactorily simulated by a defect equilibrium model taking into account the oxidation reaction

$$2Fe^{3+} + V_O + \tfrac{1}{2}O_2 = 2Fe^{4+} + O^{2-} \tag{1}$$

and disproportionation reaction of Fe^{3+} ions

$$2Fe^{3+} = Fe^{2+} + Fe^{4+} \tag{2}$$

It was revealed that barium incorporation in lanthanum-strontium ferrite made some vacancies unavailable for oxygen ions due to their size reduction [9]. Another detected effect of barium substitution for strontium was an increase in the enthalpy of both reactions (1) and (2) of defect formation.

This work, being a continuation of our research, is aimed at the analysis of barium substitution effect on partial molar enthalpy and partial molar entropy of oxygen using experimental data obtained earlier [9]. A particular purpose of the study is to verify the finding related to the ability of barium to make oxygen vacancies unavailable based on the statistical thermodynamic calculations.

2. Results and discussion

Experimental data of oxygen content in $La_{0.49}Sr_{0.5-x}Ba_xFeO_{3-\delta}$ obtained under equilibrium conditions can be used in order to calculate the chemical potential of oxygen in oxides relative to its standard state in the gas phase as a function of temperature and the partial pressure of oxygen:

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https://doi.org/10.1016/j.matlet.2018.09.168
0167-577X/

$$\Delta\mu_O = \frac{RT}{2} \cdot \ln p_{O_2} \tag{3}$$

here R is the gas constant. Isothermal dependences of $\Delta\mu_O$ on $(3-\delta)$ obtained with Eq. (3) are represented in Fig. 1 by geometric symbols. The partial molar enthalpy, $\Delta\bar{H}_O$, and partial molar entropy, $\Delta\bar{S}_O$, are related to the chemical potential of oxygen as:

$$\Delta\mu_O = \Delta\bar{H}_O - T\Delta\bar{S}_O \tag{4}$$

From (3) and (4), using the Gibbs-Helmholtz equation, the expressions for partial molar enthalpy and partial molar entropy of oxygen in oxides can be derived:

$$\Delta\bar{H}_O = \frac{\partial}{\partial(1/T)}\left(\frac{R}{2} \cdot \ln p_{O_2}\right) \tag{5}$$

$$\Delta\bar{S}_O = -\frac{\partial}{\partial T}\left(\frac{RT}{2} \cdot \ln p_{O_2}\right) \tag{6}$$

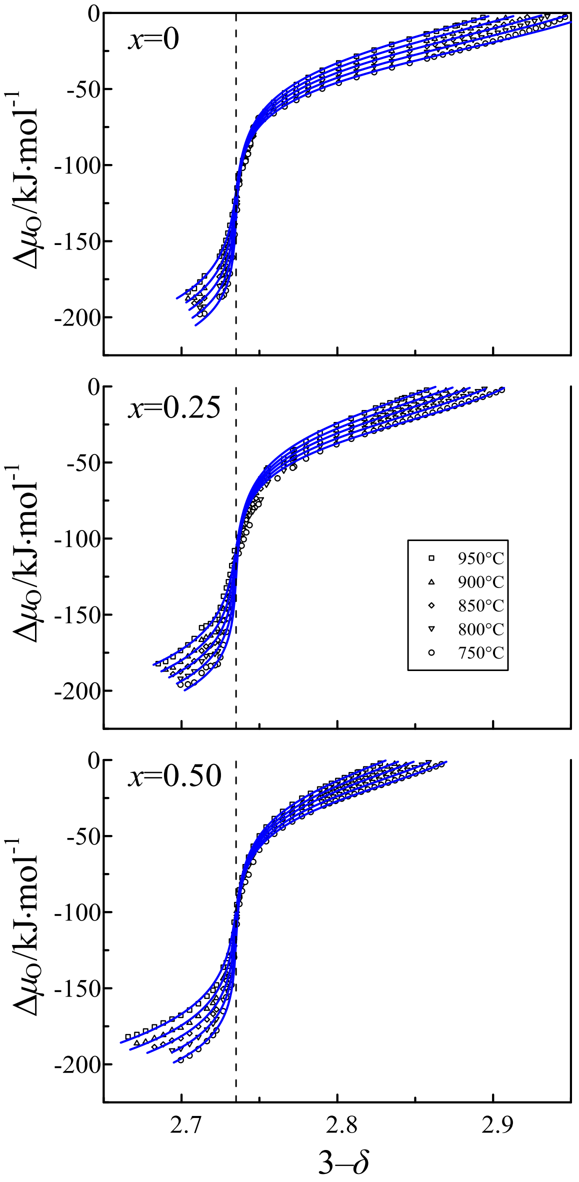

Fig. 1. Isothermal plots of $\Delta\mu_O$ depending on oxygen content in $La_{0.49}Sr_{0.5-x}Ba_xFeO_{3-\delta}$. Geometric symbols represent results, acquired with Eq. (3); curves represent results, obtained with Eq. (4) after model calculations. Dashed lines indicate oxygen content value 2.735.

Fig. 2 reveals that the dependencies of $R/2 \cdot \ln p_{O_2}$ vs. $1/T$ and $RT/2 \cdot \ln p_{O_2}$ vs. T at permanent oxygen content in $La_{0.49}Sr_{0.5}FeO_{3-\delta}$ are linear. Similar dependences are observed for other compositions. This made it possible to calculate partial molar enthalpy and partial molar entropy of oxygen in $La_{0.49}Sr_{0.5-x}Ba_xFeO_{3-\delta}$, which are represented by geometric symbols in Fig. 3(a) and (b). The observed dependences of $\Delta\bar{H}_O$ and $\Delta\bar{S}_O$ on $(3-\delta)$ look similar to those of other perovskite-related ferrites [4,10]. Thermodynamic quantities demonstrate abrupt changes in the vicinity of oxygen content 2.735 due to a sharp alteration of dominant defect species in n-p equilibrium condition. Doping with barium cations having the same oxidation state but a larger size than Sr^{2+} was shown to result in partial blocking of oxygen vacancies in $La_{0.49}Sr_{0.5-x}Ba_xFeO_{3-\delta}$ [8,9]. Being conditioned exclusively by barium concentration, the number of unavailable oxygen vacancies is assumed to be unaffected by oxygen content. Therefore, the relationship between the partial molar thermodynamic quantities of oxygen and the enthalpy and entropy of defect formation reactions in $La_{0.49}Sr_{0.5-x}Ba_xFeO_{3-\delta}$ should be similar to that of $La_{1-x}Sr_xFeO_{3-\delta}$ brought out by Mizusaki *et al.* based on statistical thermodynamic calculations [4]:

$$\Delta\bar{H}_O = \Delta H^o_{ox} - \frac{\partial n}{\partial\delta}\Delta H^o_d \tag{7}$$

and

$$\Delta\bar{S}_O = \Delta S^o_{ox} - \frac{\partial n}{\partial\delta}\Delta S^o_d + s^{conf}_O \tag{8}$$

where ΔH°_{ox}, ΔS°_{ox}, and ΔH°_d, ΔS°_d are standard enthalpy and entropy of oxidation reaction (1) and disproportionation reaction (2), respectively; n is the number of Fe^{2+} ions per formula unit. Taking into account the charge and concentration of lanthanum, strontium and barium ions, as well as the number of vacancies in the lanthanum sublattice in $La_{0.49}Sr_{0.5-x}Ba_xFeO_{3-\delta}$ ferrites, the expression for derivative $\partial n/\partial\delta$ was obtained as:

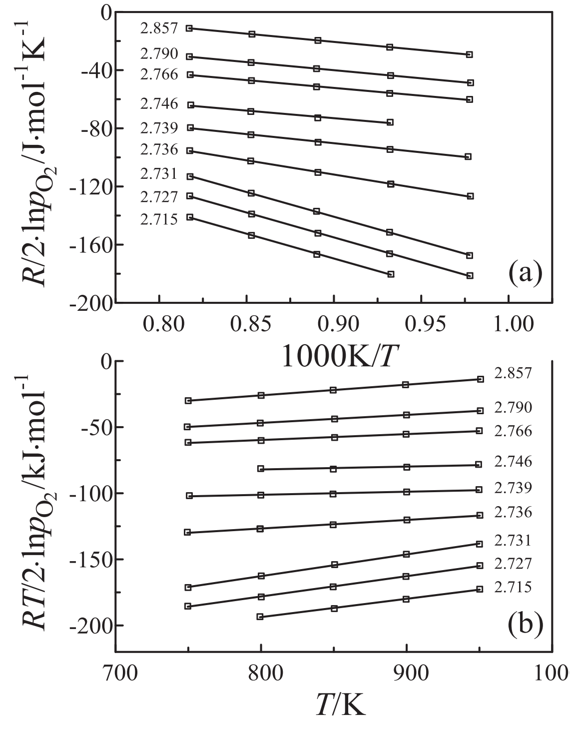

Fig. 2. Relationship of $R/2 \cdot \ln p_{O_2}$ to $1/T$ (a), and of $RT/2 \cdot \ln p_{O_2}$ to T (b) at fixed oxygen contents in $La_{0.49}Ba_{0.5}FeO_{3-\delta}$. Solid lines represent linear approximation.