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Oxygen nonstoichiometry and defect equilibria in $La_{0.49}Sr_{0.5-x}Ba_xFeO_{3-\delta}$

Alexander D. Bamburov, Alexey A. Markov, Mikhail V. Patrakeev [*], Ilia A. Leonidov

Institute of Solid State Chemistry, UB RAS, 91 Pervomaiskaya Str, 620990 Yekaterinburg, Russia

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ABSTRACT

High level of mixed-conductivity and good stability of oxide $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ make it promising for the development of functional materials for such energy-related applications as solid oxide fuel cells and membrane reactors for partial oxidation of methane. The oxygen content in $La_{0.49}Sr_{0.5-x}Ba_xFeO_{3-\delta}$ ($x = 0$, 0.25, 0.5) was measured by means of coulometric titration in the interval of partial oxygen pressure between 10^{-20} and 0.5 atm at temperatures 750–950 °C. The obtained results were employed for defect structure analysis of oxides. An ideal solution model enabled satisfactory simulation of experimental data for barium-free oxide. A reasonable data description for barium-containing oxides was achieved in the model, assuming that some of the oxygen vacancies are unavailable for oxygen ions. Partial substitution of barium for strontium was found to decrease the oxidation reaction constant of iron ions, resulting in a raised concentration of n-type electronic charge carriers and a reduced concentration of p-type carriers.

1. Introduction

Mixed oxygen ionic and electronic conductors (MIEC) have been attracting much attention owing to their potential applications as catalysts, electrodes for fuel cells and ceramic membranes for partial oxidation of methane (POM) to synthesis gas [1–3]. High ambipolar conductivity and good stability over a wide range of temperatures and partial oxygen pressures (p_{O_2}) are the most important requirements for such applications. A good combination of these properties is demonstrated by perovskite-like ferrite $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ [4]. A number of derivatives of this ferrite, obtained by partial substitution of iron ions with cations having a stable oxidation state, have been studied with the aim of further improving their properties [5–7]. This sort of substitution, however, was found to suppress both p- and n-type electron conductivity due to a decrease in charge carrier concentration as well as in the number of available states. An accompanying decrease of oxygen-ion conductivity was revealed to result from reduced mobile oxygen vacancy concentration. Partial ion substitution in the A sublattice seems greatly preferable as an alternative means of influencing ferrite transport properties since it avoids interference in the Fe–O transport network [8–10]. Taking into account the outstanding oxygen transport parameters of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, partial substitution of barium for strontium in $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ presents an interesting task. In contrast to strontium cobaltite, though, strontium substitution by barium in $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ resulted in a decrease of ion and p-type electron conductivity [8]. The reason for the observed effect is not clear. Due to the advantageous ion and electron transport parameters and good stability of $La_{0.5}Sr_{0.5-x}Ba_xFeO_{3-\delta}$ ferrites under reducing conditions, a detailed analysis of Ba–Sr ratio impact on their defect structure and thermodynamic properties is of considerable interest.

The present work, planned as part of a more complex research project, is aimed at studying oxygen nonstoichiometry in $La_{0.49}Sr_{0.5-x}Ba_xFeO_{3-\delta}$ ($x = 0$, 0.25, 0.50) over wide temperature and p_{O_2} ranges, as well as analyzing their defect structure. The charge carrier concentrations to be calculated in this work will be further employed in a profound examination of the transport properties of $La_{0.49}Sr_{0.5-x}Ba_xFeO_{3-\delta}$. The decision to create a minor deficiency in the A sublattice is related to its known positive effect on density, microstructure, and, as a result, on conducting properties of perovskite ceramics [11].

2. Experimental

The oxides $La_{0.49}Sr_{0.5-x}Ba_xFeO_{3-\delta}$, where $x = 0$, 0.25 and 0.50 were prepared using the self-combustion glycine-nitrate process with final sintering in air at 1250 °C for 10 h. Room-temperature XRD patterns were recorded with a Shimadzu XRD–7000 diffractometer (CuKα, step 0.03°, exposition 3 s) and used for unit cell parameters calculation by the Rietveld method with PCW 2.4 software [12].

The oxygen content variation in the oxides as a function of the p_{O_2} in the gas phase was measured by means of coulometric

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[*] Corresponding author.
E-mail address: patrakeev@ihim.uran.ru (M.V. Patrakeev).

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titration in a double electrochemical cell. The principles of the method and the specific features of the experiment are described in [13]. The reference values for the absolute oxygen content in the oxides were determined by assigning the inflection point of the oxygen content isotherm at 950 °C to the condition of equal concentrations of electrons and holes, i.e. to the nominal oxidation state of iron ions 3+in accordance with the formula $La^{3+}_{0.49}Sr^{2+}_{0.5-x}Ba^{2+}_xFe^{3+}O^{2-}_{2.735}$. The exact position of the inflection point was identified by the extremum of the $\partial\delta/\partial p_{O_2}$ derivative. A similar approach was employed earlier in [14].

3. Defect equilibrium

The formation of ionic and electronic defects in non-stoichiometric ferrites was shown to result from the oxidation and charge disproportionation processes involving iron ions that may acquire the oxidation states of 2+, 3+, and 4+ under considered conditions [15]. Therefore, one may write a generalized chemical formula of our ferrites as follows: $La^{3+}_{0.49}Sr^{2+}_{0.5-x}Ba^{2+}_xFe^{2+}_nFe^{3+}_aFe^{4+}_pO^{2-}_{3-\delta}$, where n, a, and p designate concentrations of respective iron ions. The oxidation reaction and respective equilibrium constant can be written as:

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

$$K_{ox} = \frac{[Fe^{4+}]^2 \cdot [O^{2-}]}{[Fe^{3+}]^2 \cdot [V_O]} p_{O_2}^{-1/2} = \frac{p^2 \cdot (3-\delta)}{a^2 \cdot \delta} p_{O_2}^{-1/2}. \tag{1}$$

The charge disproportionation reaction and its equilibrium constants are:

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

$$K_d = \frac{[Fe^{2+}] \cdot [Fe^{4+}]}{[Fe^{3+}]^2} = \frac{n \cdot p}{a^2}. \tag{2}$$

In addition, the requirement of site conservation in the iron sublattice and electroneutrality

$$a + n + p = 1, \tag{3}$$

$$n = 2\delta - 0.53 + p \tag{4}$$

should also be taken into account. The solution to the system of equations (2), (3), (4) establishes a relationship between the iron cation concentrations in different oxidation states a, n and p and oxygen nonstoichiometry δ. The relationship between p_{O_2} and oxygen content in oxide follows from Eq. 1:

$$p_{O_2}^{1/2} = \frac{p^2 \cdot (3-\delta)}{a^2 \cdot \delta \cdot K_{ox}}. \tag{5}$$

4. Results and discussion

According to X-ray diffraction, all synthesized oxides $La_{0.49}Sr_{0.5-x}Ba_xFeO_{3-\delta}$ are perovskite-like single phases. The barium-free composition exhibits rhombohedral symmetry (S.G. $R\bar{3}c$) with unit cell parameters of $a = 5.505(5)$, $b = 13.410(5)$, while $x = 0.25$ and $x = 0.50$ oxides have cubic symmetry (S.G. $Pm\bar{3}m$). For the sake of comparison, the cube root of the unit-cell volume per formula unit (a_p) has been calculated as an effective perovskite unit-cell parameter, Table 1. The observed increase in the perovskite cell parameter with increasing barium content can be attributed to ionic radius of Ba^{2+} (R_{CN12} = 1.61 Å [16]) larger than that of Sr^{2+} (R_{CN12} = 1.44 Å).

The coulometric titration data, presented in Fig. 1, display a shift of 3−δ isotherms towards high p_{O_2} with an increase in barium

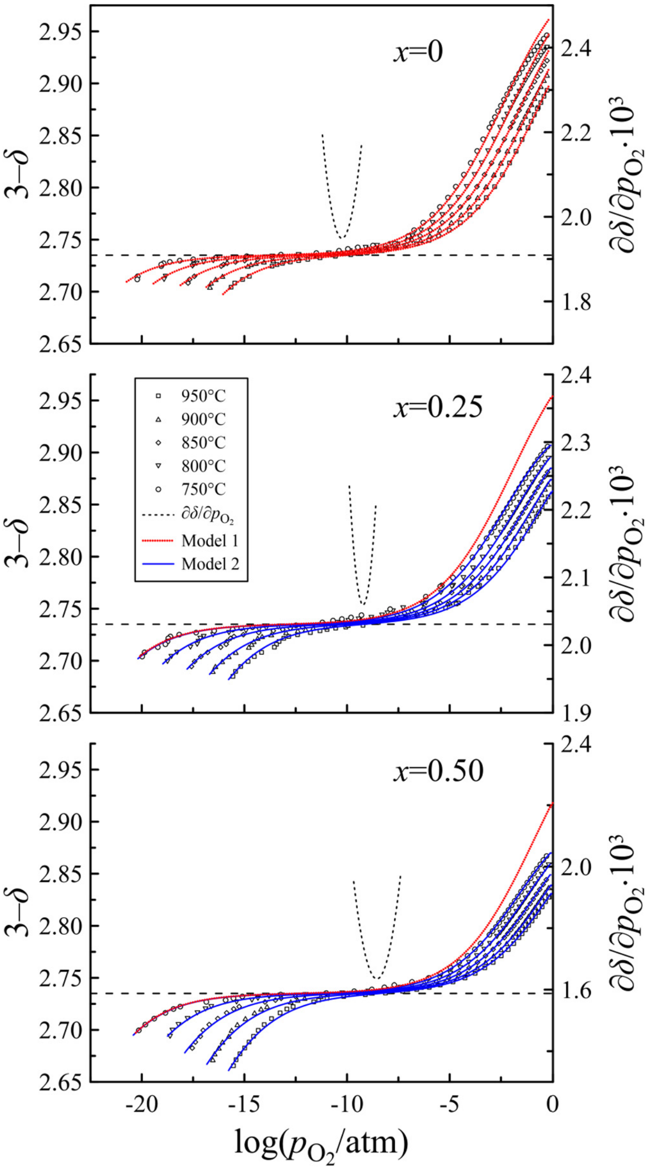

Fig. 1. Isothermal plots of oxygen content in $La_{0.49}Sr_{0.5-x}Ba_xFeO_{3-\delta}$ as a function of partial oxygen pressure at different temperatures. Solid lines represent results of model calculations. Dashed lines show fragments of derivative $\partial\delta/\partial p_{O_2}$ served for a precise locating condition of n-p equilibrium at 950 °C.

Table 1
Crystalline lattice parameter and thermodynamic parameters for defect formation reactions in $La_{0.49}Sr_{0.5-x}Ba_xFeO_{3-\delta}$.

x	a_p/A	ΔH^0_{ox}/KJ mol^{-1}	ΔS^0_{ox}/J mol^{-1} K^{-1}	ΔH^0_d/KJ mol^{-1}	ΔS^0_d/J mol^{-1} K^{-1}
0	3.885(7)*	−109 ± 2	−72 ± 2	110 ± 1	9 ± 1
0.25	3.914(5)	−103 ± 2	−70 ± 2	111 ± 2	5 ± 1
0.50	3.932(9)	−92 ± 2	−68 ± 1	133 ± 3	12 ± 3

* Reduced to the perovskite cell for comparison.