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Defect structure and defect-induced expansion of doped perovskite $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$

A.Yu. Zuev, V.V. Sereda, D.S. Tsvetkov*

Institute of Natural Sciences, Ural Federal University, Lenin av.51, 620000, Ekaterinburg, Russia

ARTICLE INFO

Article history:

Received 15 March 2014

Received in revised form

15 September 2014

Accepted 22 September 2014

Available online 16 October 2014

Keywords:

Chemical expansion

Defect structure

MIEC

Oxygen nonstoichiometry

Thermal expansion

Perovskite

ABSTRACT

The results of chemical expansion measured as a function of oxygen partial pressure, $p\text{O}_2$, and temperature by means of dilatometric technique are presented for the perovskite-type doped cobaltite $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$. The modeling of the defect structure of this perovskite was carried out. Within the framework of the model all iron sites are assumed to be occupied by localized holes whereas both electrons and holes can be localized on cobalt sites in $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$. The defect structure model proposed was shown to fit perfectly well available experimental data on oxygen nonstoichiometry of the perovskite studied. Equilibrium constants of the appropriate defects reactions were, therefore, determined and concentrations of all defect species defined within the framework of the model proposed were calculated as functions of temperature and oxygen nonstoichiometry. These concentrations were employed in the chemical expansion model derived by us earlier in order to compute the chemical expansion of the $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ lattice as a function of its oxygen nonstoichiometry. Cobalt ions transition from low spin (LS) state to high spin (HS) one induced by temperature increase was taken into account as well. The model proposed was shown to coincide completely with experimental data on chemical expansion for the $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ at all temperatures investigated. As a result, the spin state distribution of cobalt was calculated depending on temperature for the oxide studied.

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Introduction

Perovskite oxides derived from the undoped lanthanum cobaltite $\text{LaCoO}_{3-\delta}$ by substitution of alkali-earth metal and other 3d-metal for La and Co, respectively, are the state-of-the-art materials for several applications at moderate high temperatures such as solid oxide fuel cells (SOFC) and mixed ionic and electronic conducting (MIEC) membranes due to their ability to meet appropriate requirements such as high

melting point, large electronic and oxide ion conductivity, chemical and mechanical stability in both oxidizing and reducing environments. Particularly, simultaneous doping with strontium and iron was shown to enable dramatic enhance of mixed conductivity and significant decrease of thermal expansion coefficient of the lanthanum cobaltite that makes $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ suitable materials for SOFC cathodes [1,2].

The unique feature of oxides is their ability to undergo both thermal expansion and that induced by oxygen vacancies

* Corresponding author. Tel.: +7 343 251 7927; fax: +7 343 261 7411.

E-mail addresses: dmitry.tsvetkov@urfu.ru, Dmitrii.Tsvetkov@usu.ru (D.S. Tsvetkov).
<http://dx.doi.org/10.1016/j.ijhydene.2014.09.115>

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formation in the oxide lattice at high temperature and low oxygen partial pressure (pO_2). The latter measured relative to the reference state, $\epsilon_C = \frac{\Delta V}{V_0}$, is called chemical or defect-induced expansion [3]. Chemical expansion of lanthanum cobaltite simultaneously doped with strontium and iron was first measured as a function of pO_2 at different temperatures by Adler [4] for $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ using dilatometric technique. Wang et al. [5] determined later a pO_2 dependences of the pseudo-cubic cell parameter at different temperatures for another composition $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ using in situ high temperature X-ray diffraction (XRD). Chemical expansion of the compound $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ previously studied by Adler [4] was investigated later by Bishop et al. [2]. Hashimoto et al. [6] determined pseudo-cubic lattice parameter for $La_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_{3-\delta}$ ($y = 0.2, 0.4, 0.6$) depending on pO_2 and oxygen nonstoichiometry using in situ high temperature XRD. It is worth noting that all compositions $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ studied to date regarding their chemical expansion contain different amount of iron on B-site but with the same content of strontium (40 mol.%) on A-site. It seems to be of interest to study chemical expansion of $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ with different amount of the dopant, x, on A-site. On the other hand, so far there are no data on model calculations of chemical expansion for $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ that would be in satisfactory agreement with experimental results, or, in other words, the origin of chemical expansion of such oxides is still not fully understood. It is, however, recognized that the defect structure of oxide materials is of key importance for understanding the origin of their lattice strain induced by defects.

The refinement of the defect structure for selected compound $La_{0.7}Sr_{0.3}Co_{0.9}Fe_{0.1}O_{3-\delta}$ by means of the modeling on the basis of available data on the oxygen nonstoichiometry was, therefore, the first aim of the present study. The second one was to explain the chemical expansion of the doped lanthanum cobaltite investigated using the model developed by us earlier [7–10] for oxides with perovskite structure.

Experimental

Powder of $La_{0.7}Sr_{0.3}Co_{0.9}Fe_{0.1}O_{3-\delta}$ was prepared by glycerol – nitrate method using La_2O_3 , $SrCO_3$, Co, $FeC_2O_4 \cdot 2H_2O$ as starting materials. All materials used had a purity of 99.99%.

Stoichiometric mixture of starting materials was dissolved in concentrated nitric acid (99.99% purity) and required volume of glycerol (99% purity) was added as a complexing agent and a fuel. Glycerol quantity was calculated according to full reduction of corresponding nitrates to molecular nitrogen N_2 . As prepared solution was heated continuously at 100 °C until water evaporation and pyrolysis of the dried precursor. The resulting ash was subsequently calcined at 1100 °C for 10 h to get the desired oxide powder.

The phase composition of the powder sample prepared accordingly was studied at room temperature by means of X-ray diffraction (XRD) with Equinox 3000 diffractometer (Inel, France) using Cu K_α radiation. XRD showed no indication for the presence of a second phase.

Rectangular samples of $30 \times 4 \times 4$ mm³ were axially pressed at 6–7 MPa and sintered at 1200 °C for 24 h. The relative density of the sample was found to be 95%.

The experimental set up used for chemical expansion measurements is described elsewhere [8]. The accuracy of expansion measurement comes to value of ± 0.1 μ m. The sample was equilibrated at given oxygen partial pressure and temperature for several hours until a sample length ceases to change. The oxygen partial pressure was then changed in steps within range between 1 and 10^{-4} atm in both decrease and increase direction at the same temperature and the measurement procedure was repeated until equilibrium state was reached at each step.

Theory

Defect structure of $La_{0.7}Sr_{0.3}Co_{0.9}Fe_{0.1}O_{3-\delta}$

Tai et al. [1,11] were first who suggested a possible defect structure for perovskite-type oxides $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ to explain the observed unique temperature dependence of the electrical conductivity and Seebeck coefficient in air. Noteworthy feature of this defect structure is that cations Fe^{4+} are formed in preference to those Co^{4+} to compensate the negative charge of the Sr^{2+} cations. Lankhorst and Elshof [12] developed a modified rigid band model to explain obtained pO_2 dependences of oxygen nonstoichiometry of $La_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_{3-\delta}$ with $y = 0–0.6$. The particularity of this model consists in a distribution of electrons formed during oxygen vacancies formation between the conduction band (itinerant or, in other words, delocalized electrons) and iron centers (localized electrons). The energy level of Fe^{2+} was assumed to be too high to be occupied and, therefore, only Fe^{3+} and Fe^{4+} oxidation states were taken into account [12]. A fraction f_c of the electrons donated to the conduction band was supposed to be a constant irrespective of oxygen partial pressure at a given temperature [12].

Another approach was developed on the basis of iron and cobalt indistinguishability in $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ that allowed to treat neutral species, localized electrons and holes as B_{Co}^\times , B_{Co}^\bullet and B'_{Co} , respectively, using Kröger–Vink notation [13,14].

The defect structure of the undoped $LaCoO_{3-\delta}$ was earlier shown to be based on the simultaneous presence of Co^{3+} , Co^{4+} , and Co^{2+} cations in its structure [15,16]. The following defect equilibrium may, therefore, be written using the Kröger–Vink notation, which will be employed further for point defects notation.

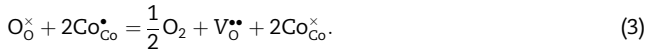


Since cobalt is more electronegative 3d-metal as compared to iron then substitution of iron for cobalt can be resulted in the following electron exchange reaction.



where Fe_{Co}^\times (Co_{Co}^\times), Co'_{Co} , and Fe_{Co}^\bullet (Co_{Co}^\bullet) are iron (cobalt) in the state of oxidation +3, +2, and +4, respectively. Charge disproportionation in the iron sublattice seems to be doubtful for $La_{0.7}Sr_{0.3}Co_{0.9}Fe_{0.1}O_{3-\delta}$ since the doping level (10 mol.%) is lower than the percolation limit for a cubic structure (~30 mol.%). However, if we assume that equilibrium in the reaction (2) is shifted significantly to the products then we can

accept that iron keeps its oxidation state +4 as constant over complete temperature and pO_2 ranges investigated. Then oxygen release by the perovskite lattice is accompanied by solely change of cobalt oxidation state that can be given, for example, as



Taking into account expressions for equilibrium constants of reactions (1) and (3), and the appropriate mass balance and electroneutrality conditions along with the definition of oxygen nonstoichiometry as $[V_O^{\bullet\bullet}] = \delta$ the following set of nonlinear equations can be given for the defect structure model.

$$\left\{ \begin{array}{l} K_3 = \frac{p_{O_2}^{1/2} [V_O^{\bullet\bullet}] [Co_{Co}^\times]^2}{[O_O^\times] [Co_{Co}^\bullet]^2} = K_3^0 \exp\left(-\frac{\Delta H_3}{RT}\right) \\ K_1 = \frac{[Co_{Co}^\bullet] [Co_{Co}^\times]}{[Co_{Co}^\times]^2} = K_1^0 \exp\left(-\frac{\Delta H_1}{RT}\right) \\ [Sr'_{La}] + [Co'_{Co}] = [Fe^\bullet_{Co}] + [Co^\times_{Co}] + 2[V_O^{\bullet\bullet}] \\ [Co^\bullet_{Co}] + [Co^\times_{Co}] + [Co'_{Co}] + [Fe^\bullet_{Co}] = 1 \\ [Fe^\bullet_{Co}] = y \\ [V_O^{\bullet\bullet}] = \delta \\ [O_O^\times] = 3 - \delta \\ [Sr'_{La}] = x \end{array} \right. \quad (4)$$

The analytical solution of the set Eq. (4) yields expression for concentration of a defect species, for instance, Co_{Co}^\bullet

$$[Co_{Co}^\bullet] = \frac{K_1(2.2 - 4\delta) + \delta - 1 - \sqrt{A(\delta)}}{4K_1 - 1}, \quad (5)$$

and the fit function of the model proposed for the defect structure of the perovskite $La_{0.7}Sr_{0.3}Co_{0.9}Fe_{0.1}O_{3-\delta}$

$$\log(p_{O_2}/\text{atm}) = 4 \cdot \log\left(\frac{\sqrt{K_3}\sqrt{3-\delta} \cdot (\sqrt{A} + 4K_1\delta - 2.2K_1 + 0.1 - \delta)}{\sqrt{\delta} \cdot (0.9 - 2\sqrt{A})}\right), \quad (6)$$

where $A(\delta) = K_1(-4\delta^2 + 0.8\delta + 0.77) + \delta^2 - 0.2\delta + 0.01$.

Since the changes in oxygen stoichiometry of the cobaltite studied were measured within relatively narrow temperature range defect formation enthalpies can be treated as constants over complete temperature range investigated. This assumption enables substitution of equilibrium constants in the fit equation (6) by their temperature dependences (see Eq. (4)) and simultaneous treatment of data on oxygen nonstoichiometry as $\delta = f(pO_2, T)$ according to the model of the defect structure proposed.

Chemical expansion modeling

Thermal expansion is a fundamental property of materials, originating from an harmonicity of the atomic vibrations, which leads to changing interatomic distances with temperature. This phenomenon can be quantified using the volumetric (α_V) and linear (α_L) coefficients of thermal expansion (CTEs)

$$\alpha_V = \frac{1}{V_0} \left(\frac{\partial V}{\partial T} \right)_P; \quad \alpha_L = \frac{1}{L_0} \left(\frac{\partial L}{\partial T} \right)_P, \quad (7)$$

where V_0 and L_0 are the values of volume and length in a selected initial (reference) state, and P is the total pressure. So-called uniaxial strain is defined as

$$\epsilon = \frac{\Delta L}{L_0} = \alpha_L \Delta T, \quad (8)$$

where ΔL is the length increment corresponding to the temperature change ΔT . In general, if thermal expansion mostly contributes to strain then the latter can be treated as a linear function of temperature. However, Strelkow [17] was first who found a significant positive deviation from linear trend of ϵ temperature dependence for several halides such as NaCl, AgCl, and AgBr just below the melting points of these compounds. He called this phenomenon as anomalous expansion. Later Mott and Gurney [18] and also Seitz [19] discussed anomalous thermal expansion in silver halides and proposed that this anomaly in expansion should be attributed to point defects arising in the crystal lattice at elevated temperatures. Later Lawson [20] plotted the logarithm of the anomalous length increase found by Strelkow [17] for silver halides versus reciprocal absolute temperature and showed that resultant points fall reasonably well on straight lines suggesting the abnormal expansion arises from an activation process. Further Lawson [20] compared the activation heat for abnormal expansion to that observed earlier for silver halides ionic conductivity and found good agreement between both heats which suggested that the anomalous expansion arises from the increase in the number of lattice defects which, in turn, are responsible for the ionic conductivity. Taking into account ionic radii Lawson [20] compared possible values of the volume expansion which could be caused by the different disordering mechanisms and found that only one calculated on the basis of Schottky defects presence is completely consistent with the values reported by Strelkow [17].

The use of CTE only is, therefore, insufficient for adequate description of solids expansion when substantial amounts of defects are formed at elevated temperatures. This is the case for mixed-conducting oxides with perovskite structure since their lattice volume is a function of both temperature and oxygen vacancies concentration. In this case lattice strain can be quantified in terms of both the standard volumetric CTE (α_V) and volumetric chemical expansivity (α_{VC}) induced by the oxygen vacancy formation [4]

$$\alpha_{VC} = \frac{1}{V_0} \left(\frac{\partial V}{\partial X_{V_o}} \right)_{T,P}, \quad (9)$$

where X_{V_o} is the oxygen vacancies mole fraction, and V_0 is the specific volume of an oxygen-stoichiometric composition at a given temperature. The former quantity is defined, for example, as $\delta/3$ for $ABO_{3-\delta}$ perovskite oxides, where δ is the oxygen nonstoichiometry. Using the aforementioned definitions, the total derivative of the uniaxial strain ϵ in the absence of additional pressure or mechanical forces can be given as

$$d\epsilon(T, X_{V_o}) = \frac{1}{3} \alpha_V dT + \frac{1}{3} \alpha_{VC} dX_{V_o}. \quad (10)$$

Equation (10) is valid under assumption that the lattice expansion is an isotropic property. Using of this equation makes it possible to determine both thermal and chemical constituents of the uniaxial strain by dilatometric measurements as shown, for instance, for Sr-substituted cobaltites $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ [21].

Despite point defects are generally recognized to be responsible for chemical expansion, its mechanism remains still controversial topic. Different reasons such as changing Coulomb forces, atomic packing, local structure, preferred coordination, association between dopants and vacancies and others are discussed in this respect [10]. Chemical expansion of the cubic perovskites was successfully described recently using the model developed on the basis of the relative change of the mean ionic radius [7–10]. Within the framework of this “dimensional” model electrons and electron holes are assumed to be localized on B–sites in $\text{ABO}_{3-\delta}$ and vacancy formation is accepted to be accompanied by the reduction of B–cations. As a result, average size of the B-site cations increases due to the apparent substitution of “large” $\text{B}^{(z-1)+}$ for smaller B^{z+} . It is worth noting that oxygen vacancy formation may also contribute to chemical expansion observed due to a change of coulomb interaction between ions. If this effect is significant then it may prevail over the effect of cation radius change.

Within the framework of the “dimensional” model the following assumptions were accepted [7–10]. (i) A closely packed lattice of oxide is formed by ions with rigid spheres. (ii) Expansion in each of three space directions is of equal value. The latter seems to be valid only for oxides with pseudo-cubic structure such as perovskites. Then the defect induced expansion can be computed by using the equation.

$$\frac{\Delta L}{L_0} = \frac{\sum_i (c_i r_i - c_{i0} r_i)}{\sum_i c_{i0} r_i}, \quad (11)$$

where c_i and r_i are the concentration and ionic radius, respectively, of an ion i of $\text{ABO}_{3-\delta}$ perovskite containing oxygen vacancies. The subscript, 0, in c_{i0} and L_0 denotes in Eq. (6) that these properties belong to the perovskite in a reference state e.g. with certain oxygen nonstoichiometry or without that ($\delta = 0$) at a given temperature. The sum is taken over all atoms belonging to the perovskite formula $\text{ABO}_{3-\delta}$ and c_i refers to the molar concentration per unit formula in this compound. The molar concentration of oxygen was assumed to have the constant value of 3. In other words, oxygen vacancy radius is believed to be identical to that of oxygen ion.

Substitution of appropriate concentrations (for cobalt species see Eqs. (4) and (5)) in general expression Eq. (11) yields the model equation of oxide chemical expansion which enables its value calculation on the basis of the defect structure accepted for a given oxide.

The crystal ionic radii accepted for all ions along with their coordination numbers are: $r_{\text{O}^{2-}} = 1.26 \text{ \AA}$ (CN = 6), $r_{\text{La}^{3+}} = 1.50 \text{ \AA}$ (CN = 12), $r_{\text{Sr}^{2+}} = 1.58 \text{ \AA}$ (CN = 12), $r_{\text{Co}^{2+}} = 0.79 \text{ \AA}$ (LS, CN = 6), $r_{\text{Co}^{3+}} = 0.885 \text{ \AA}$ (HS, CN = 6), $r_{\text{Co}^{3+}} = 0.685 \text{ \AA}$ (LS, CN = 6), $r_{\text{Co}^{3+}} = 0.75 \text{ \AA}$ (HS, CN = 6), $r_{\text{Co}^{4+}} = 0.67 \text{ \AA}$ (HS, CN = 6), and $r_{\text{Fe}^{4+}} = 0.725 \text{ \AA}$ (CN = 6), where LS and HS correspond to the low and high spin states, respectively. Crystal radii are employed in this paper, instead of effective ionic radii, due to their close correspondence to the physical size of ions in solids [22].

Results and discussion

Defect structure

Oxygen nonstoichiometry of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ measured by Cherepanov et al. [23] as a simultaneous function of temperature and $p\text{O}_2$ using thermogravimetry technique is shown in Fig. 1. The results of nonlinear surface fitting for this cobaltite using the model described by Eq. (6) are also shown in Fig. 1. The fitted parameters determined for this model along with a goodness of fit criteria, R-Squared, are summarized in Table 1 as well.

As seen the model proposed for the defect structure fits the experimental data on oxygen nonstoichiometry of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ really good over the complete $p\text{O}_2$ and temperature ranges investigated.

The values of equilibrium constants K_1 and K_3 of defects reactions (1) and (3), respectively, obtained as a result of the successful fitting procedure allowed to calculate the concentration of all defect species defined within the framework of the defect structure model for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ as a simultaneous function of oxygen partial pressure (or oxygen nonstoichiometry) and temperature. For instance, such dependencies are shown in Fig. 2 for electrons and holes localized on Co sites, and for Co species with formal neutral charge, respectively.

Fig. 2 shows that oxygen content, $3-\delta$, decrease is accompanied by sequential increase of $\text{Co}_{\text{Co}}^{\cdot}$ and decrease of $\text{Co}_{\text{Co}}^{\times}$ concentrations at a given temperature. It is of interest to note that concentration of the former becomes equal to that of the latter when the oxygen content reaches the value of 2.9 at a given temperature. At the same time, as a consequence, concentration of neutrally charged $\text{Co}_{\text{Co}}^{\times}$ as a function of oxygen nonstoichiometry has a maximum as shown in Fig. 2.

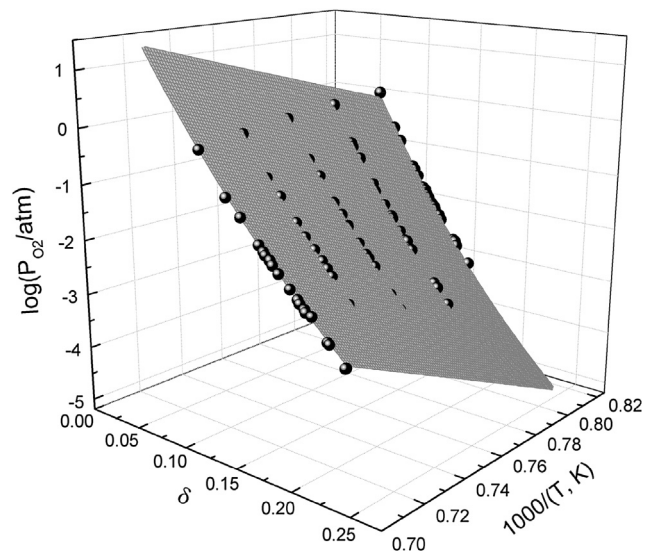


Fig. 1 – Oxygen nonstoichiometry of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ as a function of $p\text{O}_2$ and T . Points represent experimental data [23] and surface – fitted model.

Table 1 – The fitting results of the defect structure model analysis.

Compound	K_i	ΔH_i , kJ/mol	$\ln K_i^0$	R^2
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$	K_1	53.272	0.349	0.998
	K_3	102.476	9.937	

The concentration of all cobalt species defined will be employed further in order to calculate chemical expansion for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ according to the model equation (11).

Thermal and chemical expansion

The measured uniaxial strain at $p\text{O}_2 = 0.21$ atm and calculated CTE for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ are shown in Fig. 3. As seen the temperature dependence of strain starts to deviate from a linear trend in the region between 450 and 500 °C and, as a consequence, simultaneous CTE increase is observed with temperature. According to Eq. (10) one can assume that onset of the chemical expansion lies in the temperature range mentioned above.

Integration of Eq. (10) yields the following expression for uniaxial strain.

$$\Delta L/L_0 = \alpha_i(T - T_0) + \alpha_{LC}(\delta(T) - \delta_0), \quad (12)$$

where L_0 and δ_0 are length and oxygen nonstoichiometry at a reference temperature T_0 in air.

Temperature of 900 °C was selected as a reference one since this is the lowest temperature at which oxygen nonstoichiometry of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ was measured by Cherepanov et al. [23]. The value of $17.5 \cdot 10^{-6} \text{ K}^{-1}$ was estimated for CTE, α , from linear fit of the experimental data on strain measured between 200 and 450 °C in air. The value of

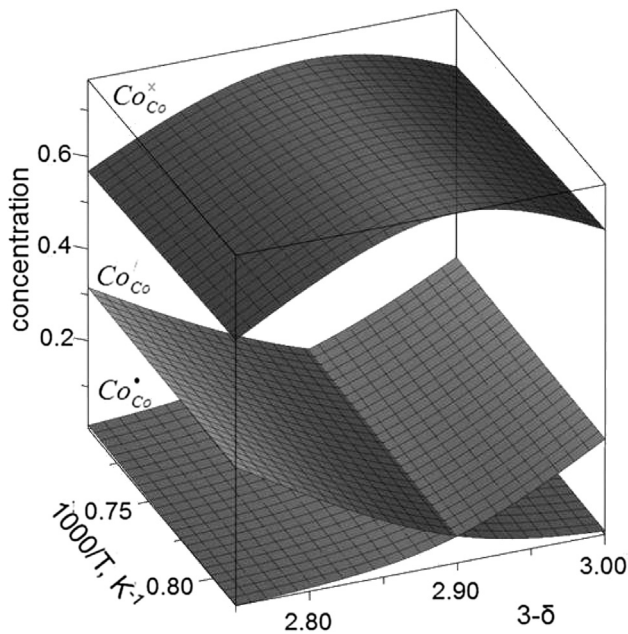


Fig. 2 – Concentration of different cobalt species as a function of δ and T calculated according to the defect structure model proposed.

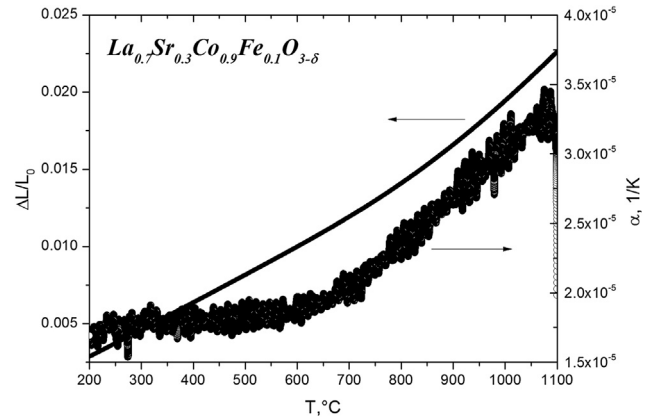


Fig. 3 – Uniaxial strain and CTE of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ as a function of temperature in air.

0.03625 was fitted for α_C according to Eq. (12) in span of δ measured between 900 and 1100 °C in air.

Fig. 4 shows, as an example, a raw trace of the relative change of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ sample length measured at 1000 °C as $p\text{O}_2$ is stepped from high value to low one and back. As seen expansion kinetic is rather fast and the sample length changes to its new equilibrium value for about two hours.

The isothermal expansion of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ measured as a function of oxygen partial pressure at different temperatures and normalized to stoichiometric composition with respect to oxygen ($\delta = 0$) is shown in Fig. 5. This figure shows that a slope coefficient of $p\text{O}_2$ dependences of chemical expansion gradually increases with temperature in range $600 \leq T, \text{ °C} \leq 700$ whereas abrupt growth of one is obviously seen between 700 and 750 °C.

The lattice chemical expansion of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ measured at different temperatures and normalized to the reference state at $\delta = 0$ is given in Fig. 6. For the sake of comparison the chemical expansion estimated on the basis of

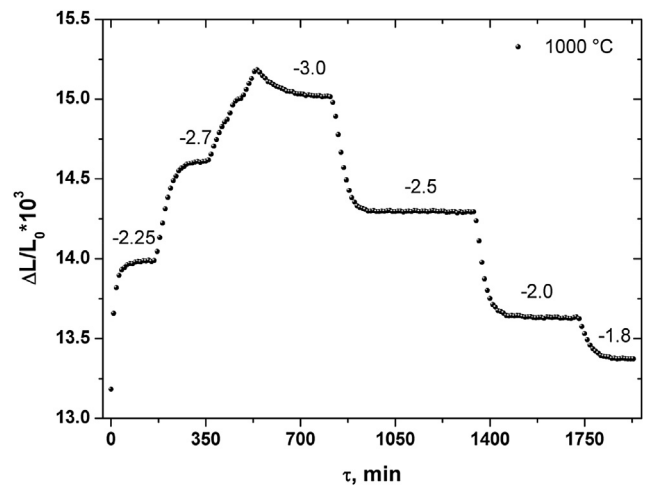


Fig. 4 – Raw trace of the isothermal expansion of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ at $T = 1000$ °C. Numbers given in figure correspond to $\log(p\text{O}_2/\text{atm})$ in ambient gas atmosphere.

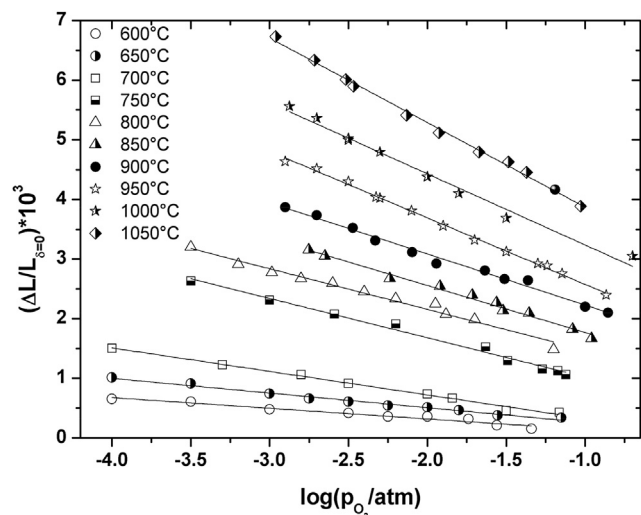


Fig. 5 – Chemical expansion of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ as a function of p_{O_2} , normalized as described in the text. The symbols represent experimental values and solid lines are given for eye guide.

Eq. (12) is given ibidem. As seen the latter exceeds somewhat the values of chemical expansion measured over complete range of oxygen nonstoichiometry. Besides the dependences of chemical expansion measured as a function of oxygen nonstoichiometry are curved in shape whereas one estimated according to Eq. (12) is straight line (see Fig. 6). However, the latter can be employed for estimation of the limit of chemical expansion value for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ lattice.

It also follows from Fig. 6 that the δ dependences of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ chemical expansion can be divided in two groups. The first group consists of the dependences measured at relatively low temperatures (between 600 and 700 °C) and the second one includes those measured at higher

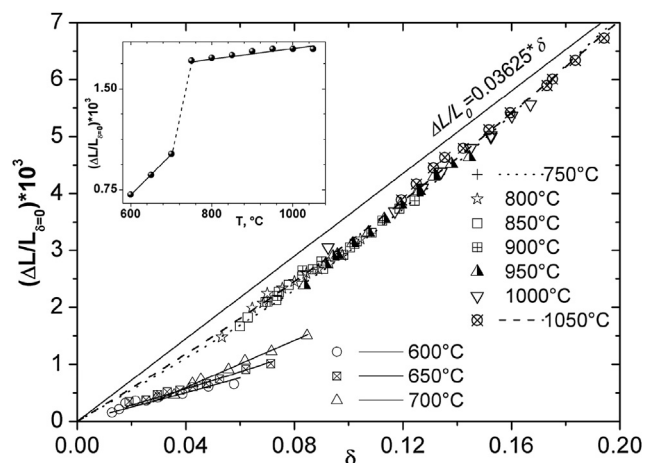


Fig. 6 – Chemical expansion of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ as a function of oxygen nonstoichiometry, normalized as described in the text. The symbols represent experimental values and lines are given by Eqs. (11), (13) and (14). Insertion is described in the text.

temperatures (between 750 and 1050 °C). Gradual increase of a slope coefficient of the δ dependences is observed for the former whereas dependences of the latter merge in a common curve in practical term. In other words, chemical expansion measured at higher temperature exceeds one measured at lower temperature but at the same value of oxygen nonstoichiometry as shown in insertion of Fig. 6, where the chemical expansion is given as a function of temperature at fixed oxygen nonstoichiometry, $\delta = 0.06$. Gradual increase of the chemical expansion observed between 600 and 700 °C (see Fig. 6) cannot be explained by an influence of the temperature dependence of equilibrium constant, K_1 , of cobalt disproportionation reaction (1) since this dependence is really weak for the substituted lanthanum cobaltite studied in contrast to the undoped $\text{LaCoO}_{3-\delta}$ as it follows from appropriate enthalpies comparison, 53 kJ (see Table 1) versus 518 kJ (see Table 1 of Ref. [12]). Abrupt growth of the chemical expansion that is seen in the narrow range $700 \leq T, \text{C} \leq 750$ in insertion of Fig. 6 seems to be inconsistent at all with a temperature dependence of the equilibrium constant.

On the other hand, it is known [12] that cobalt may exist not only in different oxidation states but also in different spin states and ionic radius of high spin (HS) cobalt species in certain oxidation state is larger significantly than that of low spin (LS) cobalt species [22].

In order to calculate the chemical expansion of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ according to the model Eq. (11) it is, therefore, necessary to decide which spin state should be accepted for Co^{2+} and Co^{3+} in the lattice of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ since their radii depend on their spins. This problem is not trivial since divalent and trivalent cobalt may exist in the low and high spin state and trivalent cobalt – in the intermediate one as well [12]. Despite the nature of spin states of cobalt in rare earth cobaltites is still a controversial topic a gradual transition from the low spin state via the intermediate state to the high one with increasing temperature is accepted for trivalent cobalt [12]. Recently we have already proposed the similar gradual transition for divalent cobalt and found that this approach is quite consistent with the chemical expansion behavior observed for variety of strontium substituted lanthanum perovskites [9,10].

Another challenge consists in definition of a crystal radius for cobalt in the intermediate spin state since one was not presented by Shannon [22]. However, Asai et al. [24] showed that a transition from the low spin state to the intermediate one for cobalt in the undoped lanthanum cobaltite is not accompanied by any anomaly during its thermal expansion. All mentioned above allows to accept the crystal radius of Co^{3+} (LS) as that of Co^{3+} (IS) and to introduce average radii of trivalent and divalent cobalt as.

$$r_{\text{Co}}^{3+} = r_{\text{Co}}^{3+}(\text{HS}, \text{CN} = 6) * a_1 + r_{\text{Co}}^{3+}(\text{LS}, \text{CN} = 6) * (1 - a_1) \quad (13)$$

and

$$r_{\text{Co}}^{2+} = r_{\text{Co}}^{2+}(\text{HS}, \text{CN} = 6) * a_2 + r_{\text{Co}}^{2+}(\text{LS}, \text{CN} = 6) * (1 - a_2), \quad (14)$$

where a_1 and a_2 are fractions of Co^{3+} and Co^{2+} , respectively, in the high spin state, $r_{\text{Co}}^{3+}(\text{LS}, \text{CN} = 6) = 0.685 \text{ \AA}$ and $r_{\text{Co}}^{2+}(\text{HS}, \text{CN} = 6) = 0.885 \text{ \AA}$ [22], are crystal radii of Co^{3+} in low spin and Co^{2+} in high spin, respectively. It is worth noting that a_1 and a_2

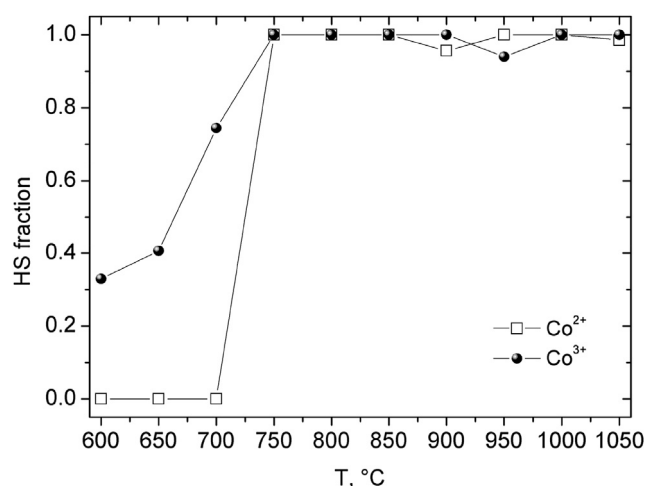


Fig. 7 – Fractions of Co ions in High Spin (HS) state in $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ as a function of temperature.

are the only parameters that have to be fitted in the model Eq. (11) using data on chemical expansion since K_1 is defined independently as a result of the defect structure modeling.

The results of model calculation of the chemical expansion according to Eqs. (11), (13) and (14) are given in Fig. 6. As seen the model proposed coincides with the experimental data on chemical expansion really good for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ at all temperatures. It is of interest to note that a slope of the calculated oxygen nonstoichiometry dependences of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ chemical expansion increases gradually with temperature at a given oxygen nonstoichiometry indicating in favor of the spin state transition from low spin to high spin state for the cobalt species with increasing temperature in the range $600 \leq T, ^\circ\text{C} \leq 700$.

The fitted values of the high spin fraction of cobalt as a function of temperature are shown in Fig. 7. Quite plausible observation follows from this figure. As seen in Fig. 7 HS fraction of Co^{3+} in $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ gradually grows with increasing temperature reaching unity at 750°C while one of Co^{2+} changes abruptly from 0 to unity in relatively narrow range $700 \leq T, ^\circ\text{C} \leq 750$.

It is worth noting that temperature of the spin transition completion for Co^{3+} in $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ is quite consistent with one found by us earlier [9,10] for other doped lanthanum cobaltites such as $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ and $(\text{La}_{0.7}\text{Sr}_{0.3})_{0.99}\text{Co}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$.

Conclusion

The chemical expansion of the oxygen deficient $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ was measured using unique dilatometric technique as a function of oxygen partial pressure p_{O_2} and temperature in the range $-4 \leq \log(p_{\text{O}_2}/\text{atm}) \leq 0$ and $600 \leq T, ^\circ\text{C} \leq 1050$, respectively. The chemical expansion model derived by us earlier [14] and based on the relative change of the mean ionic radius was employed for calculation of the $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ chemical expansion versus oxygen nonstoichiometry. In order to provide such calculation the

modeling analysis of the defect structure of the perovskite studied was carried out. Within the framework of the model applied all iron sites are assumed to be occupied by localized holes whereas both electrons and holes can be localized on cobalt sites in $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$. Defect structure model proposed was shown to fit perfectly well available experimental data on the oxygen nonstoichiometry. Equilibrium constants of the appropriate defects reactions were, therefore, determined and concentrations of all defect species defined within the frameworks of the model proposed were calculated as function of temperature and oxygen nonstoichiometry. These concentrations were employed in the chemical expansion model. Spin state transition from low spin (LS) state to high spin (HS) one for cobalt ions induced by temperature increase was taken into account as well. The model proposed was shown to coincide completely with experimental data on chemical expansion for the $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ at all temperatures investigated. As a result, the spin state distribution of cobalt was calculated depending of temperature for the oxide studied.

Acknowledgments

This work was supported by the Centers of Excellence Program at Ural Federal University, Russia and by the Ministry of Education and Science of Russian Federation (the State Task No. 4.1039.2014/K).

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