

Chapter 2

Conventional Methods for Measurements of Chemo-Mechanical Coupling

Andrey Yu. Zuev and Dmitry S. Tsvetkov

Energy-related oxide materials are often used at elevated temperatures under both oxidizing and reducing conditions and, therefore, their chemical composition with respect to oxygen may change. Due to release of lattice oxygen and simultaneous point defect formation, their lattice can undergo additional defect-induced or, in other words, chemical strain, which, in turn, affects mechanical compatibility of different components of an energy conversion device, and can cause even its damage. Thus elucidation of chemo-mechanical coupling in such materials is of key importance. In order to solve this important task, oxygen content of oxide materials and their chemical strain should be measured depending on environmental parameters. The description of the state-of-the-art methods for measuring oxygen content, such as thermogravimetry, coulometric and redox titration, as well as some examples of their employment, are given in this chapter. Dilatometry, as a conventional method for strain measurement, is described as well. Also this chapter is intended to show how insight into mechano-chemical coupling mechanisms can be established on the basis of the aforementioned measurements.

A.Yu. Zuev (✉) · D.S. Tsvetkov
Department of Chemistry, Institute of Natural Sciences, Ural Federal University,
Yekaterinburg 620000, Russia
e-mail: andrey.zuev@urfu.ru

D.S. Tsvetkov
e-mail: dmitry.tsvetkov@urfu.ru

2.1 Methods for Measuring Oxygen Content and Analysis of the Defect Structure of Oxide Materials

2.1.1 TG Analysis (*with Examples*)

Thermogravimetry (TG) is a thermal analysis method based on detection of sample mass change depending on temperature and other parameters (e.g., gas phase composition—oxides are usually studied depending on partial pressure of oxygen, pO_2). There are two ways to employ TG analysis: (i) isothermal—at constant temperature, and (ii) isobaric—when temperature is changed with time at constant gas (partial) pressure. Thermogravimetric analysis can be used to measure oxygen nonstoichiometry of oxides with low volatility and a wide homogeneity range with respect to oxygen. The former requirement is necessary because high volatility of cation species in an oxide can contribute to its irreversible mass change. The setup for TG consists of a balance for continuous weighing, furnace, instrument recording temperature, temperature controller, and software. Figure 2.1 shows a sketch of the thermobalance STA 409 PC (Netzsch GmbH, Germany), which is often used for TG analysis.

Different oxygen partial pressures are adjusted and maintained in the vicinity of the sample by using different gas mixtures (for example, N_2/O_2 or H_2/N_2). The composition of the corresponding gas mixture is controlled using precise flow controllers and the value of pO_2 is fixed by means of an yttria stabilized zirconia (YSZ) electrochemical oxygen sensor installed in close proximity to the sample surface in the TG setup (see Fig. 2.1). Alternatively the concentration of oxygen in the gas atmosphere around the sample can be adjusted using a YSZ-based electrochemical oxygen pump installed in the outer regulating unit and governed by an automatic controller. Adjusted accordingly, pO_2 is monitored by means of an installed YSZ sensor giving feedback to the control system (see Fig. 2.1). The latter method of control is more precise and flexible as well as it makes using of expensive gas cylinders unnecessary. Typically, a gas flow rate of about 30–50 ml/min is used to avoid oxygen partial pressure gradients along the sample.

The sample of studied oxide is heated first to the required temperature in an atmosphere with a given pO_2 (most often ambient air), then is equilibrated at this pO_2 and temperature for the necessary time until the sample weight ceases to change. Then measurements are carried out either in an isothermal or isobaric regime. In the case of the former, oxygen partial pressure is changed in steps within the range between initial and final values of pO_2 in both decreasing and increasing directions at the same temperature, and the measurement procedure is repeated until the equilibrium state is reached at each step, i.e., until weight curves recorded in both directions coincide with each other. In the isobaric regime, temperature is changed in steps within the range between initial and final values at the same pO_2 , and the rest of the experimental procedure is similar to that described for isothermal regime.

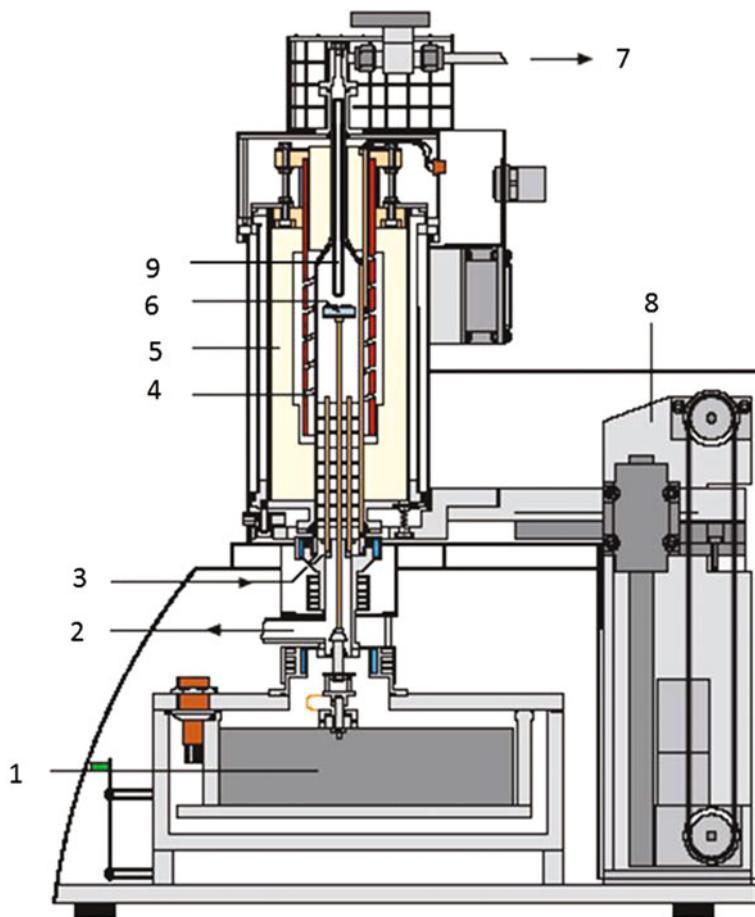
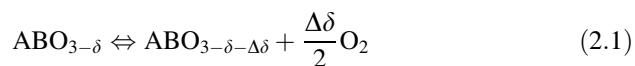


Fig. 2.1 TG setup based on thermobalance STA 409 PC: 1 weight unit, 2 vacuum flange, 3 gas inlet, 4 Al_2O_3 vacuum-tight protective tube, 5 furnace, 6 crucible with a sample studied, 7 gas outlet, 8 hoist, 9 YSZ sensor. Earlier available at <https://www.netzsch-thermalanalysis.com>

Oxygen exchange between an oxide, for example, perovskite $\text{ABO}_{3-\delta}$, and ambient gas atmosphere can be written as



where $\Delta\delta$ is a change in the oxygen content or, in other words, relative oxygen nonstoichiometry of the oxide, which can be calculated from the weight change by the following expression.

$$\Delta\delta = \frac{\Delta m_{\text{sample}}}{m_{0,\text{sample}}} \cdot \frac{M_{\text{ABO}_{3-\delta}}^0}{M_{\text{O}}} \quad (2.2)$$

where $m_{0,\text{sample}}$, Δm_{sample} , $M_{\text{ABO}_{3-\delta}}^0$, M_{O} are starting weight of the $\text{ABO}_{3-\delta}$ sample, its weight change caused by temperature or $p\text{O}_2$ variation, starting molar weight of the sample, and molar weight of oxygen (15.9994 g/mol), respectively.

In order to recalculate relative oxygen nonstoichiometry ($\Delta\delta$) on an absolute scale (δ_{total}), it is necessary to determine the absolute oxygen content in the oxide studied at some particular value of $p\text{O}_2$ and temperature lying within the range investigated. This can be implemented by means of either sample reduction by H_2 in a thermobalance (TG/ H_2) or sample redox titration. Both methods will be described further.

2.1.2 *Coulometric Titration in Solid State Electrolyte Cell (with Examples)*

Coulometric titration is the most precise method for determination of the oxygen content change in solid-oxide phases. This method can be employed to study oxides with both wide and narrow homogeneity ranges with respect to oxygen and with both high and low volatility. The method is based on using the electrochemical concentration cell (2.3) with an oxide ion conducting solid electrolyte (typically YSZ) and with gas electrodes operating at different oxygen partial pressure ($p\text{O}_2$) and separated from each other



where MeO_x is an oxide under investigation, $p\text{O}_2'$ and $p\text{O}_2''$ are oxygen partial pressure in the gas equilibrated with the oxide studied and that at the reference electrode, respectively. A schematic of the cell is shown in Fig. 2.2.

The EMF of the cell (2.3) is related to $p\text{O}_2'$ and $p\text{O}_2''$ by the Nernst equation, written below.

$$E = \frac{RT}{4F} \cdot \ln\left(\frac{p\text{O}_2''}{p\text{O}_2'}\right) \quad (2.4)$$

where F , T , $p\text{O}_2''$, $p\text{O}_2'$, 4, and R are Faraday constant (s A/mol), temperature (K), oxygen partial pressure inside the cell (Pa), oxygen partial pressure outside the cell, number of electrons taking part in the electrode reaction, and universal gas constant (J/(mol K)), respectively.

A DC current is periodically applied to the titration cell (2.3) and, as a consequence, oxygen is pumped in or out of the gas phase surrounding the oxide studied depending on polarization or, in other words, current direction by an equal

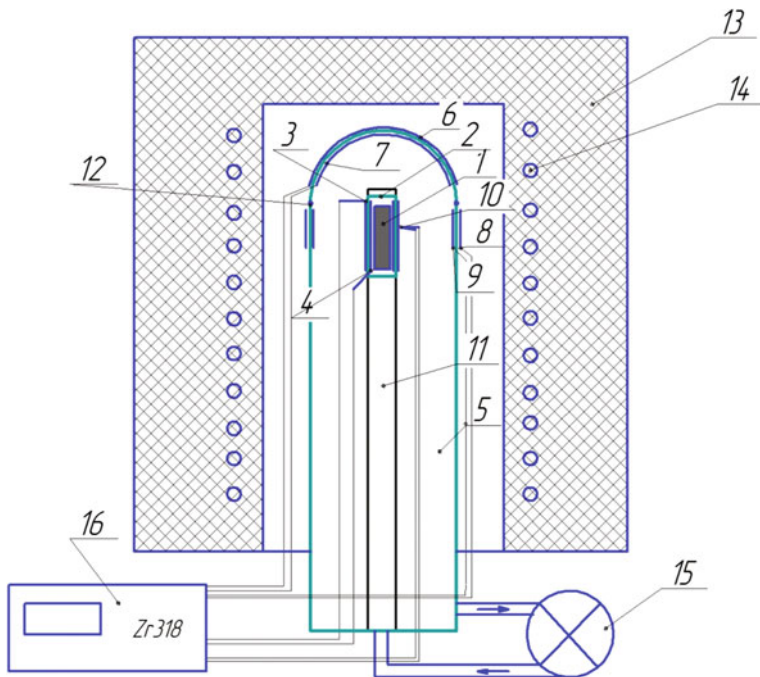


Fig. 2.2 Setup for coulometric titration: 1 sample studied; 2 YSZ coulometric cell; 3, 4 Pt electrodes of coulometric cell; 5 YSZ buffer cell; 6, 7 Pt electrodes of electrochemical pump of the buffer cell; 8, 9 Pt electrodes of electrochemical sensor of the buffer cell; 10 Pt/Rh thermocouple; 11 alumina cell holder; 12 sealing glass; 13 furnace; 14 heater; 15 gas circulation pump; 16 managing controller. Ref. [3]

proportion. Each titration step is followed by the relaxation of the sample to the equilibrium state coinciding with a new oxygen partial pressure at given temperature. The oxygen nonstoichiometry change is calculated at each titration step according to

$$\Delta\delta = \frac{2M}{m} \left[\frac{It}{4F} - \frac{V}{RT} (pO_2''(b) - pO_2''(a)) \right] \quad (2.5)$$

where M , m , I , t , V , $pO_2''(b)$, $pO_2''(a)$ are oxide investigated molar mass (g/mol), oxide sample mass (g), titration current (A), titration time (s), free volume of the coulometric cell (m^3), oxygen partial pressure before titration step (Pa), oxygen partial pressure after titration step (Pa), respectively.

In principle, a coulometric cell can be easily assembled using a dense YSZ ceramic tube closed at one side with previously deposited Pt contacts on inner and outer sides. In this case, the oxide sample is put in the inner part of the tube, which serves as a working electrode operating at pO_2'' , and its outer side serves as a reference electrode operating at pO_2' . However, a serious disadvantage of this cell

design is the so-called non-faradaic leakage of oxygen into/out of the coulometric cell due to nonnegligible electronic conduction in YSZ.

In order to prevent undesirable leakage the cell supplied by gas buffer can be used. Such a coulometric setup is shown in Fig. 2.2.

As seen the coulometric setup consists of two YSZ cells: an external one (5), which is used as a buffer, and an internal one (2), which is a coulometric cell itself. Both cells serve simultaneously as an oxygen pump (3, 4, 6, 7) and as a sensor (3, 4, 8, 9) due to platinum contacts deposited on both the inner and outer surfaces of a cell. The coulometric cell is hermetically sealed using special glass and contains a sample of the oxide investigated (1). The buffer cell (5) is used to control oxygen partial pressure around the coulometric cell using the oxygen pump (6, 7) and sensor (8, 9) in such way that a value of pO_2 outside the coulometric cell is always kept about equal to that inside it. Such design of the setup allows avoiding even very small non-faradaic leakage of oxygen into/out of the coulometric cell. In order to measure pO_2 around the sample inside the coulometric cell its oxygen sensor and that of the buffer cell are connected in series. Titration current is periodically applied to the titration cell and, as a consequence, oxygen is pumped in or out of the cell by equal portions. Each titration step is followed by the relaxation of the sample to a new equilibrium state at a new oxygen partial pressure at given temperature. The coulometric titration procedure can be fully automatized using a managing controller (16) connected to computer. Such a system enables control and adjustment of oxygen partial pressure within the range $-20 \leq \log(pO_2/\text{atm}) \leq 0$ with accuracy ± 0.01 in the immediate vicinity of the coulometric cell. Gas circulation (15) is used to avoid an oxygen partial pressure gradient along the titration cell. The oxygen nonstoichiometry change is calculated at each titration step according to Eq. (2.5).

Since Eq. (2.5) enables calculation of only the relative change of the oxygen nonstoichiometry, to get its absolute value, similar to TG analysis, an additional experiment such as H_2 reduction in a thermobalance or redox titration is needed.

It is worth noting general limitation on applicability of coulometric titration using YSZ-based cell at relatively low temperatures due to the large overpotentials at the Pt electrodes and insufficient conductivity of YSZ, making low temperature measurements difficult.

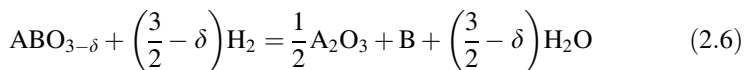
2.1.3 *Determination of the Absolute Value of Oxygen Nonstoichiometry*

As mentioned above, both TG and coulometric titration enable measurement of only the relative change of oxygen nonstoichiometry, $\Delta\delta$, in oxide compounds. The absolute value of δ can be measured using several methods, for instance, reduction of an oxide sample by hydrogen flux directly in the TG setup or chemical analysis of the sample previously quenched or slowly cooled from certain conditions

(T, pO_2). However, there is another way for the oxide compounds, which have a plateau on the pO_2 dependency of relative oxygen nonstoichiometry plotted at a given temperature. In such cases, this plateau corresponds to a certain, and as a rule, known value of the oxygen content in the oxide studied. For instance, lanthanum manganite $LaMnO_{3\pm\delta}$ has both excess ($3 + \delta$) and deficiency region ($3 - \delta$) with respect to oxygen content depending on temperature and pO_2 and its absolute oxygen nonstoichiometry is exactly equal to zero when the plateau between these regions is reached during coulometric titration or TG procedure (see Fig. 2.5).

2.1.3.1 Direct Reduction of Oxide Sample by Hydrogen

A sample of the oxide studied is heated in a thermobalance chamber to the required temperature in atmosphere with a given pO_2 (most often ambient air) and then is equilibrated at this pO_2 and temperature for the necessary time until the sample weight ceases to change. Afterwards hydrogen flow is passed through the chamber previously purged with an inert gas until the weight of the sample becomes unchangeable. The value of this weight is used for calculation of absolute oxygen nonstoichiometry of the oxide compound according to the products of its reduction. Products of the reduction are determined by XRD of the sample cooled down fast after the completion of the reduction procedure. For example, if the sample of a perovskite $ABO_{3-\delta}$ is reduced in hydrogen flux according to the following reaction



then the oxygen nonstoichiometry δ can be calculated as

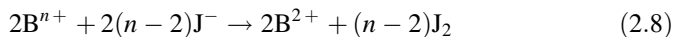
$$\delta = \frac{m_{\text{red}} \cdot M_{\text{st}} - m_{\text{ox}} \cdot \left(\frac{M_{A_2O_3}}{2} + M_B\right)}{m_{\text{red}} \cdot M_O} \quad (2.7)$$

where m_{red} , m_{ox} , M_{st} , $M_{A_2O_3}$, M_B , and M_O are weight of the reduced and oxidized (before reduction) sample, molar weight of the ABO_3 stoichiometric with respect to oxygen, molar weight of oxide A_2O_3 , metal B, and elemental oxygen, respectively.

2.1.3.2 Iodometric Determination of the Absolute Oxygen Nonstoichiometry

Iodometric method is based on Ox–Red processes related to reduction of iodine into iodide ions or in oxidation of iodide ions into molecular iodine. Normally the sample is dissolved in an acidic solution containing an excess of iodide ions. Molecular iodine obtained as a result of interaction between the oxidant and iodide ions is titrated with standard sodium thiosulfate solution. Both oxide dissolution

and successive titration should be carried out under an inert gas protective atmosphere to prevent iodide oxidation by oxygen from the air. Now let us consider the following example. Suppose we have a B cation in a perovskite $\text{ABO}_{3-\delta}$ in a mixed state of oxidation $n+$, and during dissolution and simultaneous interaction with iodide ions it reduces to B^{2+} while the A cation and oxygen do not change their oxidation states, then the following reactions can be written



Since the thiosulfate volume spent for iodine titration is known, the mean state of oxidation $n+$ of B cation in the perovskite $\text{ABO}_{3-\delta}$ can be calculated using the obvious relation

$$n = \frac{(CV)_{\text{S}_2\text{O}_3^{2-}}}{v} + 2, \quad (2.11)$$

where v , $C_{\text{S}_2\text{O}_3^{2-}}$, $V_{\text{S}_2\text{O}_3^{2-}}$ are number of moles of B cation, molarity, and volume of thiosulfate solution used, respectively.

The absolute oxygen nonstoichiometry in the perovskite $\text{A}^{z+}\text{B}^{n+}\text{O}_{3-\delta}^{2-}$ studied is calculated on the basis of electroneutrality condition as

$$\delta = 3 - \frac{z+n}{2}. \quad (2.12)$$

2.1.4 Some Examples of the Study of Oxygen Nonstoichiometry by TG and Coulometric Titration Methods

Typical results of TG analysis demonstrating sample weight change caused by temperature variation at a given $p\text{O}_2$ or $p\text{O}_2$ variation at a given temperature are shown in Fig. 2.3.

Taking into account weight changes of the sample $\text{GdBaCo}_2\text{O}_{6-\delta}$ obtained in an analogous way for different $p\text{O}_2$ within the range investigated, the relative change of the oxygen nonstoichiometry can be calculated according to the relation analogous to Eq. (2.2) and then recalculated on an absolute scale on the basis of the results of TG/ H_2 reduction or/and Ox-Red titration. As a result, the oxygen nonstoichiometry (δ) of the double perovskite $\text{GdBaCo}_2\text{O}_{6-\delta}$ measured [1] as a function of $p\text{O}_2$ and temperature in the ranges $-6 \leq \log(p\text{O}_2/\text{atm}) \leq -0.68$ and

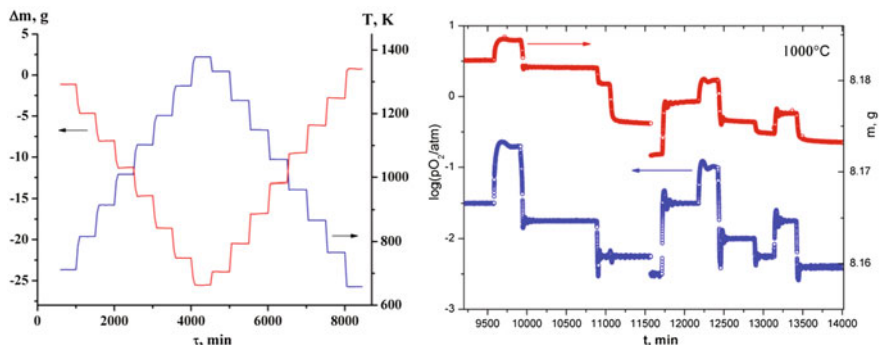


Fig. 2.3 Raw trace of sample weight for $\text{GdBaCo}_2\text{O}_{6-\delta}$ as a function of temperature in air (*left*) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ as a function of $p\text{O}_2$ at 1000 °C (*right*)

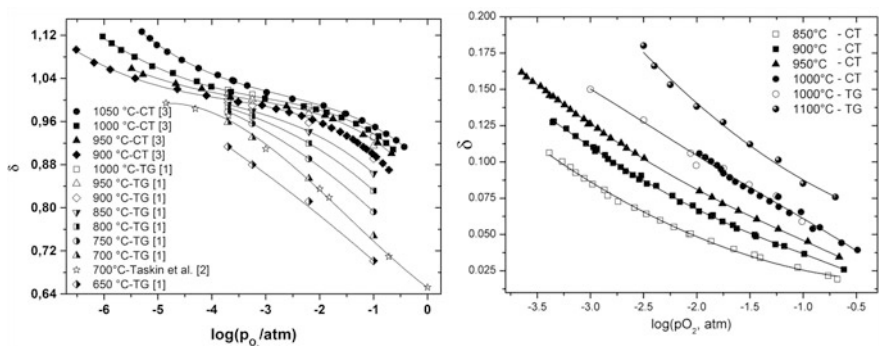


Fig. 2.4 Oxygen nonstoichiometry of $\text{GdBaCo}_2\text{O}_{6-\delta}$ (*left*) [1] and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ (*right*) [17] as a function of $p\text{O}_2$ at different temperatures. *Points* are experimental data and *lines* are given for eye guide. *CT* coulometric titration, *TG* thermogravimetry

923 $\leq T$, K $\leq$ 1323, respectively, is given in Fig. 2.4 in comparison with the data reported by Taskin et al. [2]. As seen there is good agreement between the values of oxygen nonstoichiometry obtained by TG [1] and those measured by Taskin et al. [2]. It also follows from Fig. 2.4 that oxygen nonstoichiometry determined by means of the coulometric titration technique [3] and one measured by the TG method [1] are completely coincident with each other.

Another example of successful joint employment of TG and coulometric techniques is shown in Fig. 2.4 where oxygen nonstoichiometry of the perovskite $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ is given as a function of $p\text{O}_2$ and temperature as well. As seen in the figure, the oxygen nonstoichiometry values determined by both techniques are completely coincident with each other, as likewise demonstrated for those for $\text{GdBaCo}_2\text{O}_{6-\delta}$ discussed above.

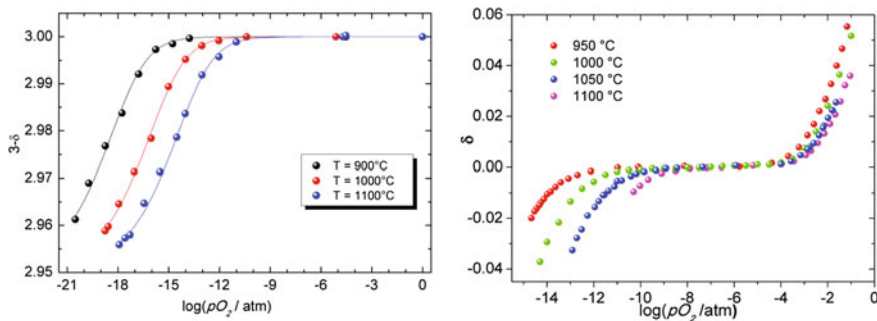


Fig. 2.5 Oxygen nonstoichiometry of $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_{3-\delta}$ (left) [5] and $\text{LaMnO}_{3\pm\delta}$ (right) [15] as a function of $p\text{O}_2$ at different temperatures. Points are experimental data and lines are given for eye guide

Another couple of examples are given in Fig. 2.5 where the experimental data on oxygen nonstoichiometry are given for perovskites $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_{3-\delta}$ and $\text{LaMnO}_{3\pm\delta}$ investigated by TG and coulometric method, respectively.

2.2 Analysis of the Oxide Defect Structure Using Data on Oxygen Content

It is known that the important properties of advanced oxide materials, such as oxide ion and electronic conductivity, catalytic and electrochemical activity as well as chemical expansion are directly related to their defect structure. Thus determination of a defect structure is of key importance for understanding and, therefore, governing their fascinating properties. In order to establish the valid defect structure it is necessary first to carry out its modeling analysis and then verify the model proposed using available data on properties of the oxides studied.

Before we begin the analysis let us first define some concepts of defect chemistry that we will use. Point defects (zero-dimensional defects) mean the disturbance within or around one site of the crystal lattice. It can be either a vacant site, called *vacancy*, or an atom (ion) in the *interstitial* site. The impurity species can be also treated as point defects. Often electronic defects are also ascribed to this group, especially if the electronic charge carriers are localized. In order to specify point defects, Kröger–Vink notation [4] is often used in the literature. In this notation, a lattice constituent is denoted, for example, for perovskite $\text{A}^{3+}\text{B}^{3+}\text{O}_3^{2-}$ as $\text{A}_\text{A}^\times$, $\text{B}_\text{B}^\times$, or $\text{O}_\text{O}^\times$. Here the subscript denotes the chemical identity of the sublattice site, and cross as superscript index denotes neutral effective charge of the constituent in the ideal crystal ABO_3 where all available sites are occupied by native species. The effective charge of the defect within the Kröger–Vink approach is equal to the change of real charge of the whole crystal as a result of the defect formation.

As the real charge of the crystal may change only on integer number of elementary charges, an effective charge may accept only an integer value. Thus vacancies in A-, B-, or O-sublattice of ABO_3 crystal are denoted as $V_A^{///}$, $V_B^{///}$, or $V_O^{..}$ (point—unit positive charge, dash—unit negative charge), respectively.

A thermodynamic approach can be applied to describe concentrations of point defects in thermodynamic equilibrium. Within the framework of this approach, the point defects and their simplest associates are treated as chemical species. The processes of the defect formation and disappearance can be presented in a form of *quasi-chemical* reactions with corresponding equilibrium constants

$$K = \frac{\prod_j [j]^{v_j}}{\prod_i [i]^{v_i}}, \quad (2.13)$$

where i - and j -symbols in brackets correspond to the equilibrium concentration of products and the starting reagents, respectively, of the defect reaction and v_i and v_j are corresponding stoichiometric coefficients.

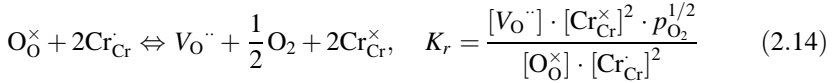
The rules for *quasi-chemical* reactions are the same as for the normal chemical reactions, namely mass balance and electroneutrality conditions. One extra requirement appears, however, for crystalline solids where the ratio of sites in the crystal structure must be constant and must satisfy the stoichiometric formula. This means that if in the ABO_3 crystal one site for A atom is formed, then automatically one B-site and three O-sites appear as well, regardless of their occupancy. Let us note that the point defects and/or the processes of their formation are classified into two groups: stoichiometric and nonstoichiometric. The first type processes do not disturb the stoichiometric ratio of components constituting the crystal, which, in turn, is a closed thermodynamic system. The second one leads to the nonstoichiometric compounds by exchanging the components between the crystal and its environment, whilst the crystal constitutes an open system.

Now let us consider the procedure of the defect structure modeling in detail on some examples.

2.2.1 Doped Lanthanum Chromites



A relatively simple defect structure was found for doped lanthanum chromites [5, 6]. The characteristic feature of the defect structure of the chromites containing Ca, Sr, or Mg as a dopant is that tetravalent chromium is formed under oxidizing conditions as a result of charge compensation due to acceptor doping. The process of oxygen release from the chromite lattice under reducing conditions is, therefore, accompanied by the transition of Cr^{4+} to Cr^{3+} according to the “small polaron” reaction



where $\text{V}_0^{\cdot\cdot}$ is an oxygen vacancy, $\text{Cr}_{\text{Cr}}^\cdot$ and $\text{Cr}_{\text{Cr}}^\times$ are tetra- and trivalent chromium, respectively, written in the aforementioned Kröger–Vink notation, and brackets indicate concentration.

It should be noted here that reaction Eq. (2.14) is common for all chromites doped with divalent metals and does not depend on their composition, if they are able to release or uptake oxygen [7]. This behavior is described as a “small polaron” model, because the electron transport (polaron conduction) in chromites can be understood in terms of a charge transfer reaction where an electron hole is transferred from a chromium ion in the high oxidation state Cr^{4+} to a neighbor ion in the low oxidation state Cr^{3+} . Substitution of the species concentrations in Eq. (2.14) by the use of evident relation $[\text{V}_0^{\cdot\cdot}] = \delta$, electroneutrality condition $[\text{Cr}_{\text{Cr}}^\cdot] = x + y - 2\delta$, and mass conservation law $[\text{Cr}_{\text{Cr}}^\times] = 1 - z - y - [\text{Cr}_{\text{Cr}}^\cdot]$, where z and y are concentration of Al and Mg, respectively, yields finally the modeling expression

$$\log(p_{\text{O}_2}/\text{atm}) = \frac{\sqrt{K_r} \cdot (x + y - 2\delta) \cdot \sqrt{3 - \delta}}{(1 - z - 2y - x + 2\delta) \cdot \sqrt{\delta}} \quad (2.15)$$

which allows to verify the model proposed for doped chromites $\text{La}_{1-x}\text{Me}_x\text{Cr}_{1-y-z}\text{Al}_z\text{Mg}_y\text{O}_{3-\delta}$ using data on their oxygen nonstoichiometry. Since the changes in oxygen stoichiometry of oxides are usually measured within a relatively narrow temperature range, defect formation enthalpies can be treated as constants over the complete temperature range investigated. This assumption enables substitution of the equilibrium constant in the model using Eq. (2.15) by its temperature dependence as following

$$K_r = K_r^0 \exp\left(-\frac{\Delta H_r^\circ}{RT}\right) \quad (2.16)$$

and treatment of data on oxygen nonstoichiometry obtained at different temperatures simultaneously as $\delta = f(p_{\text{O}_2}, T)$ according to the model of the defect structure proposed.

The results of nonlinear surface fitting for some chromites using the model described by Eq. (2.15) are shown in Fig. 2.6.

As seen the model proposed fits the experimental data on oxygen nonstoichiometry really well over the complete p_{O_2} and temperature ranges investigated. The nonlinear surface fitting parameters determined for these chromites according to the model proposed for their defect structure are summarized in Table 2.1. As seen, values of goodness of fit criterion, R^2 , which are very close to unity, confirm excellent agreement between the experimental data and the model proposed. The value of the equilibrium constant K_r of the defect reaction (2.14) obtained as a result

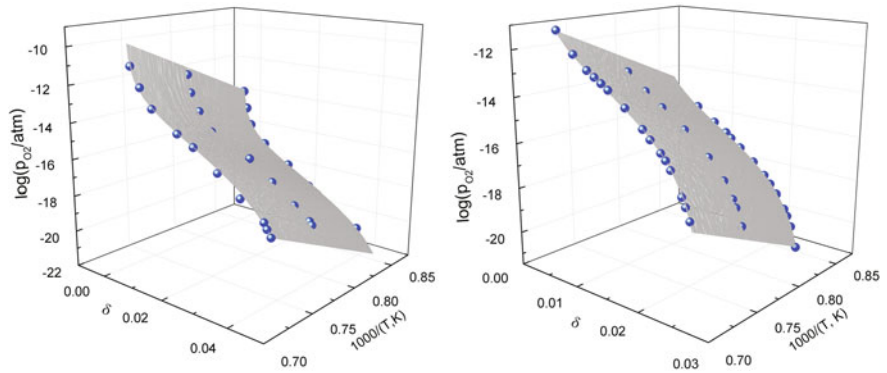


Fig. 2.6 Oxygen nonstoichiometry of $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_{3-\delta}$ (left) and $\text{La}_{0.95}\text{Ca}_{0.05}\text{Cr}_{0.84}\text{Al}_{0.16}\text{O}_{3-\delta}$ (right) versus p_{O_2} and T . Points experimental data, surface fitted model [6]

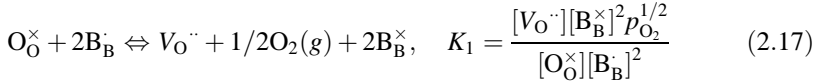
Table 2.1 The results of the defect structure analysis according to the models described in the text

Compound	K_i	ΔH_i^0 , kJ/mol	$\ln K_i^0$	R^2
$\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_{3-\delta}$	K_r	295.6	9.9	0.998
$\text{La}_{0.95}\text{Ca}_{0.05}\text{Cr}_{0.84}\text{Al}_{0.16}\text{O}_{3-\delta}$	K_r	231.8	5.9	0.999
$\text{LaMnO}_{3-\delta}$	K_1	384.8	20.7	0.999
	K_2	-7.2	-5.0	
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$	K_1	102.476	9.937	0.998
	K_2	53.272	0.349	

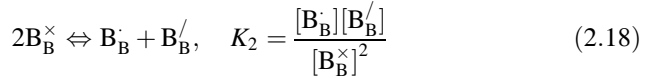
of the successful fitting procedure enable calculation of the concentration of all defect species defined within the framework of the defect structure model as a simultaneous function of oxygen partial pressure (or oxygen nonstoichiometry) and temperature.

2.2.2 Perovskite Structured Oxides $\text{La}_{1-y}\text{Sr}_y\text{B}_{1-x}\text{B}'_x\text{O}_{3-\delta}$
(**B=Mn, Fe, Co, and Ni; B'=Other 3d–Metal**)

It is generally recognized that the defect structure of the oxygen deficient perovskites $\text{LaBO}_{3-\delta}$ ($\text{B} = \text{Mn, Fe, and Co}$) is based on the simultaneous presence of B-species in different oxidation states such as B^{3+} , B^{4+} , and B^{2+} cations in their structure. The following defect equilibria may, therefore, be written



and



where $[\text{B}_\text{B}^\times]$, $[\text{B}_\text{B}^\cdot]$, and $[\text{B}_\text{B}'/]$ correspond to concentration of B^{3+} , B^{4+} , and B^{2+} , respectively.

Reactions (2.17) and (2.18) completely describe the defect structure for the oxide compositions without other 3d-metals different from a host metal. For oxides with partial substitution of other 3d-metal for a host metal on B-site the defect structure can be more complicated due to an electron exchange between this metal and a host metal because of difference in their electronegativity. However, different simplifications can be suitable depending on the nature of a dopant and a host metal. For instance, for the lanthanum cobaltite simultaneously doped with strontium on A-site and nickel on B-site one can accept as a first approximation that Ni keeps a constant oxidation state 2+ over the whole range of $p\text{O}_2$ and temperature investigated, as it is a more electronegative element as compared to cobalt. In contrast to that, one can treat iron as cation Fe^{4+} in the lanthanum cobaltite simultaneously doped with strontium on A-site and iron on B-site since iron is less electronegative element as compared to cobalt.

Model of the defect structure can be represented by a set of equations consisting of expressions for equilibrium constants of appropriate defect reactions as well as necessary mass balance and electroneutrality conditions along with the definition of oxygen nonstoichiometry as $[\text{V}_\text{O}^{\cdot\cdot}] = \delta$. The following set of independent equations describing the selected defect model can be given, for instance, for the doped lanthanum cobaltite $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$

$$\left\{ \begin{array}{l} K_1 = \frac{p_{\text{O}_2}^{1/2}[\text{V}_\text{O}^{\cdot\cdot}][\text{Co}_\text{Co}^\times]^2}{[\text{O}_\text{O}^\times][\text{Co}_\text{Co}^\cdot]^2} = K_1^0 \exp\left(-\frac{\Delta H_1^\circ}{RT}\right) \\ K_2 = \frac{[\text{Co}_\text{Co}^\cdot][\text{Co}_\text{Co}'/]}{[\text{Co}_\text{Co}^\times]^2} = K_2^0 \exp\left(-\frac{\Delta H_2^\circ}{RT}\right) \\ [\text{Sr}'_\text{La}] + [\text{Co}'_\text{Co}] = [\text{Co}_\text{Co}^\cdot] + [\text{Fe}_\text{Co}^\cdot] + 2[\text{V}_\text{O}^{\cdot\cdot}] \\ [\text{Co}_\text{Co}^\cdot] + [\text{Co}_\text{Co}^\times] + [\text{Co}_\text{Co}'/] + [\text{Fe}_\text{Co}^\cdot] = 1 \\ [\text{Fe}_\text{Co}^\cdot] = y \\ [\text{V}_\text{O}^{\cdot\cdot}] = \delta \\ [\text{O}_\text{O}^\times] = 3 - \delta \\ [\text{Sr}'_\text{La}] = x \end{array} \right. \quad (2.19)$$

This set can be solved analytically. An obvious advantage of an analytical solution is an explicit form of the fit expression. For instance, a solution of the set (2.19) for $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ($y = 0$) is the following

$$[\text{Co}_{\text{Co}}] = \frac{4K_2(1 - 2\delta + x) + 2\delta - x - \sqrt{A(\delta)}}{2(4K_2 - 1)} \quad (2.20)$$

where $A(\delta) = 16K_2\delta(x - \delta) + 4\delta(\delta - x) + 4K_2(1 - x^2) + x^2$ and K_2 is the equilibrium constant for the reaction (2.18) written for $B = \text{Co}$. The further obvious substitutions in the expression of K_1 yields the necessary fit expression

$$p_{\text{O}_2}^{1/4} = \frac{\sqrt{K_1}\sqrt{3 - \delta}(4K_2(1 - 2\delta + x) + 2\delta - x - \sqrt{A(\delta)})}{2\sqrt{\delta}(-1 + \sqrt{A(\delta)})} \quad (2.21)$$

where K_1 is the equilibrium constant for reaction (2.17) written for $B = \text{Co}$.

The aforementioned assumption enables the substitution of equilibrium constants in the modeling Eq. (2.21) by their temperature dependences (see Eq. 2.19) and, as a consequence, simultaneous treatment of experimental data on oxygen nonstoichiometry as $\delta = f(p_{\text{O}_2}, T)$ according to the model of the defect structure proposed.

As an example, the results of nonlinear surface fitting for $\text{LaMnO}_{3\pm\delta}$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ using the models proposed for their defect structure are shown in Fig. 2.7. One can see that the model surfaces are in good agreement with the experimental data on oxygen nonstoichiometry over the complete p_{O_2} and temperature ranges investigated for these perovskites. The fitted parameters of these models along with a goodness fit criteria, R^2 , are also summarized in Table 2.1.

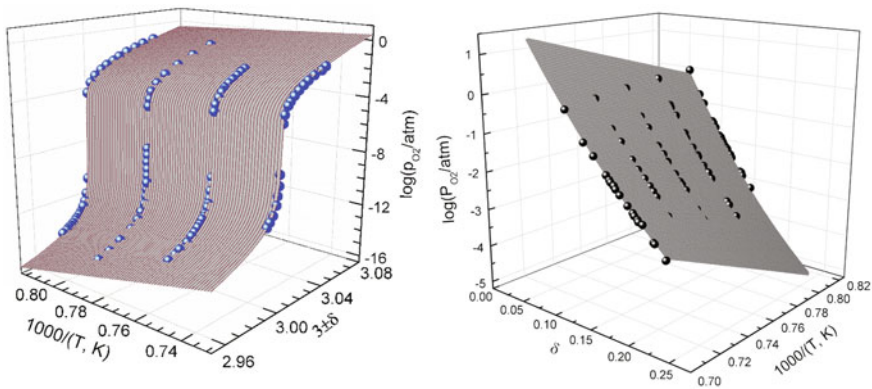


Fig. 2.7 Oxygen nonstoichiometry of $\text{LaMnO}_{3\pm\delta}$ (left) [15] and $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ (right) [18] versus p_{O_2} and temperature. Points experimental data, surfaces fitted models

2.3 Methods for Measuring Thermal and Chemical Expansion of Oxide Materials

2.3.1 Dilatometric Measurements in Air

Thermal expansion is a fundamental property of materials originating from the anharmonicity 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) under assumption on constant sample composition:

$$\alpha_V = \frac{1}{V_0} \left(\frac{\partial V}{\partial T} \right)_P \quad (2.22)$$

$$\alpha_L = \frac{1}{L_0} \left(\frac{\partial L}{\partial T} \right)_P \quad (2.23)$$

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. The so-called uniaxial strain is defined as

$$\varepsilon = \frac{\Delta L}{L_0} = \alpha_L \Delta T \quad (2.24)$$

where ΔL is the length increment corresponding to the temperature change ΔT . In general, CTE can be treated as a linear function of temperature, at least, as a first approximation. The thermal expansion of solids depends on their structure symmetry and may be iso- or anisotropic. For example, graphite has a layered structure and its expansion in the direction perpendicular to the layers is quite different from that in the layers. For isotropic materials, $\alpha_V \approx 3\alpha_L$ and their CTE can be easily determined by means of dilatometric measurements using a dilatometer. In anisotropic solid materials, the total volume expansion is distributed unequally among the three crystallographic axes and, as a rule, should be measured on single crystalline sample or using in situ X-ray diffraction (XRD) to determine temperature dependence of the lattice parameters.

The most typical dilatometer setup consists of a displacement transducer, which is connected via pushrod to the sample, furnace, instrument recording temperature, temperature controller, and software. Figure 2.8 shows a sketch of dilatometer DIL 402 C (Netzsch GmbH, Germany), which is often used for uniaxial strain measurements.

The uniaxial strain measured in air 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, as an example, in Fig. 2.9. The uniaxial strain along with oxygen content measured in air for $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ as functions of temperature are shown in this figure as well. As seen the temperature dependence of strain starts to deviate from a linear trend in the region between 450 and 500 °C for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ and, as a consequence, a simultaneous CTE increase is

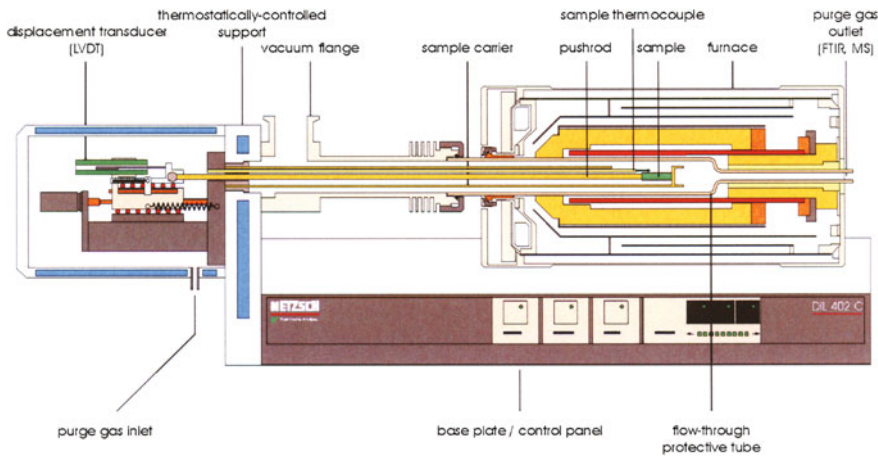


Fig. 2.8 Sketch of dilatometer DIL 402 C. Earlier available at <https://www.netzsch-thermalanalysis.com/us/products-solutions/dilatometry/>

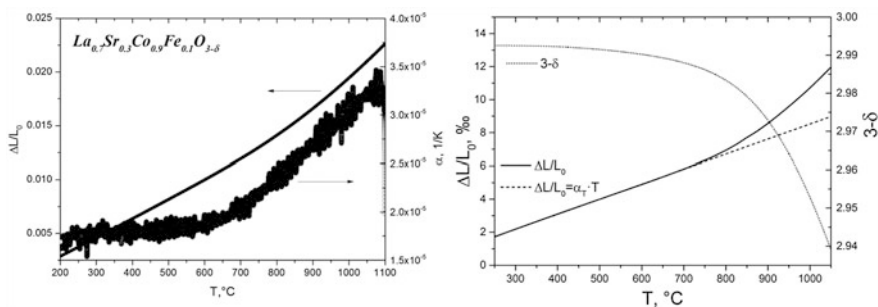


Fig. 2.9 Uniaxial strain of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ (left) [18] and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ (right) [17] as a function of temperature in air

observed with temperature. Such deviation is observed also for $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ between 700 and 750 °C. It is worth noting that an onset of deviation from the linear trend for $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ thermal expansion occurs at the same time as significant oxygen release from its lattice (see Fig. 2.9). Therefore, the deviation mentioned above is caused mostly by the change in the chemical composition with temperature and can be attributed to the chemical lattice strain induced by oxygen vacancy formation. 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 [8–10].

$$\alpha_{VC} = \frac{1}{V_0} \left(\frac{\partial V}{\partial X_{V_O}} \right)_{T,P} \quad (2.25)$$

where X_{V_o} is the oxygen vacancy mole fraction, and V_0 is the specific volume in a reference state, for instance one 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 by the following equation.

$$d\varepsilon(T, X_{V_o}) = \frac{1}{3} \alpha_v dT + \frac{1}{3} \alpha_{vC} dX_{V_o} \quad (2.26)$$

Equation (2.26) is valid under the assumption that the lattice expansion is an isotropic property. Use of this equation makes it possible to determine both thermal and chemical constituents of the uniaxial strain by dilatometric measurements. Integration of Eq. (2.26) yields the following expression for uniaxial strain.

$$\Delta L/L_0 = \alpha_L(T - T_0) + \alpha_{LC}(\delta(T) - \delta_0) \quad (2.27)$$

where L_0 and δ_0 are length and oxygen nonstoichiometry at a reference temperature T_0 and reference oxygen partial pressure (often in air). The result of calculating the chemical expansion contribution using Eq. (2.27) will be discussed below.

2.3.2 *Dilatometric Measurements in Gas Atmosphere with Controlled Oxygen Partial Pressure*

Since oxygen content in the oxide depends on oxygen partial pressure at a given temperature, and this content change may induce chemical strain of its lattice, then dilatometric measurements in gas atmospheres with controlled oxygen partial pressure are essential.

The experimental setup for chemical strain measurements depending on pO_2 is shown in Fig. 2.10. The main feature of the device developed is the control and adjustment of oxygen partial pressure by means of YSZ electrochemical oxygen pump (2) and sensor (3) using the automatic pO_2 controller. Such a system allows control of oxygen partial pressure within the range $-20 \leq \log(pO_2/\text{atm}) \leq 0$ with accuracy ± 0.01 in the immediate vicinity of the sample (4), and avoids use of a gas mixing equipment. Gas circulation (9) is used to prevent an oxygen partial pressure gradient along the sample. The sample studied (4) and an expansion sensor (8) are connected by means of alumina rod (5).

The accuracy of expansion measurement is $\pm 0.01 \mu\text{m}$. The sample is equilibrated first at a given oxygen partial pressure and temperature for 2–7 h until the sample length ceases to change. The oxygen partial pressure is then changed in steps within the range between starting and final values in both a decreasing and increasing direction at the same temperature, and the measurement procedure is repeated until an equilibrium state is reached at each step.

Fig. 2.10 Experimental setup for measuring the chemical expansion.
 1 furnace, 2 oxygen pump, 3 oxygen sensor, 4 sample, 5 alumina rod/pushrod, 6 thermocouple, 7 water cooling, 8 expansion sensor/displacement transducer, 9 gas circulation system [21]

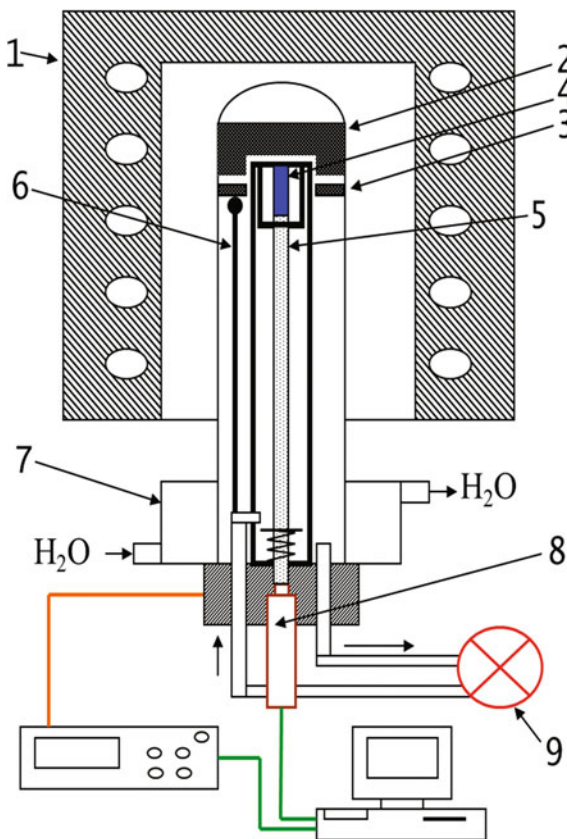


Figure 2.11 shows, as an example, a raw trace of the relative change of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ sample length measured at 1000 °C as p_{O_2} is stepped from high value to low one and back.

As seen expansion kinetics is rather fast, as the sample length changes to its new equilibrium value in about two hours. The chemical strain 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. 2.12. This figure shows that the slope of the p_{O_2} dependence of chemical expansion gradually increases with temperature in the range $600 \leq T, \text{ } ^\circ\text{C} \leq 700$, whereas an abrupt growth of the slope is obviously seen between 700 and 750 °C. The possible reason of such behavior will be discussed in the next section.

Fig. 2.11 Raw trace of the chemical strain of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ at $T = 1000^\circ\text{C}$ [18]. Numbers given in figure correspond to $\log(p\text{O}_2/\text{atm})$ in ambient gas atmosphere

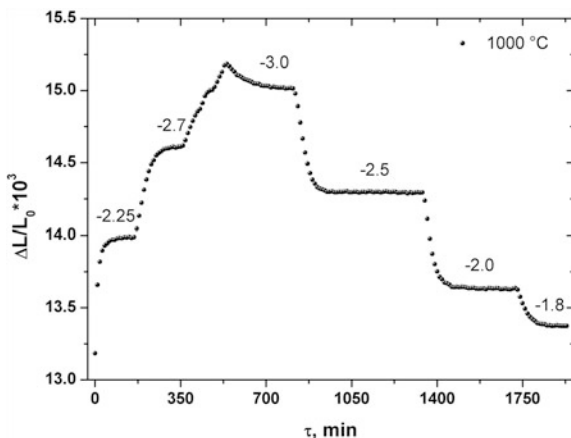
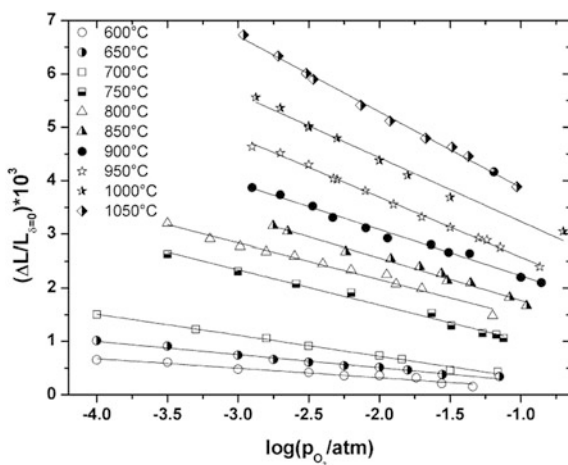


Fig. 2.12 Raw trace of the chemical strain of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ at $T = 1000^\circ\text{C}$ [18]. Numbers given in figure correspond to $\log(p\text{O}_2/\text{atm})$ in ambient gas atmosphere



2.4 Application of the Oxide Defect Structure for the Chemical Expansion Estimation

To date, partially substituted perovskites $\text{ABO}_{3-\delta}$, where A and B are rare earth and 3d-transition metal cations, respectively, are the extensively studied oxides with respect to their chemical expansion. However, the thermodynamic approach given by Eq. (2.27) does not reveal a chemical expansion mechanism.

Though it is generally recognized that point defects are responsible for isothermal expansion, the chemical expansion mechanism is 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 [6]. If electronic defects have a localized nature, then their impact on ion size is another source of chemical expansivity. Within the

framework of such assumptions, the oxygen vacancy formation is accepted to be accompanied by the reduction of 3d-metal cations. As a result, the average size of the B-site cations increases due to the apparent substitution of “large” $B^{(z-1)+}$ for smaller B^{z+} . 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 [11]. One can conclude, therefore, that the question on the nature of chemical expansion in oxides including perovskite structured ones still remains open. The aim of this section is to explain the origin of the chemical strain of the perovskite structured oxides selected using the defect structure models proposed for them.

Within the framework of the “dimensional” model, the following assumptions can be accepted. (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 a subset of perovskites with a high degree of symmetry. It is worth noting here that despite the fact that the approximation of hard sphere ions with Shannon radii is not accurate and has no solid physical (quantum mechanical) foundation—this approximation is quite efficient in describing the actual changes in unit cell volumes (expansion or contraction) by partial substitution of a host cation with another one with different size and charge or by change of the oxidation state (and thus also size) of the host cation (reduction/oxidation) [12]. Then the defect-induced expansion can be computed using the equation

$$\frac{\Delta L}{L_0} = \frac{\sum_i (c_i r_i - c_{i_0} r_i)}{\sum_i c_{i_0} r_i} \quad (2.28)$$

where c_i and r_i are the concentration and ionic radius, respectively, of an ion i of $ABO_{3-\delta}$ perovskite containing oxygen vacancies. The subscript, 0, in c_{i_0} and L_0 denotes in Eq. (2.28) 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 $ABO_{3-\delta}$ and c_i refers to the molar concentration per unit formula in this compound.

Let us illustrate the physical meaning for the model used for the chemical expansion calculation. For the sake of simplicity let us consider a closely packed 2D-lattice consisting of two types of ions with different radii, for example, 0.69 Å and 1.26 Å (see Fig. 2.13). The cell parameter is obviously equal to 3.9 Å or double distance between the adjacent ions (1.95 Å). From the dimensional point of view the equivalent lattice can be reproduced if real ions are substituted by ions with averaged radius as shown in Fig. 2.13. The cell parameter will be obviously the same. The averaged ion radius is equal to weighted sum of real ionic radii

$$R_{\text{avg}} = \frac{c_1 R_1 + c_2 R_2}{c_1 + c_2} = \frac{\sum c_i R_i}{\sum c_i} \quad (2.29)$$

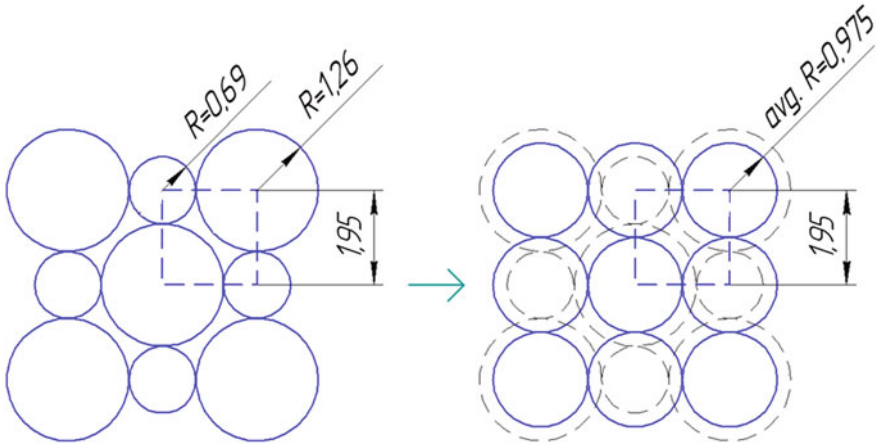


Fig. 2.13 Representations of closely packed 2D-lattice: built from ions as is (*left*) and built from ions with averaged radius (*right*)

where c_1 and c_2 are numbers (or concentrations in general case) of real ions in 2D-lattice and R_1 and R_2 are their real radii.

Any change of the real ion radii will, therefore, lead to corresponding change of an averaged ion radius. The cell parameter equals R_{avg} multiplied by 4 in our example. Therefore, normalized change of the lattice parameter is given by

$$\frac{\Delta a}{a_0} = \frac{4(R_{\text{avg}} - R_{\text{avg}}^0)}{4R_{\text{avg}}^0} = \frac{\sum c_i R_i - \sum c_i^0 R_i^0}{\sum c_i^0 R_i^0} \quad (2.30)$$

where c_i and R_i are concentration and radius of i -ion, respectively, in the oxide lattice, and c_i^0 and R_i^0 are concentration and radius of i -ion in the one under reference conditions. Comparing Eqs. 2.28 and 2.30 one can conclude that they are identical.

Appropriate concentrations of defect species can be calculated easily within the framework of the defect structure found for the oxide studied. For example, concentration of cobalt species in the doped lanthanum cobaltite $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ can be calculated according to Eqs. 2.19 and 2.20. Shannon crystal radii should be employed as the radii of ions in the calculation according to Eq. 2.28 instead of effective ionic radii, due to the former's close correspondence to the physical size of ions in solids [13]. However, there is the challenge regarding the radius of an oxygen vacancy. In reality oxygen vacancy radius is not identical to that of oxygen ion. The exact size of an oxygen vacancy and, a fortiori, its shape are believed to be very difficult to determine [12]. It seems to be difficult to define the volume of a given vacancy when that is examined on the atomic level [12]. An effective vacancy radius estimated using different approaches reflects, in the best case, the volumetric effect of the vacancy in interaction with the nearest 2–3 coordination shells and not

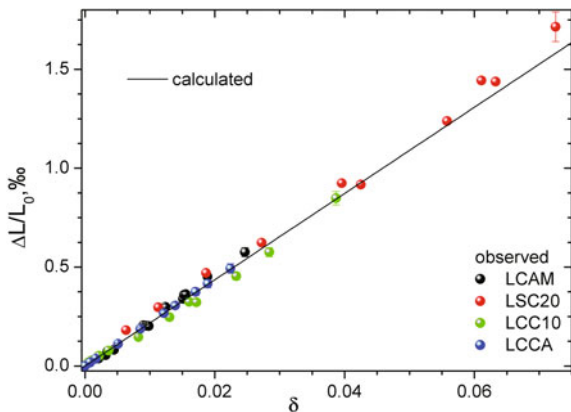
the physical size and shape of the real vacancy. For this reason, the estimated radius of oxygen vacancy should be treated as “the effective oxide vacancy radius.” The latter was found [12] to be useful in describing and rationalizing at the macroscopic level the changes of volume of lattice unit cell induced by redox processes. It is worth noting that the effective oxide vacancy radius in doped perovskites was found [12] to be close to the size of the oxide ion. The similar conclusion was made recently by Marrocchelli et al. [14]. For this reason one can accept, as a first approximation, that oxygen vacancy radius is identical to that of oxygen ion in perovskite oxides. It enables substitution of the concentration of oxygen in Eq. (2.28) by a value of 3.

2.4.1 Doped Lanthanum Chromites



The chemical expansion of selected chromites $\text{La}_{1-x}\text{Me}_x\text{Cr}_{1-y-z}\text{Al}_z\text{Mg}_y\text{O}_{3-\delta}$ ($\text{Me} = \text{Ca}, \text{Sr}$) measured at 1273 K [5, 7] is given in Fig. 2.14 as a deviation from the reference state normalized to the length of a sample with stoichiometric composition regarding oxygen ($\delta_0 = 0$) replotted versus oxygen nonstoichiometry using $p\text{O}_2$ - T - δ diagrams available for this perovskites (see, for example, Fig. 2.6). This length was accepted as a reference state as well. The remarkable features of the dependences shown in Fig. 2.14 are the following: (i) they are linear in shape and (ii) they all belong to a common line. Taking into account the defect structure model accepted for $\text{La}_{1-x}\text{Me}_x\text{Cr}_{1-y-z}\text{Al}_z\text{Mg}_y\text{O}_{3-\delta}$ ($\text{M} = \text{Sr}, \text{Ca}$) (see Sect. 2.1) appropriate concentrations can be substituted in the model Eq. (2.28) and the latter can be transformed, for instance, for $z = 0$ and $y = 0$ to the following equation

Fig. 2.14 Chemical expansion of $\text{La}_{1-x}\text{Me}_x\text{Cr}_{1-y-z}\text{Al}_z\text{Mg}_y\text{O}_{3-\delta}$ ($\text{Me} = \text{Ca}, \text{Sr}$) as a function of the oxygen nonstoichiometry at 1273 K, normalized as described in the text. The *points* represent experimental values and *line* is given by Eq. (2.31). LCAM— $\text{LaCr}_{0.79}\text{Al}_{0.16}\text{Mg}_{0.05}\text{O}_{3-\delta}$; LSC20— $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_{3-\delta}$; LCC10— $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_{3-\delta}$; LCCA— $\text{La}_{0.95}\text{Ca}_{0.05}\text{Cr}_{0.84}\text{Al}_{0.16}\text{O}_{3-\delta}$



$$\frac{\Delta L}{L_0} = \frac{(r_{\text{Cr}^{3+}} - r_{\text{Cr}^{4+}})2\delta}{(r_{\text{Cr}^{4+}} - r_{\text{Cr}^{3+}} - r_{\text{La}^{3+}} + r_{\text{Me}^{2+}})x + r_{\text{Cr}^{3+}} + r_{\text{La}^{3+}} + 3r_{\text{O}^{2-}}} \quad (2.31)$$

where x is a dopant concentration.

As follows from Eq. (2.31) predicted chemical expansion of doped lanthanum chromites (i) is really a linear function with respect to their oxygen nonstoichiometry and (ii) it does not depend on temperature. The slope of the linear relationship Eq. (2.31) depends on the doping level of a lanthanum chromite in strict sense. However, calculation according to Eq. (2.31) using crystal radii values $r_{\text{Cr}^{3+}} = 0.755 \text{ \AA}$ (CN = 6), $r_{\text{Cr}^{4+}} = 0.69 \text{ \AA}$ (CN = 6), and $r_{\text{Ca}^{2+}} = 1.48 \text{ \AA}$ (CN = 12) [13] yields, for instance, the slope values of 0.02157 and 0.02163 for $x = 0.1$ and 0.3 in $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$, respectively. Replacement of Sr ($r_{\text{Sr}^{2+}} = 1.58 \text{ \AA}$ (CN = 12) [13]) for Ca results in the slope values of 0.02154 and 0.02153 for $x = 0.1$ and 0.3, respectively. By comparing these results, it is evident that the computed oxygen nonstoichiometry coefficient of isothermal expansion can be regarded as a constant irrespective of the dopant nature and level. As seen in Fig. 2.14 the predicted expansion behavior according to Eq. (2.31) completely coincides with that observed for the doped lanthanum chromites. Calculated values of chemical expansion are seen to be in very good agreement with those experimentally measured.

Thus aforementioned agreement gives rise to draw a conclusion that chemical lattice expansion of the doped lanthanum chromites observed with deviation from their stoichiometric composition with respect to oxygen is solely caused by the mean ionic radius increase.

2.4.2 *Perovskite Structured Oxides* $\text{La}_{1-y}\text{Sr}_y\text{B}_{1-x}\text{B}'_x\text{O}_{3-\delta}$ ($\text{B}=\text{Mn, Fe, and Co}$; $\text{B}'=3\text{d-Metal}$)

The chemical expansion measured at different temperatures and normalized to the stoichiometric composition with respect to oxygen ($\delta = 0$) for the undoped lanthanum manganite [15] is given as a function of oxygen nonstoichiometry in Fig. 2.15. It is noteworthy that dependences shown in Fig. 2.15 are not linear in shape and chemical expansion values measured at the same value of oxygen nonstoichiometry but at different temperatures differ from each other in strict sense.

Aforementioned particularities obviously indicate that the chemical expansion behavior for the undoped lanthanum cobaltite and manganite does not coincide with that for the doped lanthanum chromites discussed above.

Taking into account the defect structure model accepted for undoped $\text{LaBO}_{3-\delta}$ ($\text{B} = \text{Mn, Co}$) appropriate concentrations can be substituted in the model Eq. (2.28) which can be transformed, as a result, to the following equation

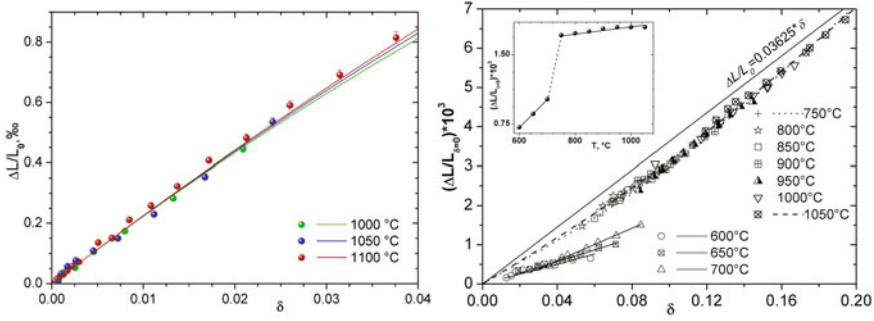


Fig. 2.15 Chemical expansion of $\text{LaMnO}_{3-\delta}$ [15] (left) and $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ [18] (right) as a function of the oxygen nonstoichiometry normalized as described in the text. The *points* represent experimental values and *lines* the model calculations. Insertion (right) is described in the text

$$\frac{\Delta L}{L_0} = \frac{(2r_{\text{B}^{3+}} - r_{\text{B}^{4+}} - r_{\text{B}^{2+}}) \cdot (\sqrt{\delta^2 - 4K_2\delta^2 + K_2} - \sqrt{K_2}) + \delta(4K_2 - 1) \cdot (r_{\text{B}^{2+}} - r_{\text{B}^{4+}})}{(2\sqrt{K_2} - 1)(r_{\text{B}^{3+}} + \sqrt{K_2}(r_{\text{B}^{4+}} + r_{\text{B}^{2+}})) + (4K_2 - 1)(3r_{\text{O}^{2-}} + r_{\text{La}^{3+}})} \quad (2.32)$$

where K_2 is the equilibrium constant of the reaction (2.18).

Two particularities can be highlighted with respect to the model function Eq. (2.32). The first one consists in that chemical expansion calculated according to Eq. (2.32) is not a linear function of oxygen nonstoichiometry unlike that for the doped lanthanum chromites. The second particularity is that chemical strain $\frac{\Delta L}{L_0} = f(\delta)$ may change distinctly with temperature at a given value of oxygen nonstoichiometry, if equilibrium constant K_2 depends on temperature significantly. It is worth noting that, generally speaking, model Eq. (2.32) can be fitted to the experimental data on the chemical expansion of $\text{LaBO}_{3-\delta}$ given, for example, in Fig. 2.15 for B = Mn. However, computation of a chemical expansion using the values of the equilibrium constant K_2 determined independently on the basis of oxygen nonstoichiometry measurements seems to be more preferable, since such approach allows to reveal unambiguously whether the isothermal expansion of $\text{LaBO}_{3-\delta}$ is solely caused by the dimensional effect. The parameters of temperature dependences of K_2 given in Table 2.1 were, therefore, employed for model calculations according to Eq. (2.32). The crystal ionic radii [13] 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), $r_{\text{Mn}^{2+}} = 0.81 \text{ \AA}$ (LS, CN = 6), $r_{\text{Mn}^{3+}} = 0.785 \text{ \AA}$ (HS, CN = 6), $r_{\text{Mn}^{4+}} = 0.67 \text{ \AA}$ (CN = 6), where LS and HS correspond to the low and high spin states, respectively.

The chemical expansion calculated using Eq. (2.32) is shown in Fig. 2.15 for $\text{LaMnO}_{3-\delta}$. This figure shows obviously that there is very good agreement between the experimental data and those predicted on the basis of the model proposed for the

perovskite. Such coincidence implies obviously that the chemical strain of $\text{LaMnO}_{3-\delta}$ observed with deviation from its stoichiometric composition with respect to oxygen at a given temperature is solely caused by the mean ionic radius increase. The latter occurs due to the partial substitution of “large” $\text{B}^{(n-1)+}$ cation for smaller B^{n+} that as a result of the reduction. On the other hand, aforementioned agreement seems to be regarded as an additional evidence of the localized nature of electronic defects or, in other words, small polarons existence in the undoped lanthanum manganite.

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 (see Fig. 2.12) and normalized to the reference state at $\delta = 0$ is given in Fig. 2.15 as well. For the sake of comparison, the chemical expansion estimated on the basis of Eq. (2.27) is given ibidem. As seen, the latter exceeds somewhat the values of chemical expansion measured over the complete range of oxygen nonstoichiometry. Besides the dependence of chemical expansion measured as a function of oxygen nonstoichiometry are curved in shape whereas the one estimated using Eq. (2.27) is a straight line (see Fig. 2.15). 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. 2.15 that the δ dependence 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 into two groups. The first group consists of the dependence measured at relatively low temperatures (between 600 and 700 °C) and the second one includes those measured at higher temperatures (between 750 and 1050 °C). A gradual increase of the slope coefficient of the δ dependence is observed for the former whereas the dependence of the latter merges in a common curve for all practical purposes. In other words, the chemical expansion measured at higher temperature exceeds the one measured at lower temperature, but at the same value of oxygen nonstoichiometry, as shown by the inset of Fig. 2.15, where the chemical expansion is given as a function of temperature at fixed oxygen nonstoichiometry, $\delta = 0.06$. A gradual increase of the chemical expansion observed between 600 and 700 °C as well as the abrupt growth of the chemical expansion in the narrow range $700 \leq T, \text{C} \leq 750$ (see Fig. 2.15) cannot be explained by an influence of the temperature dependence of equilibrium constant, K_2 , of cobalt disproportionation reaction (2.18) 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 a comparison of enthalpies, 53 kJ (see Table 2.1) versus 518 kJ (see Table 1 of Ref. [16]). On the other hand, it is well-known [6] that cobalt may exist not only in different oxidation states but also in different spin states, and that the ionic radius of high spin (HS) cobalt species in certain oxidation states is significantly larger than that of low spin (LS) cobalt species [13].

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. (2.28) it is, therefore, necessary to decide which spin state should be accepted for Co^{2+} and Co^{3+} in the lattice of the cobaltite 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 [6]. Though 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 [6]. Recently, we have proposed a similar gradual transition for divalent cobalt and found that this approach is quite consistent with the chemical expansion behavior observed for a variety of strontium substituted lanthanum perovskites [6, 17–19].

Another challenge consists in definition of a crystal radius for cobalt in the intermediate spin state since one was not presented by Shannon [13]. However, Asai et al. [20] 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. The above mentioned discussion allows one 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

$$r_{\text{Co}}^{3+} = r_{\text{Co}}^{3+}(\text{HS}, \text{CN} = 6) * a_1 + r_{\text{Co}}^{3+}(\text{LS}, \text{CN} = 6) * (1 - a_1) \quad (2.33)$$

and

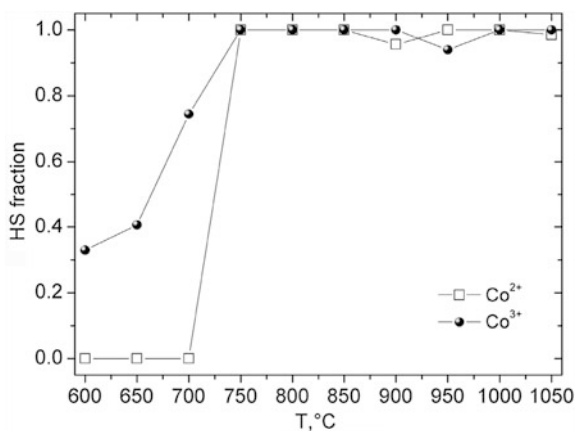
$$r_{\text{Co}}^{2+} = r_{\text{Co}}^{2+}(\text{HS}, \text{CN} = 6) * a_2 + r_{\text{Co}}^{2+}(\text{LS}, \text{CN} = 6) * (1 - a_2) \quad (2.34)$$

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 $r_{\text{Co}}^{2+}(\text{HS}, \text{CN} = 6) = 0.885 \text{ \AA}$ [13], 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 are the only parameters that have to be fitted in the model Eq. (2.27) using data on chemical expansion since K_2 is defined independently as a result of the defect structure modeling.

The results of model calculation of the chemical expansion according to Eqs. (2.28), (2.33), and (2.34) are given in Fig. 2.15. As seen the model proposed coincides with the experimental data on chemical expansion very well 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. 2.16. Quite plausible observation follows from this figure. As seen 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 that of Co^{2+} changes abruptly from 0 to unity in relatively narrow range $700 \leq T, ^\circ\text{C} \leq 750$.

Fig. 2.16 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 [18]



2.5 Summary

State-of-the-art methods for measurement of oxygen content, such as TG, coulometric and redox titration, direct reduction in hydrogen flux, as well as some examples of their employment in analyzing defect chemistry were discussed in this chapter. Conventional dilatometry was demonstrated to be an effective method for measuring the oxide lattice strain dependence on temperature and oxygen partial pressure. It was shown that the defect structure of an oxide material can be developed and verified on the basis of measured oxygen content. A quantitative model of chemical strain was developed as an example of mechano-chemical coupling in oxide materials.

References

1. Tsvetkov, D. S., Ananjev, M. V., Eremin, V. A., Zuev A. Yu., & Kurumchin, E. K. (2014). Oxygen nonstoichiometry, defect structure and oxygen diffusion in the double perovskite $\text{GdBaCo}_2\text{O}_{6-\delta}$. *Dalton Transaction*, 43, 15937–15943.
2. Taskin, A. A., Lavrov, A. N., & Ando, Y. (2005). Achieving fast oxygen diffusion in perovskites by cation ordering. *Applied Physics Letters*, 86, 091910.
3. Tsvetkov, D. S., Sereda, V. V., & Zuev, A. Yu. (2010). Oxygen nonstoichiometry and defect structure of the double perovskite $\text{GdBaCo}_2\text{O}_{6-\delta}$. *Solid State Ionics*, 180(40), 1620–1625.
4. Kroeger, F. A., & Vink, H. J. (1956). Relations between the concentrations of imperfections in crystalline solids. *Solid State Physics*, 3, 307–435.
5. Hilpert, K., Steinbrech, R. W., Boroomand, F., et al. (2003). Defect formation and mechanical stability of perovskites based on LaCrO_3 for solid oxide fuel cells (SOFC). *Journal of the European Ceramic Society*, 23(16), 3009–3020.
6. Zuev, A. Yu., & Tsvetkov, D. S. (2013). In J. Zhang & H. Li (Eds.), *Perovskite: crystallography, chemistry and catalytic performance* (p. 141). New York: Nova Science Publisher.

7. Zuev, A. Yu., Singheiser, L., & Hilpert, K. (2002). Defect structure and isothermal expansion of A-site and B-site substituted lanthanum chromites. *Solid State Ionics*, 147(1), 1–11.
8. Laredo, E. (1969). Etude par rayons X de la dilatation de NaCl a haute temperature. *Journal of Physics and Chemistry of Solids*, 30(5), 1037–1042.
9. Lidiard, A. (1957). *Ionic conductivity*. Berlin: Springer.
10. Adler, S. B. (2001). Chemical expansivity of electrochemical ceramics. *Journal of the American Ceramic Society*, 84(9), 2117–2119.
11. Bishop, S. R., Duncan, K. L., & Wachsman, E. D. (2010). Thermo-chemical expansion in strontium-doped lanthanum cobalt iron oxide. *Journal of the American Ceramic Society*, 93(12), 4115–4121.
12. Chatzichristodoulou, C., Norby, P., Hendriksen, P. V., & Mogensen, M. B. (2015). Size of oxide vacancies in fluorite and perovskite structured oxides. *Journal of Electroceramics*, 34(1), 100–107.
13. Shannon, R. D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography*, 32(5), 751–767.
14. Marrocchelli, D., Perry, N. H., & Bishop, S. R. (2015). Understanding chemical expansion in perovskite-structured oxides. *Physical Chemistry Chemical Physics*, 17(15), 10028–10039.
15. Zuev, A. Yu., & Tsvetkov, D. S. (2010). Oxygen nonstoichiometry, defect structure and defect-induced expansion of undoped perovskite $\text{LaMnO}_{3\pm\delta}$. *Solid State Ionics*, 181(11), 557–563.
16. Zuev, A. Yu., Petrov, A. N., Vylkov, A. I., & Tsvetkov, D. S. (2007). Oxygen nonstoichiometry and defect structure of undoped and doped lanthanum cobaltites. *Journal Materials Science*, 42, 1901–1908.
17. Zuev, A. Yu., Sereda, V. V., & Tsvetkov, D. S. (2014). Oxygen nonstoichiometry, defect structure, thermal and chemical expansion of pseudo-cubic $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ and double perovskite $\text{GdBaCo}_2\text{O}_{6-\delta}$. *Journal of the Electrochemical Society*, 161(11), F3032–F3038.
18. Zuev, A. Yu., Sereda, V. V., & Tsvetkov, D. S. (2014). Defect structure and defect-induced expansion of doped perovskite $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$. *International Journal of Hydrogen Energy*, 39(36), 21553–21560.
19. Zuev, A. Yu., Sereda, V. V., & Tsvetkov, D. S. (2012). Defect structure and defect-induced expansion of MIEC oxides: Doped lanthanum cobaltites. *Journal of the Electrochemical Society*, 159(9), F594–F599.
20. Asai, K., Yoneda, A., Yokokura, O., Tranquauda, J. M., Shirane, G., & Kohn, K. (1998). Two spin-state transitions in LaCoO_3 . *Journal of the Physical Society of Japan*, 67(1), 290–296.
21. Zuev, A. Yu., Vylkov, A. I., Petrov, A. N., & Tsvetkov, D. S. (2008). Defect structure and defect-induced expansion of undoped oxygen deficient perovskite $\text{LaCoO}_{3-\delta}$. *Solid State Ionics*, 179, 1876–1879.

Electro-Chemo-Mechanics of Solids

Bishop, S.R.; Perry, N.; Marrocchelli, D.; Sheldon, B.
(Eds.)

2017, IX, 192 p. 71 illus., 50 illus. in color., Hardcover

ISBN: 978-3-319-51405-5