



Oxygen thermodynamics and defect chemistry of nonstoichiometric manganites $\text{Ca}_{0.6-y}\text{Sr}_{0.4}\text{La}_y\text{MnO}_{3-\delta}$



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ABSTRACT

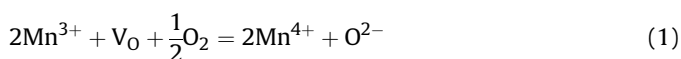
The chemical potential of oxygen $\Delta\mu_{\text{O}}(\delta, y, T)$ relative to the standard state is calculated from experimental data for equilibrium oxygen content in $\text{Ca}_{0.6-y}\text{Sr}_{0.4}\text{La}_y\text{MnO}_{3-\delta}$ at different values of temperature and oxygen partial pressure in the gaseous phase. The respective values of partial molar enthalpy $\Delta\bar{H}_{\text{O}}(\delta, y)$ and entropy $\Delta\bar{S}_{\text{O}}(\delta, y)$ are derived from the linear plots for $\Delta\mu_{\text{O}}(\delta, y, T)$ vs. temperature. Based on the ideal solution approximation, the equations are obtained that show interrelation of $\Delta\bar{H}_{\text{O}}(\delta, y)$ and $\Delta\bar{S}_{\text{O}}(\delta, y)$ with thermodynamic parameters of defect formation reactions and concentration of defects. It is shown that thermal excitation of Mn^{4+} cations considerably impacts equilibration of defect species in the crystal structure of $\text{Ca}_{0.6-y}\text{Sr}_{0.4}\text{La}_y\text{MnO}_{3-\delta}$.

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1. Introduction

The perovskite-like manganites $A_{1-y}\text{Ln}_y\text{MnO}_{3-\delta}$, where A is Ca, Sr and Ln is a lanthanide metal, attract attention as promising materials for SOFCs cathodes [1,2], thermoelectric converters [3,4] and oxidation catalysts [5]. The ability of the manganites to reversibly exchange oxygen with the gaseous phase is favorable for their using as oxygen-carrier materials in combustion processes [6–9]. The interesting properties combination in the manganites reflect coexistence of Mn^{3+} and Mn^{4+} cations that appear in response to doping [10,11] and changes of oxygen nonstoichiometry [12,13]. Therefore, practically important are the data concerning variations of oxygen nonstoichiometry (δ) with temperature (T), oxygen pressure (p_{O_2}) and concentration of donors (y). Moreover, the analysis of the respective dependencies $\delta(T, p_{\text{O}_2}, y)$ can be used in order to determine thermodynamic functions of oxygen in manganites, and provide insight into defect formation reactions that govern concentration of oxygen vacancies and manganese cations. For instance, the partial molar enthalpy of oxygen $\Delta\bar{H}_{\text{O}}$ may weakly depend on δ when predominant reaction in the oxide is oxidation of transition metal cations [14–18]. Quite

differently, strong variations of $\Delta\bar{H}_{\text{O}}$ with δ may signal large contribution from charge disproportionation of 3d metal cations [19,20] as is the case also for $\text{CaMnO}_{3-\delta}$ [21] and $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{MnO}_{3-\delta}$ [22]. It is important to notice that simultaneous reactions of oxidation



and thermal excitation



are sufficient to explain the δ dependent behavior of partial oxygen enthalpy $\Delta\bar{H}_{\text{O}}$ and entropy $\Delta\bar{S}_{\text{O}}$ in $\text{CaMnO}_{3-\delta}$ [21,23] and $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{MnO}_{3-\delta}$ [22]. According to electron structure calculations [24], the reaction of thermal excitation may be related to the transition of electrons from half-filled t_{2g} to empty e_g states of Mn^{4+} cations. Therefore, the enthalpy for reaction (2) must be nearly equal to the band gap [25,26]. On the other hand, the thermal excitation results in appearance of appreciable amount of Mn^{3+} cations in $\text{CaMnO}_{3-\delta}$ already at 720–890 K, i.e., in conditions where oxygen non-stoichiometry δ can be safely neglected. As a result, the activation energy of 0.36 eV for electrical conductivity in CaMnO_3 [27] occurs considerably larger compared to electron doped

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manganites with doping induced (extrinsic) mechanism of conductivity [3,4,10]. It is worth to note that as expected the conductivity activation energy equals almost exactly to a half band gap [25] and, respectively, is close to the half enthalpy for reaction (2) [26]. Also the competing reactions (1) and (2) appear to be operative in a more complicated case of doped derivatives $\text{Ca}_{1-x-y}\text{Sr}_x\text{La}_y\text{MnO}_{3-\delta}$, where they help to explain experimental $\delta(T, p_{\text{O}_2}, y)$ plots [28] and obtain the enthalpy value for reaction (2) in a good correspondence with the forbidden energy gap [25].

In this work, we use reactions (1) and (2) and the experimental data obtained earlier for $\delta(T, p_{\text{O}_2}, y)$ [28] in order to derive partial molar thermodynamic functions of oxygen in $\text{Ca}_{1-x-y}\text{Sr}_x\text{La}_y\text{MnO}_{3-\delta}$, where $x = 0.4$ and $0 \leq y \leq 0.15$. The obtained dependencies $\Delta\bar{H}_{\text{O}}(\delta, y)$ and $\Delta\bar{S}_{\text{O}}(\delta, y)$ show that reaction (2) plays an important role in equilibration of the manganites with gaseous phase at heating. This finding can be helpful in development of oxide thermo-electric manganites and oxygen carriers for such redox processes as chemical-looping combustion.

2. Results and discussion

2.1. Oxygen partial molar enthalpy and entropy in $\text{Ca}_{0.6-y}\text{Sr}_{0.4}\text{La}_y\text{MnO}_{3-\delta}$

For the sake of convenience the experimental data [28] are shown in Fig. 1 (insets) for equilibrium oxygen content ($3-\delta$) in $\text{Ca}_{0.6-y}\text{Sr}_{0.4}\text{La}_y\text{MnO}_{3-\delta}$. They can be used for calculations of the chemical potential of oxygen $\Delta\mu_{\text{O}}(\delta, T)$ in $\text{Ca}_{0.6-y}\text{Sr}_{0.4}\text{La}_y\text{MnO}_{3-\delta}$ relative to the gas phase oxygen according to

$$\Delta\mu_{\text{O}}(\delta, T) \equiv \mu_{\text{O}}(\text{oxide}) - 1/2\mu_{\text{O}_2}^{\circ} = 1/2RT \cdot \ln p_{\text{O}_2} \quad (3)$$

where $\mu_{\text{O}_2}^{\circ}$ is the chemical potential of gas phase oxygen in standard state ($p_{\text{O}_2} = 1$ atm and $T = 298$ K) and R is the gas constant. The respectively derived plots $\Delta\mu_{\text{O}}(\delta, T)$ vs. temperature at constant δ 's are straight lines in respective temperature limits, Fig. 1. Hence, the known relation

$$\Delta\mu_{\text{O}}(\delta, T) = \Delta\bar{H}_{\text{O}}(\delta) - T\Delta\bar{S}_{\text{O}}(\delta) \quad (4)$$

can be used in order to obtain partial molar thermodynamic quantities $\Delta\bar{H}_{\text{O}}(\delta, y)$ and $\Delta\bar{S}_{\text{O}}(\delta, y)$ in Fig. 2 and Fig. 3, respectively. It is seen that incorporation of lanthanum in the crystalline lattice is accompanied with an appreciable decrease of the enthalpy $\Delta\bar{H}_{\text{O}}(\delta, y)$. In other words, the increase in lanthanum content results in stronger bonding of oxygen in $\text{Ca}_{0.6-y}\text{Sr}_{0.4}\text{La}_y\text{MnO}_{3-\delta}$. The values of $\Delta\bar{H}_{\text{O}}(\delta, y)$ at large δ 's approach the oxidation enthalpy $\Delta H_{\text{Ox}}^{\circ}$ for reaction (1), Table 1. At the same time, the increase of $\Delta\bar{H}_{\text{O}}(\delta, y)$ at $\delta \rightarrow 0$ may be understood as manifestation of reaction (2). In contrast to the enthalpy behavior, the entropy $\Delta\bar{S}_{\text{O}}(\delta, y)$ variations with lanthanum content are rather small, Fig. 3. Only in the limit $\delta \rightarrow 0$ one can see stronger changes of $\Delta\bar{S}_{\text{O}}(\delta, y)$ plots. This behavior may signal an increasing contribution of the configuration entropy as it occurs in other perovskite-like oxides [14,15,21,22].

2.2. Thermodynamic relationships

Taking in view possible charge states of manganese cations the manganite formula can be represented as $\text{Ca}_{1-x-y}\text{Sr}_x\text{La}_y\text{Mn}_{\text{n}}^{3+}\text{Mn}_{\text{g}}^{4+}\text{Mn}_{\text{p}}^{5+}\text{O}_{3-\delta}$. Then, the free Gibbs energy, G , in the manganite can be expressed as

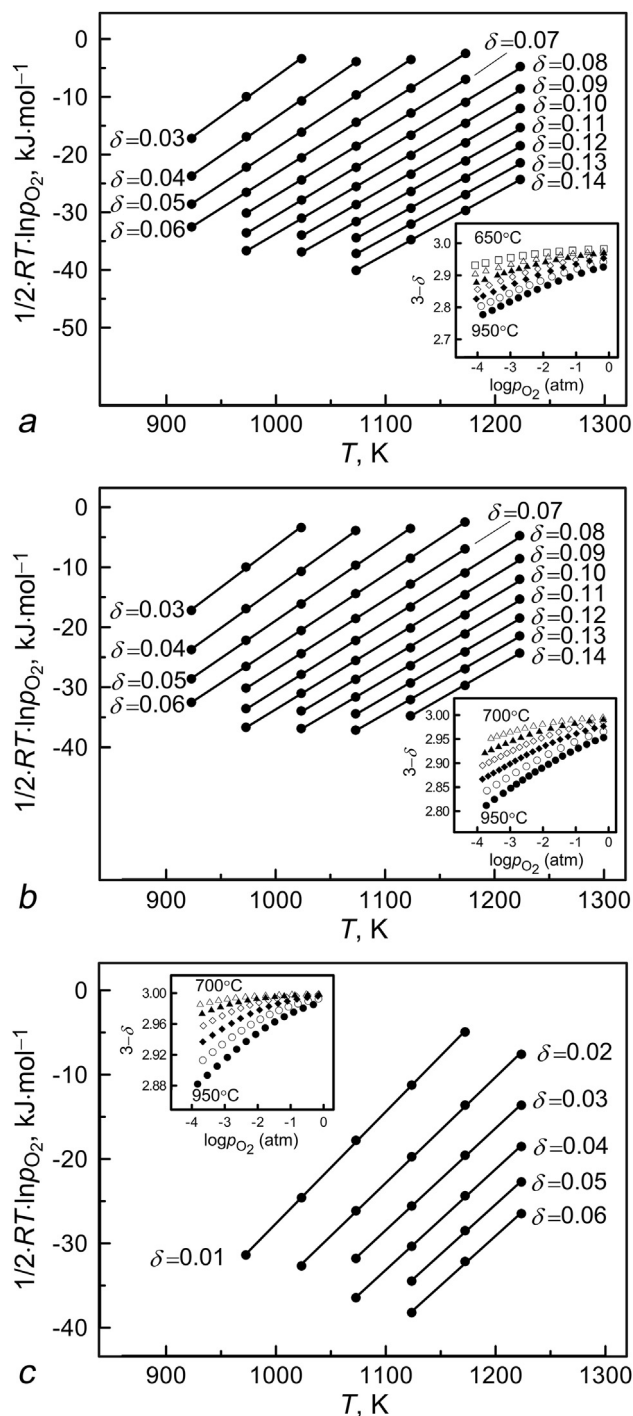


Fig. 1. The oxygen chemical potential vs. temperature plots for $\text{Ca}_{0.6-y}\text{Sr}_{0.4}\text{La}_y\text{MnO}_{3-\delta}$ at different values of oxygen nonstoichiometry: (a) $y = 0$; (b) $y = 0.05$; (c) $y = 0.15$. The insets show isothermal changes of oxygen content in $\text{Ca}_{0.6-y}\text{Sr}_{0.4}\text{La}_y\text{MnO}_{3-\delta}$ at variations of oxygen partial pressure. The temperature step between the isotherms is 50°C [23].

$$G = G^\circ + (1-x-y)\mu^\circ(\text{Ca}^{2+}) + x\mu^\circ(\text{Sr}^{2+}) + y\mu^\circ(\text{La}^{3+}) + n\mu^\circ(\text{Mn}^{3+}) + g\mu^\circ(\text{Mn}^{4+}) + p\mu^\circ(\text{Mn}^{5+}) + (3-\delta)\mu^\circ(\text{O}^{2-}) + \delta\mu^\circ(\text{V}_\text{O}) - TS(\text{conf}) \quad (5)$$

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