Thermochemistry of Perovskites in the Lanthanum - Strontium - Manganese - Iron Oxide System

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Abstract

The enthalpies of formation from binary oxides of perovskites (ABO_3) based on lanthanum strontium manganite $\text{La}(\text{Sr})\text{MnO}_3$ (LSM) and lanthanum strontium ferrite $\text{La}(\text{Sr})\text{FeO}_3$ (LSF) and mixed lanthanum strontium manganite ferrite $\text{La}(\text{Sr})\text{Mn}(\text{Fe})\text{O}_3$ (LSMF) were measured by high temperature oxide melt solution calorimetry. Using iodometric titration, the oxygen content was derived. The perovskites with A-site cation deficiency have greater oxygen deficiency than the corresponding A-site stoichiometric series. Stability of LSMF decreases with increasing iron content. Increasing oxygen deficiency clearly destabilizes the perovskites. The results suggest an enthalpy of oxygen incorporation that is approximately independent of composition.

Keywords: perovskite, calorimetry, SOFC

1. Introduction

Perovskites (ABO_3) based on lanthanum strontium manganite $\text{La}(\text{Sr})\text{MnO}_3$ (LSM) and lanthanum strontium ferrite $\text{La}(\text{Sr})\text{FeO}_3$ (LSF) and mixed lanthanum strontium manganite ferrite $\text{La}(\text{Sr})\text{Mn}(\text{Fe})\text{O}_3$ (LSMF) are receiving considerable attention because of their unusual electronic and magnetic properties [1,2] and promising applications as cathodes for solid oxide fuel cells (SOFC) [3-5]. LSM satisfies most requirements for fuel cell electrodes due to its high electrical conductivity and minimum reactivity and interdiffusion [6]. A disadvantage of LSM is the lack of oxide ion conduction at working temperatures [7]. LSF materials exhibit substantial ionic and electronic conductivity, good catalytic activity for oxygen reduction [8,9] and tend to react more slowly with the yttria-stabilized zirconia (YSZ) electrolyte than LSM [10,11]. $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$ (LSMF), belongs to a family of mixed-valence ($\text{Mn}^{3+/4+}$) manganite perovskites, exhibiting unique magnetic and electrical properties [8,12,13]. For both A and B site doping, strong correlation between electronic properties and the valence and the ionic radius of the doping atoms has been observed [14]. The iron content strongly influences the magnetic and transport properties of LSMF [15-17] due to the progressive suppression of ferromagnetic ordering [12,15,18]. The number of Mn^{4+} ions in LSMF is fixed not only by doping, but also by the oxygen nonstoichiometry (δ) in the formula, $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ [19]. δ depends on composition, temperature, and oxygen fugacity and is a key factor in determining defect chemistry and transport properties.

The substitutions and defect equilibria are controlled by the thermodynamics of the perovskite. In a previous study of $\text{La}_{0.70}\text{Sr}_{0.30}\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$ solid solutions, Kemik et al. [20] investigated the main factors governing the energetics of the solid solution in this system

when $0 < y < 1$. They found that the symmetry of the perovskite structure, the valence of the transition metal and the energetics are highly interdependent. Kinderman et al [21] reported on chemical compatibility between some orthoferrite - based perovskites and the solid electrolyte zirconia (ZrO_2) doped with 8 mol % yttria (Y_2O_3) (8YSZ) with consideration of the thermodynamic activities, tolerance factor, and oxygen ion migration energies. Some correlations between the nonstoichiometry and the thermodynamic data, as well as some information about the oxygen transport kinetics in the LSMF system were presented in several papers [21-25]. Although some thermodynamic data (relative partial molar free energy, enthalpy, and entropy of oxygen, as well as the partial pressure of oxygen, enthalpy of formation, enthalpy of oxidation) [20,22,23] have been reported for certain compositions in the LSMF system, the data are incomplete and not systematic. In particular, fundamental understanding of how the thermodynamic data of appropriate substitutions in LSMF could be correlated with the change of the charge compensation mechanism and the oxygen nonstoichiometry of the samples is still needed.

The purpose of this study is to measure enthalpies of formation of a set of LSMF perovskites, well characterized in terms of structure, composition, and oxygen nonstoichiometry and to seek systematics in thermodynamic parameters as a function of cationic composition and oxygen content. We employed iodometric titration to obtain oxygen content and mean oxidation state of manganese for all materials. The oxygen nonstoichiometry values at different levels of Fe doping in LSMF are discussed to obtain information on the influence of oxygen vacancies on thermodynamic stability. High temperature oxide melt solution calorimetry using $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ as solvent has been applied to determine enthalpies of formation, $\Delta H_{f, \text{ox}}$ of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($y = 0, 0.2, 0.5, 0.7$) and $(\text{La}_{1-x}\text{Sr}_x)_{0.95}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($x = 0.25, 0.30; y = 0, 0.2, 0.7$) from their oxide components at

25 °C. Some of the previously reported data by Tanasescu et al. [22,23] referring to the relative partial molar free energies, enthalpies and entropies of oxygen dissolution in the perovskite phase, which were obtained by electromotive force measurements (EMF), are discussed to clarify the relationship between the average Mn valence, and thermodynamic behavior of the perovskites. A simplified approach gives a general picture of thermodynamic properties as a function of composition and oxygen stoichiometry. Simplified trends in the measured enthalpies of formation, oxidation, and defect formation are identified and discussed.

2. Experimental Methodology

2.1. Sample Preparation and Characterization

The initial powders of the perovskite specimens, $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($y = 0, 0.2, 0.5, 0.7$) (LS3MF), $(\text{La}_{1-x}\text{Sr}_x)_{0.95}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($x = 0.3; y = 0, 0.2, 0.7$) ((LS3).95MF) and $(\text{La}_{1-x}\text{Sr}_x)_{0.95}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($x = 0.25; y = 0, 0.2$) ((LS25).95MF), were supplied by Haldor Topsae A/S, Lyngby, Denmark. Samples were prepared as described in detail previously by drip pyrolysis of aqueous nitrate solutions and glucose or glycine as a combustion fuel [26-28] followed by sintering at 1150 °C in air for 24 h.

Powder X-ray diffraction (XRD) patterns were recorded using a Bruker-AXS D8 Advance diffractometer (Bruker-AXS, Inc., Fitchburg, WI) operating at an accelerating voltage of 40 kV and emission current of 40 mA with Cu $K\alpha$ radiation. Data were acquired in the range 20 – 80 ° (2 θ) using a step size of 0.02 ° (2 θ) and a collection time of 1 s/step. The sample was rotated at 15 rpm during data collection. Whole pattern fitting as implemented in MDI Jade software was used to refine the lattice parameters.

Electron microprobe analysis: Chemical composition was determined using a Cameca SX100 electron microprobe, operating at a beam current of 20 nA and a beam size of 1 mm, with LaPO_4 , SrTiO_3 , Fe_2O_3 and Mn metal as standards. Analyzed compositions were in good agreement with nominal composition (Table 1). There was no evidence of heterogeneity or impurity phases. We use the nominal cation compositions for further calculations. The oxygen content is based on iodometric titrations, see below.

2.2. Oxygen Content Determination

The average formal B-site ions valence, and hence the total oxygen content, was determined using a standard iodometric method [29,30]. This gives the total number of highly oxidized species present, but does not confirm the identity of the oxidized species. The procedure described by Birkner et al. [31] was modified slightly by replace the use of H_2SO_4 with concentrated HCl. The samples, which weighed 50 – 70 mg, were completely and homogeneously dissolved in HCl under gradual heating. The method involves reacting the manganese oxide with a high excess of I^- in acidic medium to produce I^{3-} which is then titrated with a standardized solution of $\text{S}_2\text{O}_3^{2-}$. The number of moles of thiosulfate that react with the I^{3-} provides the number of moles of B-site ions that had been reduced during the process of iodide oxidation by B-site ions species greater than +2 oxidation state. Nitrogen sparged 18 M Ω /cm deionized water was used for all preparations, with the goal of removing dissolved oxygen and avoiding oxidation of reagents. All determinations were performed in triplicate. In terms of oxygen deficiency values, δ , the precision can be ± 0.01 or less when sufficient sample is used. This value increases slightly for samples high in iron.

2.3. High Temperature Oxide Melt Solution Calorimetry

High temperature drop solution calorimetry was performed in a custom built twin Calvet type microcalorimeter using sodium molybdate ($3\text{Na}_2\text{O}-4\text{MoO}_3$) as the solvent. The

equipment and experimental procedures have been described in detail previously by Navrotsky [32, 33]. Before dropping, the samples were equilibrated for one month in the calorimetry suite that maintains a controlled environment for constant temperature (25 ± 1 °C) and relative humidity (50 ± 3 %).

Oxygen was flushed through the calorimeter glassware assembly at 60 mL/min. Samples were pressed into pellets (about 5 mg) and dropped from room temperature into solvent in the calorimeter at 702 °C. The molten solvent was agitated by bubbling oxygen gas through it (8 ml/min) to facilitate dissolution and under this condition, all dissolved iron and manganese were in the trivalent state [16]. The resulting heat effect represents the drop solution enthalpy, ΔH_{ds} , and is equal to the heat content of the sample from 25 to 702 °C, the enthalpy of dissolution of oxides plus the enthalpy associated with the reduction of Mn^{4+} present in the samples to +3 valence states in the solvent. The calorimeter was calibrated using the known heat content of 5 mg Al_2O_3 pellets as a standard laboratory protocol.

3. Results

3.1. Structure and Composition

X-ray diffraction patterns of all annealed samples show single phase perovskites, with R-3c space group. Lattice parameters determined by a full-profile (Rietveld) refinement are shown in Table 1. The variation of molar volume with composition is presented in Fig. 1. The trend of molar volume dependence on Fe content for LS3MF series is in good agreement with results obtained by Kemik et al.²⁰ Comparing the three series of perovskites, the molar volume decreases with increasing Sr content because the average A–O bond length is shortened, the radius of Sr^{2+} being smaller than that of the host La^{3+} . Furthermore the oxidation of a part of Mn^{3+} to Mn^{4+} with smaller ionic radius accompanying strontium

substitution results in a decrease of the average ionic radius of the B-site cation and consequent lattice shrinkage. There appears to be an exception for the $(\text{La}_{0.7}\text{Sr}_{0.3})_{0.95}\text{Mn}_{0.3}\text{Fe}_{0.7}\text{O}_{2.89}$ sample which has a smaller molar volume than the corresponding sample in the LS3MF series (LS3MF7). This may occur because this sample has the highest concentration of oxygen vacancies, which could cause local structural distortions [19, 34]. Accordingly, the number of Mn^{4+} ions in the samples is fixed not only by the introduction of a given amount of Sr^{2+} into the structure, but also by the oxygen and A-site nonstoichiometry. Then, the observed decrease in the molar volume with the increasing Sr content for the A-site non-stoichiometric samples, at the same oxygen nonstoichiometry and Fe content, is linked to the difference in Mn^{4+} content.

Using iodometric titration, oxygen content was derived (Table 1). δ denotes the average number of vacant oxygen sites per nominal ABO_3 formula unit and is called the level of oxygen nonstoichiometry. The oxygen content in each sample depends on the doping level of Sr and nonstoichiometry in the A-site for $(\text{La}_{1-x}\text{Sr}_x)_{0.95}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ series. The perovskites with A-site cation deficiency have greater oxygen deficiency than the LS3MF series. The oxygen stoichiometry of studied samples imposes a formal valence for iron and manganese (B-site ions). It is assumed that in LSMF systems Fe^{4+} is not formed, taking into account that the enthalpy of oxidation for Mn is more exothermic than for Fe, therefore the oxidation of Mn^{3+} is favored over Fe^{3+} [20]. The valence state of the Fe^{3+} cation within the perovskite structure has been also confirmed in similar $\text{LaSr}(\text{MnFe})\text{O}_3$ manganites by Mössbauer spectroscopy [14].

In the LS3MF series, the contribution of oxygen vacancies to charge compensation increases by doping with 20 % Fe and then remains almost constant at higher iron content. In A-site nonstoichiometric perovskite samples, the formation of oxygen vacancies reaches a

maximum for $(\text{La}_{0.70}\text{Sr}_{0.30})_{0.95}\text{Mn}_{0.30}\text{Fe}_{0.70}\text{O}_{3-\delta}$. This is the only sample in the whole series for which about half (51 %) of the total defects is represented by oxygen vacancies.

3.2. Calorimetry

Enthalpies of drop solution (ΔH_{ds}) and the corresponding enthalpies of formation from oxides are summarized in Table 2. ΔH_{ds} for the reference phases, -228.26 ± 3.16 kJ/mol for La_2O_3 [35], 155.47 ± 1.13 kJ/mol for Mn_2O_3 [36], 96.8 ± 1.8 kJ/mol for Fe_2O_3 [37], -138.3 ± 2.48 kJ/mol for SrO [38], 124.92 ± 1.03 kJ/mol for MnO_2 [39], and 21.84 kJ/mol the heat content of oxygen from 25°C to 702°C , calculated by integrating the heat capacity over T : $C_p = 56.58 - 5.255 \cdot 10^{-3} T + 6.856 \cdot 10^{-5} T^2 - 578 T^{-0.5} + 1.113 \times 10^{-6} T^2$ J/(mol·K) [40], are taken from earlier works. Using the thermodynamic cycles below (Tables 3 and 4) the enthalpy of formation from binary oxides (Mn_2O_3 , Fe_2O_3 , La_2O_3 , SrO and O_2 gas) and oxygen for these perovskites at room temperature, $\Delta H_{\text{f,ox}}$, was calculated (Table 2). The exothermic formation enthalpies show the stability of each sample with respect to its component oxides. The thermodynamic cycles contain an exothermic contribution from an oxidation enthalpy, namely the incorporation of oxygen that converts Mn^{3+} to Mn^{4+} . Eliminating the enthalpy of oxidation by calculating the formation enthalpy from Mn_2O_3 , MnO_2 , Fe_2O_3 , La_2O_3 , SrO (thermodynamic cycles shown in Tables 5 and 6) results in values of $\Delta H_{\text{f,ox}}^*$, less exothermic than $\Delta H_{\text{f,ox}}$ (Table 2).

Fig. 2 shows that for the A site stoichiometric samples with $\text{Sr} = 0.3$, both $\Delta H_{\text{f,ox}}$ and $\Delta H_{\text{f,ox}}^*$ become less exothermic with increasing iron content, as noted previously by Kemik [20]. For these compositions a roughly linear trend in both $\Delta H_{\text{f,ox}}$ and $\Delta H_{\text{f,ox}}^*$ with iron content is seen and can be approximated by the following equations, values in kJ/mol.

For LS3MF nonstoichiometric series (our samples)

$$\Delta H_{\text{f,ox}} = (-97.68 \pm 1.41) + (11.50 \pm 3.20)y \quad (1)$$

$$\Delta H_{f,ox}^* = (-85.73 \pm 0.74) + (6.9 \pm 1.70)y \quad (2)$$

For the LS3MF series reported by Kemik [20]:

$$\Delta H_{f,ox} = (-99.20 \pm 0.73) + (13.5 \pm 1.60)y \quad (3)$$

Using our and Kemik's [20] points together:

$$\Delta H_{f,ox} = (-98.16 \pm 0.73) + (12.10 \pm 1.60)y \quad (4)$$

The scatter around the trends probably arises from the differences in oxygen stoichiometry. The A-site deficient samples are clearly less stable in enthalpy. Their variation with iron content appears to parallel that of the stoichiometric samples but there are not enough points for a meaningful fit.

Variation of enthalpy of formation with oxygen nonstoichiometry, δ , is shown in Fig.

3. Increasing oxygen deficiency clearly destabilizes the perovskites. The data for $x = 0.3$ (can be fit by a straight line, giving an enthalpy of oxygen incorporation of -199 ± 28 kJ per mole of oxygen vacancy or -398 ± 56 kJ per mole of O_2). The two sets of Sr-deficient samples have higher oxygen nonstoichiometry and less exothermic enthalpies of formation but there are too few points for accurate fitting of individual trends, although lines are shown to guide the eye.

4. Discussion

Upon substitution of strontium for lanthanum, the difference in ionic charge between Sr^{2+} and La^{3+} is compensated by creation of oxygen vacancies (Eq. 5) and/or internal oxidation of Mn^{3+} to Mn^{4+} (Eq. 6). These reactions together represent the charge balanced substitution that is related to the enthalpy of formation from oxides.

or, in Kroger - Vink notation

The oxidative substitution creating Mn^{4+} can be separated from the ionic substitution creating vacancies by noting that reaction (6) is the sum of reaction (5) and the reaction

or in Kroger - Vink notation

This imparts an oxygen fugacity dependence on reaction (5) and on the content of Mn^{4+} in the perovskite. We assume that Fe^{4+} is not significant in these perovskites at iron substitutions of less than 0.7, as argued by Kemik et al. [20]. Thus the major defects in the studied perovskites are A-site dopant and nonstoichiometry, Sr_{La}'' , V_{La}''' , oxygen vacancy, V_{O}'' , and Mn^{4+} , Mn_{Mn}' , where Kröger - Vink notation is used [41].

These results are supported by previously reported partial molar thermodynamic data of oxygen dissolution obtained by Tanasescu et al. [22,23] from electromotive force (EMF) measurements performed in the temperature range of use of these materials (700 - 1000 °C). The energy and entropy of O_2 in the oxide can be interpreted to describe the defect structure considering that the partial molar enthalpy of oxygen dissolution, $\Delta\bar{H}_{\text{O}_2}$ can be regarded as a measure of the binding strength of O^{2-} in the oxide and $\Delta\bar{S}_{\text{O}_2}$ as a measure of O^{2-} ordering. In Fig. 4, the partial molar enthalpy $\Delta\bar{H}_{\text{O}_2}$ and partial molar entropy $\Delta\bar{S}_{\text{O}_2}$ of oxygen collected from references [22] and [23] are shown as a function of iron content. At the same Sr content, Fe not only controls valence, but also appears to have strong interactions with the oxygen sublattice, leading to composition dependence in the partial molar enthalpy and entropy of

oxygen. These observations are in agreement with the variation of the oxidation enthalpy determined calorimetrically (Fig. 2) which tends to more endothermic values with increasing Fe content. However, for the compounds with A-site stoichiometry of 1.0, a maximum in the $\Delta\bar{H}_{O_2}$ is seen at 50 % iron, even though the difference between the enthalpy values for $y = 0.5$ and $y = 0.7$ is only $\sim 10 \text{ kJ mol}^{-1}$. At reduced A-site stoichiometry of 0.95, the values of $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ increase from 20 % iron to 70 % iron by $\sim 30 \text{ kJ mol}^{-1}$ and $\sim 45 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The same trend is found in the variation of the enthalpy of formation (Fig. 2). This behavior suggests that the energetically favorable long-range interactions between the charged defects that trap the oxygen vacancies become dominant at higher Fe doping, probably leading to changes in the extent of oxygen vacancy order. According to the EMF data, the effect of the decreased A-site stoichiometry at the same Sr content ($x = 0.3$) is the decrease of the dissolution enthalpy of oxygen. However, the increase of the $\Delta\bar{S}_{O_2}$ values suggests a change of order in the oxygen sublattice by the reduction in A-site stoichiometry.

These results clearly show that in LSMF materials the mechanism of charge compensation for the introduced Sr and Fe cations involves not only the oxidation of a fraction of M^{3+} to M^{4+} , but also the creation of oxygen vacancies, which leads to high concentrations of mobile electronic and ionic charge carriers at elevated temperatures ($>700^\circ\text{C}$).

In order to obtain the enthalpy related to variation in oxygen nonstoichiometry, δ , ΔH_δ [20,42], the enthalpies of formation from oxides, $\Delta H_{f, \text{ox}}$, for all samples are plotted vs. the oxygen deficiency (Fig. 3). If one combines all the data for the three systems, excluding the point at highest oxygen deficiency, a straight line with similar slope: $175 \pm 24 \text{ kJ per mole}$ of oxygen vacancy or $350 \pm 48 \text{ kJ per mole of O}_2$ (Fig. 3) is obtained. This suggests that

constant enthalpy of oxygen incorporation (Eq. 6) is a reasonable approximation for all these systems. This value is much more exothermic than that the $\text{Mn}^{3+}/\text{Mn}^{4+}$ oxidation enthalpy in the $\text{Mn}_2\text{O}_3 - \text{MnO}_2$ equilibrium, -168.1 kJ per mole of O_2 [40, 43, 44]. This difference is not surprising and confirms that substitution of large divalent cations in perovskites tends to stabilize higher transition metal oxidation states [45-47], and indeed these perovskites contain mainly Mn^{4+} to charge balance Sr^{2+} ($0 < \delta < 0.07$).

The enthalpy of oxygen incorporation can then be used to calculate the enthalpy of formation of samples in which all the manganese is trivalent, and the stoichiometry is charge balanced by vacancies. For all samples with $\text{La} + \text{Sr} = 1$ and with stoichiometry $\text{La}_{0.7}\text{Sr}_{0.3}\text{MO}_{2.85}$ ($\text{M} = \text{Fe}$ or Mn) the enthalpy of formation from La_2O_3 , SrO , Mn_2O_3 , and Fe_2O_3 is between -71 and -73 kJ/mol, with no clear dependence on iron content (Table 7). Taking -72 kJ/mol as a representative value, we can calculate the enthalpy of the reaction

with $\Delta H_{11} = \Delta H_f(\text{La}_{0.7}\text{Sr}_{0.3}\text{MO}_{2.85}) - \Delta H_f(\text{LaMO}_3)$. The enthalpy of formation from oxides of LaFeO_3 is -64.58 ± 3.32 kJ/mol [8, 35] and that of $\text{LaMnO}_{3.16}$ is -77.85 ± 1.95 kJ/mol [48]. Vradman and Navrotsky [48] argue that “ LaMnO_3 ” is in fact always slightly oxidized to $\text{LaMnO}_{3+\delta}$ and that variations in its measured heat of formation may reflect slightly different oxygen contents. They suggest that the enthalpy of oxidation is roughly -87 kJ per mol of excess O. similar to that of the oxidation of Mn_2O_3 to MnO_2 , and thus not reflecting stabilization of higher oxidation state by alkaline earth ions, which, in this case, are not present. Using this value one obtains the enthalpy of formation of stoichiometric LaMnO_3 of -63.9 kJ/mol, similar to that of LaFeO_3 . Thus the enthalpy of reaction 11 is estimated to be $-72 + 64 = -8$ kJ/mol, with no significant dependence on iron content and an uncertainty on the order of ± 10 kJ/mol when one propagates the individual errors. This suggests the charge

balanced vacancy forming substitution without manganese oxidation is energetically close to neutral, supporting the idea that oxygen vacancy formation in perovskites does not carry a large energetic penalty. We can associate this value with the enthalpy of reaction (7) as well. These calculations, though very approximate, clearly show that manganese oxidation in the presence of Sr substitution is the major stabilizing factor in these perovskites.

For samples which are cation deficient ($\text{La} + \text{Sr} = 0.95$), there are presumably cation vacancies as well as oxygen vacancies. We could not separate the effects of these two types of defects and did not analyze those data further. According to the EMF data, at the same Sr content ($x = 0.3$), for the $\text{Sr} + \text{La} = 0.95$ samples having greater oxygen deficiency, the dissolution enthalpy is smaller than that for $\text{Sr} + \text{La} = 1$.

5. Conclusions

A systematic separation of energetics of manganese oxidation from those of vacancy formation has been enabled by calorimetric measurements. The oxygen content in each sample depends on the doping level of Sr and nonstoichiometry in the A-site for the $(\text{La}_{1-x}\text{Sr}_x)_{0.95}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ series. In the A-site stoichiometric series, the contribution of oxygen vacancies to charge compensation increases by doping with 20 % Fe and then remains almost constant at higher iron content. $(\text{La}_{0.70}\text{Sr}_{0.30})_{0.95}\text{Mn}_{0.30}\text{Fe}_{0.70}\text{O}_{3-\delta}$ sample is the only one in the whole series for which about half (51 %) of the total defects is represented by oxygen vacancies. These perovskites contain mainly Mn^{4+} to charge balance Sr^{2+} ($0 < \delta < 0.07$). The charge balanced vacancy forming substitution without manganese oxidation is energetically close to neutral, supporting the idea that oxygen vacancy formation in perovskites does not carry a large energetic penalty.

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Table 1. Composition, oxygen deficiency, and lattice parameters of perovskites studied

Sample	Oxygen		Lattice			
	content,	Total cation weight %	parameters (Å)*			
	3-δ	Nominal	Measured (± two std dev.)	a	c	Molar volume (cm ³ /mol)
La _{0.70} Sr _{0.30} MnO _{3-δ}	3.00±0.01	78.80	78.50 ± 0.70	5.502	13.352	35.127
(La _{0.70} Sr _{0.30}) _{0.95} MnO _{3-δ}	2.93±0.01	78.61	78.80 ± 1.14	5.504	13.358	35.170
(La _{0.75} Sr _{0.25}) _{0.95} MnO _{3-δ}	2.93±0.01	78.84	-	5.516	13.363	35.336
La _{0.70} Sr _{0.30} Mn _{0.80} Fe _{0.20} O _{3-δ}	2.97±0.01	78.99	-	5.511	13.364	35.280
(La _{0.70} Sr _{0.30}) _{0.95} Mn _{0.80} Fe _{0.20} O _{3-δ}	2.92±0.01	78.68	78.90 ± 0.66	5.515	13.369	35.338
(La _{0.75} Sr _{0.25}) _{0.95} Mn _{0.80} Fe _{0.20} O _{3-δ}	2.92±0.01	78.92	-	5.525	13.376	35.492
La _{0.70} Sr _{0.30} Mn _{0.50} Fe _{0.50} O _{3-δ}	2.96±0.01	79.07	-	5.515	13.377	35.367
La _{0.70} Sr _{0.30} Mn _{0.30} Fe _{0.70} O _{3-δ}	2.96±0.01	79.09	-	5.493	13.545	35.521
(La _{0.70} Sr _{0.30}) _{0.95} Mn _{0.30} Fe _{0.70} O _{3-δ}	2.89±0.01	78.90	-	5.520	13.394	35.478

*The errors for a and c parameters are in the fourth decimal place.

Table 2. Thermochemical data for the $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ and $(\text{La}_{1-x}\text{Sr}_x)_{0.95}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ series

Sample	ΔH_{ds}	$\Delta H_{\text{f,ox}}$	$\Delta H_{\text{f,ox}}^*$
	(kJ/mol)	(kJ/mol)	(kJ/mol)
	calorimetry	calorimetry	calorimetry
$\text{La}_{0.70}\text{Sr}_{0.30}\text{MnO}_3$	58.33 ± 0.95 (8)*	-99.05 ± 1.73	-86.37 ± 1.71
$(\text{La}_{0.70}\text{Sr}_{0.30})_{0.95}\text{MnO}_{2.93}$	54.33 ± 1.18 (14)	-89.10 ± 1.82	-76.63 ± 1.80
$(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{MnO}_{2.93}$	50.57 ± 0.70 (9)	-84.50 ± 1.56	-74.03 ± 1.53
$\text{La}_{0.70}\text{Sr}_{0.30}\text{Mn}_{0.80}\text{Fe}_{0.20}\text{O}_{2.97}$	46.47 ± 0.96 (8)	-93.45 ± 1.71	-83.30 ± 1.70
$(\text{La}_{0.70}\text{Sr}_{0.30})_{0.95}\text{Mn}_{0.80}\text{Fe}_{0.20}\text{O}_{2.92}$	45.52 ± 0.79 (9)	-86.34 ± 1.57	-74.71 ± 1.56
$(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Mn}_{0.80}\text{Fe}_{0.20}\text{O}_{2.92}$	42.84 ± 0.72 (8)	-82.81 ± 1.54	-73.19 ± 1.52
$\text{La}_{0.70}\text{Sr}_{0.30}\text{Mn}_{0.50}\text{Fe}_{0.50}\text{O}_{2.96}$	35.95 ± 0.62 (11)	-91.94 ± 1.56	-82.64 ± 1.56
$\text{La}_{0.70}\text{Sr}_{0.30}\text{Mn}_{0.30}\text{Fe}_{0.70}\text{O}_{2.96}$	28.27 ± 0.77 (10)	-90.20 ± 1.67	-80.89 ± 1.68
$(\text{La}_{0.70}\text{Sr}_{0.30})_{0.95}\text{Mn}_{0.30}\text{Fe}_{0.70}\text{O}_{2.89}$	30.38 ± 0.60 (9)	-86.36 ± 1.55	-77.27 ± 1.55

For ΔH_{ds} , errors are two standard deviations of the mean. For ΔH_{f} , errors are propagated errors. Number in () is the number of calorimetric experiments performed, Uncertainties in partial molar enthalpies are estimated as 0.5 kJ/mol and in partial molar entropies as 1.5 J/mol K, with data from (22, 23)

Table 3. Thermochemical cycle for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($y = 0, 0.2, 0.5, 0.7$) series from La_2O_3 , SrO , Mn_2O_3 , Fe_2O_3 and oxygen at 25 °C ($\Delta H_{f,ox}$)

Reaction	ΔH
La_2O_3 (xl, 25 °C) $\rightarrow$ La_2O_3 (sol, 702 °C) ^a	$\Delta H (1) = \Delta H_{ds} (\text{La}_2\text{O}_3)$
Mn_2O_3 (xl, 25 °C) $\rightarrow$ Mn_2O_3 (sol, 702 °C)	$\Delta H (2) = \Delta H_{ds} (\text{Mn}_2\text{O}_3)$
Fe_2O_3 (xl, 25 °C) $\rightarrow$ Fe_2O_3 (sol, 702 °C)	$\Delta H (3) = \Delta H_{ds} (\text{Fe}_2\text{O}_3)$
SrO (xl, 25 °C) $\rightarrow$ SrO (sol, 702 °C)	$\Delta H (4) = \Delta H_{ds} (\text{SrO})$
O_2 (g, 25 °C) $\rightarrow$ O_2 (g, 702 °C)	$\Delta H (5) = \Delta H_{25-702} (\text{O}_2)^b$
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (xl, 25 °C) $\rightarrow$	$\Delta H (6) = \Delta H_{ds} (\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta})$
$0.35 \text{La}_2\text{O}_3$ (sol, 702 °C) + $\frac{1-y}{2} \text{Mn}_2\text{O}_3$ (sol, 702 °C) + 0.3	
SrO (sol, 702 °C) + $\frac{y}{2} \text{Fe}_2\text{O}_3$ (sol, 702 °C)	
+ $\frac{0.15-\delta}{2} \text{O}_2$ (g, 702 °C)	
$0.35 \text{La}_2\text{O}_3$ (xl, 25 °C) + $\frac{1-y}{2} \text{Mn}_2\text{O}_3$ (xl, 25 °C)	$\Delta H (7) = \Delta H_{f,ox} (\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta})$
+ 0.3 SrO (xl, 25 °C) + $\frac{y}{2} \text{Fe}_2\text{O}_3$ (xl, 25 °C) + $\frac{0.15-\delta}{2} \text{O}_2$	
(g, 25 °C) $\rightarrow$ $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (xl, 25 °C)	
$\Delta H (7) = 0.35 \Delta H (1) + \frac{1-y}{2} \Delta H (2) + \frac{y}{2} \Delta H (3) + 0.3 \Delta H (4) + \frac{0.15-\delta}{2} \Delta H (5) - \Delta H (6)$	

^axl = crystalline solid, g = gas, sol. = solution in Na_2MoO_4

^bHeat content of O_2 from 25 to 702 °C

Table 4. Thermochemical cycle for $(\text{La}_{1-x}\text{Sr}_x)_{0.95}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($x = 0.25, 0.3$; $y = 0, 0.2, 0.5, 0.7$) series from La_2O_3 , SrO , Mn_2O_3 , Fe_2O_3 and oxygen at 25 °C ($\Delta H_{f,ox}$)

Reaction	ΔH
La_2O_3 (xl, 25 °C) $\rightarrow$ La_2O_3 (sol, 702 °C) ^a	ΔH (1) = ΔH_{ds} (La_2O_3)
Mn_2O_3 (xl, 25 °C) $\rightarrow$ Mn_2O_3 (sol, 702 °C)	ΔH (2) = ΔH_{ds} (Mn_2O_3)
Fe_2O_3 (xl, 25 °C) $\rightarrow$ Fe_2O_3 (sol, 702 °C)	ΔH (3) = ΔH_{ds} (Fe_2O_3)
SrO (xl, 25 °C) $\rightarrow$ SrO (sol, 702 °C)	ΔH (4) = ΔH_{ds} (SrO)
O_2 (g, 25 °C) $\rightarrow$ O_2 (g, 702 °C)	ΔH (5) = ΔH_{25-702} (O_2) ^b
$(\text{La}_{1-x}\text{Sr}_x)_{0.95}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (xl, 25 °C) $\rightarrow$	ΔH (6) = ΔH_{ds} ($(\text{La}_{1-x}\text{Sr}_x)_{0.95}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$)
$\frac{(1-x)0.95}{2} \text{La}_2\text{O}_3$ (sol, 702 °C) + $\frac{1-y}{2} \text{Mn}_2\text{O}_3$ (sol, 702 °C) +	
$0.95x\text{SrO}$ (sol, 702 °C) + $\frac{y}{2} \text{Fe}_2\text{O}_3$ (sol, 702 °C)	
+ $\frac{0.075+0.475x-\delta}{2} \text{O}_2$ (g, 702 °C)	
La_2O_3 (xl, 25 °C) + $\frac{1-y}{2} \text{Mn}_2\text{O}_3$ (xl, 25 °C) + $0.95x \text{SrO}$	ΔH (7) = $\Delta H_{f, ox}$ ($(\text{La}_{1-x}\text{Sr}_x)_{0.95}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$)
(xl, 25 °C) + $\frac{y}{2} \text{Fe}_2\text{O}_3$ (xl, 25 °C) + $\frac{0.075+0.475x-\delta}{2} \text{O}_2$	
(g, 25 °C) $\rightarrow$ $(\text{La}_{1-x}\text{Sr}_x)_{0.95}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (xl, 25 °C)	
$\Delta H(7) = \frac{(1-x)0.95}{2} \Delta H(1) + \frac{1-y}{2} \Delta H(2) + \frac{y}{2} \Delta H(3) + 0.95x \Delta H(4) + \frac{0.075+0.475x-\delta}{2} \Delta H(5) - \Delta H(6)$	

^axl = crystalline solid, g = gas, sol. = solution in Na_2MoO_4

^bHeat content of O_2 from 25 to 702 °C

Table 5. Thermochemical cycle for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($y = 0, 0.2, 0.5, 0.7$) series from La_2O_3 , SrO , Mn_2O_3 , MnO_2 , and Fe_2O_3 ; reaction does not involve oxygen gas ($\Delta H_{f,ox}^*$)

<i>Reaction</i>	<i>ΔH</i>
$\text{La}_2\text{O}_3 (\text{xl}, 25^\circ\text{C}) \rightarrow \text{La}_2\text{O}_3 (\text{sol}, 702^\circ\text{C})^a$	$\Delta H (1) = \Delta H_{ds} (\text{La}_2\text{O}_3)$
$\text{Mn}_2\text{O}_3 (\text{xl}, 25^\circ\text{C}) \rightarrow \text{Mn}_2\text{O}_3 (\text{sol}, 702^\circ\text{C})$	$\Delta H (2) = \Delta H_{ds} (\text{Mn}_2\text{O}_3)$
$\text{Fe}_2\text{O}_3 (\text{xl}, 25^\circ\text{C}) \rightarrow \text{Fe}_2\text{O}_3 (\text{sol}, 702^\circ\text{C})$	$\Delta H (3) = \Delta H_{ds} (\text{Fe}_2\text{O}_3)$
$\text{SrO} (\text{xl}, 25^\circ\text{C}) \rightarrow \text{SrO} (\text{sol}, 702^\circ\text{C})$	$\Delta H (4) = \Delta H_{ds} (\text{SrO})$
$\text{MnO}_2 (\text{xl}, 25^\circ\text{C}) \rightarrow 0.5\text{Mn}_2\text{O}_3 (\text{sol}, 702^\circ\text{C}) + 0.25\text{O}_2 (\text{sol}, 702^\circ\text{C})$	$\Delta H (5) = \Delta H_{ds} (\text{MnO}_2)$
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta} (\text{xl}, 25^\circ\text{C}) \rightarrow$ $0.35 \text{La}_2\text{O}_3 (\text{sol}, 702^\circ\text{C}) + (0.7-y+2\delta)/2 \text{Mn}_2\text{O}_3 (\text{sol}, 702^\circ\text{C}) + 0.3$ $\text{SrO} (\text{sol}, 702^\circ\text{C}) + \frac{y}{2} \text{Fe}_2\text{O}_3 (\text{sol}, 702^\circ\text{C}) +$ $(0.3 - 2\delta) \text{MnO}_2 (\text{sol}, 702^\circ\text{C})$	$\Delta H (6) = \Delta H_{ds} (\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta})$
$0.35 \text{La}_2\text{O}_3 (\text{xl}, 25^\circ\text{C}) + (0.7-y+ 2\delta)/2 \text{Mn}_2\text{O}_3 (\text{xl}, 25^\circ\text{C})$ $+ 0.3 \text{SrO} (\text{xl}, 25^\circ\text{C}) + \frac{y}{2} \text{Fe}_2\text{O}_3 (\text{xl}, 25^\circ\text{C}) +$ $(0.3 - 2\delta) \text{MnO}_2 (\text{xl}, 25^\circ\text{C}) \rightarrow \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta} (\text{xl}, 25^\circ\text{C})$	$\Delta H (7) = \Delta H_{f,ox}^* (\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta})$
$\Delta H (7) = 0.35 \Delta H (1) + (0.7-y+ 2\delta)/2 \Delta H (2) + \frac{y}{2} \Delta H (3) + 0.3 \Delta H (4) + (0.3 - 2\delta) \Delta H (5) - \Delta H (6)$	

Table 6. Thermochemical cycle for $(\text{La}_{1-x}\text{Sr}_x)_{0.95}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($x = 0.25, 0.3; y = 0, 0.2, 0.5, 0.7$) series from La_2O_3 , SrO , Mn_2O_3 , MnO_2 , and Fe_2O_3 ; reaction does not involve oxygen gas ($\Delta H_{f,ox}^*$)

Reaction	ΔH
La_2O_3 (xl, 25 °C) $\rightarrow$ La_2O_3 (sol, 702 °C) ^a	$\Delta H (1) = \Delta H_{ds} (\text{La}_2\text{O}_3)$
Mn_2O_3 (xl, 25 °C) $\rightarrow$ Mn_2O_3 (sol, 702 °C)	$\Delta H (2) = \Delta H_{ds} (\text{Mn}_2\text{O}_3)$
Fe_2O_3 (xl, 25 °C) $\rightarrow$ Fe_2O_3 (sol, 702 °C)	$\Delta H (3) = \Delta H_{ds} (\text{Fe}_2\text{O}_3)$
SrO (xl, 25 °C) $\rightarrow$ SrO (sol, 702 °C)	$\Delta H (4) = \Delta H_{ds} (\text{SrO})$
MnO_2 (xl, 25 °C) $\rightarrow$ $0.5\text{Mn}_2\text{O}_3$ (sol, 702 °C)+ 0.25O_2 (sol, 702 °C)	$\Delta H (5) = \Delta H_{ds} (\text{MnO}_2)$
$(\text{La}_{1-x}\text{Sr}_x)_{0.95}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (xl, 25 °C) $\rightarrow$ $\frac{(1-x)0.95}{2}\text{La}_2\text{O}_3(\text{sol}, 702\text{ °C}) + (1 - y - x \cdot 0.95 + 2\delta - 0.15)/2$ Mn_2O_3 (sol, 702 °C) + $0.95x\text{SrO}$ (sol, 702 °C) + $\frac{y}{2}\text{Fe}_2\text{O}_3$ (sol, 702 °C) + $(x \cdot 0.95 - 2\delta + 0.15)\text{MnO}_2$ (sol, 702 °C)	$\Delta H (6) = \Delta H_{ds} (\text{La}_{1-x}\text{Sr}_x)_{0.95}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta})$
$\frac{(1-x)0.95}{2}\text{La}_2\text{O}_3$ (xl, 25 °C) + $(1 - y - x \cdot 0.95 + 2\delta - 0.15)/2$ Mn_2O_3 (xl, 25 °C) + $0.95x\text{SrO}$ (xl, 25 °C) + $\frac{y}{2}\text{Fe}_2\text{O}_3$ (xl, 25 °C) + $(x \cdot 0.95 - 2\delta + 0.15)\text{MnO}_2$ (xl, 25 °C) $\rightarrow$ $(\text{La}_{1-x}\text{Sr}_x)_{0.95}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (xl, 25 °C)	$\Delta H (7) = \Delta H_{f,ox}^* (\text{La}_{1-x}\text{Sr}_x)_{0.95}\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3-\delta})$
$\Delta H(7) = \frac{(1-x)0.95}{2} \Delta H(1) + (1 - y - x \cdot 0.95 + 2\delta - 0.15)/2 \Delta H(2) + \frac{y}{2} \Delta H(3) + 0.95x \Delta H(4) +$ $(x \cdot 0.95 - 2\delta + 0.15) \Delta H(5) - \Delta H(6)$	

Table 7. Calculated enthalpies of formation of perovskites, $\text{La}_{0.7}\text{Sr}_{0.3}\text{MO}_{2.85}$, containing no tetravalent manganese

Fe/(Fe+Mn)	ΔH_f (kJ/mol)
0	-72.8
0.2	-72.5
0.5	-72.2
0.7	-70.9

Figure captions

Fig. 1 Molar volume of the LS3MF, (LS3).95MF and (LS25).95MF solid solutions as a function of Fe/(Fe+Mn) ratio, y

Fig. 2 (a) $\Delta H_{f, ox}$ and **(b)** $\Delta H_{f, ox}^*$ vs. iron content, y

Fig.3 Enthalpy of formation, $\Delta H_{f, ox}$, of LS3MF, (LS3).95MF and (LS25).95MF perovskites from oxides vs. oxygen deficiency, δ . Solid lines represent fits to each set of data individually (not well constrained for Sr-poor samples. Dashed line represents fit to all but last (most oxygen deficient) point.

Fig. 4 (a) $\Delta \bar{H}_{O_2}$ as a function of iron content **(b)** $\Delta \bar{S}_{O_2}$ as a function of iron content

Fig. 1 Molar volume of the LS3MF, (LS3).95MF and (LS25).95MF solid solutions as a function of Fe/(Fe+Mn) ratio, y

Fig. 2 (a) $\Delta H_{f,ox}$ and (b) $\Delta H_{f,ox}^*$ vs. iron content, y .

Fig.3 Enthalpy of formation, $\Delta H_{f,ox}$, of LS3MF, (LS3).95MF and (LS25).95MF perovskites from oxides vs. oxygen deficiency, δ . Solid lines represent fits to each set of data individually (not well constrained for Sr-poor samples. Dashed line represents fit to all but last (most oxygen deficient) point.

Fig. 4 (a) $\Delta \bar{h}_{O_2}$ as a function of iron content (b) $\Delta \bar{s}_{O_2}$ as a function of iron content