



# Redox energetics of perovskite-related $\text{La}(\text{B}_{1-x}\text{B}'_x)\text{O}_{3-\delta}$ oxides where $\text{BB}'$ is FeCo, MnCo, MnNi and CoCu

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## ABSTRACT

The enthalpy of oxidation of  $\text{La}(\text{B}_{1-x}\text{B}'_x)\text{O}_{3-\delta}$  ( $x = 0.25$  and  $0.75$  for  $\text{BB}' \equiv \text{FeCo}$ ,  $\text{MnCo}$ ,  $\text{MnNi}$  and  $x = 0.2$  for  $\text{BB}' \equiv \text{CoCu}$ ) has been derived using solid solution models to analyse thermogravimetric measurements of oxygen non-stoichiometry vs.  $\log(p\text{O}_2)$  at 1273 K. For selected samples the enthalpy of oxidation has also been measured by TG-DSC, and the direct heat measurements agree well with the results from the solution models. The affinity for oxygen decreases when  $x$  in  $\text{La}(\text{B}_{1-x}\text{B}'_x)\text{O}_{3-\delta}$  increases from 0.25 to 0.75. This trend may be extended to a larger range of  $x$ -values ( $x \in [0,1]$ ) when isotherms from the literature are included in the solution modelling. For the materials investigated in this work, the affinity for oxygen decreases in the order  $\text{Mn}_{0.75}\text{Ni}_{0.25} > \text{Mn}_{0.75}\text{Co}_{0.25} > \text{Fe}_{0.75}\text{Co}_{0.25}$  (for  $x = 0.25$ ) and in the order  $\text{Mn}_{0.25}\text{Co}_{0.75} > \text{Fe}_{0.25}\text{Co}_{0.75} > \text{Mn}_{0.25}\text{Ni}_{0.75}$  (for  $x = 0.75$ ). The  $\text{Co}_{0.80}\text{Cu}_{0.20}$  containing material has the smallest affinity for oxygen among all the samples.

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## 1. Introduction

Many perovskite-related oxides show large variations in oxygen non-stoichiometry and defect concentrations and they have thus rich redox chemistry with variable oxidation states of the metal cations at the B-site in the  $\text{ABO}_{3-\delta}$  structure. The perovskites have many possible applications in e. g. electrolytes, membranes for gas separation, catalysts and in sensors [1] and in most applications the redox properties are important. A recent example [2,3] is the use of perovskite-related oxides as oxygen carrier materials in power production based on chemical looping combustion (CLC) [4]. Other examples are hydrogen production using membrane reactors or chemical looping reforming processes [3,5,6]. In these technologies the enthalpy of oxidation of the perovskite determines the heat balance of the process when the material is exposed to either the reducing fuel conditions or the oxidizing air conditions. The redox chemistry and the stability of the perovskites in reducing and oxidizing environments are thus important properties for a large number of applications. From systematic studies of the variation of enthalpy of oxidation with the composition of the perovskite, it should to a large extent be possible to predict the composition that is suitable for a certain process application.

In a previous report, trends in the enthalpy of oxidation (from  $\text{B}^{3+}$  to  $\text{B}^{4+}$ ) for the  $\text{La}_{1-x}\text{Ae}_x\text{BO}_{3-\delta}$  ( $\text{Ae} \equiv \text{Ca}$ ,  $\text{Sr}$  and  $\text{B} \equiv \text{Cr}$ ,  $\text{Mn}$ ,  $\text{Fe}$ ,  $\text{Co}$ ) systems have been derived by fitting solid solution models to non-

stoichiometry- $\log(p\text{O}_2)$  isotherms [7]. In the present work a similar approach is used to extract the enthalpy of oxidation from measured non-stoichiometry isotherms. For selected compositions the enthalpies of oxidation are also measured by TG-DSC.

In this work, the redox chemistry of  $\text{La}(\text{B}_{1-x}\text{B}'_x)\text{O}_{3-\delta}$  ( $x = 0.25$  and  $0.75$  for  $\text{BB}' \equiv \text{FeCo}$ ,  $\text{MnCo}$ ,  $\text{MnNi}$  and  $x = 0.2$  for  $\text{BB}' \equiv \text{CoCu}$ ) is investigated. For simplicity, these systems will be denoted by their  $\text{B}_{1-x}\text{B}'_x$  cations. The crystal structures at room temperature for the  $\text{Fe}_{1-x}\text{Co}_x$  [8,9],  $\text{Mn}_{1-x}\text{Co}_x$  [10,11] and  $\text{Mn}_{1-x}\text{Ni}_x$  [12] systems change from orthorhombic to hexagonal when  $x$  increases. The transitions occur at approximately  $x \sim 0.5$ , and the systems are single phases in the whole compositional range. The solid solution in the  $\text{Co}_{1-x}\text{Cu}_x$  system is limited to  $x \leq 0.2$ , and the crystal structure is hexagonal in the single phase region [13]. There is limited information about the redox properties of these mixed B-cation systems in the literature. However, for the  $\text{Fe}_{0.1}\text{Co}_{0.9}$  composition the oxygen non-stoichiometry vs.  $\log(p\text{O}_2)$  has been measured at 1273–1423 K and the standard, partial molar enthalpy and entropy of oxygen have been derived. [14]. TPR measurements show, as expected, that the  $\text{Fe}_{1-x}\text{Co}_x$  [9],  $\text{Mn}_{1-x}\text{Ni}_x$  [15] and  $\text{Co}_{1-x}\text{Cu}_x$  [16] materials are more easily reduced when  $x$  increases.

## 2. Experimental

### 2.1. Synthesis

Ceramic powders of  $\text{La}(\text{B}_{1-x}\text{B}'_x)\text{O}_{3-\delta}$  were synthesized using a method derived from the complexation-polymerization route known as the Pechini method [17]. Nitrate salts were used as starting agents, citric acid as a complexing agent and ethylene glycol for polymerization.

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**Table 1**

Nitrate salts used for powder synthesis. The cation contents in the salts were obtained by thermogravimetric standardizations.

Nitrate salt	Provider	Purity	mmol cation/g salt
La(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	Merck	≥99	2.309
Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	Fluka	≥99	2.475
Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Fluka	≥98	3.436
Mn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	Merck	≥98.5	3.984
Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Merck	≥99	3.439
Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	Merck	≥99.5	4.125

Nitrate salts of La, Fe, Co, Mn and Ni were standardized by thermal decomposition to the respective oxides (La<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub> and NiO) at 973 or 1073 K for 6 h in ambient air. The copper nitrate was standardized by reducing the salt to metallic Cu at 873 K in a gas mixture of 5% hydrogen and 95% argon. The nitrate salts with standardized cation content are listed in Table 1.

For each synthesis, the standardized nitrate salts were dissolved in RO-water (18 MΩ) in stoichiometric ratios at a concentration of ~0.5 M. After stirring for ~30 min citric acid (Sigma-Aldrich, ≥99.5%) was added in a molar ratio (citric acid:cation) of 1.1:1. After mixing for additional 60 min (or more) ethylene glycol (Aldrich, 99.8%) was added in a molar ratio of 1:1 with respect to citric acid.

The solutions were heated to 393 K under stirring for 60 min and further evaporated to form dry polymeric gels. Upon heating to 473–523 K self-ignition occurred and the gels decomposed in a smoldering process. The volatility varied for the different compositions. The dried gels were pre-calcined at 673 K, gently crushed in a mortar before further calcinations/annealing at 1073–1273 K for 6 h in ambient air. The resulting powders were analyzed by X-ray diffraction (XRD) (Siemens D5000) with Cu K<sub>α</sub> radiation through a primary monochromator to determine crystal structure and phase purity. XRD of the synthesized powders of Fe<sub>0.75</sub>Co<sub>0.25</sub>, Fe<sub>0.25</sub>Co<sub>0.75</sub>, Mn<sub>0.75</sub>Co<sub>0.25</sub>, Mn<sub>0.25</sub>Co<sub>0.75</sub> and Mn<sub>0.75</sub>Ni<sub>0.25</sub> identified single phase perovskite structures after annealing at 1073 K. XRD of the powder of Co<sub>0.8</sub>Cu<sub>0.2</sub> indicated presence of a secondary phase after annealing at 1073 K, however, single phase perovskite structure was obtained after annealing at 1273 K. For the Mn<sub>0.25</sub>Ni<sub>0.75</sub> sample traces (<1%) of NiO was detected by XRD after annealing at 1273 K, and the impurity was not removed by annealing at an even higher (1373 K) temperature. The obtained unit cell dimensions of the synthesized samples are in fairly good agreement with literature data, see Table 2.

## 2.2. Thermogravimetry

The oxygen non-stoichiometry vs. log(*p*O<sub>2</sub>) at 1273 K was measured by a SETARAM Setsys Evolution TGA with an in-house gas

**Table 2**

Unit cell dimensions and crystal structure (O≡orthorhombic, H≡hexagonal) for La(B<sub>1-x</sub>B'<sub>x</sub>)O<sub>3-δ</sub> (x=0.25, 0.75 for BB'≡FeCo, MnCo, MnNi and x=0.2 for BB'≡CoCu).

Sample	Crystal structure	a/Å	b/Å	c/Å	Reference
Fe <sub>0.75</sub> Co <sub>0.25</sub>	O	5.511(4)	7.784(5)	5.48(1)	This study
Fe <sub>0.75</sub> Co <sub>0.25</sub> *	O	5.46	7.76	5.43	[18]
Fe <sub>0.25</sub> Co <sub>0.75</sub>	H	5.452(2)	–	13.147(6)	This study
Fe <sub>0.25</sub> Co <sub>0.75</sub> *	H	5.45	–	13.12	[18]
Mn <sub>0.75</sub> Co <sub>0.25</sub>	O	5.460(4)	5.519(2)	7.770(2)	This study
Mn <sub>0.75</sub> Co <sub>0.25</sub> *	O	5.533	5.518	7.805	[10]
Mn <sub>0.25</sub> Co <sub>0.75</sub>	H	5.469(3)	–	13.151(8)	This study
Mn <sub>0.25</sub> Co <sub>0.75</sub> *	H	5.475	–	13.163	[10]
Mn <sub>0.75</sub> Ni <sub>0.25</sub>	O	5.57(3)	5.523(8)	7.775(5)	This study
Mn <sub>0.75</sub> Ni <sub>0.25</sub>	O	5.531	5.504	7.792	[12]
Mn <sub>0.25</sub> Ni <sub>0.75</sub>	H	5.49(1)	–	13.23(6)	This study
Mn <sub>0.25</sub> Ni <sub>0.75</sub>	H	5.480	–	13.198	[12]
Co <sub>0.8</sub> Cu <sub>0.2</sub>	H	5.471(1)	–	13.131(4)	This study
Co <sub>0.8</sub> Cu <sub>0.2</sub>	H	5.451	–	13.09	[13]

\* Cell parameters are obtained by interpolation between experimental results.

mixing system for O<sub>2</sub>(g), N<sub>2</sub>(g), CO<sub>2</sub>(g) and H<sub>2</sub>(g). A set of Bronkhorst [19] mass flow controllers were used to feed the gases. Mixtures of O<sub>2</sub>(g) with N<sub>2</sub>(g) were used in the log(*p*O<sub>2</sub>) range from 0 to approximately –5, and mixtures of H<sub>2</sub>(g), CO<sub>2</sub>(g) and N<sub>2</sub>(g) were used in the reducing conditions from log(*p*O<sub>2</sub>)≈–5 to –20. The *p*O<sub>2</sub> was measured in-situ using an oxygen sensor from Econox [20] that was fitted into the TGA furnace. The absolute stoichiometries of the samples were determined by decomposing the compounds to products with known compositions at 1273 K.

The samples were re-oxidized in-situ in the TGA after the last non-stoichiometry measurement, and characterization by XRD at room temperature gave single phase perovskite-type materials (except for the Mn<sub>0.25</sub>Ni<sub>0.75</sub> compound with traces of NiO from the synthesis). The samples were not cooled down in reducing atmosphere in the TGA since the TGA has platinum parts that do not tolerate H<sub>2</sub>(g) at low temperature. A new experimental set-up is thus under construction to study phase relations at high defect concentrations where the perovskites may start to decompose. The results will be presented in a future contribution.

## 2.3. TG-DSC measurements

Measurements of the enthalpies of oxidation at 1273 K were performed using a SETARAM Setsys Evolution TGA with a combined TG-DSC set-up (DSC rod S60/37334). Gas mixtures were introduced using an in-house gas-mixing system (different from the TGA gas mixing system previously described) with computer controlled valco valves [21] to perform rapid changes between the reducing and oxidizing gases. In all the experiments the total gas flow was kept constant at 200 ml min<sup>-1</sup>. The enthalpies of oxidation were measured using sample masses of typically 50 mg, placed on top of 20 mg Al<sub>2</sub>O<sub>3</sub> powder in a Pt sample container. In general, the measurement was performed as follows: 1) heating the sample to 1273 K in air, 2) flushing with Ar, 3) reducing the sample, 4) flushing with Ar and finally 5) exposing the sample to oxidizing conditions. Both the heat release and the weight change were monitored when the sample was oxidized. The heats of oxidation of the La(B<sub>1-x</sub>B'<sub>x</sub>)O<sub>3-δ</sub> samples were measured for low oxygen vacancy concentrations (3–δ close to 3), and the relevant *p*O<sub>2</sub> ranges for each experiment were taken from the isotherm data measured by the TGA, see above. The gas mixtures used for reduction and oxidation were therefore varied from one sample to another. Blank experiments with only Al<sub>2</sub>O<sub>3</sub> powder in the sample holder were performed to subtract the weight change caused by the buoyancy effect for all the gas mixtures used for the oxidation. Certain oxygen pressures are difficult to obtain and the heats of oxidation for the Mn<sub>0.25</sub>Co<sub>0.75</sub> and the Mn<sub>0.75</sub>Ni<sub>0.25</sub> samples could not be measured due to limitations in the present gas mixing system.

The TG-DSC set-up was heat calibrated by means of earlier reported enthalpies of melting of metals [22] with melting points that covered the temperature range of interest. Ag (T<sub>fus</sub> = 1234.93 K) and Au (T<sub>fus</sub> = 1337.33 K) were chosen for this purpose. The metal was placed on top of 20 mg Al<sub>2</sub>O<sub>3</sub> in a Pt crucible to mimic the procedure used for the perovskite samples. The masses of the metals were adjusted so that the heat consumption matched the heat liberation caused by the oxidations of the perovskites. At least three experiments for each metal were performed. The oxidation of the perovskite is an exothermic process as opposed to melting of a metal which consumes heat. Since it is not ideal to use an endothermic process for calibration of an exothermic process, the calibration of the instrument was validated by measuring the enthalpies of oxidation of CaMnO<sub>3-δ</sub> and SrFeO<sub>3-δ</sub> and comparing with already reported values. The obtained values for CaMnO<sub>3-δ</sub> and SrFeO<sub>3-δ</sub> (–295 ± 6 and –157 ± 20 kJ/(mol O<sub>2</sub>)<sup>-1</sup>, respectively) agree well with the reported values (–327 ± 15 [23], –325 ± 11 and –356 ± 7 kJ/(mol O<sub>2</sub>)<sup>-1</sup> [24] for CaMnO<sub>3-δ</sub> and –160 [25] and –140 ± 20 kJ/(mol O<sub>2</sub>)<sup>-1</sup> [26] for SrFeO<sub>3-δ</sub>).

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