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Oxygen non-stoichiometry determination of perovskite materials by a carbonation process

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ABSTRACT

A new and easy method is developed to determine the oxygen non-stoichiometry of perovskite materials under equilibrium conditions. The method is based on the complete decomposition of the powder to stoichiometric metal oxides and/or metal carbonates by using CO_2 as reacting gas. The oxygen non-stoichiometry is calculated from the mass change caused by this reaction. Its applicability is demonstrated by using $SrCoO_{3-\delta}$, $BaCoO_{3-\delta}$, $BaFeO_{3-\delta}$ and $BaCeO_{3-\delta}$ as representative materials. The oxygen non-stoichiometry (δ) values at 950 °C in air were determined as 0.48, 0.36, 0.43 and 0.03 respectively. These values can be used as reference points for oxygen non-stoichiometry analysis at other temperatures.

1. Introduction

An important issue in defect chemistry is the study of the oxygen non-stoichiometry of metal oxides, especially for materials with high oxygen deficiency [1–3]. Examples are several perovskite systems with general formula $ABO_{3-\delta}$, where δ represents the oxygen non-stoichiometry value. Several methods are developed to measure this oxygen non-stoichiometry as function of temperature and oxygen partial pressure [4]. All these methods are based on the analysis of the change in oxygen non-stoichiometry Δ(δ) as function of temperature or oxygen partial pressure, which are briefly reviewed as the following.

For the measurement of Δ(δ) thermal gravimetric analysis (TGA) is the most popular and frequently used method [5]. In this method it is assumed that the only reason for mass change is the release or incorporation of oxygen at varying temperatures or oxygen partial pressures. The mass change of the sample can then easily be converted to Δ(δ). Another technique to measure Δ(δ) is coulometric titration [4], where samples are placed in a sealed vessel made from yttria-stabilized zirconia (YSZ). One part of the YSZ (connected with electrolytes) is used as an oxygen pump, while another separate part is used as oxygen sensor. A defined amount of oxygen is pumped out/in quantitatively by applying a fixed electrical potential over the pump part of the vessel. The change in oxygen partial pressure in the vessel is not only related to the amount of oxygen removed by pumping, because oxygen is also released from the powder sample during pumping. From the difference between the measured oxygen partial pressure in the vessel and the amount of oxygen pumped out Δ(δ) can be calculated. A method similar to coulometric titration is solid electrolyte coulometry (SEC). The difference however is that in the latter case the experiment can be done in open systems or in a gas flowing mode. Details can be found in Teske, Bode and Vashook's work [6–8].

It should be mentioned that in order to determine the absolute oxygen non-stoichiometry for both the TGA and the coulometric titration method, an absolute value of δ at a fixed temperature and oxygen partial pressure is necessary (called reference point). A traditional way to obtain such a reference point is iodometric titration [9]. Here samples are dissolved in HCl with the presence of an excess of KI and heated in an oxygen-free (nitrogen) environment. During this process, the transition metal ions (such as Co^{3+}, Co^{4+}, Fe^{3+}, and Fe^{4+}) were reduced, and I^- was oxidized to I_2. The amount of I_2 released is quantitatively determined by redox titration using $Na_2S_2O_3$ as the titrant agent. The oxygen non-stoichiometry was calculated based on the amount of I_2 formed. Another way to measure the reference point is hydrogen reduction [10], by making use of the phenomenon that at elevated temperatures (~700 °C) several cations in oxides will react with hydrogen to the metallic state or to the metal oxides, and the absolute content of oxygen in these oxides is determined by monitoring the mass loss of the sample in a hydrogen containing gas with a TGA setup, while the final products are determined by X-ray diffraction (XRD).

In this paper a new and convenient method is reported to measure the absolute oxygen content (3−δ) of perovskite materials at a thermodynamic equilibrium state. Since several metal oxides, especially perovskite structured oxides, contain alkaline earth metals, which are very sensitive to CO_2, these materials easily decompose at elevated temperature in a CO_2 containing atmosphere [11]. After complete reaction and obtaining stoichiometric products the oxygen non-stoichiometry can easily be calculated. To demonstrate this method, $SrCoO_{3-\delta}$, $BaCoO_{3-\delta}$, $BaFeO_{3-\delta}$ and $BaCeO_{3-\delta}$ were chosen as representative materials in

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this study, because of their relative simple compositions, while products after reaction with CO_2 can easily be identified. However, it is expected that this method can also successfully be applied for other perovskite materials with well-defined reaction products.

2. Experimental

$SrCoO_{3-\delta}$, $BaCoO_{3-\delta}$, $BaFeO_{3-\delta}$ and $BaCeO_{3-\delta}$ were synthesized using an EDTA complexation/pyrolysis process as described in detail in [12]. In this work metal nitrates were dissolved in demineralized water under stirring at a stoichiometric ratio. EDTA, dissolved in ammonia, was added and after chelating for several minutes citric acid was added. The molar ratio of total metal ions: citric acid: EDTA was 1.0:1.5:1.0. The pH value of the solution was adjusted to 6 by adding ammonia. Subsequently NH_4NO_3 was added as an ignition aid at an amount of 100 g NH_4NO_3 per 0.1 mol of metal ions. This final solution was heated at 120–150 °C under stirring to evaporate water until it changed into a viscous gel, which was transferred to a stainless steel vessel and heated on a hot plate at a temperature of around 500 °C, while a vigorous combustion took place, resulting in a fluffy powder. The powder was collected and calcined in a room furnace at 950 °C for 5 h at a heating and cooling rate of 3 °C/min.

Isothermal gravimetric analyses were carried out on a Netzsch TG 449 F3 Jupiter®. About 20 mg of powder was weighed in an alumina crucible and placed in the TGA setup. The temperature was increased to 950 °C in flowing air (79 ml/min N_2 and 21 ml/min O_2) at a heating rate of 10 °C/min. The system was isothermally held in air at 950 °C for 1 h in order to reach a steady equilibrium state, indicated by a constant mass of the sample at this holding. Subsequently the gas was switched to a CO_2/N_2 mixture (80 ml/min CO_2 and 20 ml/min N_2; N_2 is used as protective gas for the setup). After completion of the reaction between powder and CO_2 (when no mass change was observed), the system was cooled to room temperature in the same CO_2/N_2 mixture at a cooling rate of 10 °C/min. All TGA experiments were based on a correction file measured with a blank crucible to exclude background data. After TGA measurements the samples were ground with a mortar and the phase composition was analyzed by X-ray diffraction (Bruker D2 PHASER with Cu K_α radiation, accelerate voltage 30 KV, current 10 mA, step size 0.02, time per step 1 s). For comparison the X-ray diffraction patterns of freshly synthesized powders (after calcination) were analyzed as well.

After obtaining the oxygen non-stoichiometry value (δ) in air at 950 °C the values of δ at other temperatures were determined by simple TGA experiments in air. In these experiments the temperature was stepwise increased from 550 °C to 950 °C in flowing air (79 ml/min N_2 and 21 ml/min O_2) and held at intervals of 100 °C. Based on the reference point at 950 °C, oxygen non-stoichiometry at other temperatures was calculated.

3. Results

Isothermal gravimetric analysis is a convenient way to study quantitatively the reaction between perovskite materials and CO_2 [13], and the results are given in Fig. 1. It can be seen that the reactions are very fast for all four materials, resulting in a final increase in weight of respectively 119.04%, 114.18%, 108.92% and 113.67%. In order to make sure that the reactions were completely finished, the systems were held for a longer time at 950 °C before cooling. During this cooling procedure in the same CO_2/N_2 atmosphere no mass change was observed.

The phase composition of powder samples before and after TGA experiments was examined by X-ray diffraction and the results are shown in Fig. 2. From this figure it can be seen that the characteristic peaks of the perovskite materials were not present any more after CO_2 exposure, indicating that the decomposition reaction is complete. By indexing the XRD patterns of CO_2-treated powders, products of the carbonation reactions can be determined. Tables 1–4 summarize the XRD data to prove the degree of matching of the XRD signals of standard materials with those of the products after reaction. In these tables only characteristic peaks are given, however full indexing of the XRD data was performed in this work. From these data it is concluded that the diffraction angles (2θ) match very well. The slight deviations in intensities for some signals might be caused by the overlap of different peaks for the products obtained after the decomposition reaction. For example, in the case of $SrCoO_{3-\delta}$ after reaction with CO_2 (Fig. 2c), the characteristic peaks of CoO (111) and $SrCO_3$ (112) are so close to

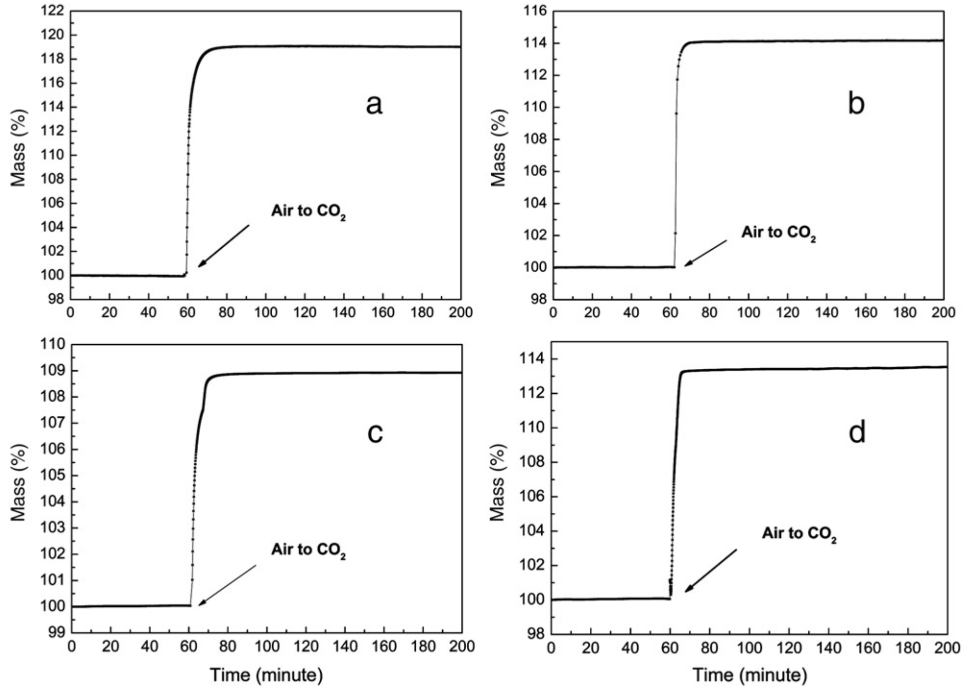

Fig. 1. Normalized plot of mass change of (a) $SrCoO_{3-\delta}$, (b) $BaCoO_{3-\delta}$, (c) $BaFeO_{3-\delta}$ and (d) $BaCeO_{3-\delta}$ in air/CO_2 at 950 °C.

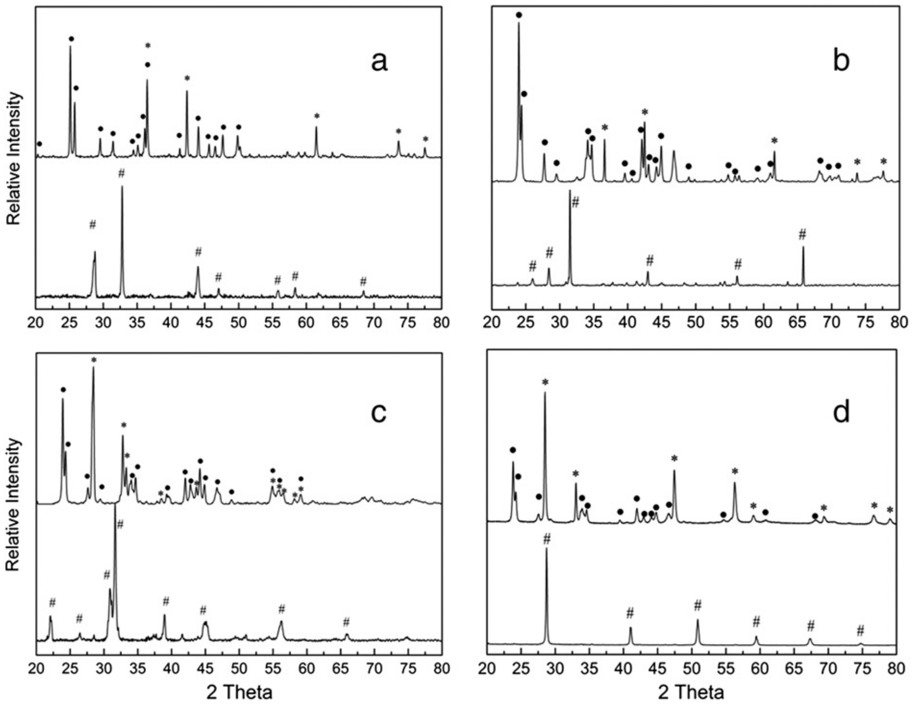

Fig. 2. X-ray diffraction pattern of (a) $SrCoO_{3-\delta}$, (b) $BaCoO_{3-\delta}$, (c) $BaFeO_{3-\delta}$ and (d) $BaCeO_{3-\delta}$ before (lower) and after (upper) CO_2 treatment at 950 °C. #: As prepared samples; ● in (a): $SrCO_3$; ● in (b–d):$BaCO_3$; * in (a–d): CoO, CoO, $BaFe_2O_4$, and CeO_2.

each other that it is impossible to separate them, which makes the intensity of CoO (111) even higher than that of CoO (200) (see Table 1).

According to the XRD results, the reactions between $SrCoO_{3-\delta}$, $BaCoO_{3-\delta}$, $BaFeO_{3-\delta}$, $BaCeO_{3-\delta}$ and CO_2 at 950 °C can be described as follow:

$$SrCoO_{3-\delta}+CO_2\rightarrow SrCO_3+CoO+\frac{1-\delta}{2}O_2 \tag{1}$$

$$BaCoO_{3-\delta}+CO_2\rightarrow BaCO_3+CoO+\frac{1-\delta}{2}O_2 \tag{2}$$

$$2BaFeO_{3-\delta}+CO_2\rightarrow BaFe_2O_4+BaCO_3+\frac{1-2\delta}{2}O_2 \tag{3}$$

$$BaCeO_{3-\delta}+CO_2\rightarrow BaCO_3+CeO_2-\frac{\delta}{2}O_2 \tag{4}$$

As shown by XRD, in our case the products (CoO, $SrCO_3$, $BaCO_3$, CeO_2 and $BaFe_2O_4$) are stoichiometric and the reactions are complete. The following equation, describing the mass change during the reaction, can then be established:

$$\frac{m_1}{MW_{ABCoO_{3-\delta}}}=\frac{m_2}{MW_{ss}} \tag{5}$$

Where m_1 and $MW_{ABO3-\delta}$ represent the mass and molecular weight before reaction with CO_2; m_2 and MW_{SS} are the mass and the sum of the molecular weights of the products after reaction. For example, MW_{SS} for reaction (1) is the sum of mole weight of $SrCO_3$ and CoO. Since MW_{SS} is known and m_1 and m_2 can be determined from the TGA results, the molecular weight of $ABO_{3-\delta}$ can be calculated according to Eq. (5) and subsequently the oxygen non-stoichiometry (δ) is determined to be 0.48, 0.36, 0.43 and 0.03 for $SrCoO_{3-\delta}$, $BaCoO_{3-\delta}$, $BaFeO_{3-\delta}$ and $BaCeO_{3-\delta}$ respectively, which is in agreement with literature [14–16].

Table 1
Comparison of XRD patterns of $SrCoO_{3-\delta}$ after reaction with CO_2 at 950 °C with standard XRD peaks (Cu Kα radiation).

Materials	XRD peaks (2θ)	Normalized peak intensity (Area, %)	Characteristic peaks for pure material (2θ)	Peak intensity for pure material (%)	(h k l)
			ICDD PDF No.: 78-0431		
CoO	36.51	117	36.49	68	(111)
	42.40	100	42.38	100	(200)
	61.50	56	61.49	45	(220)
	73.65	35	73.66	16	(311)
	77.55	25	77.52	11	(222)
			ICDD PDF No.: 05-0418		
$SrCO_3$	25.16	100	25.17	100	(111)
	25.80	46	25.80	70	(021)
	36.17	35	36.18	34	(112)
	36.51	75	36.53	40	(130)
	44.09	24	44.08	50	(221)
	47.69	20	47.69	35	(132)
	49.89	34	49.92	31	(113)

Table 2
Comparison of XRD patterns of $BaCoO_{3-\delta}$ after reaction with CO_2 at 950 °C with standard XRD peaks (Cu Kα radiation).

Materials	XRD peaks (2θ)	Normalized peak intensity (Area, %)	Characteristic peaks for pure material (2θ)	Peak intensity for pure material (%)	(h k l)
			ICDD PDF No.: 78-0431		
CoO	36.59	54	36.49	68	(111)
	42.49	100	42.38	100	(200)
	61.58	54	61.49	45	(220)
	73.75	19	73.66	16	(311)
	77.61	27	77.52	11	(222)
			ICDD PDF No.: 71-2394		
$BaCO_3$	23.98	100	23.90	100	(111)
	24.39	48	24.31	52	(021)
	34.13	25	34.10	21	(112)
	34.70	23	34.61	25	(130)
	42.09	27	42.00	28	(221)
	44.94	22	44.92	23	(132)
	46.78	19	46.80	18	(113)

Table 3
Comparison of XRD patterns of $BaFeO_{3-\delta}$ after reaction with CO_2 at 950 °C with standard XRD peaks (Cu Kα radiation).

Materials	XRD peaks (2θ)	Normalized peak intensity (Area, %)	Characteristic peaks for pure material (2θ)	Peak intensity for pure material (%)	(h k l)
			ICDD PDF No.: 25-1191		
$BaFe_2O_4$	28.27	99	28.22	54	(402)
	28.47	100	28.41	100	(212)
	32.79	80	32.70	56	(610)
	33.32	38	33.22	27	(020)
	44.19	50	44.12	21	(422)
			ICDD PDF No.: 71-2394		
$BaCO_3$	23.90	100	23.90	100	(111)
	24.33	57	24.31	52	(021)
	34.05	28	34.10	21	(112)
	34.64	19	34.61	25	(130)
	42.03	27	42.00	28	(221)
	44.88	22	44.92	23	(132)
	46.70	31	46.80	18	(113)

Based on the reference point measured at 950 °C in air, oxygen non-stoichiometry (δ) at other temperatures can be acquired according to Eq. (6).

$$\frac{m_T}{MW_T} = \frac{m_{950}}{MW_{950}} \tag{6}$$

Where m_T and MW_T represent the mass and molecular weight of $ABO_{3-\delta}$ at temperature T, m_{950} and MW_{950} are the mass and molecular weight at 950 °C. In this study, the temperature was stepwise increased to 950 °C in air, and at each measuring point (550 °C, 650 °C, 750 °C, 850 °C, and 950 °C) the temperature was kept constant until a steady state was reached. The results, as given in Fig. 3, clearly indicate that equilibrium was really obtained during these holding temperatures as no weight loss is observed prior to the next heating step. The oxygen non-stoichiometry was calculated according to Eq. (6) and results are shown in Fig. 4. For $BaCeO_{3-\delta}$, due to extremely small mass change during heating, we could not do the same analysis as above with our equipment, so the result for $BaCeO_{3-\delta}$ was not given in this study.

4. Discussion

The principle of this method is similar to the hydrogen reduction method, because in both cases the perovskite materials react with a sweeping gas resulting in stoichiometric products, subsequently the oxygen non-stoichiometry is calculated from the mass change. However, the reaction mechanism is completely different, one is reduction and

Table 4
Comparison of XRD patterns of $BaCeO_{3-\delta}$ after reaction with CO_2 at 950 °C with standard XRD peaks (Cu Kα radiation).

Materials	XRD peaks (2θ)	Normalized peak intensity (Area, %)	Characteristic peaks for pure material (2θ)	Peak intensity for pure material (%)	(h k l)
			ICDD PDF No.: 43-1002		
CeO_2	28.55	100	28.55	100	(111)
	33.08	26	33.08	27	(200)
	47.49	53	47.48	46	(220)
	56.33	48	56.34	34	(311)
	76.66	15	76.70	12	(331)
			ICDD PDF No.: 71-2394		
$BaCO_3$	23.89	100	23.90	100	(111)
	24.27	73	24.31	52	(021)
	34.02	35	34.10	21	(112)
	34.68	15	34.61	25	(130)
	42.01	21	42.00	28	(221)
	44.95	20	44.92	23	(132)
	46.65	17	46.80	18	(113)

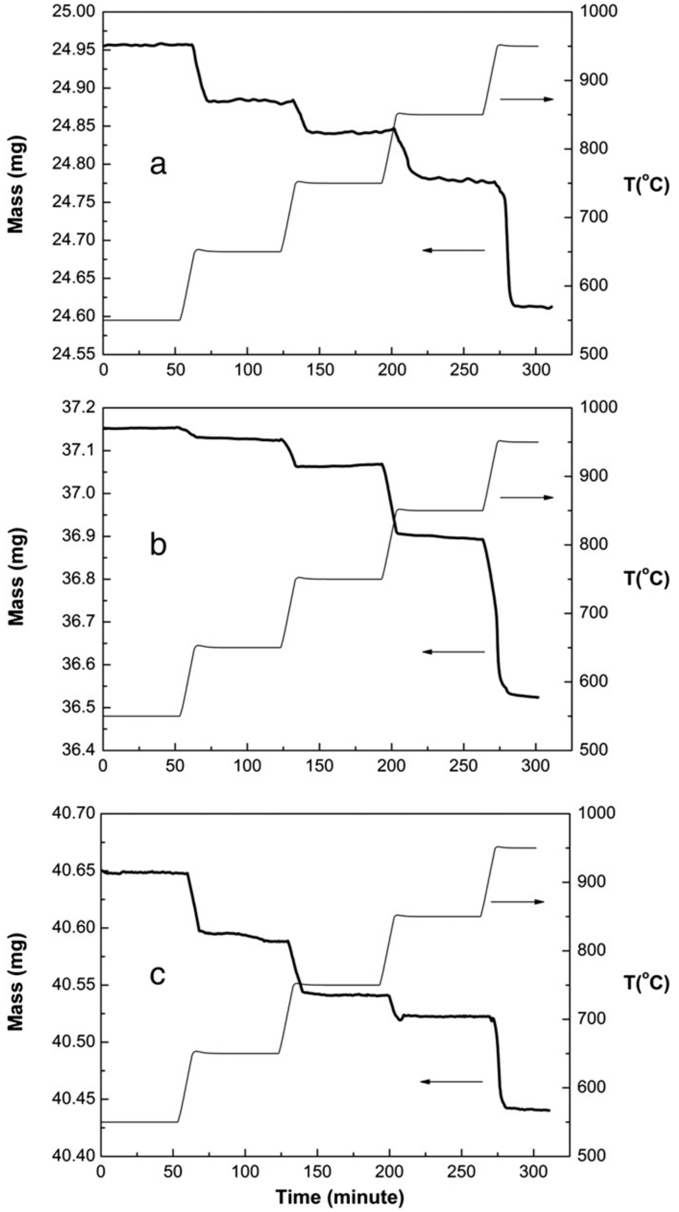

Fig. 3. Mass change of powder sample in air as function of temperature; (a) $SrCoO_{3-\delta}$, (b) $BaCoO_{3-\delta}$ and (c) $BaFeO_{3-\delta}$.

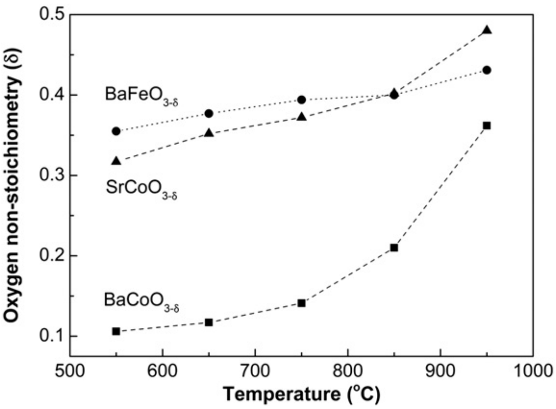

Fig. 4. Temperature dependence of oxygen non-stoichiometry (δ) in $SrCoO_{3-\delta}$ (▲), $BaCoO_{3-\delta}$ (■) and $BaFeO_{3-\delta}$ (●) in air. Dashed lines are guides to the eye.

another one is carbonation. Due to this difference, some materials that do not react with CO_2 may react with hydrogen, and some materials that do not react with hydrogen may react with CO_2, which gives the idea that we can choose an appropriate method for a certain material. For example, $BaCeO_{3-\delta}$ is a well-known perovskite material for hydrogen separation and it is very stable in hydrogen containing atmosphere, indicating that we cannot use hydrogen reduction method to determine its oxygen non-stoichiometry, however this material is very sensitive to CO_2 and we can analyze the oxygen non-stoichiometry by CO_2 method.

An accurate analysis of the phase composition of the reaction products is of great importance, which in this work was examined by room-temperature XRD. It should be pointed out that there might be some phase transitions during the cooling process, meaning that the phase composition at 950 °C could be different. However, as in this work no mass change was observed during cooling, the assumption can be made that the products of the reactions (1–4) at 950 °C are the same as those analyzed at room temperature and can be used to calculate the oxygen non-stoichiometry by Eq. (5). Nevertheless, high temperature XRD in a CO_2 atmosphere is the best way to identify the phase composition. This might be possible, because CO_2 is not explosive and toxic and it is therefore safe to conduct XRD experiments under such conditions, which is not the case for the explosive properties of hydrogen at the higher temperatures of interest.

Evaluation of the accuracy of the method is also important, especially when the oxygen non-stoichiometry change is very small, like for $BaCeO_{3-\delta}$. The cumulative error of this method may arise from different steps in the experiment, but the most important one is weighing part. In this study, the weighing error of our TGA equipment is around 0.01% (20–50 mg powder was used), and it will cause 0.01 deviation in the oxygen non-stoichiometry calculation. Generally, there are two ways to increase the accuracy of this method. The first one is to increase the accuracy of the TGA setup, however this is limited, due to current technology; e.g.: the best accuracy for an electronic balance is 0.001 mg. Alternatively, one can use more powder to increase the accuracy as well. In some other studies, around 1 g or even 3–4 g was used for TGA measurements [17,18]. If for example in this study 200 mg powder was used and weighed with the same accuracy, the deviation of $3-\delta$ would be reduced to 0.001.

5. Conclusion

A new method to determine the oxygen non-stoichiometry of perovskite materials under equilibrium state has been developed and demonstrated by using $SrCoO_{3-\delta}$, $BaCoO_{3-\delta}$, $BaFeO_{3-\delta}$ and $BaCeO_{3-\delta}$ as representative materials. The oxygen non-stoichiometry (δ) of these 4 materials at 950 °C in air was measured to be 0.48, 0.36, 0.43 and 0.03 respectively. Based on these reference points, the oxygen non-stoichiometry at other temperatures was also measured, while this method is expected to be successful for other perovskite materials as well. This method is not only restricted for analysis of δ in air, large variations in oxygen partial pressures can also be used, because the equilibrium state for all partial pressures can easily be attained at (sufficient) high temperatures.

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