Dependence of Lattice Constant of Ba, Co-Contained Perovskite Oxides on Atmosphere, and Measurements of Water Content

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Abstract:

In this work, water content of Ba$_{0.5}$Sr$_{0.5}$Co$_x$Fe$_{1-x}$O$_{3-\delta}$ and PrBaCo$_2$O$_{5+\delta}$ were measured by Karl-Fischer titration method. Dependence of lattice constants of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ and PrBaCo$_2$O$_{5+\delta}$ on atmosphere was investigated by high temperature X-ray diffraction (HT-XRD) measurements. The results revealed that the lattice volumes of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ and PrBaCo$_2$O$_{5+\delta}$ increased when the atmosphere was altered from O$_2$ to Ar, due to a releasing of oxygen from lattice in a reducing atmosphere. Significantly low water contents were measured for both Ba$_{0.5}$Sr$_{0.5}$Co$_x$Fe$_{1-x}$O$_{3-\delta}$ and PrBaCo$_2$O$_{5+\delta}$ by Karl-Fischer titration method.

Keywords: Ba$_{0.5}$Sr$_{0.5}$Co$_x$Fe$_{1-x}$O$_{3-\delta}$, PrBaCo$_2$O$_{5+\delta}$, perovskite, hydration, proton conduction
1. Introduction

New types of fuel cells operating at lower temperatures are getting great attention. A promising one is protonic ceramic fuel cells (PCFCs) using proton conductive oxides as electrolytes, such as Y-doped BaZrO$_3$ (BZY), which exhibits high proton conductivity exceeding $10^{-2}$ S cm$^{-1}$ in a humidified atmosphere at 600 °C [1, 2]. The most ideal cathode material for PCFCs should be a mixed proton and electron conductor, enabling the reactive area of the cathodic reaction to be extended to the whole surface of cathode [3, 4]. In a recent thermogravimetry study by Grimaud et al., weight increase of 0.6 wt% and 0.1 wt% for Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ and PrBaCo$_2$O$_{5+\delta}$, respectively, was reported, which was attributed to water incorporation in a humidified atmosphere [5]. Based on the mechanism of proton conduction in perovskite oxides [6, 7], the work of Grimaud et al. [5] implies possible proton conduction, and therefore, a potentially mixed proton and electron conduction in Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ and PrBaCo$_2$O$_{5+\delta}$. In this work, we measured water content of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{1-x}$O$_{3-\delta}$ and PrBaCo$_2$O$_{5+\delta}$ hydrated in humidified atmospheres by Karl-Fischer titration method. Dependence of lattice constants of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ and PrBaCo$_2$O$_{5+\delta}$ on atmosphere was also investigated.

2. Experimental

2.1 Sample Synthesis

Ba$_{0.5}$Sr$_{0.5}$Co$_x$Fe$_{1-x}$O$_{3-\delta}$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$), and PrBaCo$_2$O$_{5+\delta}$ were synthesized by solid state
reaction method. Required amounts of BaCO$_3$, SrCO$_3$, CoCO$_3$·0.5H$_2$O and Fe$_2$O$_3$ powders for Ba$_{0.5}$Sr$_{0.5}$Co$_x$Fe$_{1-x}$O$_{3-\delta}$, Pr$_6$O$_{11}$, BaCO$_3$, and CoCO$_3$·0.5H$_2$O powders for PrBaCo$_2$O$_{5+\delta}$ were mixed and ball-milled for 24 h. Mixtures were pressed into pellets under 9.8 MPa, and heated for 10 h at 900 °C and 1000 °C for Ba$_{0.5}$Sr$_{0.5}$Co$_x$Fe$_{1-x}$O$_{3-\delta}$ and PrBaCo$_2$O$_{5+\delta}$, respectively. Then, samples were ball-milled for 24 h, and mixed with a binder solution [4]. After that, samples were pressed into pellets at 392 MPa, and subsequently heat-treated for 8 h at 600 °C to remove the binder solution. Finally, a heat-treatment at 1100 °C for 10 h in air was performed for sintering. The sample was furnace-cooled at the cooling rate of 5 °C min$^{-1}$. Dense pellets with the size of 10 mm in diameter and 1.7 mm in thickness were obtained.

2.2 X-ray Diffraction Analysis

Powder X-ray diffraction (XRD) analysis with CuK$\alpha$ radiation using X’Pert-ProMPD (PANalytical, Netherlands) was applied for phase identification. High temperature XRD (HT-XRD) measurements were performed using a HTK 1200N high-temperature chamber (Anton Paar, Austria) in the temperature range of 30 to 900 °C. Two continuous batches of HT-XRD measurements were performed in dry O$_2$ and dry Ar in sequence. During the heating and cooling processes, samples were heated up and cooled down to the set temperature at heating and cooling rates of 150 and 50 °C min$^{-1}$, respectively, and then kept for 30 min at each temperature before collecting an XRD pattern, which took 7 min. Average heating and cooling rates are estimated to be both about 1.35 °C min$^{-1}$. Rietveld refinements were performed using a commercial software X’Part HighScore Plus.
2.3 Thermogravimetry Analysis

Thermogravimetry (TG) analysis was performed in dry O$_2$ using a standard instrument, TG8120 (Rigaku, Japan) to measure weight change of a hydrated Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ powder sample, which was preliminarily kept in O$_2$ - 5% H$_2$O at 200 °C for 72 h and then in O$_2$ - 3.12% H$_2$O at 200 °C for 24 h. During the TG analysis, the sample was heated from 200 °C to 1000 °C and subsequently cooled to 200 °C at a rate of 2 °C min$^{-1}$.

2.4 Water Content Measurement

Karl-Fischer titration method was applied to determine water content in the samples. The sintered pellets were broken into pieces about 2 mm in length, and hydrated in O$_2$ - 5% H$_2$O or Ar - 5% H$_2$O for 72 h at 600°C. Readers are referred to our previous work [4] for detailed procedures.

3 Results and Discussions

3.1 Identification of Crystal Structure of Ba$_{0.5}$Sr$_{0.5}$Co$_x$Fe$_{1-x}$O$_{3-\delta}$ and PrBaCo$_2$O$_{5+\delta}$

A cubic perovskite structure (JCPDS 00-055-0563) was identified for Ba$_{0.5}$Sr$_{0.5}$Co$_x$Fe$_{1-x}$O$_{3-\delta}$ with Co content varying from 0 to 0.8. For Ba$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$, a single phase with a hexagonal structure (JCPDS 01-071-2453) was identified. The lattice constants, which were measured at room
temperature, of the samples with the cubic structure after the heat-treatments at 900 °C and 1100 °C, are shown in Fig. 1. Single phase with tetragonal structure (JCPDS 00-053-0131) was identified for the PrBaCo$_2$O$_{5+\delta}$ samples.

3.2 Water Content of Ba$_{0.5}$Sr$_{0.5}$Co$_x$Fe$_{1-x}$O$_{3-\delta}$ and PrBaCo$_2$O$_{5+\delta}$

As shown in Fig. 2, very poor capacity for water incorporation was confirmed by Karl-Fischer titration method for all the Ba$_{0.5}$Sr$_{0.5}$Co$_x$Fe$_{1-x}$O$_{3-\delta}$ samples. For example, water content of only 0.0054 wt% was measured for Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ after hydration in O$_2$ – 5% H$_2$O at 600 °C for 72 h. Similarly, very small water content of 0.0064 and 0.0008 wt% was measured for PrBaCo$_2$O$_{5+\delta}$, which was preliminarily heated at 600 °C for 72 h in O$_2$ – 5% H$_2$O and Ar – 5% H$_2$O, respectively. The results in our work were greatly different from the TG study by Grimaud et al. [5].

Then, in this work, a TG experiment was also performed on Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ powder sample which was preliminarily hydrated in wet O$_2$. And a weight loss of 0.4 wt% was observed after this sample was heated and then cooled in dry O$_2$ at a rate of 2 °C min$^{-1}$. This result was comparable with that of Grimaud et al. [5].

The Karl-Fischer titration method is a highly water-sensitive method [4], so we believe that the water content determined by this method is reliable. In addition, Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ is known for its high conductivity of oxide ions [8], and is reported to absorb and release oxygen when it is heat-treated [9]. Therefore, the weight loss observed in the TG analyses, in which heating and
cooling rates are not sufficiently slow, should be mainly attributed to the variation of the amount of oxygen, rather than water in Ba$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Fe$_{x}$O$_{3-\delta}$. The heating and cooling rates in the TG analysis of 2 °C min$^{-1}$ in this work, and 1 °C min$^{-1}$ in the work of Grimaud et al. [5], were supposed to be not slow sufficiently to allow the system approaching an equilibrium state on releasing and absorbing oxygen.

3.3 Thermal Behavior Observation

(1) Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$

The lattice constants of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ samples heat-treated at 900 °C were smaller than those heat-treated at 1100°C, as shown in Fig. 1. HT-XRD measurements were thereby performed to give a further insight into the thermal behavior of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$. Profiles of (112) diffraction peak collected at various temperatures are shown in Fig. 3. During the heating process in dry O$_2$, only a splitting of the diffraction peak from radiations of CuK$\alpha_1$ and CuK$\alpha_2$ was observed at all the temperatures. However, during the cooling process, when the temperature was lower than 300 °C, three distinguishable vertexes were observed. When the sample was subsequently heated in dry Ar, the peak shape containing three vertexes remained in the temperature range between 30 and 200 °C, and merged into a two vertex appearance when the temperature was elevated over 200 °C. The peak shape of two vertexes was kept during the rest of heating process and the subsequent cooling process in dry Ar. Obviously, the peak having three vertexes does not belong to a single
cubic structure. We considered the possibility of structure distortion, and attempted the models of tetragonal ($P4/mmm$) [10] and hexagonal ($P63/mmc$) [10] structures for Rietveld refinement, but failed to get any reasonable result because the calculated profile deviated from the observed pattern apparently. Since all the other diffraction peaks collected at 30 – 200 °C during cooling in dry O$_2$ and heating in dry Ar also exhibited a similar peak shape which is especially obvious in the high angle range, we consider that it is more reasonable to attribute this peak splitting to a coexistence of two Ba$_{0.5}$Sr$_{0.5}$Co$_x$Fe$_{1-x}$O$_{3-\delta}$ phases. It is difficult to identify the structures of the two Ba$_{0.5}$Sr$_{0.5}$Co$_x$Fe$_{1-x}$O$_{3-\delta}$ phases, but since Ba$_{0.5}$Sr$_{0.5}$Co$_x$Fe$_{1-x}$O$_{3-\delta}$ can maintain the cubic perovskite structure with a wide range of oxygen non-stoichiometry [11, 12], we here assume, which will be discussed lately, that this three-vertex peak shape was generated due to the coexistence of two cubic perovskite phases with different lattice constants. As an example, the fitting profile by using the model of two cubic perovskite structures ($Pm\overline{3}m$) to simulate the (112) diffraction peak collected at 30 °C during the cooling process in dry O$_2$ are shown in Fig. 4, and the calculated profile fits well with the observed one. Then, models of a single cubic perovskite structure ($Pm\overline{3}m$) [11] and two cubic perovskite structures ($Pm\overline{3}m$) [11] were adopted to simulate the diffraction patterns, where the peak shape of two and three vertexes were observed, respectively. The lattice constants are plotted in Fig. 5.

Although these models fitted well in most cases, fitting quality of the diffraction patterns collected between 600 and 700 °C seems to be insufficient, and the lattice constants calculated in this
temperature range by using the single cubic perovskite structure \((Pm\bar{3}m)\) model shows an obvious deviation from the tendency of lattice constant variation estimated from other temperature ranges. Possibility of structural distortion, such as hexagonal \((P63/mmc)\) [10] and tetragonal perovskite \((P4/mmm)\) [10], was taken into consideration, but no improvement in fitting quality was obtained. The reason is not clear, and further investigation is expected in future.

As shown in Fig. 5, the lattice constant in dry Ar is larger than that in dry O\(_2\) at the same temperature. It is due to the releasing of oxygen in a reducing atmosphere [9, 11, 13], resulting in a reduction of a part of the Co and Fe cations to a lower valence state with larger radii. Coexistence of two \(\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{x}\text{Fe}_{1-x}\text{O}_{3-\delta}\) phases with different lattice constants was identified at the low temperature range of 30 – 200 °C during cooling in O\(_2\) and heating in Ar. And based on the discussion above, this phenomenon should be due to the different concentration of oxide ions in these two phases, which was induced by insufficient diffusion of oxide ions at low temperature.

(2) \(\text{PrBaCo}_2\text{O}_{5+\delta}\)

In XRD analysis of \(\text{PrBaCo}_2\text{O}_{5+\delta}\), we did not observe a separation into three or more vertexes as the case for \(\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}\). A tetragonal perovskite-type structure \((P4/mmm)\) model [9] was used in Rietveld refinements to calculate the lattices constants of \(\text{PrBaCo}_2\text{O}_{5+\delta}\). As shown in Fig. 6, similar to the case for \(\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}\), apparent increase in lattice volume was confirmed for \(\text{PrBaCo}_2\text{O}_{5+\delta}\) when cooling in dry Ar, compared with cooling in dry O\(_2\). It implies a partial
reduction of multivalent cations in reducing atmosphere. We therefore consider that the larger water content determined by Grimaud et al. [5] might be an improper interpretation of the TG data without carefully considering the uptake of oxygen in PrBaCo2O5+δ.

4. Conclusions

In this work, we investigated the dependence of lattice constants of Ba0.5Sr0.5Co0.8Fe0.2O3-δ and PrBaCo2O5+δ on atmosphere, and measured water content of these two kinds of materials. Expansion of lattice volume was observed for Ba0.5Sr0.5Co0.8Fe0.2O3-δ and PrBaCo2O5+δ when the atmosphere was altered from O2 to Ar, which was induced by a releasing of oxygen from the lattice. Significantly low water contents were measured for both Ba0.5Sr0.5Co0.8Fe0.2O3-δ and PrBaCo2O5+δ by Karl-Fischer titration method.

5. Acknowledgements

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References


Fig. 1. Lattice constants of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{x}\text{Fe}_{1-x}\text{O}_{3-\delta}$ ($x = 0, 0.2, 0.4, 0.6, 0.8$) heat-treated at 900 °C and subsequently at 1100 °C, for synthesizing and sintering, respectively.
Fig. 2. Proton concentration of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ hydrated in $\text{O}_2$ - 5% $\text{H}_2\text{O}$ and $\text{Ar}$ - 5% $\text{H}_2\text{O}$ at 600 °C for 72 h. Samples sintered at 1100 °C were used for hydration.
Fig. 3. (112) diffraction peaks of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ collected by HT-XRD measurements from 30 to 900 °C in (a) dry O$_2$ and (b) dry Ar. For HT-XRD measurements, a sample sintered at 1100 °C was used.
Fig. 4. Rietveld refinement results by fitting the diffraction peaks collected at 30 °C during the cooling process in dry O\textsubscript{2}, by using the model of two cubic perovskite. Fitting of the (112) diffraction peak profile is highlighted in the inset. Observed profile (blue), calculated profile (red), difference (black, at bottom), and Bragg peaks for the candidate two cubic perovskite phases (Green and purple vertical lines) are shown. Solid and dash vertical lines in the inset are the Bragg peaks for the candidate phases from the CuK\textalpha{}1 and CuK\textalpha{}2 radiations, respectively. For HT-XRD measurements, a sample sintered at 1100 °C was used.
Fig. 5. Lattice constants of Ba\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3-δ} determined by using Rietveld refinement to analyze the XRD patterns collected in HT-XRD measurements in dry O\textsubscript{2} and dry Ar. For HT-XRD measurements, a sample sintered at 1100 °C was used.
Fig. 6. Lattice volume of PrBaCo$_2$O$_{5+\delta}$ determined by using Rietveld refinements to analyze the XRD patterns collected by HT-XRD measurements in dry O$_2$ and dry Ar. For HT-XRD measurements, a sample sintered at 1100 °C was used.