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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 $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ and $\text{PrBaCo}_2\text{O}_{5+\delta}$ were measured by Karl-Fischer titration method. Dependence of lattice constants of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and $\text{PrBaCo}_2\text{O}_{5+\delta}$ on atmosphere was investigated by high temperature X-ray diffraction (HT-XRD) measurements. The results revealed that the lattice volumes of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and $\text{PrBaCo}_2\text{O}_{5+\delta}$ 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 $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ and $\text{PrBaCo}_2\text{O}_{5+\delta}$ by Karl-Fischer titration method.

Keywords: $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$, $\text{PrBaCo}_2\text{O}_{5+\delta}$, 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 BaZrO₃ (BZY), which exhibits high proton conductivity exceeding 10^{-2} Scm⁻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-δ} and PrBaCo₂O_{5+δ}, 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-δ} and PrBaCo₂O_{5+δ}. In this work, we measured water content of Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-δ} and PrBaCo₂O_{5+δ} 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-δ} and PrBaCo₂O_{5+δ} on atmosphere was also investigated.

2. Experimental

2.1 Sample Synthesis

Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-δ} ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$), and PrBaCo₂O_{5+δ} were synthesized by solid state

reaction method. Required amounts of BaCO_3 , SrCO_3 , $\text{CoCO}_3 \cdot 0.5\text{H}_2\text{O}$ and Fe_2O_3 powders for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$, Pr_6O_{11} , BaCO_3 , and $\text{CoCO}_3 \cdot 0.5\text{H}_2\text{O}$ powders for $\text{PrBaCo}_2\text{O}_{5+\delta}$ 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 $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ and $\text{PrBaCo}_2\text{O}_{5+\delta}$, 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 $\text{CuK}\alpha$ 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

(PANalytical, Netherlands) to determine lattice constants.

2.3 Thermogravimetry Analysis

Thermogravimetry (TG) analysis was performed in dry O₂ 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-δ} powder sample, which was preliminarily kept in O₂ - 5% H₂O at 200 °C for 72 h and then in O₂ - 3.12% H₂O 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 O₂ - 5% H₂O or Ar - 5% H₂O 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_xFe_{1-x}O_{3-δ} and PrBaCo₂O_{5+δ}

A cubic perovskite structure (JCPDS 00-055-0563) was identified for Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-δ} with Co content varying from 0 to 0.8. For Ba_{0.5}Sr_{0.5}CoO_{3-δ}, 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 $\text{PrBaCo}_2\text{O}_{5+\delta}$ samples.

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

As shown in **Fig. 2**, very poor capacity for water incorporation was confirmed by Karl-Fischer titration method for all the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ samples. For example, water content of only 0.0054 wt% was measured for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ after hydration in $\text{O}_2 - 5\% \text{H}_2\text{O}$ at 600 °C for 72 h. Similarly, very small water content of 0.0064 and 0.0008 wt% was measured for $\text{PrBaCo}_2\text{O}_{5+\delta}$, which was preliminarily heated at 600 °C for 72 h in $\text{O}_2 - 5\% \text{H}_2\text{O}$ and $\text{Ar} - 5\% \text{H}_2\text{O}$, 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 $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ 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, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ 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 $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$. The heating and cooling rates in the TG analysis of $2\text{ }^\circ\text{C min}^{-1}$ in this work, and $1\text{ }^\circ\text{C min}^{-1}$ 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) $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$

The lattice constants of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ samples heat-treated at $900\text{ }^\circ\text{C}$ 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 $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$. 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 $\text{CuK}\alpha_1$ and $\text{CuK}\alpha_2$ was observed at all the temperatures. However, during the cooling process, when the temperature was lower than $300\text{ }^\circ\text{C}$, 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 $200\text{ }^\circ\text{C}$, and merged into a two vertex appearance when the temperature was elevated over $200\text{ }^\circ\text{C}$. 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 O₂ 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_xFe_{1-x}O_{3-δ} phases. It is difficult to identify the structures of the two Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-δ} phases, but since Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-δ} can maintain the cubic perovskite structure with a wide range of oxygen non-stoichiometry [11, 12], we here assume, which will be discussed later, 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 ($Pm\bar{3}m$) to simulate the (112) diffraction peak collected at 30 °C during the cooling process in dry O₂ are shown in **Fig. 4**, and the calculated profile fits well with the observed one. Then, models of a single cubic perovskite structure ($Pm\bar{3}m$) [11] and two cubic perovskite structures ($Pm\bar{3}m$) [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 O₂ 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 Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-δ} phases with different lattice constants was identified at the low temperature range of 30 – 200 °C during cooling in O₂ 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) PrBaCo₂O_{5+δ}

In XRD analysis of PrBaCo₂O_{5+δ}, we did not observe a separation into three or more vertexes as the case for Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}. A tetragonal perovskite-type structure ($P4/mmm$) model [9] was used in Rietveld refinements to calculate the lattices constants of PrBaCo₂O_{5+δ}. As shown in **Fig. 6**, similar to the case for Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}, apparent increase in lattice volume was confirmed for PrBaCo₂O_{5+δ} when cooling in dry Ar, compared with cooling in dry O₂. 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 $\text{PrBaCo}_2\text{O}_{5+\delta}$.

4. Conclusions

In this work, we investigated the dependence of lattice constants of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ and $\text{PrBaCo}_2\text{O}_{5+\delta}$ on atmosphere, and measured water content of these two kinds of materials. Expansion of lattice volume was observed for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and $\text{PrBaCo}_2\text{O}_{5+\delta}$ when the atmosphere was altered from O_2 to Ar, which was induced by a releasing of oxygen from the lattice. Significantly low water contents were measured for both $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ and $\text{PrBaCo}_2\text{O}_{5+\delta}$ by Karl-Fischer titration method.

5. Acknowledgements

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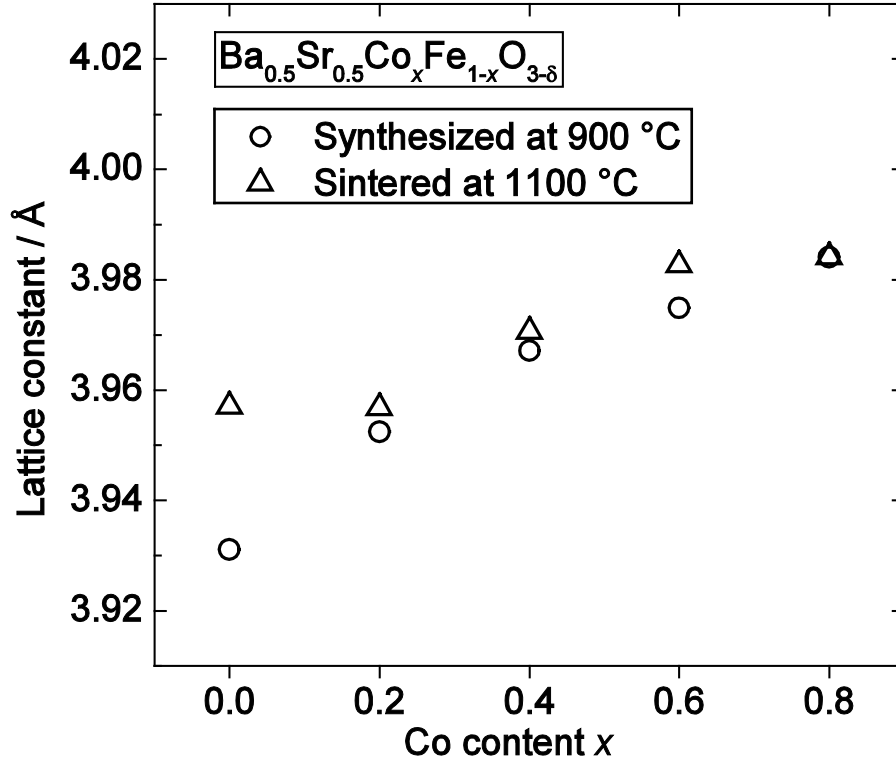


Fig. 1. Lattice constants of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ ($x = 0, 0.2, 0.4, 0.6, 0.8$) heat-treated at 900 °C and subsequently at 1100 °C, for synthesizing and sintering, respectively.

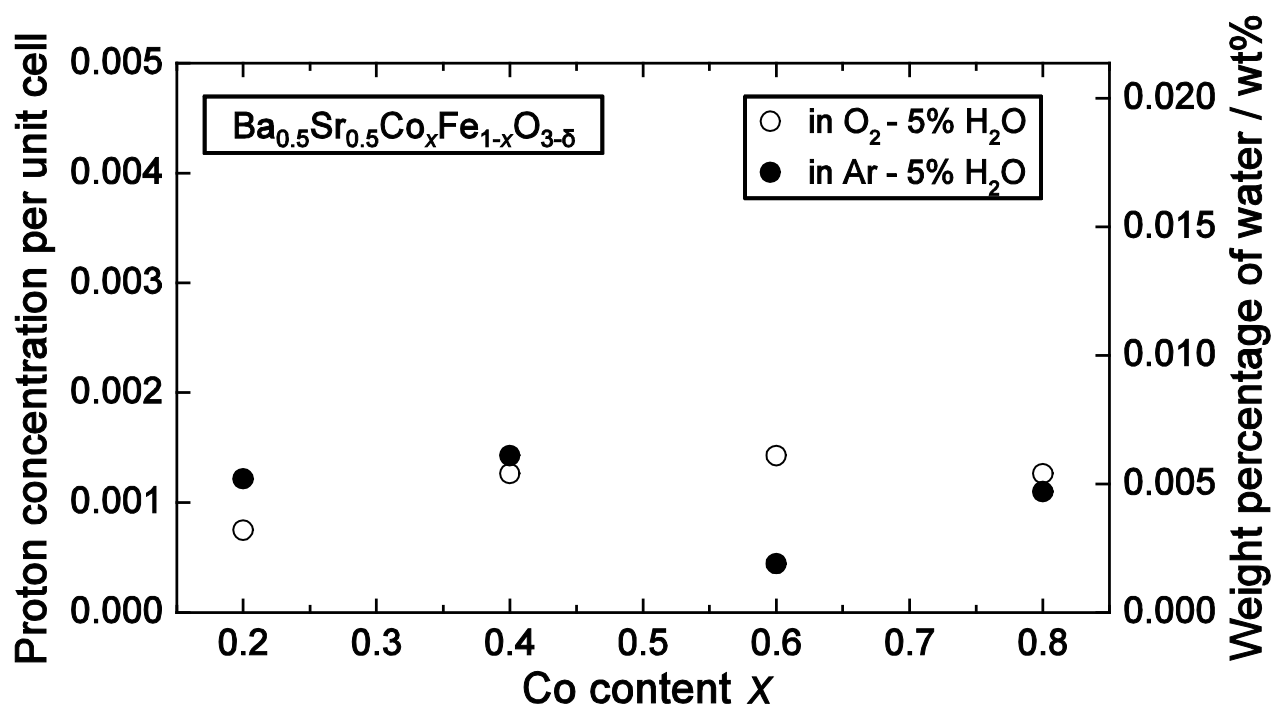


Fig. 2. Proton concentration of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_X\text{Fe}_{1-X}\text{O}_{3-\delta}$ hydrated in $\text{O}_2 - 5\% \text{H}_2\text{O}$ and $\text{Ar} - 5\% \text{H}_2\text{O}$ at 600°C for 72 h. Samples sintered at 1100°C were used for hydration.

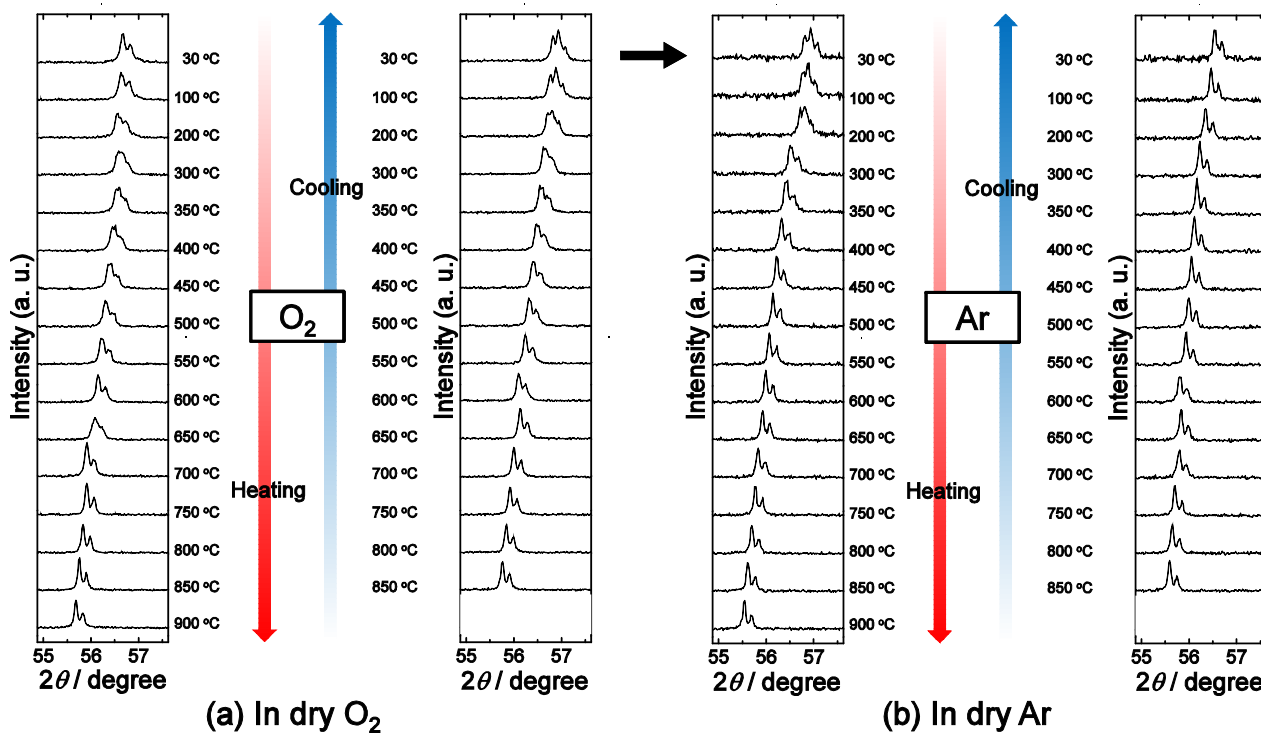


Fig. 3. (112) diffraction peaks of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ collected by HT-XRD measurements from 30 to 900 °C in (a) dry O_2 and (b) dry Ar. For HT-XRD measurements, a sample sintered at 1100 °C was used.

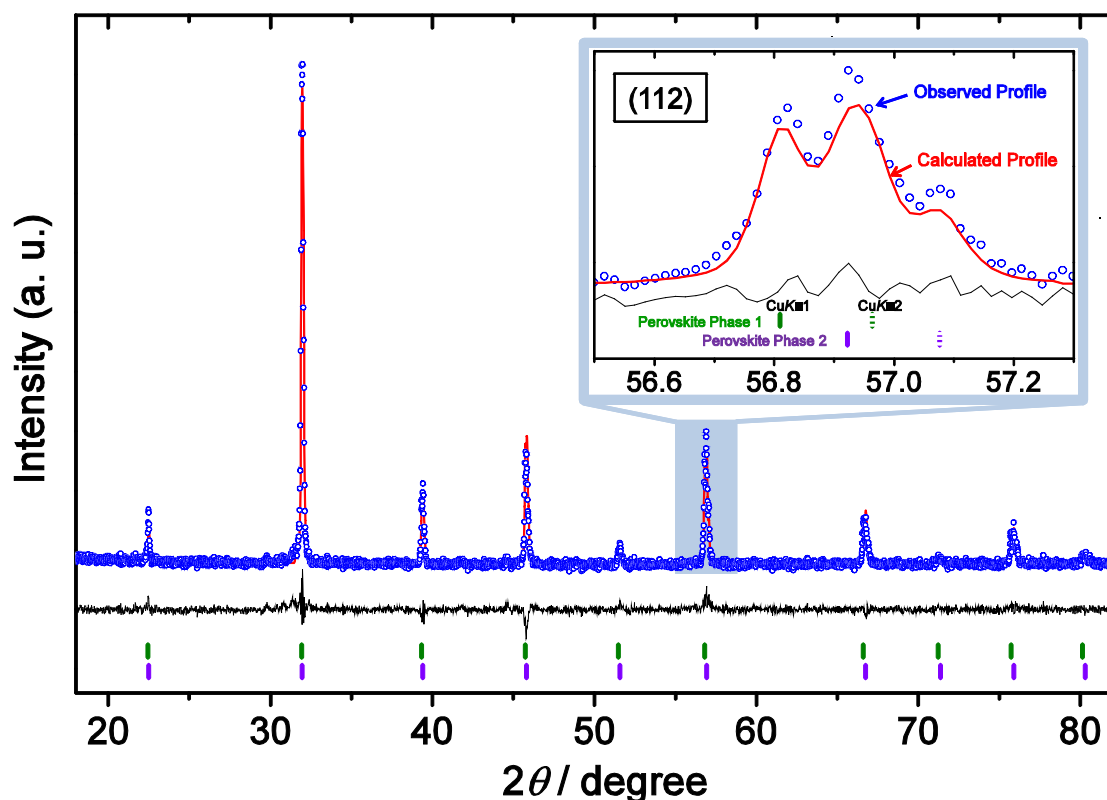


Fig. 4. Rietveld refinement results by fitting the diffraction peaks collected at 30 °C during the cooling process in dry O₂, by using the model of two cubic perovskite. Fitting of the (112) diffraction peak profile is highlighted in the inset. Observed profile (blue), calculated profile (red), difference (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 α 1 and CuK α 2 radiations, respectively. For HT-XRD measurements, a sample sintered at 1100 °C was used.

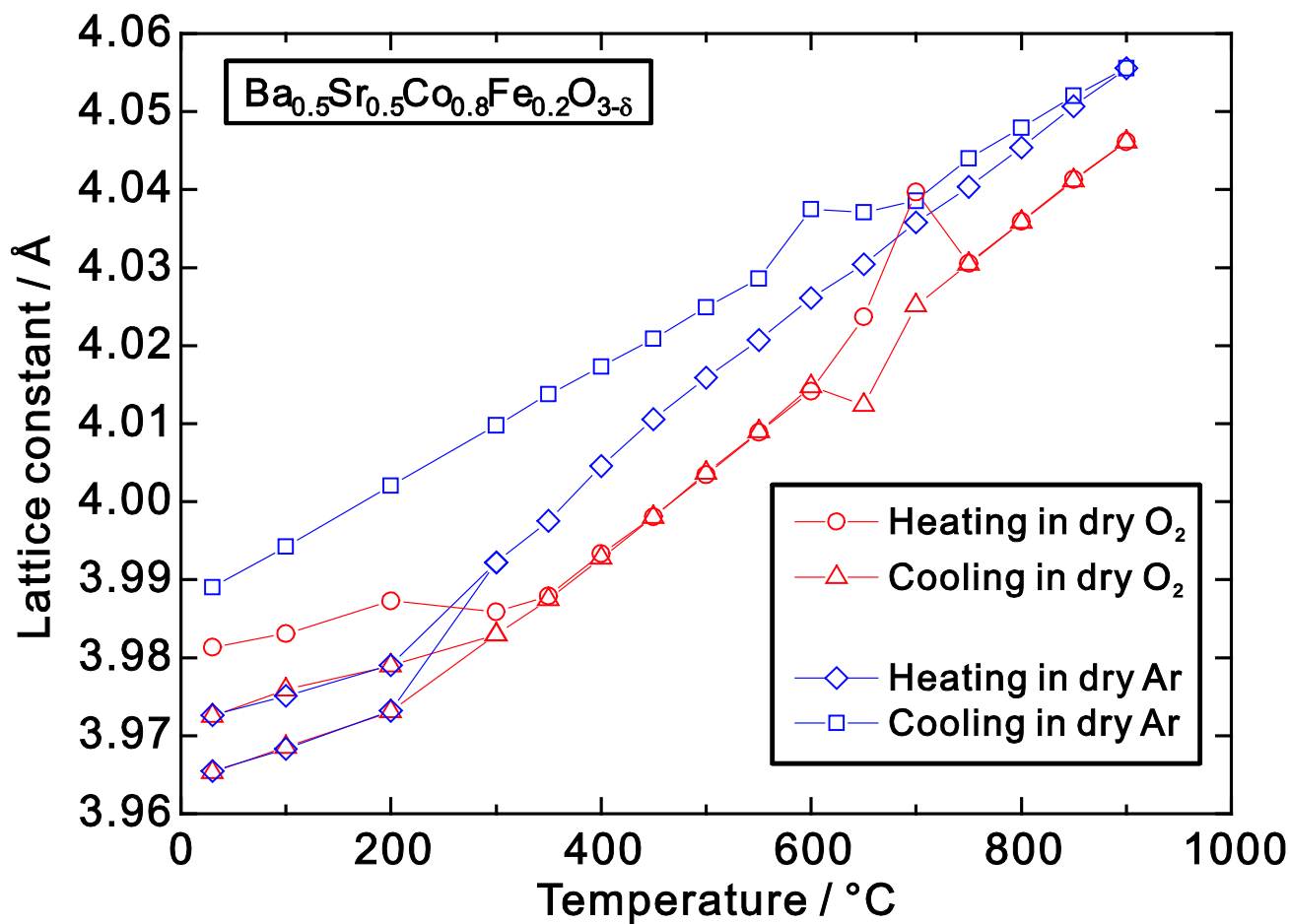


Fig. 5. Lattice constants of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ determined by using Rietveld refinement to analyze the XRD patterns collected in HT-XRD measurements in dry O_2 and dry Ar. For HT-XRD measurements, a sample sintered at 1100 °C was used.

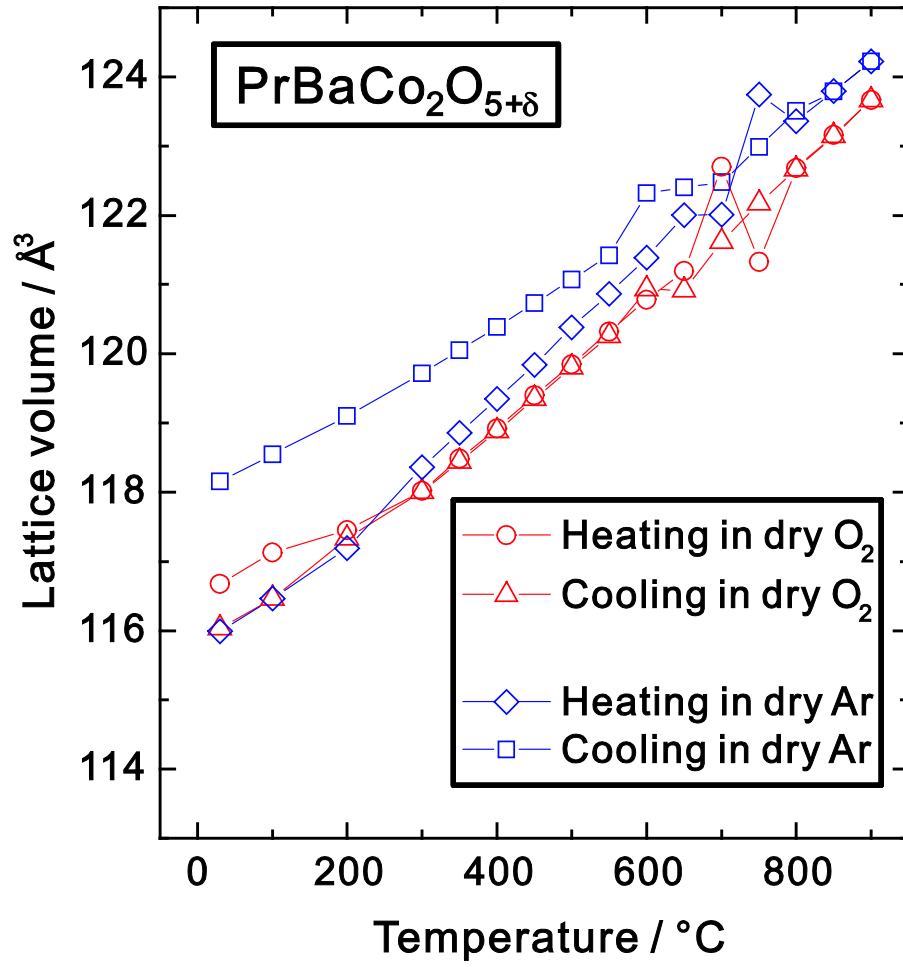


Fig. 6. Lattice volume of PrBaCo₂O_{5+δ} determined by using Rietveld refinements to analyze the XRD patterns collected by HT-XRD measurements in dry O₂ and dry Ar. For HT-XRD measurements, a sample sintered at 1100 °C was used.