Role of temperature and oxygen content on structural and electrical properties of $\text{LaBaCo}_2\text{O}_{5+\delta}$ thin films

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The role of temperature and the oxygen content in the structural transformation and electrical conductivity of epitaxial double perovskite $\text{LaBaCo}_2\text{O}_{5+\delta}$ ($0 \leq \delta \leq 1$) thin films was systematically investigated. Reciprocal space mapping and ω - 2θ x-ray diffraction performed at different temperatures in vacuum indicate that oxygen vacancies in the films become ordered at high temperature in a reducing environment. The changes of the oxygen content and the degree of oxygen vacancy ordering in the films result in a strong in-plane anisotropic lattice deformation and a large thermal expansion coefficient along the c-axis direction. The electrical conductivity measurements reveal that these behaviors are related to the degree of oxygen vacancy formation and lattice deformation in the films. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5009245>

Perovskite oxides show many interesting physical phenomena including a metal-insulator transition, giant magnetoresistance, spin blockade, etc., due to their strongly correlated charge, spin, orbitals, and lattice.^{1–3} Of particular recent interest is double perovskite cobaltite in the form of $\text{LnBaCo}_2\text{O}_{5+\delta}$ (LBCO) (Ln = La, Pr, Eu, etc.). This class of perovskite oxides exhibits excellent mixed ionic electronic conductivity (MIEC), making them suitable for applications in solid oxide fuel cells, gas sensors, gas separation, and energy storage systems as well as many others.^{4–7} However, fundamental understanding of $\text{LnBaCo}_2\text{O}_{5+\delta}$ (LBCO) at high temperature is still very limited. For instance, chemical expansion or “stoichiometric expansion” due to the large variable oxygen content of the lattice is a critical issue for device applications but not well studied. Such an expansion can lead to many unpredicted issues in device design and fabrication such as cracking and delamination of layers causing mechanical instability.^{8–10} These structural and chemical changes also have a large impact on the electronic and ionic conductivity.^{11,12}

Interest in $\text{LaBaCo}_2\text{O}_{5+\delta}$ (LBCO) in particular stems from the material forming both A-site ordered and A-site disordered structures due to the La and Ba ions being similar in size.^{13,14} In the disordered structure, La and Ba ions are distributed randomly at the A-sites leading to a cubic like perovskite structure.¹⁵ The ordered structure is made up of alternating layers of LaAlO_3 (LaO) and BaO, giving a tetragonal structure with the unit cell doubling in the c-axis direction, known as the double perovskite structure.^{2,16} As oxygen vacancies are created in the lattice oxygen pyramids, octahedra will be randomly distributed throughout the lattice.¹⁷ This change in the lattice leads to tilts, rotations, and distortions of the oxygen octahedra, which affects the ionic and electronic conductivity.^{18,19} The oxygen vacancies tend to order themselves in

LaO_δ layers due to the slightly smaller size of the La ion relative to the Ba ion.²⁰ This ordering of oxygen vacancies forms alternating rows of oxygen octahedra and pyramids, not only changing the lattice parameter along the c-axis but also causing an expansion in the b-axis direction of the crystal which makes it possible to form different crystal structures such as orthorhombic.^{21,22} To gain a fundamental understanding of the role of the oxygen vacancy in the physical properties, systematic studies were performed on the epitaxial thin films of $\text{LaBaCo}_2\text{O}_{5+\delta}$ on the LaAlO_3 (LAO) substrate. We use non-ambient high temperature HRXRD to establish the structural phase transition in low oxygen partial pressure at high temperature. The electrical conductivity is also measured in a reducing environment to explore the potential effects of the vacancy ordering on the electrical conductivity.

Epitaxial thin films of $\text{LaBaCo}_2\text{O}_{5+\delta}$ (LBCO) were deposited on LaAlO_3 (LAO) by pulsed laser deposition. Details about the film fabrications can be found in previous reports.^{23–25} Briefly, a KrF excimer laser with a wavelength of 248 nm and a fluence of 2.0 J/cm^2 was used to grow films with a thickness of $\sim 100 \text{ nm}$. The substrate was held at 800°C during the deposition. A constant oxygen pressure of 250 mTorr was maintained. After deposition of the film, the oxygen pressure was raised to 500 Torr and held at the deposition temperature for 15 min, after which the sample was cooled at a rate of 5°C/min to room temperature. X-ray diffraction (XRD) measurements were carried out using a PANalytical Empyrean X-ray Diffractometer with an Anton Parr DHS1100 heated stage. The film was placed in a graphite dome where the vacuum was maintained at 40 mTorr while structural measurements were performed. The film resistance was measured by attaching platinum electrodes to the surface of the film with silver conductive paste. The film was placed in a tube furnace, and separate gas flows of oxygen and argon were introduced and maintained at $\sim 200 \text{ sccm}$ as the film was heated and cooled from room temperature to 750°C at a rate of 2°C/min .

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FIG. 1. (a) Full set of scans from 30 to 700 °C showing expansion of the c -axis. (b) c -axis lengths vs. T ; the inset shows possible LBCO structures at different levels of oxidation.

XRD ω - 2θ scans were carried out on an LBCO film under a vacuum of 40 mTorr ($P(O_2)$ of 1×10^{-5} atm) from room temperature up to 700 °C as shown in Fig. 1. The scans were focused on the (004) LBCO peak as this was the most intense peak. As illustrated in our previous report, LBCO films show c -axis orientation with respect to the (001) oriented LAO substrate. Furthermore, the appearance of a weak diffraction at a 2θ angle of 47.3° potentially indicates a strained layer at the interface.^{26,27} From these scans, the lattice parameter along the c -axis can be derived and can be used to estimate the total expansion in the out-of-plane direction due to thermal and chemical effects. At room temperature, the c -axis lattice parameter is 7.8180 Å, which is slightly larger than the bulk value of 7.7145 Å.¹⁶ This indicates that there is a partial unreleased out-of-plane strain of 1.34% in the film due to a small lattice mismatch of about 2.32% between the LBCO film and the LAO substrate. The c -axis lattice parameters were plotted against temperature as shown in Fig. 1(b). From about 150 °C to 500 °C, the expansion in the c -axis is almost linear with a maximum value of 8.0183 Å, after which the expansion appears to be stabilized which could indicate a structural transition from oxygen vacancy ordered orthorhombic to disordered tetragonal. A linear fit of this region was used to calculate the thermal expansion coefficient (TEC) of the LBCO thin film. The TEC was found to be $59.4 \times 10^{-6} \text{ °C}^{-1}$ as compared to the bulk value of $24.3 \times 10^{-6} \text{ °C}^{-1}$. All TEC values are summarized in Table I.^{28,29} This large difference over the bulk value may result from two key factors: the so called “clamping” effect from the substrate and the expansion due to the density change of oxygen vacancies in the film at different temperatures. First, the epitaxial clamping effect induces a larger expansion in the out-of-plane direction versus that of the in-plane direction since the thermal expansion coefficient of LAO is less than that of LBCO.^{30,31} In addition, as the material loses oxygen at different temperatures, the valence of the cobalt ions is reduced and the lattice expands, and for bulk LBCO, the contribution to the volume expansion is minimal; however, further study is required for LBCO thin films.^{29,32} To ensure that the TEC values for the

film were correct, we also calculated the TEC of the substrate as $9.32 \times 10^{-6} \text{ °C}^{-1}$ which is very close to the typical value of crystalline LAO,³³ as seen in Table I.

To further determine the lattice structures of the film at high temperatures, asymmetric reciprocal space maps (RSMs) were taken under the same conditions to assess the effects of oxygen vacancies on the in-plane directions of the film. RSMs of the (106) and (016) planes were taken in vacuum at 30 °C, 400 °C, and 600 °C, and the scans at 30 °C and 600 °C are shown in the inset of Fig. 2. In the scans performed at 30 °C, the film peaks are located in the same place, meaning that the a and b -axes lattice parameters are approximately of the same length, 3.84 Å. This indicates that the structure is tetragonal with a small compressive strain. As the temperature is increased, oxygen loss occurs in the film, resulting in expansions in the in-plane direction just as in the out-of-plane direction. However, after analysis of the RSM and calculation of the lattice parameters (Fig. 2), there appears to be a preferential expansion in the b -axis direction, indicating that the structure has become slightly orthorhombic. This may indicate that oxygen vacancy ordering occurs. As oxygen vacancies are created, they tend to occur in the LaO_δ layers due to the La ions being smaller than the Ba ions. If the vacancies are well ordered, the structure will contain alternating rows of oxygen pyramids and octahedra causing an expansion in one of the in-plane directions. Again from these data, the TEC can be calculated for each lattice direction; in the a -axis, the TEC is

FIG. 2. Lattice parameters calculated from reciprocal space map (RSM) scans vs. T . The inset shows RSM of (106) and (016) planes at 30 °C and 600 °C.

TABLE I. Thermal expansion coefficients ($\times 10^{-6} \text{ °C}^{-1}$) of the LBCO film and LAO substrate compared to their bulk values.

Material	a -axis	b -axis	c -axis	Bulk
LBCO	18.1	34.9	59.4	24.3
LAO			9.32	10.7

$18.1 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ near the bulk value, but the *b*-axis TEC is much larger at $34.9 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$.

To better understand the effects of the structure on the electrical transport property, measurements were conducted under different ambient annealing environments. The first data-set was collected in flowing oxygen as the sample was heated from room temperature to 750°C at a rate of $2^\circ\text{C}/\text{min}$, after being held at 750°C for 20 min, the sample was cooled to room temperature at the same rate. This temperature ramp profile was used for all resistance measurements. Subsequently, the sample was measured multiple times in argon, and between these data collections, the sample was re-oxidized by heating the sample to 500°C in O_2 and holding the sample at this temperature for 3 h and then cooling to room temperature at a rate of $1^\circ\text{C}/\text{min}$. After the last measurements on the oxidized sample in argon, the argon annealed sample was again measured in argon. As seen in Fig. 3, the data from the measurements in argon differ greatly from the flowing oxygen and argon annealed measurements.

Upon heating, the resistance of the sample in all conditions drops following the behavior of a p-type semiconductor with the Co^{4+} ions providing the holes as the main charge carrier. For these perovskite oxides, a small polaron hopping mechanism is employed to describe the conduction. By applying the small polaron hopping model ($\ln(\rho/T) \propto 1/T$) and constructing an Arrhenius plot, the activation energies can be found for the region of $30\text{--}200^\circ\text{C}$. For the oxidized sample in flowing argon, activation energies (E_a) of 0.075 eV and 0.098 eV were found; these agree with values previously found for LBCO thin films on SrTiO_3 substrates.^{34,35} The E_a of the sample in flowing oxygen was slightly lower at 0.063 eV due to a difference in the starting lattice oxygen content, and the E_a for the argon annealed sample was found to be much larger at 0.330 eV which is expected due to the reduced oxygen content of the film.

The behavior of the oxidized film in argon is of particular interest as the reduced oxygen partial pressure environment is similar to the XRD measurement environment. Such measurements are most likely to show the effects of the structural transitions on the electrical transport property. As

FIG. 3. Film resistance vs. Temperature solid lines represent the heating data, and the open symbols represent the cooling data. The inset shows the Arrhenius plot of the linear region from $30\text{--}200^\circ\text{C}$ with the small polaron fitting applied (dashed lines).

shown in Fig. 3, for the measurements in flowing argon (red and black), the resistance rises sharply in the range of 150°C to 320°C . This is due to the large loss of oxygen resulting from the low oxygen partial pressure or the reduction from the stoichiometric $\text{LaBaCo}_2\text{O}_6$ to $\text{LaBaCo}_2\text{O}_{5.5}$.²⁴ As oxygen vacancies are created, the cobalt ions are reduced to the Co^{3+} state with the vacancy creation reaction represented with Kröger-Vink notation

The electrons from the oxygen vacancies compensate the holes and the resistivity increases. From 320°C to 400°C , there is a drop of the resistance indicating that the film continues to lose oxygen causing a partial reduction from the stoichiometric $\text{LaBaCo}_2\text{O}_{5.5}$ to $\text{LaBaCo}_2\text{O}_{5.0}$.^{24,36} This would appear to agree with the RSM data collected showing evidence of the orthorhombic structure indicative of oxygen vacancy ordering. In this case, the ordering has the effect of increasing the Co-O-Co bond angle allowing for better charge transport.³⁷ However, at 400°C , the slope of the resistance curve changes dramatically likely associated with a structural ordering transition from the oxygen vacancy ordered orthorhombic phase back to a disordered tetragonal state.^{12,38} A step around this temperature in the symmetric XRD data is also visible, indicating that a structural transition occurs in this temperature range.

For a comparison to the behavior of the oxidized sample being reduced, the oxidized sample was also measured under a flow of oxygen, and the reduced film was measured in a flow of argon. The film in oxygen shows a slow drop in resistance to about 200°C similar to the oxidized film in argon; as seen in the inset, the slope of the Arrhenius plot is similar to that for the data collected under argon indicating similar behavior. After further heating, the resistance levels out before continuing to drop at approximately 300°C , and this is due to the loss of the adsorbed oxygen on the film surface.²⁴ The reduced film under a flow of argon behaves similarly initially. Upon heating, the resistance drops steadily until leveling out around 350°C , and as previously mentioned, due to the reduced oxygen content, the activation energy is much lower than that of the oxidized film.^{34,35} There is however a noticeable change in the resistance curve at around 400°C , likely due to the transition from the oxygen vacancy ordered orthorhombic structure to the disordered tetragonal structure.

In summary, epitaxial thin films of $\text{LaBaCo}_2\text{O}_{5+\delta}$ were grown on LAO substrates and were structurally characterized by non-ambient XRD. Symmetric scans showed rapid expansion in the out-of-plane direction as expected due to the substrate clamping effect, with a stabilization of the expansion above 500°C . RSM scans showed a preferential expansion of the *b*-axis of the film indicating potential oxygen vacancy ordering. From this, the thermal expansion coefficients were calculated and shown to be larger than those of the bulk values. The electrical transport property was studied under similar conditions and showed remarkable behavior consistent with potential oxygen vacancy ordering. These findings provide additional information for fuel cell research and energy device development.

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