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Ultrafast Chemical Dynamic Behavior in Highly Epitaxial LaBaCo$_2$O$_{5+δ}$ Thin Films

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Abstract

The redox reactions of highly epitaxial LaBaCo$_2$O$_{5+\delta}$ (LBCO) thin films exposed to the switching flow of reducing (H$_2$) and oxidizing (O$_2$) gases were examined at various temperatures between 260 – 700 °C by measuring their electrical resistance using a precise ac bridge measurement system. The as-grown LBCO films have very good electrical conductivity at low/medium temperatures between 400 – 700 °C, and are extremely sensitive to the reducing/oxidizing environments with superfast redox dynamics. The LBCO thin films show more complex redox reactions at low temperatures (300 – 350 °C) suggesting the occurrence of conducting-to-insulating-to-conducting transitions during the redox reactions. In particular, the insulating-to-conducting transition under oxidation process is superfast with the largest resistance change of up to 3x10$^7$Ω/s even at low temperature of 300 °C. The extremely short response time, the giant resistance change, and the excellent chemical stability in a broad temperature range of 260 – 700°C suggests that the highly epitaxial LBCO thin-film can be an excellent candidate for low-temperature solid oxide fuel cells, chemical sensors, and catalyst applications.

Keywords: LaBaCo$_2$O$_{5+\delta}$; epitaxial thin film; mixed conductor; redox reaction; gas sensor; catalyst
1. Introduction

Recently the 112-type cobalt oxides LnBaCo$_2$O$_{5.5}$ (LnBCO) (Ln = rare earth) with perovskite structure have become a subject of intense studies, both theoretically and experimentally, due to their unusual magnetic and electrical transport properties suitable.$^{1,2,3,4}$ The structure of the double-perovskite LnBaCo$_2$O$_{5+\delta}$ has the layer sequence of [LnO$_\delta$] [CoO$_2$] [BaO] [CoO$_2$] along the $c$ axis. With the ideal oxygen stoichiometry of 5.5 per formula unit (i.e., $\delta = 0.5$), the average oxidation state of Co is +3. LnBaCo$_2$O$_{5+\delta}$ with different extents of oxygen deficiency gives rise to ordered, nano-ordered, and disordered phases. The ionic/electronic conductivities of LnBaCo$_2$O$_{5+\delta}$ depend on the extent of oxygen deficiency thereby leading to a family of mixed ionic/electronic conducting materials with different physical/chemical properties.$^{5,6,7,8,9,10}$ Taskin et al. observed that the A-site ordered GdBaCo$_2$O$_{5.5+\delta}$ significantly enhances oxygen diffusivity.$^{11}$ The previous studies found that the A-site ordered PrBaCo$_2$O$_{5.5+\delta}$ exhibits ultrafast oxygen transport kinetics at low temperatures ranging $300 - 500 \, ^\circ C$. $^{12,13,14}$ The size difference between La$^{3+}$ and Ba$^{2+}$ is small, which makes it difficult for the La$^{3+}$ and Ba$^{2+}$ ions to order, but the ordered 112-type LaBaCo$_2$O$_{5+\delta}$ (LBCO) can be prepared under specific synthesis conditions. Rautama et al. successfully fabricated and characterized the nanoscale-ordered and disordered forms of the fully oxidized LaBaCo$_2$O$_6$ as well as the ordered form of the oxygen-deficient LaBaCo$_2$O$_{5.5}$. $^{15,16}$ With different synthesis methods, many studies have found that the oxygen content in the Ln/Ba ordered perovskites LnBaCo$_2$O$_x$ can be varied from $x = 6$ to $x = 4.5$, which leads to a change of the average cobalt oxidation state from +3.5 to +2.$^{17,18}$ In addition, Seddon et al. found the ground samples of YBaCo$_2$O$_5$ and LaBaCo$_2$O$_5$ are reduced by a strong reductant NaH to form YBaCo$_2$O$_{4.5}$ and LaBaCo$_2$O$_{4.25}$, respectively.$^{19}$ Recently, we
have successfully obtained the highly epitaxial LnBCO thin films and systematically studied the epitaxial nature and their electrical transport, magnetic and chemical properties. When these films are exposed to the switching flow of reducing (4% H$_2$ + 96% N$_2$, which will be referred to as H$_2$ for simplicity) and oxidizing (O$_2$) gases, their electrical resistance exhibits a ultrafast and dramatic change in a very broad temperature range varying from 400 to 800 °C, which reflects the change in the oxidation states of the cobalt atoms under the different redox environments. In this paper, we carry out resistance measurements on the highly epitaxial LBCO thin films under the switching flow of H$_2$ and O$_2$ gases in the temperature range of 260 – 800 °C to find the occurrence of a conducting-to-insulating transition at medium temperatures (400~700 °C) and a conducting-to-insulating-to-conducting transition at lower temperatures (300 and 350 °C). These observations are expected to be of potential importance developing the up-to-date low temperature SOFC cathode, chemical sensors and vehicle exhaust catalyst.

2. Experiments

LBCO thin films were epitaxially grown on (001) LaAlO$_3$ (LAO) single crystal ($c_{\text{LAO}} = 0.3788$ nm) substrates by using a KrF excimer (a wavelength of 248 nm) pulsed laser deposition (PLD) system. An energy density of 2.0 J/cm$^2$ and a laser repetition rate of 5 Hz were adopted during the film deposition. A high density, single phase, stoichiometric (LaBa)Co$_2$O$_{5+\delta}$ target was purchased from MTI Crystal Inc. Highly epitaxial LBCO thin films were achieved in an optimized growth condition at 850 °C with oxygen pressure of 250 mTorr. The as-grown films were in situ annealed in 200 Torr oxygen for 15 min at 850 °C and
cooled down to room temperature at a rate of 5 °C/min. The microstructure and crystallinity of the as-grown LBCO films were examined by a routing x-ray diffraction technique and characterized by cross sectional and plan-view transmission electron microscopy, details of which are given in the previous reports. The chemical dynamic measurements on the LBCO films were conducted by using a Lake Shore 370 AC Precise Resistance Bridge System in the temperatures ranging from 260 to 700 °C under pure oxygen or mixture of 5% hydrogen and 95% nitrogen (H-N mixture) in a pressure of 1 atm. Platinum leads were glued on the film surface with high temperature silver paste, were air-dried at room temperature and were annealed at 800 °C before measurements.

3. Results and discussion

3.1. Medium temperature transitions

The ac conductivity measurements indicate that at medium temperatures (400~700 °C), the resistance of the LBCO thin films changes drastically during the redox reactions. Under oxidizing environments of O₂, the LBCO thin films are good electrical conductors with resistance R less than 1000 Ω. Liu et al. studied the temperature dependence of the electrical resistivity of the LBCO thin films and found the linear relation between ln(ρ/T) and 1/T, which corresponds to the resistivity behavior of small polarons. Thus, the conductivity of the LBCO thin films comes from the coexistence of Co³⁺ and Co⁴⁺ ion according to the mechanism of small-polaron hopping conduction of most mixed-valence transition metal oxides. As the gas flow was switched from O₂ to the H₂, the Co⁴⁺ ions become reduced to Co³⁺ ions. As the reduction of the LBCO thin films proceeds,
the amount of Co$^{4+}$ decreases directly lowering the amount of small-polarons as carriers and hence raising the resistance of the LBCO thin films. Finally, almost all Co$^{4+}$ ions are reduced to Co$^{3+}$ ions making the LBCO thin films insulating with resistance greater than $10^7$ Ω. Note that the resistance does not change any more even if the reduction time is increased at medium temperature above 400 °C. This is different from the low temperature (260~350°C) phenomenon (see below). The change in the resistance R under the switching flow of the reducing/oxidizing gas at 500 °C is shown in Fig. 1(a), and the associated dR/dt in Fig. 1(b). As the gas flow is switched from H$_2$ to O$_2$, the oxidation from Co$^{3+}$ to Co$^{4+}$ occurs, and the resistance decreases ultrafast with rate much larger than the reduction reaction. This indicates that the reduced LBCO thin films have a large number of oxygen vacancies and Co$^{3+}$ ions are extremely sensitive to O$_2$. Furthermore, at 500 °C, the LBCO thin films show excellent chemical stability with good reproducibility of the conducting-to-insulating transitions.

3.2. Low temperature transitions

While monitoring the resistance change during the redox reactions at low temperatures (260~400°C), we found that the LBCO thin films go through more complex transitions involving three obvious states with a sudden change in the resistance. Fig. 2 shows the R vs. t and dR/dt vs. t curves at 350 °C. As shown in Fig. 2(a), there is a peak in the R vs. t curve during each reduction cycle under H$_2$ and during each oxidation cycle under O$_2$. This phenomenon suggests that each transition between conducting and insulating states in the early part of the reduction reaction cycle is followed by a transition between insulating and conducting states. These transitions are also reversible through the redox reactions. Under the
repetitive switching of the redox environments, the reduction and oxidation processes of the LBCO films are highly reversible as can be seen from Fig. 2 for the case of the redox reactions at 350 °C. Fig. 2b shows that, as the gas flow is switched from O₂ to H₂, the resistance R of LBCO increases to the maximum value and then decreases gradually to the equilibrium value. As the gas flow is switched from H₂ back to O₂, the resistance rapidly reaches its maximum value with the maximum rate of $\sim 10^9 \Omega/s$ and then quickly decreases to the stable value. These resistance changes are attributed to the average Co oxidation states on the surface of the films. In pure O₂ environment, LBCO can be fully oxidized to become ErBaCo₂O₆ with the Co average oxidation state of +3.5. As the gas flow changes from O₂ to H₂, LBCO would be reduced to become LaBaCo₂O₅(OH) and then LaBaCo₂O₅.₅ (by losing oxygen in terms of H₂O) with average Co oxidation state of +3, which explains the sharp increase in the resistance. A further reduction under H₂ would lead LBCO to LaBaCo₂O₄.₅(OH) and then LaBaCo₂O₅ with average Co oxidation state of +2.₅, which explains the sharp decrease in the resistance.

Fig. 3 (a) and (b) show the detailed R vs. t measurements for the reduction and oxidation cycles at various temperatures which indicate that at a given temperature the resistance change of the LBCO films under oxidation is much faster than that under reduction. When the gas flow is switched from H₂ to O₂, the resistance drops down by a few orders of magnitude, and this change depends sensitively on the temperature. The resistance under O₂ or H₂ is much higher at low temperatures than that at high temperatures. Below $\sim 400$ °C the reduction under H₂ occurs in one step at high temperatures, but in two steps (i.e., a very sharp increase followed by a gradual decrease).
The observed resistance of the LBCO films under the flow of the redox gases can be understood by considering the average Co oxidation state. The resistance should be low when the average Co oxidation state is fractional (e.g., +3.5 and +2.5) because it signals the presence of mixed valence cobalt ions (e.g., Co$^{3+}$/Co$^{4+}$ and Co$^{2+}$/Co$^{3+}$, respectively) and hence the occurrence of either hopping with low activation energy or metallic conductivity. In contrast, the resistance of the LBCO films should be high when the average Co oxidation state is an integer (e.g., +3 and +2) because electron-hopping is difficult in the case of single valence. The average Co oxidation state is +3.5 for LaBaCo$_2$O$_6$, +3 for LaBaCo$_2$O$_{5.5}$, and +2.5 for LaBaCo$_2$O$_5$. Our first principles density functional theory calculations for LaBaCo$_2$O$_6$ and various probable structures of LaBaCo$_2$O$_{5.5}$ and LaBaCo$_2$O$_5$(OH) show that hydrogen atoms are present in LBCO as bound to oxygen forming O-H bonds. Then, the average Co oxidation state is +3 for LaBaCo$_2$O$_5$(OH), +2.5 for LaBaCo$_2$O$_{4.5}$(OH), and +2 for LaBaCo$_2$O$_{3.5}$(OH)$_2$.

### 3.3. Redox equations

In general, any state transition of the LBCO thin films should arise from the chemical reactions. The reduction reaction of the LBCO thin films corresponding to their conducting-to-insulating transition can be expressed as

$$H_2 + O_o^* + 2Co^{4+} \rightarrow H_2O + 2Co^{3+} + V_o^{**} + 2e^\cdot.$$  \hspace{1cm} (1)

While the oxidation reaction corresponding to the insulating-to-conducting transition can be expressed as

$$O_2 + 2V_o^{**} + 4Co^{3+} + 4e^\cdot \rightarrow 2O_o^* + 4Co^{4+}.$$  \hspace{1cm} (2)
The LBCO thin films are stabilized at the insulating state with Co\(^{3+}\) ions under H\(_2\) at medium
temperatures, probably because the oxygen potential (i.e., the Gibbs energy of formation \(\Delta G\))
of H\(_2\)O is lower than that of the LBCO films with Co\(^{4+}\) ions but higher than that of LBCO
films with Co\(^{3+}\) ions. However, the oxygen potentials are temperature-dependent, so it is
possible that the oxygen potential of H\(_2\)O might become lower than that of the LBCO films
with Co\(^{3+}\) ions. In fact, a further reduction reaction of the LBCO thin films following the
reaction (1) does continue according to the sudden change in the resistance at low
temperatures. The further reduction reaction can be expressed as

\[
H_2 + O_2^{\bullet\bullet} + 2Co^{3+} \rightarrow H_2O + 2Co^{2+} + V_0^{\bullet\bullet} + 2e^{\bullet}\,.(3)
\]

As a result of the reaction (3), the LBCO thin films are converted from the insulating to a
conducting state, in which new small polarons might play the role of new carriers, as depicted
in Fig 2(c). The oxidation reaction corresponding to the semiconducting-to-insulating
transition can be expressed as

\[
O_2 + 2V_0^{\bullet\bullet} + 4Co^{2+} + 4e^{\bullet} \rightarrow 2O_2^{\bullet\bullet} + 4Co^{3+}\,.(4)
\]

3.4. Analysis of the cycling stability

Usually, changes in the oxygen vacancy concentration of the LBCO thin films are
expected to bring about expansion, contraction or even destruction of their structures.
Nevertheless, as shown in Fig. 2(a) and Fig. 4(a), the transitions among the different states
has good reproducibility during five to seven reduction/oxidation cycles at low temperatures.
The repeatable R vs. t curves in these cycles reflects a repeatable change in the oxygen
vacancy concentration and the variation of the Co oxidation states, and also reveals good
stability of the chemical properties of the LBCO thin films under the reducing/oxidizing
environments. The latter may benefit from the stable frame structure of the epitaxial thin films. According to the neutron diffraction studies of Seddon et al., the LaBaCo$_2$O$_{4.25}$ prepared by a low-temperature reduction of LaBaCo$_2$O$_5$ using NaH contains cobalt in three distinct coordination environments, namely, CoO$_4$ tetrahedra (50%), CoO$_5$ square-pyramids (25%), and CoO$_4$ square-planes (25%). Owing to the weak reducing capacity of the H$_2$ environment, the oxygen vacancy concentration of the LBCO thin film under H$_2$ is much lower than that found for LaBaCo$_2$O$_{4.25}$. Thus, as shown in Fig. 5, it is probable that, in the LBCO thin films under H$_2$, CoO$_4$ tetrahedra or square planes are not present, but CoO$_5$ square pyramids are. Obviously, the expansion and contraction of the LBCO thin films would be much less for the change between CoO$_5$ square pyramids and CoO$_6$ octahedra than between CoO$_4$ tetrahedra/square-planes and CoO$_6$ octahedra.

3.5. Chemical dynamics analysis

From the perspective of the dR/dt vs. t curves, the LBCO thin films possess ultrafast chemical dynamics during the oxidation cycle, with largest change above $10^7$ Ω/s even at 300 °C, as shown in Fig. 4(b). In particular, the oxidation reaction (4) at 300 °C has a very short reaction time and a greater change in dR/dt than does the oxidation reaction (2) at either 300 °C or 500 °C. The ultrafast oxidation from Co$^{2+}$ to Co$^{3+}$ can be understood as arising from the higher oxygen vacancy concentration and higher reducibility of the LBCO thin films with Co$^{2+}$.

To further understand the dynamic nature of the ultrafast oxidation from Co$^{2+}$ to Co$^{3+}$, our data were analyzed by employing the Avrami equation. For a solid-state phase
transformation, the degree of its completion is defined as the volume fraction $f$ of a new phase in solid phase. A solid-gas reaction consists of several steps such as the adsorption of gaseous molecules on the surface of solid, the dissociation of the molecules, and the atomic diffusion and nucleation, with the rate of the reaction determined by the slowest step. The volume fraction $f$ as a function of the reaction time can be expressed as

$$f(t) = 1 - \exp[-(t / \tau)^n].$$  \hspace{1cm} (5)

where $f(t)$ is the volume fraction, $n$ the nucleation factor representing the nucleation type, and $\tau$ the time for which $f(t) = 0$. Normally, $n = 4$ when nucleation occurs at a constant nucleation rate, $n = 3$ if the transformation is only the three-dimensional growth of the nuclei after the preformation of the nuclei, $n = 3 - 4$ if the nucleation rate decreases with time, and $n > 4$ if the nucleation rate increases with time. For the solid reaction dynamics, it is common to use the resistance change to calculate the volume fraction $f(t)$ as

$$f(t) = \frac{R_1 - R_0}{R_1 - R_0}$$

(6)

where $R_0$, $R_0$, and $R_1$ are the resistances of the solid at time $t$, at the start ($t = 0$) and at the end of the reaction, respectively. For the oxidation reaction from $\text{Co}^{2+}$ to $\text{Co}^{3+}$, the resistance increases from $R_{\text{min}}$ to $R_{\text{max}}$. Thus, by using equation (5) and (6), the resistance at time $t$ can be expressed as

$$R = R_{\text{max}} - (R_{\text{max}} - R_{\text{min}}) \exp[-(t / \tau)^n].$$  \hspace{1cm} (7)

The analysis of our data using the equation (7) indicates that the oxidation reaction at 300 °C is controlled by the nucleation rate, and the whole reaction can be completed in 3 seconds, as shown in Fig. 4(c).

The phase transition involving the change from the oxidation state $\text{Co}^{2+}$ to $\text{Co}^{3+}$ is highly
dependent upon the oxidation temperature. The time constants and the nucleation factors obtained by fitting the resistance curves with the equation (7) are plotted in Fig. 6. The reaction rate for the transition from $\text{Co}^{2+}$ to $\text{Co}^{3+}$ increases with increasing the temperature (from 260 to 350 °C). From the curve of $n$ we can find that the nucleation type also varies entirely with temperature. The extraordinary values of $n >> 4$ signify that a large numbers of oxygen vacancy sites, which act as potential oxidation nucleation centers, are generated during the reduction process above 300 °C. At 280 °C, nucleation occurs only at the start of the transformation. At 260 °C, the oxidation process from $\text{Co}^{2+}$ to $\text{Co}^{3+}$ is reduced in reaction rate and is not nucleation-controlled any longer.

4. Conclusions

The redox dynamics of the epitaxial LBCO thin films exposed to the switching flow of $\text{H}_2$ and $\text{O}_2$ gases at 260 – 700 °C were systematically studied by ac resistance measurements. At medium temperatures (400~700 °C), the LBCO thin films are sensitive to the reducing/oxidizing environments, exhibiting a conducting-to-insulating transition in each oxidation/redox cycle. At low temperatures (260~350 °C) under $\text{H}_2$ environment, the LBCO thin films undergo a conducting-to-insulating-to-conducting transition, which corresponds to the variation of the oxidation states, $\text{Co}^{4+}/\text{Co}^{3+}$ to $\text{Co}^{3+}$ to $\text{Co}^{3+}/\text{Co}^{2+}$. The oxidation reaction from $\text{Co}^{2+}$ to $\text{Co}^{3+}$ at low temperatures is faster than that from $\text{Co}^{3+}$ to $\text{Co}^{4+}$. The time required to change from the $\text{Co}^{2+}$ to $\text{Co}^{3+}$ state decreases from 30 to 3 s with increasing the temperature from 260 to 350 °C. The nucleation rate of the reaction at 300 and 350 °C increases with time during their very short reaction process. The ultrafast redox reactions at
300 – 700 °C indicates that the epitaxial LBCO thin films are a promising candidate for low-temperature SOFC cathodes, chemical gas sensors, effective deoxidizers, and vehicle exhaust catalysts.

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Figure Captions

Fig. 1. (a) R vs. t and (b) dR/dt vs. t curves measured for the LBCO thin films under oxidizing/reducing atmospheres at 500 °C.

Fig. 2. Resistance changes vs. the gas flow time, R vs. t, of an epitaxial LBCO thin film: (a) During the reduction (under H₂) cycle at various temperatures. (b) During the oxidation (under O₂) cycle at various temperatures.

Fig. 3. (a) R vs. t and (b) dR/dt vs. t curves measured for the LBCO thin films under oxidizing/reducing atmospheres measured at 350°C. (c) A zoomed-in view of the R vs. t curve for one oxidation/reduction cycle showing the variation of the Co oxidation state as a function of t. The dR/dt vs. t curves for the (d) reduction and (e) oxidation processes of the reduction/oxidation cycle presented in (c).

Fig. 4. Redox reactions of the LBCO thin films under the switching flow of reducing/oxidizing gas flow at 300 °C: (a) R vs. t and (b) dR/dt vs. t curves. (c) Avrami analysis of the oxidation reactions associated with the oxidation state change from Co²⁺ to Co³⁺.

Fig. 5. Polyhedral representations of the crystal structures of LaBaCo₂O₆, LaBaCo₂O₅.₅ and LaBaCo₂O₅.

Fig. 6 The n and τ values obtained from the Avrami analysis for the oxidation reactions associated with the change in the Co oxidation state Co²⁺ to Co³⁺ at temperatures between 260 – 350 °C.
Fig. 1
Figure 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6


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