

Thermal and chemical expansion of mixed conducting $\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$

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The thermal and chemical expansion properties of $\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, a potential candidate for oxygen permeable membranes and cathodes in solid oxide fuel cells (SOFC), are reported here. The isothermal expansion measurements were repeated over the oxygen partial pressure range of $10^{-4} \leq p\text{O}_2/\text{atm} \leq 0.21$ and the temperature range of $700 \leq T/^\circ\text{C} \leq 1000$. The high-temperature chemical expansion of LSCF1982 was attributed to both volume expansion due to the increased ionic radii of the B-site cations and the increase of the oxygen nonstoichiometry.

Key word: thermal expansion, perovskite, isothermal expansion,

Introduction

$\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) materials are potential candidates as the cathode in solid oxide fuel cells (SOFC) and oxygen permeation membranes. Ishihara *et al* [1], reported that when LSCF1982 ($\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$) surface catalyst was applied onto aliovalent, cation-doped, $\text{Pr}_2\text{NiO}_{4+\delta}$ -based, oxide specimens, the oxygen permeation flux increased significantly. Because the binding energy for oxygen of Co ions on B-sites is smaller than that of Fe ions, the oxygen nonstoichiometry is expected to increase with increasing Co content in LSCF [2, 3].

LSCF1982 readily undergoes oxygen deficiency because B-site quadrivalent cations are easily reduced to trivalent cations, leading to charge compensation by oxygen vacancies. The effective charge defect formation results in a chemical expansion as a function of the oxygen partial pressure ($p\text{O}_2$) because of electrostatic repulsion between defects and their surrounding atoms, as well as the larger crystal radius of the reduced B-site cation compared to that of the unreduced B-site cation [3]. This induces stresses in composites or constrained bodies that, in turn, affect conductivity and possibly result in mechanical failure of the system [4, 5]. Therefore, the purpose of the present study was to determine the isothermal expansion of LSCF1982 as a function of temperature and $p\text{O}_2$.

Experimental

Mixed oxygen ion-electron conducting LSCF1982 powders were prepared by a solution method with

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich, 99.99%), $\text{Sr}(\text{NO}_3)_2$ (Aldrich, 99.99%), $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Aldrich, 99.9%), and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aldrich, 99.9%) as starting materials. Stoichiometric amounts of the components were dissolved in distilled water, dried under stirring conditions and calcined at 1100°C for 6 h in air. The calcined powder was then planetary ball-milled with stabilized zirconia balls for 4 h at 180 rpm, cold isostatically pressed at 150 MPa, and sintered at 1250°C for 8 h in air. The X-ray diffraction (D/Max vitina III, Rigaku Japan) spectra revealed that the LSCF1982 structure consisted of a single phase. The primary particle size, d , was estimated from the X-ray line width by the Scherrer formula, $d = 0.9\lambda/\beta_{1/2}\cos\theta$, where λ is the X-ray wavelength, $\beta_{1/2}$ the corrected width of the main diffraction peak at half-height and λ the diffraction angle. The d values of the powders were ≈ 32 nm [6]. For isothermal dilatometry, a parallelepiped specimen of dimensions $1 \times 5 \times 10$ mm³ was cut out of the sintered samples with a low-speed diamond saw. The one-dimensional displacement in the direction of the specimen length was measured using a Netzsch L75 PT1600 dilatometer from room temperature to 1000°C at $2 \text{ K}\cdot\text{minute}^{-1}$ with an air purge at a flow rate of $50 \text{ cc}\cdot\text{minute}^{-1}$. The detecting rod was pushed against the specimen with a load of 0.02 N. The overall measurements were repeated over the $p\text{O}_2$ range of $10^{-4} \leq p\text{O}_2/\text{atm} \leq 0.21$ and the temperature range of $700 \leq T/^\circ\text{C} \leq 1000$. The $p\text{O}_2$ values were controlled by flowing O_2/N_2 gas mixtures, and monitored with a zirconia-based oxygen sensor.

Results and Discussion

The surface microstructures of as-sintered specimens are shown in Fig. 1. The morphological evolutions that occurred revealed the attainment of high densification at a sintering temperature of 1170°C because the presence of cobalt and iron assisted in the sintering process in the LSCF system

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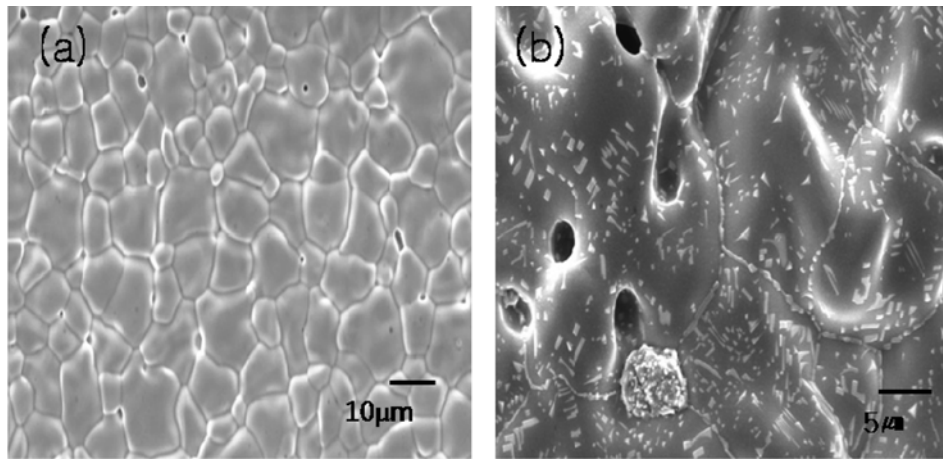
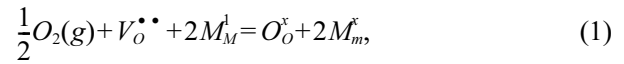


Fig. 1. Surface micrographs of $\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ after measurements up to at (a) 1000 °C, (b) 1100 °C.

due to liquid phase sintering. Furthermore, after dilatometry measurements up to 1100 °C, some nanocrystalline grains were found to be uniformly precipitated within the core grains. It has been reported that the precipitation of nanocrystalline grains at the time of recrystallization is only observed for heavily A-site Sr rich LSCF [7]. Because of the nanocrystalline grain formation on the surface, the isothermal dilatometry measurements were performed below 1000 °C.

The thermal expansion of LSCF1982 in the temperature range of $20 < T/^{\circ}\text{C} < 1100$ in air is shown in Fig. 2. The measurements were made at heating and cooling rates of $2 \text{ K}\cdot\text{minute}^{-1}$. The temperature was held constant between each segment. The expansion of the sample was constant ($\pm 0.1\%$) in the isothermal regions. The inflexion that appeared at about 600 °C, and was also revealed by the DTA data [6], was attributed to the thermally induced loss of lattice oxygen and the formation of oxygen vacancies due to cobalt cation reduction from Co^{3+} to Co^{2+} for charge neutrality from the external reaction with the atmosphere, according to the following reaction:



The average thermal expansion coefficient (TEC) was about $13 \times 10^{-6} \text{ K}^{-1}$ below 600 °C, and about $22 \times 10^{-6} \text{ K}^{-1}$ between 650 °C and 1000 °C. The total DC conductivity and the weight change in a thermal gravimetric analysis (TGA) experiment both begin to decrease at this temperature [8, 9, 10]. The expansion curve deviated from linearity, as indicated by the dashed lines and this change in linear dimension was completely reversible during heating/cooling cycling in air. The hysteresis in the cooling and heating processes evidenced the reversibility of the oxygen uptake process, along with the phase transition.

Furthermore, raw traces of the relative isothermal dilatometry measurements at various temperatures are shown in Fig. 3 as $p\text{O}_2$ is stepped from 10^{-4} atm to air. The sample was first heated to 700 °C in air and allowed to reach constant length. The sample expansion due to oxygen loss was then measured after switching off the gas stream. The kinetic parameters could not be extracted from the transient dilatometry measurements because the gas switch-out time was too long to fit reliable oxidation and reduction kinetics. The chemical expansion of LSCF1982 with the change in $p\text{O}_2$ with good reversibility suggests that the external redox reaction reflects the change in the nonstoichiometry of LSCF1982 [11, 12].

The $p\text{O}_2$ dependence of the chemical expansion at various temperatures between air and an ultra-high pressure N_2 atmosphere is shown in Fig. 4. The chemical expansion increased linearly with decreasing $p\text{O}_2$, suggesting that the oxygen nonstoichiometry with $p\text{O}_2$ was directly correlated with the chemical expansion. The expansion of the oxide specimen with $p\text{O}_2$ showed that the volume of LSCF1982 increased with the increase in oxygen nonstoichiometry. However, the isothermal expansion of LSCF1982 was not only solely dominated by oxygen nonstoichiometry but also by the change in the crystal ionic radii of the B-site cations due to the reduction shown in Eq. 1. The crystal ionic radii accepted for cations along with their coordination numbers

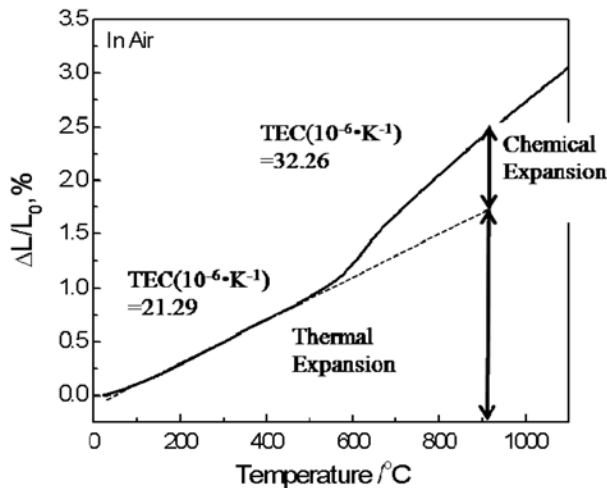


Fig. 2. Thermal expansion curve for $\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ in the temperature range of 20-1000 °C.

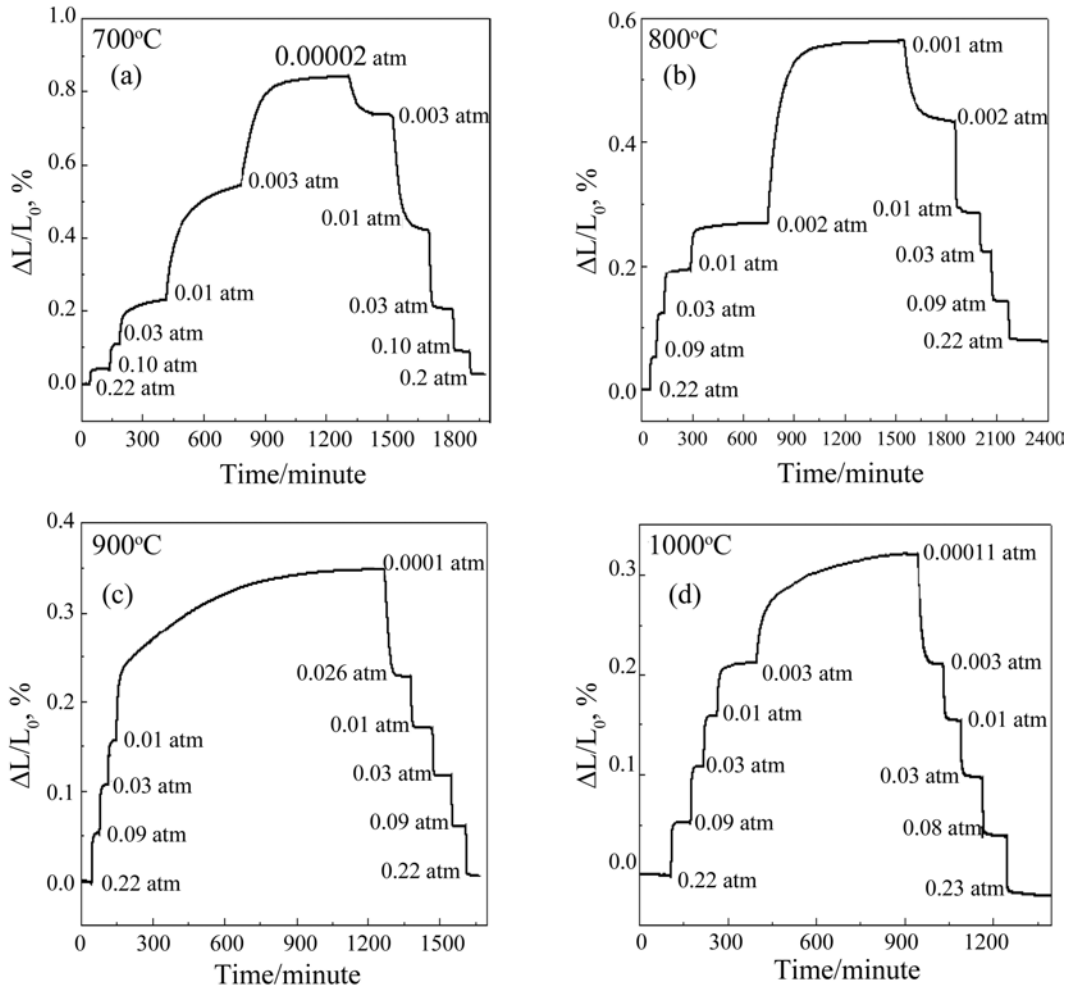


Fig. 3. Raw traces of the isothermal expansion of $\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ at various temperatures.

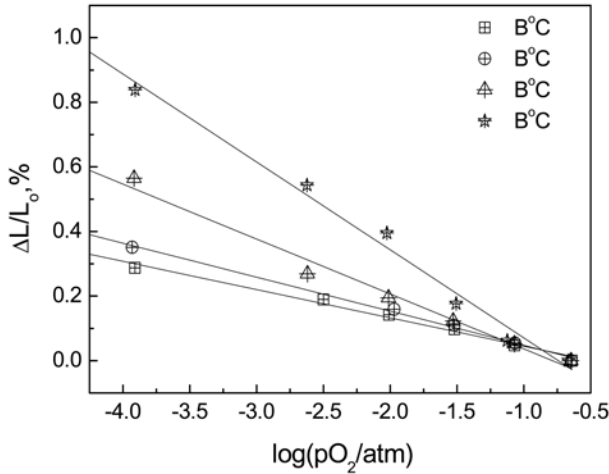


Fig. 4. Chemical expansion of $\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ vs. $\log(p\text{O}_2/\text{atm})$.

were: $r_{\text{O}^{2-}} = 1.26 \text{ \AA}$ (CN = 6), $r_{\text{La}^{3+}} = 1.50 \text{ \AA}$ (CN = 12), $r_{\text{Co}^{2+}} = 0.79 \text{ \AA}$ (LS, CN = 6), $r_{\text{Co}^{3+}} = 0.75 \text{ \AA}$ (HS, CN = 6), and $r_{\text{Co}^{4+}} = 0.67 \text{ \AA}$ (HS, CN = 6), where LS and HS correspond to the low and high spin states, respectively [13]. The reduced cobalt cation had a larger crystal radius than its

unreduced (quadrivalent) state, and the effective negative charged reduced cobalt ions in the lattice have electrostatic charges that repel their nearest oxygen atoms. Therefore, the high-temperature chemical expansion of LSCF1982 can be attributed to both volume expansion due to the increased ionic radii of the B-site cations and the increase of oxygen nonstoichiometry.

Conclusions

The isothermal expansion of $\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ was measured over the oxygen partial pressure range of $10^{-4} \leq p\text{O}_2/\text{atm} \leq 0.21$ and the temperature range of $700 \leq T/^\circ\text{C} \leq 1000$. The average thermal expansion coefficient (TEC) was about $13 \times 10^{-6} \text{ K}^{-1}$ below 600°C , and about $22 \times 10^{-6} \text{ K}^{-1}$ between 650°C and 1000°C , which consists of the previous total DC conductivity and the weight change in a thermal gravimetric analysis (TGA) experiment. The chemical expansion increased linearly with decreasing $p\text{O}_2$, suggesting that the high-temperature chemical expansion of LSCF1982 was attributed to both volume expansion due to the increased ionic radii of the B-site cations and the increase of the oxygen nonstoichiometry.

Acknowledgments

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