

Thermal and chemical expansion properties of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-x}$

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Abstract

The thermal and chemical expansion coefficients for $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-x}$ were measured at $800 \leq T \leq 1200$ °C and at $\sim 1 \times 10^{-15} \leq p\text{O}_2 \leq 0.21$ atm. Measurements of the total expansion coefficient in air, on heating and cooling between room temperature and 1200 °C, are reproducible. The average thermal expansion coefficient of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-x}$ is $9.3 \pm 1.1 \times 10^{-6} \text{ K}^{-1}$ over the whole temperature range, similar to the values reported for other titanium substituted perovskites and yttria-stabilized zirconia. The chemical expansion coefficients measured at 800 °C vary linearly with the degree of oxygen non-stoichiometry. At higher temperatures, the chemical expansion shows a pronounced non-linear dependence on stoichiometry. At oxygen partial pressures below $\sim 10^{-6}$ atm, the expansion shows evidence of the slow kinetic behavior previously observed in stoichiometry and conductivity measurements.

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1. Introduction

The mixed ionic electronic conductors, $(\text{La},\text{Sr})(\text{Fe},\text{Ti})\text{O}_{3-x}$, have been studied because of the possibility of their practical applications in ion transport membranes, pressure driven oxygen generators, partial oxidation reactors, and as electrodes for solid oxide fuel cells (SOFCs) [1,2]. In contrast, the related compositions, $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-x}$, have a high level of mixed conductivity, relatively high thermal expansion coefficients (TECs), but poor stability both in highly reducing conditions and with respect to reaction with YSZ [3–7].

The partial substitution of lanthanum for strontium on the A site lowers the thermal expansion coefficient and enhances the stability [4,5,7]. The electrical conductivity and oxygen non-stoichiometry of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-x}$ have been investigated previously [8]. The total conductivity at $p\text{O}_2 = 1$ atm is $\sim 14 \text{ Scm}^{-1}$ at ~ 400 °C and the ionic conductivity is $\sim 0.03 \text{ Scm}^{-1}$ at 900 °C with an activation energy of 0.63

eV. The chemical and structural stability in low $p\text{O}_2$ environments is a critical requirement for application in ion transport membranes for syngas generation. Consequently, we have determined the thermal and chemical expansion of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-x}$ at different temperatures and oxygen partial pressures to complement our other studies of this composition. Thermal expansion coefficients of related compositions have been reported but no information, to the best of our knowledge, concerning the chemical expansion is available.

2. Experimental details

$\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-x}$ powder, synthesized by using the spray pyrolysis method, was obtained from Praxair Specialty Ceramics (Woodinville, WA). The details of the sample characterization, conductivity and stoichiometry were reported previously [8]. Rectangular sample bars ($14.38 \times 4.47 \times 5.33$ mm) sintered at 1450 °C for 10 h were used for dilatometry measurements (NETZSCH, DIL 402C). Thermal expansion measurements were performed at $25 \leq T \leq 1200$ °C with a heating and cooling rate of 3 K

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min^{-1} . Purified air was flowed through the furnace at 80 ml/min. The chemical expansion data were obtained by switching the gas from air to pure argon or by using mixed gases (5% H_2/N_2 , CO_2 , and argon) in the temperature range between 800 and 1000 °C. The flow rate of the each gas was controlled by using mass flow controllers (MKS, 247C). An oxygen analyzer (AMETEK, TM-1B) was connected to the outlet of the dilatometer. The oxygen partial pressure (p_{O_2}) was recorded every minute by reading the emf of the oxygen analyzer with an HP 3468A multimeter. The oxygen partial pressure (p_{O_2}) was calculated using the Nernst equation with air as a reference gas.

For additional X-ray diffraction studies, samples were heated to 900 °C in different oxygen partial pressures and then quenched by rapidly transferring them from the furnace into ambient air. Samples were quenched from $p_{\text{O}_2} \sim 1.3 \times 10^{-4}$, 1.1×10^{-7} , 1.2×10^{-10} , and 6.7×10^{-14} atm and analyzed by X-ray powder diffraction (Scintag XDS 2000).

3. Results and discussion

3.1. Thermal expansion behavior

The thermal expansion of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-x}$ in the temperature range $25 \leq T \leq 1200$ °C in air is shown in Fig. 1a. The measurements were made over two heating and cooling cycles at heating and cooling rates of 3 K min^{-1} . The temperature was held constant between each segment (see Fig. 1a). The expansion of the sample is constant ($\pm 0.1\%$) in the isothermal regions. The sample expansion as a function of temperature is shown in Fig. 1b. The data obtained on heating and cooling are reproducible. The change in slope of the thermal expansion data at ~ 320 °C (see inset in Fig. 1b) is attributed to the onset of oxygen loss upon heating and slow re-oxidation kinetics on cooling. The discontinuity is more pronounced on heating. The total DC conductivity and the weight change in a TGA experiment both begin to decrease at this temperature [8]. Similar changes in sample expansion due to oxygen loss have been reported previously, for example, in $\text{Sr}_{0.97}\text{Ti}_{1-x}\text{Fe}_x\text{O}_{3-x}$ by Kharton and co-workers [3,5–7].

Based on the dilatometry data, the thermal expansion coefficients (TECs) can be calculated from:

$$\alpha_i = \text{Limit}_{T_i T_0} \frac{L_t - L_0}{L(T_t - T_0)} = \frac{1}{L} \frac{dL}{dT} \quad (1)$$

where α_i is the instantaneous coefficient of linear thermal expansion/degree, L_t and L_0 are the specimen length at temperature T_t and T_0 , respectively [9].

The results obtained by taking the derivative of dL/L with respect to temperature are shown in Fig. 2 for the two cycles of heating and cooling (the data has been smoothed

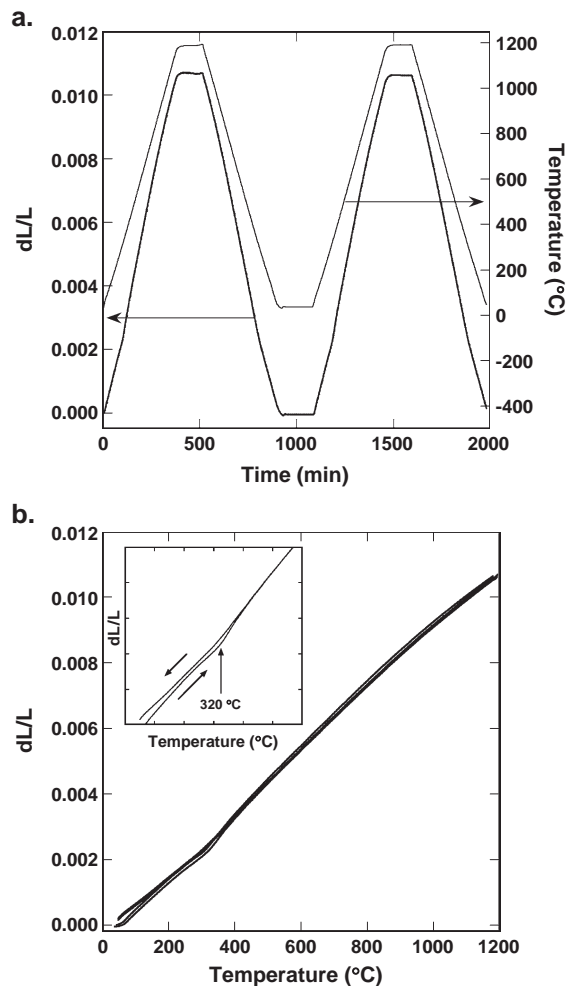


Fig. 1. Thermal expansion data for $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-x}$. In (a) the thin line indicates the temperature profile. In (b) the insert shows the behavior in the vicinity of the temperature at which oxygen loss occurs on heating.

to eliminate some of the noise in the derivative). The data are reproducible for the two heating cycles and the two cooling cycles but show some differences below 550 °C presumably due to the differences in the relative rates of oxygen loss or re-oxidation. It is interesting to note that the heating and cooling curves cross over at 320 °C, the temperature at which the kinetics of oxygen insertion or removal becomes limiting. On heating, the thermal expansion coefficient reaches a maximum value of $\sim 12 \times 10^{-6} \text{ K}^{-1}$ and then falls to $\sim 10 \times 10^{-6} \text{ K}^{-1}$ at 550 °C. Above 750 °C, the expansion coefficient drops smoothly to $\sim 8 \times 10^{-6} \text{ K}^{-1}$ at 1100 °C. The average TEC of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.55}\text{Ti}_{0.45}\text{O}_{3-x}$ over the whole temperature range is $9.3 \pm 1.1 \times 10^{-6} \text{ K}^{-1}$. The introduction of titanium ions on the B sites of LSFO clearly has a strong effect in reducing the thermal expansion coefficient, in part due to the restriction imposed on the extent of oxygen non-stoichiometry. Low thermal expansion coefficients of related titanates have been reported by Fagg et al. [5]. A low TEC is an important property for the use of the material

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