Synthesis and evaluation of effective parameters in thermal expansion coefficient of $\text{Ln}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{M}_{0.8}\text{O}_{3-\delta}$ ($\text{Ln} = \text{La}, \text{Nd}$ and $\text{M} = \text{Mn}, \text{Fe}$) perovskite oxide

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Abstract. In this study, oxides $\text{Ln}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{M}_{0.8}\text{O}_{3-\delta}$ ($\text{Ln} = \text{La}, \text{Nd}$ and $\text{M} = \text{Mn}, \text{Fe}$) have been prepared and characterized to study the influence of the different cations on thermal expansion coefficient (TEC). TEC decreases favourably with replacement of Nd^{3+} and Mn^{3+} ions in the lattice. Nd^{3+} leads to decreasing ionicity of the $\text{Ln}-\text{O}$ bond and phase transition from rhombohedral to orthorhombic. Structural parameters of compounds have been determined by X-ray diffraction (XRD). FT-IR analysis has been used to compare the bond strength of different cations in the lattice. Variations of lattice parameters of compounds have been monitored by *in-situ* XRD at different temperatures in order to study the thermo-chemical expansivity. Concentration of oxide ion vacancy has been determined by high temperature gravimetry. The results show more stability of Mn^{4+} ions in high temperature in comparison with Fe^{4+} ions, which suppresses the tendency to lose oxygen from the lattice with the increase in temperature.

Keywords. Thermal expansion coefficient; perovskite; bond strength, chemical expansion.

1. Introduction

In solid oxide fuel cells (SOFCs) the cathode functions as the site for the electrochemical reduction of oxygen. Therefore, the cathode must have high electronic conductivity, adequate porosity, stability under an oxidizing atmosphere and high catalytic activity. In addition, it is crucial for the cathode to have matched thermal expansion coefficient (TEC) and chemical compatibility with both the electrolyte and interconnect materials. Hence, care should be taken to match TECs and avoid undesirable interface reactions.^{1–5}

The chemical reactivity and thermal expansion mismatch among the components as well as the limited choice of interconnect and cathode materials at the conventional operating temperatures (1000°C) of SOFC have created enormous interest in recent times in intermediate temperature (500–800°C) SOFC.⁶

Perovskite materials—particularly of the LaMO_3 type, where M is typically a transition metal, have been widely used as cathode materials in SOFCs.^{1,2} For most of the perovskite materials used as cathodes in SOFCs, the A-site cation is a mixture of rare and alkaline earths (such as La and Sr, Ca or Ba), while the B-site cation is a reducible transition metal such as Mn, Fe, Co or Ni (or a mixture thereof). In general, most cathode materials rely on doping of both the A- and B-sites in order to improve the difference in the performance.^{1,2,7}

In $\text{Ln}_{1-x}\text{Sr}_x\text{M}^{3+}\text{O}_{3-\delta}$ the oxygen vacancies arise either from replacement of A^{3+} by A^{2+} or from the partial reduction of B^{3+} or B^{4+} to B^{2+} and B^{3+} , respectively. Oxygen mobility through vacancies is the basis of oxide ion conductivity.^{8,9}

Nonstoichiometric oxides are known to not only undergo lattice expansion as a function of temperature, but also based on changes in oxygen partial pressure, P_{O_2} , and the correlated changes in oxygen content (nonstoichiometry) at elevated temperatures.^{10–12} This thermochemical expansion affects the compatibility with other components.

Chemical expansion has been investigated in various nonstoichiometric oxides such as LaMnO_3 ,¹³ $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF),¹² $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ (LSF),¹¹ A- and B-site-doped $\text{LaCrO}_{3-\delta}$,¹⁴ LaMnO_3 ¹³ and $\text{Pr}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$.¹⁵ While an increase in lattice parameter, and thus thermal lattice expansion is induced through enhanced vibration of lattice atoms upon heating, the origin of chemical expansion in nonstoichiometric oxides has been correlated to the formation of oxygen vacancies and changes in the oxidation state of the metal cations.¹⁶ Upon reduction of the oxide material under reductive atmosphere and with increasing temperature, oxygen vacancies are introduced in the lattice, which is accompanied by the reduction of the metal cations to maintain charge neutrality.¹⁷

The formation of oxygen vacancies is considered to cause lattice expansion through electrostatic repulsion as positively charged cations are no longer shielded by negatively charged oxygen ions in the crystallattice of the perovskite

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material.^{16,17} Additionally, the reduction of the metal cation results in an increase in ionic radius, and the lattice expands due to steric effects.¹⁶

Riza *et al*¹⁸ and Lee and Manthiram⁶ investigated the effect of element replacement on TEC. They found that the replacement of Nd, Sm, Pr and Gd in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ results in decrease of the TEC.

This study attempted to identify the effective factors and mechanisms in the TEC of perovskite ($\text{Ln}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{M}_{0.8}\text{O}_{3-\delta}$; Ln = La, Nd and M = Mn, Fe). Therefore, structural parameters, bond strength, oxygen deficiency, lattice parameter variations and approximate thermal and chemical parameters have been investigated.

2. Material and methods

The $\text{Ln}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{M}_{0.8}\text{O}_{3-\delta}$ (Ln = La, Nd and M = Mn, Fe) cathode samples were synthesized by the conventional solid-state reaction method. Required amounts of the lanthanide oxides La_2O_3 , Nd_2O_3 , SrCO_3 , Fe_2O_3 , Co_3O_4 and Mn_2O_3 were thoroughly mixed with ethanol using an agate mortar and pestle, and calcined in air first at 900°C for 12 h. The calcined powders were then ground, pressed into pellets, and finally sintered at 1300°C for 24 h.

For the phase identification, X-ray diffraction (XRD) profile was equipped with a Philips Cu K α radiation ($\lambda = 1.5404 \text{ \AA}$). All XRD experiments were performed with step size of 0.02° and a step time of 2 s. The lattice parameter was determined by fitting the observed reflection with a least-squares refinement program. The lattice parameters of different compounds were also converted to those as pseudo-cubic via lattice volume of trigonal and orthorhombic. Variations in lattice parameters with increasing temperature were monitored by high-temperature X-ray diffraction analysis (HT-XRD) (Philips Co-K α 1.5404 $\text{\AA}$ radiation at 10 kV and 10 mA). The measurements were carried out at $25\text{--}800^\circ\text{C}$ and each sample was put on to a platinum heater directly in the chamber. The TECs of sintered samples were measured from room temperature to 800°C with a heating/cooling rate of $10^\circ\text{C min}^{-1}$ by Dilatometry 402ENETZSCH. The absolute values of oxygen content in the specimens were precisely confirmed by high temperature gravimetry (Linseis-STAPT1000).¹⁹ Field emission scanning electron microscopy (FE-SEM) Philips XL30S FEG with the accelerating voltage of 5 kV was used for the morphological study. Fourier-transform infrared (FT-IR) spectra of the powder samples (in the KBr pellets) were recorded from 150 to 700 cm^{-1} by a Bruker Fourier-transform infrared spectrometer (Perkin Elmer, Spectrum 400, resolution 2 cm^{-1}).

3. Results and discussion

3.1 TEC of different samples

Figure 1 shows the average TECs of the different compounds which were measured in air and in the temperature range of

Figure 1. Variations of thermal expansion coefficient vs. temperature in different compounds in air.

Figure 2. XRD patterns of different compounds.

$25\text{--}800^\circ\text{C}$. It has been noted that the substitution of Nd for La (A-site) and Mn for Fe (B-site) decreases the TEC. The maximum reduction in coefficient of thermal expansion was followed by simultaneous replacement of these elements in NSCM compound.

3.2 The effect of structural parameters on TEC

Figure 2 shows XRD patterns of synthesized compounds and their structural properties have been summarized in table 1. All specimens were single phase, LSCF and LSCM compounds were indexed as rhombohedral (trigonal) perovskite phase with the $R3c$ space group, NSCF and NSCM compounds were indexed as orthorhombic perovskite phase with the $Pnma$ space group. When La^{3+} is replaced by smaller Nd^{3+} ions (La^{3+} : $1.36 \text{ \AA}$ and Nd^{3+} : $1.27 \text{ \AA}$), ionic radius, unit cell volume and Goldschmidt's tolerance factor were decreased. In a perfect cubic perovskite structure the B–O–B

Table 1. Lattice parameters, lattice volume, pseudocubic lattice parameter (a_{pc}) and tolerance factor (t) different compounds.

Compounds	Structure	a (Å)	b (Å)	c (Å)	V (Å) ³	a_{pc} (Å)	t
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF)	Rhombohedral	5.47	—	13.69	350.46	3.88	0.97
$\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (NSCF)	Orthorhombic	5.35	5.57	7.48	222.9	3.54	0.90
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.8}\text{O}_{3-\delta}$ (LSCM)	Rhombohedral	5.43	—	13.01	329.95	3.80	0.97
$\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.8}\text{O}_{3-\delta}$ (NSCM)	Orthorhombic	5.46	5.24	7	206.88	3.45	0.90

Figure 3. SEM micrographs for fractured surface of (a) LSCF, (b) NSCF, (c) LSCM and (d) NSCM.

chains are linear, i.e., the bond angle is 180° . Deviation from cubic symmetry results in tilting of the BO_6 octahedra and reduction of the B–O–B bond angles. Tilting of the BO_6 octahedra leads to phase transition from cubic to rhombohedral and then to orthorhombic. Tai *et al.*²⁰ have shown that phase transition in perovskite ferro-cobaltite from rhombohedral to orthorhombic decreases TEC.

Radaelli *et al.*²¹ have shown using the expression $V \approx Z(2B-O \cos \omega)^3$ that the unit cell volume directly proportional to the B–O and tilt angle (ω). The ω also represents the distortion of the BO_6 octahedra with respect to the cubic

phase ($\omega = 0^\circ$). The tilt angle is therefore calculated using an expression, $\omega = (180^\circ - \text{B–O–B})/2$, where B–O–B is the bond angle.

Using smaller Nd^{3+} ions led to an increase in tilting of the BO_6 octahedra and a decrease in unit cell volume. Consequently, more compaction crystal structure has been observed in this compound. In addition, decreasing tolerance factor is an indication of phase transition from rhombohedral to orthorhombic. It has been noted that replacement of Mn in the system has no significant impact on the structure and compaction of lattice. Figure 3 shows SEM micrographs for

fractured surface of different compounds. Particles have been found almost spherical in all samples and the average size of particles has been decreased with replacement of Mn in the lattice.

3.3 Relationship between bond strength and TEC

In general, ionic bonds have a larger thermal expansion than the covalent bonds. Therefore, the variations in TEC can be understood by considering the ionic character of the Ln–O bonds. Mori *et al*²² have also discussed the variations of TEC in the analogous lanthanum manganites $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ A = alkaline earth in terms of the ionic character of the A–O bond. The per cent ionic character of a bond is related to the electronegativity difference between the bonded atoms A and B in the A–B bond by the following empirical relationship:²³

$$\text{Ionicity } \% = [1 - \exp(-0.25 (X_A - X_B)^2)] \times 100, \quad (1)$$

where X_A and X_B are the electronegativities of the A and B atoms, respectively. Based on the Pauling electronegativity values,²⁴ one can therefore, understand that the decreasing TEC in compounds containing Nd is due to the increasing electronegativity of Nd and the decreasing ionic character of the Ln–O bond. Elements in the B-sites have strong covalent bond. In order to compare the bond strength of these elements, their capacity of change in system should be considered. According to Pauling bond strength law, tetravalent ions create stronger bond in BO_6 octahedra, reduce the size and unit cell volume of the octahedra and decrease the TEC. Hence, in order to bond strength of different elements, the infrared spectroscopy study is carried out for different compounds and the results are presented in figure 4. The FT-IR spectra of different compounds are similar to those of rhombohedral perovskites pure and doped LaMnO_3 .^{25,26} Therefore, an irreducible representation for the optical mode can be represented as $\Gamma_{\text{opt}} = \Gamma_{\text{Raman}} + \Gamma_{\text{IR}} + \Gamma_{\text{Inactive}} + \Gamma_{\text{Acoustic}}$. $\Gamma_{\text{Raman}} = A_{1g} + 4E_g$ corresponds to Raman active modes. $\Gamma_{\text{IR}} = 3A_{2u} + 5E_u$ indicates IR active modes. Γ_{Inactive}

($= 2A_{1u} + 3A_{2g}$) and $\Gamma_{\text{Acoustic}} (= A_{2u} + E_u)$ are acoustic and inactive modes, respectively. Figure 4 shows that using Nd instead of La in NSCF and NSCM samples resulted in transfer of the peak associated with the bending vibration of A–O in vibrational modes of E_u^1/A_u^1 to the larger wavenumber (from 166 to 168 cm^{-1} in La–O to 166 to 178 cm^{-1} in Nd–O). Results of Mn-containing samples shows that the stretching and bending vibrations of B–O bond in E_u^2/A_u^2 and E_u^3/A_u^3 mod happen in larger wavenumber, which is due to the decrease in bond length of Mn–O compared to Fe–O. It has been observed that replacement of Nd and Mn cause a shift of the atomic vibrations peaks to the larger wavenumber which indicates a decrease in bond length, unit cell volume, and thus the TEC.

3.4 Relationship between oxygen deficiency and TEC

The variations in TEC could also be related to the tendency to form oxide ion vacancies as the sample is heated, which is accompanied by the reduction of the metal cations to maintain charge neutrality. The formation of oxygen vacancies was considered to cause lattice expansion through electrostatic repulsion as positively charged cations are no longer shielded by negatively charged oxygen ions in the crystal lattice of the perovskite material.^{14–17} Results of oxygen deficiency vs. temperature in different compounds are shown in figure 5. As could be seen in all compounds, increasing temperature has increased the oxygen deficiency. Oxygen deficiency in LSCF and NSCM compounds is more compared to LSCM and NSCF compounds, which indicates the role of Mn in decreasing amount of oxygen deficiency and greater stability of Mn^{4+} ions in relation to Fe^{4+} ions at higher temperatures. It is evident that Nd slightly reduced the amount of oxygen vacancies which is associated with more bond strength in Nd–O compared with La–O.

Kilner and Brook²⁷ noted that for an oxide ion to jump between two oxygen sites, it must pass through a gap bordered by three cations and named the radius of this gap the critical radius, r_c .

Figure 4. FT-IR spectra of different compounds.

Figure 5. Oxygen nonstoichiometry, $3-\delta$, as a function of temperature.

Decreasing the critical radius in the system causes more difficulty for diffusion of oxygen and reduces the tendency of the systems to lose oxygen, which acts in favour of reduction of TEC. Variations of R_c with the increase in temperature is shown in figure 6. LSCF and NSCF compounds have largest and lowest R_c , respectively. The presence of Nd and Mn in system limits the R_c which lead to a decrease in TEC.

3.5 Thermal and chemical lattice expansion

Nonstoichiometric oxides contain two types of expansions. Thermal lattice expansion that is induced through enhanced

Figure 6. Variations of R_c as a function of temperature in different compounds.

Figure 7. Pseudocubic lattice parameter of different compounds as a function of temperature.

Table 2. Thermal lattice expansion $(\partial a_{pc}/\partial T)_\delta$, reference lattice parameter, a_{ref} (equation (1)); lattice parameter at room temperature in air, a_0 , thermal expansion coefficients, α_{th} and lattice parameter constant A (equation (4)) for different compounds.

Compounds	($\text{\AA} \text{K}^{-1}$)	a_0 ($\text{\AA}$)	a_{ref} ($\text{\AA}$)	$\alpha_{Thermal}$ (K^{-1})	$A = (a_{ref} - a_0)/a_0$
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF)	1×10^{-4}	3.87	3.83	2.58×10^{-5}	-1×10^{-2}
$\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (NSCF)	7×10^{-5}	3.55	3.52	1.97×10^{-5}	-8×10^{-3}
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.8}\text{O}_{3-\delta}$ (LSCM)	6×10^{-5}	3.86	3.84	1.55×10^{-5}	-5×10^{-3}
$\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.8}\text{O}_{3-\delta}$ (NSCM)	7×10^{-5}	3.45	3.42	2.02×10^{-5}	-8×10^{-3}

vibration of lattice atoms upon heating. The origin of chemical expansion in nonstoichiometric oxides has been correlated to the formation of oxygen vacancies and changes in the oxidation state of the metal cations.¹⁶ In fact variations in the lattice constant with the increase in temperature is due to thermal and chemical expansion of lattice. Pseudocubic lattice parameter of different compounds as a function of temperature has been shown in figure 7.

With replacement of smaller Nd^{3+} ions to La^{3+} in the lattice, lattice constants declined significantly at different temperatures. The effect of using Mn^{3+} instead of Fe^{3+} ions is perceptible with the increase in temperature which is attributed to the reduced chemical expansion.

The pseudocubic lattice parameter can be expressed by the thermally and chemically induced change in lattice parameter with respect to a reference state, a_{ref} , e.g., at 0 K (-2°C) and $\delta = 0$.^{16,17,19}

$$a_{pc} = (\partial a_{pc}/\partial T)_\delta T + (\partial a_{pc}/\partial \delta)_T \delta + a_{ref}. \quad (2)$$

The TEC $(\partial a_{pc}/\partial T)_\delta$ was determined for $\delta = 0$ as the slope of the linear fit of the pseudocubic lattice parameter as a function of temperature (figure 7). The reference lattice parameter was determined by extrapolation to -25°C (0 K) in figure 7 and is given in table 2. The lattice expansion is expressed as the linear expansion rate $\Delta l/l$.

$$\Delta l/l = \Delta a/a_0 = (a - a_0)/a_0 = ((\partial a_{pc}/\partial T)_\delta T)/a_0 + ((\partial a_{pc}/\partial \delta)_T \delta)/a_0 + (a_{ref} - a_0)/a_0, \quad (3)$$

$$\Delta l/l = \alpha_{th} T + \alpha_{ch} \delta + A \quad (4)$$

with α_{th} and α_{chem} the thermal and chemical expansion coefficients and the pseudocubic lattice parameter at room temperature is a_0 .^{16,19}

Variations of the proportion of chemical expansion ($\alpha_{ch}\delta$) for different compounds are shown in figure 8. As can be seen, Nd^{3+} is present in the lattice and establish stronger bond with oxygen ions. Oxygen ions in the lattice become more stable and chemical expansion has decreased. Also greater stability of the Mn^{4+} ions compared with Fe^{4+} led to a significant reduction in the proportion of chemical expansion of containing Mn samples.

4. Conclusion

Effective factors and mechanisms in TEC of perovskite with composition of $\text{Ln}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{M}_{0.8}\text{O}_{3-\delta}$ ($\text{Ln} = \text{La}, \text{Nd}$ and

Figure 8. Variations of proportion chemical expansion ($\alpha_{ch}\delta$) vs. temperature in different compounds in air.

M = Mn, Fe) have been evaluated. Using Nd^{3+} instead of La^{3+} led to tilting of the BO_6 octahedra, phase transition from rhombohedral to the orthorhombic and consequently a decrease in volume unit cell. Moreover, increasing electronegativity of Nd and decreasing ionic character of the Ln–O bond led to an increase in the bond strength and more stable oxygen ions. All of these factors have significant effect on the reduction of TEC. Main role of Mn in the lattice is due to greater stability of the Mn^{4+} ions compared with Fe^{4+} . Tetravalent ions form stronger bond in BO_6 octahedra and reduce the size of the octahedra with concomitant decrease in TEC. Also stability of the Mn^{4+} in high temperature led to a significant reduction in the chemical expansion of Mn-containing compounds.

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