

Comparison of Thermal Expansion Coefficient in $\text{Ln}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{M}_{0.8}\text{O}_{3-\delta}$ (Ln=La,Nd,Sm and M=Fe,Ni,Mn) as Cathode Materials for Solid Oxide Fuel Cell

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ABSTRACT

In this study, Thermal expansion coefficient variation of $\text{Ln}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{M}_{0.8}\text{O}_{3-\delta}$ (Ln=La,Nd,Sm and M=Fe,Ni,Mn) perovskite oxide were evaluated. Different compounds were prepared and thermal expansion coefficient were measured in different temperature by means of dilatometer analysis. Structural parameters of compounds were determined by X-ray diffraction and Field Emission Scanning Electron Microscopy (FE-SEM) was used for the morphological study. Using Nd^{3+} instead of La^{3+} led to tilting of the BO_6 octahedra, phase transition from rhombohedral to the orthorhombic. Experimental results showed TEC decreases favorably with substitution of Nd^{3+} and Mn^{3+} ions in the lattice.

1. INTRODUCTION

The solid oxide fuel cell (SOFC) is an all solid energy conversion device with high efficiency and very low greenhouse emissions. Thus, the use of SOFC technologies can significantly reduce the production of greenhouse gases and improve our environment[1-3]. A typical SOFC consists of a dense layer of an oxygen ion conducting electrolyte, separating a cathode, on which oxygen molecules react with electrons to produce oxygen anions, from an anode on which the fuel is oxidized (see Figure 1.) The electrons that are produced during the oxidation of fuels are transported through an external load back to the cathode[4,5]. The materials used as the SOFC cathodes should have high electrical conductivity and oxygen ion conductivity, they should also meet the requirements of chemical and thermal stability in oxidizing environment, chemical and thermal compatibility with the electrolyte, and high catalytic activity toward oxygen reduction reactions at intermediate temperatures[4-6]. 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 intermediate temperature (500–800°C) SOFC in the recent years[7].

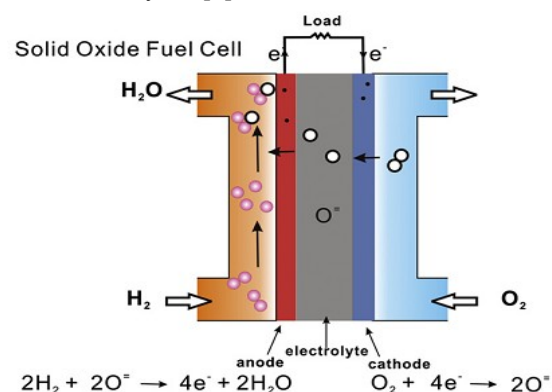


Figure 1. Schematic of operating principle of a solid oxide fuel cell.

The traditional view of the perovskite lattice is, it consists of small B cations within oxygen octahedra, and larger A cations which are XII fold coordinated by oxygen. 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 in A site. 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.

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According to Pauling's rules, tetravalent ions create stronger bond in BO_6 octahedra, reduce the size and unit cell volume of the octahedra and decrease the TEC.

Mixed ionic and electronic conducting (MIEC) oxides with perovskite structures have been the focus of the recent research activities for being used as the SOFC cathodes. These MIEC oxides, including (La,Sr) MnO_3 (LSM) [8] (La,Sr) CoO_3 (LSC) [9-11], (La,Sr) $(\text{Co,Fe})\text{O}_3$ (LSCF) [12,13], (Sm,Sr) Co_3 (SSC) [14,15,16,4], (Ba,Sr) $(\text{Co,Fe})\text{O}_3$ (BSCF) [18], and (GdBaCoO_3) [6,17,20] demonstrated very high electrochemical performance. Besides containing MIECs which have received considerable attention, a few other new cathode materials have been developed, including pyrochlore oxides [18-22], Ruddlesden-Popper type oxides [23,24], and $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ (LNF) based oxides [25,26]. Development of new cathode materials for IT-SOFC is still an area of intense research.

In the present work, we tried to study variation of thermal expansion coefficient and structural parameters

in $\text{Ln}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{M}_{0.8}\text{O}_{3-\delta}$ ($\text{Ln}=\text{La,Nd,Sm}$ and $\text{M}=\text{Fe,Ni,Mn}$) perovskite oxide.

2. EXPERIMENTAL

The material sources for the powder synthesis were La_2O_3 , Nd_2O_3 , Sm_2O_3 , SrCO_3 , Fe_2O_3 , Co_3O_4 , NiO and Mn_2O_3 . The stoichiometry of the different compounds were summarized in Table 1. Different compounds were synthesized by the conventional solid-state reaction methods. Raw materials were thoroughly mixed with ethanol by using an agate mortar and pestle, and calcined in air at 900°C for 12 hs. The calcined powders were pressed by using a uniaxial hydraulic press into $20\text{ mm} \times 20\text{ mm}$ disc specimens at final pressure of 60 MPa pressed into pellets and finally sintered at 1300°C for 24 h in an electrical furnace at a heating rate of $5^\circ\text{C}/\text{min}$. For the phase identification, X-ray diffraction profile was equipped using 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.

TABLE 1. stoichiometry of the different compounds

Compounds	Sample code	La_2O_3 (2811) mol%	SrCO_3 (1633) mol%	Co_3O_4 (1308049) mol%	Fe_2O_3 (3924) mol%	Nd_2O_3 (131397) mol%	Sm_2O_3 (11229) mol%	Mn_2O_3 (145737) mol%	NiO (2010) mol%
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$	LSCF	0.3	0.4	0.06	0.4	-	-	-	-
$\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$	NSCF	-	0.4	0.06	0.4	0.3	-	-	-
$\text{Sm}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$	SSCF	-	0.4	0.06	0.4	-	0.3	-	-
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.8}\text{O}_3$	LSCM	0.3	0.4	0.06	-	-	-	0.4	-
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Ni}_{0.8}\text{O}_3$	LSCN	0.3	0.4	0.06	-	-	-	-	0.4
$\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.8}\text{O}_3$	NSCM	-	0.4	0.06	-	0.3	-	0.4	-

The lattice parameter was determined by fitting the observed reflection with a least squares refinement program. The TECs of sintered samples were measured from room temperature to 800°C with a heating/cooling rate of $10^\circ\text{C}/\text{min}$ by Dilatometry 402ENETZSCH. Field Emission Scanning Electron Microscopy (FE-SEM) Philips XL30S FEG with the accelerating voltage of 5kV was used for the microstructure study.

3. RESULT AND DISCUSSION

3-1. Thermal expansion coefficient of different compounds

The average thermal expansion coefficients (TECs) of the different compounds measured in the range of $25\text{-}800^\circ\text{C}$ in air are given in Figure 2.

substitution of Nd for La (A site) decreased the thermal expansion coefficient whereas substitution of Sm for La (A site) increased it. 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.[27] also discussed the variations of TEC in the analogous lanthanum manganites $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ where A = alkaline-earth in terms of the ionic character of the A-O

bond. The percent ionic character of a bond is related to the electro negativity difference between the bonded atoms A and B in the A-B bond by the following empirical relationship:[28]

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

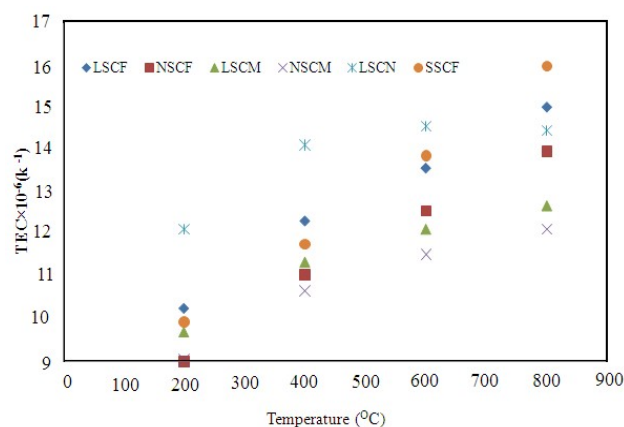


Figure 2. The variations of thermal expansion coefficient versus temperature in different compounds in air.

where x_A and x_B are the electro negativities of the A and B atoms, respectively. Based on the Pauling electro

negativity values, [29] one can understand that the TEC values in compounds containing Nd is due to the increase in electro negativity of Nd and the decrease in ionic character of the Ln–O bond. Substitution of Ni for Fe (B site) increased the coefficient of thermal expansion of the compounds, however substitution of Mn ions for Fe (B site) decreased TEC favorably.

Elements in the B sites have strong covalent bond. In order to compare the bond strength of these elements, changes of their capacity in system should be considered. According to Pauling's rules bond strength, tetravalent ions create stronger bond in BO_6 octahedra, reduce the size and unit cell volume of the octahedra and decrease the TEC. Simultaneous use of Nd and Mn in $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.8}\text{O}_{3-\delta}$ (NSCM) led to the lowest TEC. Figure 2. The variations of thermal expansion coefficient versus temperature in different compounds in air.

3.2. Phase evaluation Figure 3. shows the XRD profile of different compounds. The XRD pattern of LSCF was compared with JCPDS file nos.00-050-0308 and was indexed as rhombohedral (trigonal) perovskite phase with the $R3c$ space group. NSCF and SSCF compounds were compared with JCPDS file nos.01-088-0060 and were indexed as orthorhombic perovskite phase with the $Pnma$ space group. It can be seen that LSCF, NSCF, SSCF compounds are single phase.

Compounds containing Mn were single phase with a rhombohedral (trigonal) perovskite phase with the $R3c$ space group with JCPDS file nos.00-050-0308. It can be seen that compound containing Ni was not a single phase and NiO , LaNiO_3 and La_2NiO_4 phases precipitated. NSCM compound was compared with JCPDS file nos.01-088-0060. It was indexed as orthorhombic perovskite phase with the $Pnma$ space group.

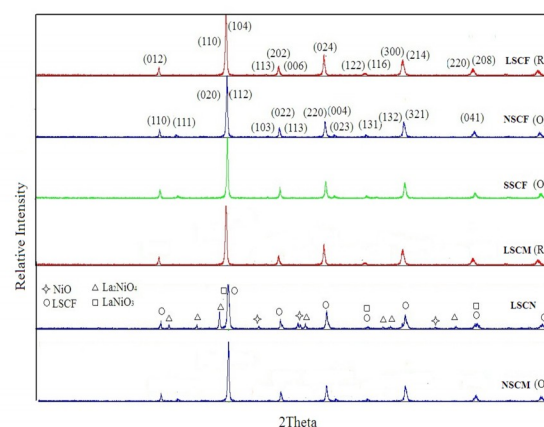


Figure 3. XRD profiles of different compounds.

Structural properties of single phase compounds were summarized in Table 2. With substitution of smaller ions in the A site, lattice parameter, unit cell volume and Goldschmidt's tolerance factor were decreased and successive tilting of the BO_6 octahedra was increased and unit cell volume was decreased. As a result in these compounds a more compact crystal structure can be seen. In addition, decreasing tolerance factor is an expression of phase transition from rhombohedral to orthorhombic. Moreover, increasing electro negativity of Nd and decreasing ionic character of the Ln–O bond led to an increase in bond strength and more stable oxygen ions. As it has been seen with substitution of Mn in the B site, lattice parameter and unit cell volume were decreased. All of these factors have a significant effect on the reduction of thermal expansion coefficient. Tetravalent ions form stronger bonds in BO_6 octahedra and reduce the size of the octahedra with concomitant decrease in TEC. Greater stability of the Mn^{4+} ions compared to Fe^{4+} led to a decrease in TEC of compounds containing Mn.

TABLE 2. Lattice parameters, lattice volume, pseudocubic lattice parameter (a_{pc}) and tolerance factor (t) of 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
$\text{Sm}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (SSCF)	Orthorhombic	5.50	5.40	6.88	204.34	3.44	0.89
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.8}\text{O}_{3-\delta}$ (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

3.3. Microstructural evaluation Figure 4. and 5. show SEM micrographs for fractured surface of

different compounds. In order to evaluate the distribution of different elements in grains and grain

boundaries, line scan analysis was carried out. The scan analysis from NSCF and SSCF compounds could be seen in Figure 6. As can be seen, Nd was distributed in grains and grain boundaries uniformly, but Sm was more concentrated in the grain boundaries region. It seems using Sm in the lattice creat more stress compared to Nd, which is due to greater difference in ionic radius of Sm in comparison to Sr. As a result, Sm migrates to the grain boundaries to reduce the lattice energy. The concentration of Sm in the garin boundaries led to behavior change of SSCF compounds. By comparing the microstructure of different compounds one can understand average size of particles were decreased by using Mn in the lattice.

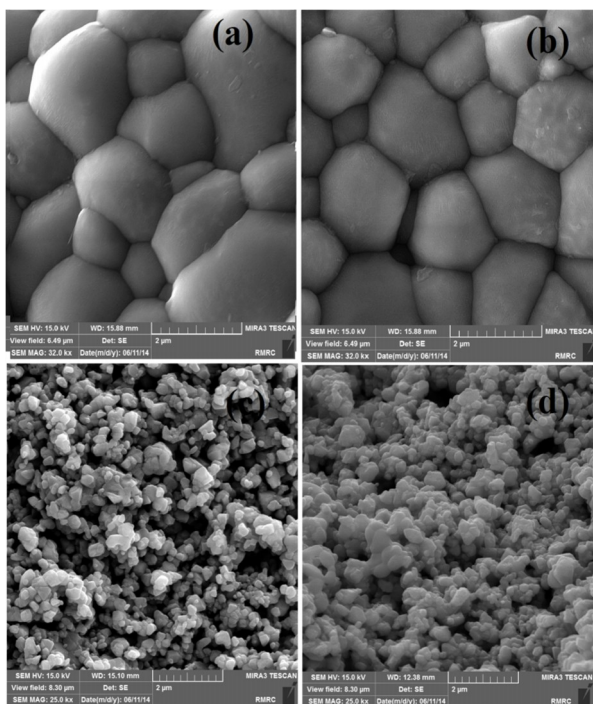


Figure 4. SEM micrographs for fractured surface of (a) LSCF, (b) NSCF, (c) LSCM and (d) NSCM.

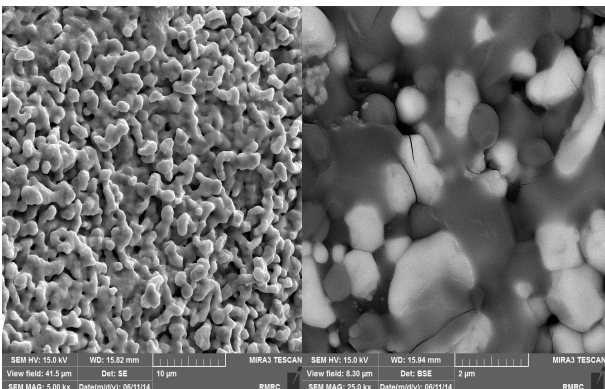


Figure 5. SEM micrographs for fractured surface of LSCN.

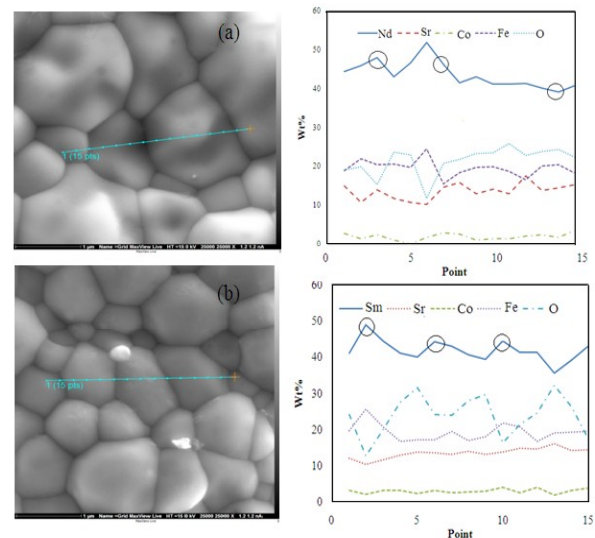


Figure 6. Line Scan analysis of (a) NSCF and (b) SSCF compounds.

4. CONCLUSION

Thermal expansion coefficient of perovskite with composition of $\text{Ln}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{M}_{0.8}\text{O}_{3-\delta}$ ($\text{Ln}=\text{La},\text{Nd},\text{Sm}$ and $\text{M}=\text{Mn},\text{Fe},\text{Ni}$) were 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 decrease in volume unit cell. Using Sm in the lattice creat more stress compared to Nd, which is due to greater difference in ionic radius of Sm in comparison to Sr. As a result, Sm migrates to the grain boundaries to reduce the lattice energy. Compounds containing Mn were single phase, but compound containing Ni was not single phase and NiO , LaNiO_3 and La_2NiO_4 phases were precipitated. Simultaneous using of Nd and Mn in $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.8}\text{O}_3$ (NSCM) led to lowest TEC.

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