

Electrical conductivity and thermal expansion of $\text{La}_{0.8}\text{Sr}_{0.2}(\text{Mn,Fe,Co})\text{O}_{3-\delta}$ perovskites

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Abstract

$\text{La}_{1-x}\text{Sr}_x\text{MeO}_3$ (Me=Mn, Co, Fe) perovskites are used as cathodes and are also attractive materials for application as the contact layer between cathode and interconnect in solid oxide fuel cells. In this contribution, three perovskite series, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ (series 1), $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ (series 2) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x/2}\text{Fe}_{(1-x)/2}\text{Co}_x\text{O}_{3-\delta}$ (series 3) with $x=0, 0.25, 0.5, 0.75$ and 1 were re-investigated under identical synthesis and measurement conditions with the aim of obtaining a full overview of the quasi-ternary system $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ – $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ – $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$. The distribution of the different crystallographic phases in the selected series, the DC electrical conductivity and the thermal expansion coefficients are presented.

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1. Introduction

Published data on the physical properties of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MeO}_{3-\delta}$ perovskites with Me=Mn, Fe and Co reveal that different authors adopt different synthesis and measurement procedures, thereby reporting data with sometimes significant variation. Since these perovskites are suitable candidates for application as cathode material and as cathodic contact layers in SOFCs, comparisons of their functional properties are significant only when the processing conditions are identical. There are a number of reports comparing the electrical and thermal expansion properties of compositions in single series within the quasi-ternary system $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ – $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ – $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$. However, a collective attempt is made here to evaluate these properties under identical conditions for the whole $\text{La}_{0.8}\text{Sr}_{0.2}(\text{Mn,Fe,Co})\text{O}_{3-\delta}$ system. In this contribution, as a first step, three series of compositions originating from this system were investigated. Variations in

Table 1

Crystalline phases observed after sintering at 900, 1100 and 1300 °C

Perovskite systems	x	Phases after calcination at 900 °C for 6 h	Phases after calcination at 1100 °C for 6 h	Phases after calcination at 1300 °C for 6 h
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ (series 1)	0	$\text{P}_{\text{hex}} + \text{La}_2\text{O}_3$	$\text{P}_{\text{hex}} + \text{La}_2\text{O}_3$	P_{hex}
	0.25	$\text{P}_{\text{hex}} + \text{La}_2\text{O}_3$	$\text{P}_{\text{hex}} + \text{La}_2\text{O}_3$	$\text{P}_{\text{hex}} + \text{La}(\text{OH})_3$
	0.5	$\text{P}_{\text{hex}} + \text{La}_2\text{O}_3$	P_{hex}	P_{hex}
	0.75	$\text{P}_{\text{hex}} + \text{La}_2\text{O}_3, \text{Co}_3\text{O}_4$	$\text{P}_{\text{hex}} + \text{La}(\text{OH})_3, \text{Co}_3\text{O}_4$	$\text{P}_{\text{hex}} + \text{Sr}_2\text{MnO}_{4-6}$
	1	P_{hex}	P_{hex}	P_{hex}
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ (series 2)	0	P_{or}	P_{or}	P_{or}
	0.25	P_{hex}	P_{hex}	P_{hex}
	0.5	P_{hex}	P_{hex}	P_{hex}
	0.75	P_{hex}	P_{hex}	P_{hex}
	1	P_{hex}	P_{hex}	P_{hex}
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x/2}\text{Fe}_{(1-x)/2}\text{Co}_x\text{O}_{3-\delta}$ (series 3)	0	$\text{P}_{\text{or}} + \text{La}_2\text{O}_3$	$\text{P}_{\text{or}} + \text{La}_2\text{O}_3$	$\text{P}_{\text{or}} + \text{La}(\text{OH})_3$
	0.25	$\text{P}_{\text{or}} + \text{La}_2\text{O}_3$	$\text{P}_{\text{hex}} + \text{La}_2\text{O}_3$	$\text{P}_{\text{hex}} + \text{La}(\text{OH})_3$
	0.5	$\text{P}_{\text{hex}} + \text{La}_2\text{O}_3, \text{Co}_3\text{O}_4$	$\text{P}_{\text{hex}} + \text{La}_2\text{O}_3$	$\text{P}_{\text{hex}} + \text{Sr}_2\text{MnO}_{4-6}$
	0.75	$\text{P}_{\text{hex}} + \text{La}_2\text{O}_3, \text{Co}_3\text{O}_4, \text{Sr}_2\text{MnO}_{4-6}$	$\text{P}_{\text{hex}} + \text{Sr}_2\text{MnO}_{4-6}$	$\text{P}_{\text{hex}} + \text{Sr}_2\text{MnO}_{4-6}$
	1	P_{hex}	P_{hex}	P_{hex}

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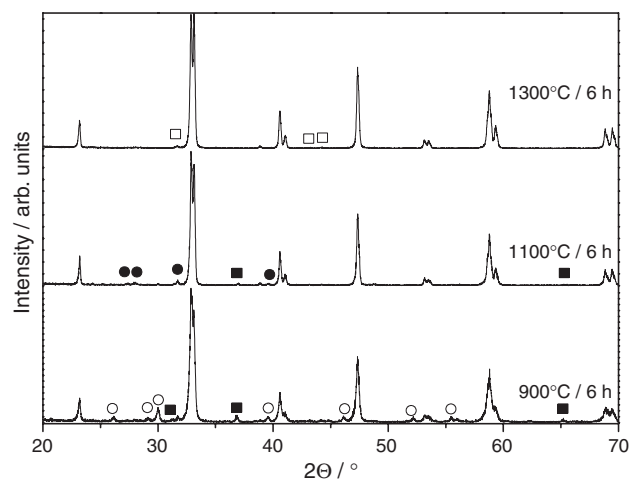


Fig. 1. XRD patterns of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.25}\text{Co}_{0.75}\text{O}_{3-\delta}$ after sintering at different temperatures for 6 h in air. (Open circles: La_2O_3 ; closed squares: Co_3O_4 ; closed circles: $\text{La}(\text{OH})_3$ and open squares: $\text{Sr}_2\text{MnO}_{4-\delta}$).

thermal expansion coefficient between 30 and 1000 °C as well as in the DC-electrical conductivity at 800 °C in air as a function of compositions are presented and compared with results in the literature.

2. Experimental

Powders of compositions in three perovskite series, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ (series 1), $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ (series 2) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x/2}\text{Fe}_{1-x/2}\text{Co}_x\text{O}_{3-\delta}$ (series 3) with $x=0, 0.25, 0.5, 0.75$ and 1, were synthesized by the Pechini method [1] using nitrate solutions of La, Sr, Co, Mn and Fe and calcined at 600 °C for 3 h in air. A detailed description of the synthesis process is given in Ref. [2]. The crystal phase composition of the powders was determined by X-ray diffraction (XRD) analysis using a Siemens D5000 diffractometer and CuK_α radiation after sintering at 900, 1100 and 1300 °C for 6 h in air. The raw powders were uniaxially pressed to form rectangular bars and sintered at 1300 °C for

6 h in air. The total electrical conductivity (σ) of the sintered samples was measured by a 4-probe DC technique at temperatures between 200 and 900 °C in air using silver wires and silver paste as contacts. Data were corrected taking into account the porosity of the test specimens. The thermal expansion between 30 and 1000 °C was determined using a Netzsch DIL 402C dilatometer.

3. Results and discussion

3.1. XRD analysis

The XRD results of the samples heat-treated at 900, 1100 and 1300 °C for 6 h, summarized in Table 1, reveal that the main phase within the series is a perovskite in all cases. However, a small amount of impurities (La_2O_3 , $\text{La}(\text{OH})_3$, Co_3O_4 and $\text{Sr}_2\text{MnO}_{4-\delta}$) can be detected in the compositions of the series 1 and 3. The $\text{La}(\text{OH})_3$ results from the hydration of La_2O_3 during storage in ambient air. The sample with $x=0.75$ of series 1 contains the highest amount of impurities related to the intensity of reflections in the XRD patterns as shown in Fig. 1. For the sintering temperature of 1300 °C only traces of $\text{Sr}_2\text{MnO}_{4-\delta}$ (open squares) are detectable in the pattern, whereas at 1100 °C very small amounts of $\text{La}(\text{OH})_3$ and Co_3O_4 (close circles and squares, respectively) are visible. Only at 900 °C a higher amount of impurities (La_2O_3 and Co_3O_4) can be detected. The compositions of series 2 exhibit pure perovskite without any impurity phases. In an earlier publication [3] on $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$, the reported crystallographic phases contained CoO as an impurity along with the perovskite even after sintering at 1250 °C for 4–6 h, whereas in the present study it is demonstrated that the pure perovskite phase is already formed even after sintering at 900 and 1100 °C for 6 h. The crystallographic structures detected in compositions $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ are in good agreement with the results presented in Ref. [3]. The samples of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.25}\text{Co}_{0.75}\text{O}_{3-\delta}$, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.125}\text{Fe}_{0.125}\text{Co}_{0.75}\text{O}_{3-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.25}\text{Fe}_{0.25}\text{Co}_{0.5}\text{O}_{3-\delta}$ contained Co_3O_4 as an additional impurity. Tetragonal $\text{Sr}_2\text{MnO}_{4-\delta}$ [4] was detected as

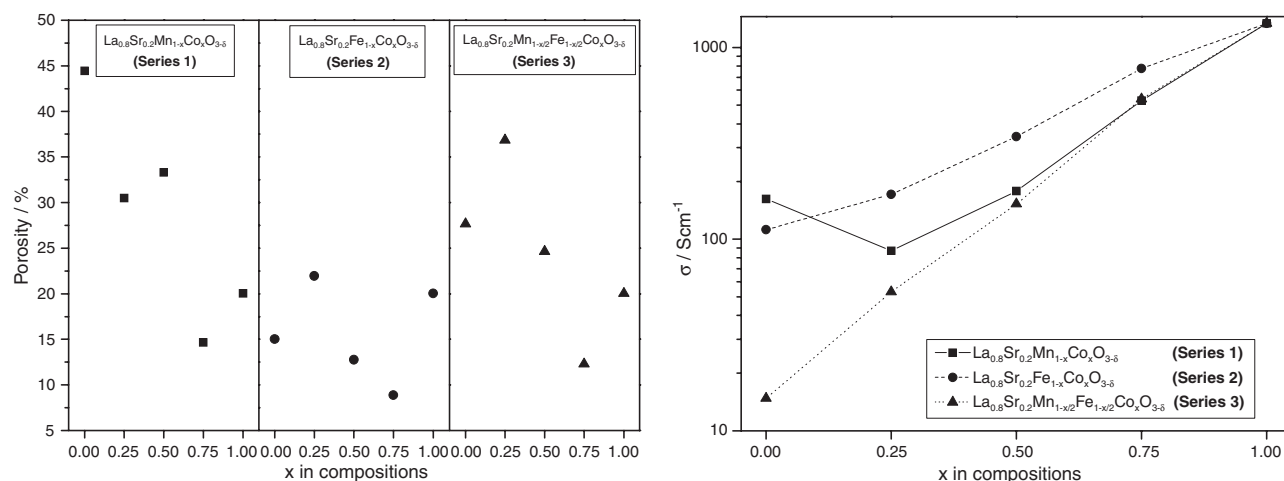


Fig. 2. Left — porosity of the samples used for DC-electrical conductivity measurements. Right — corrected electrical conductivity at 800 °C in air.

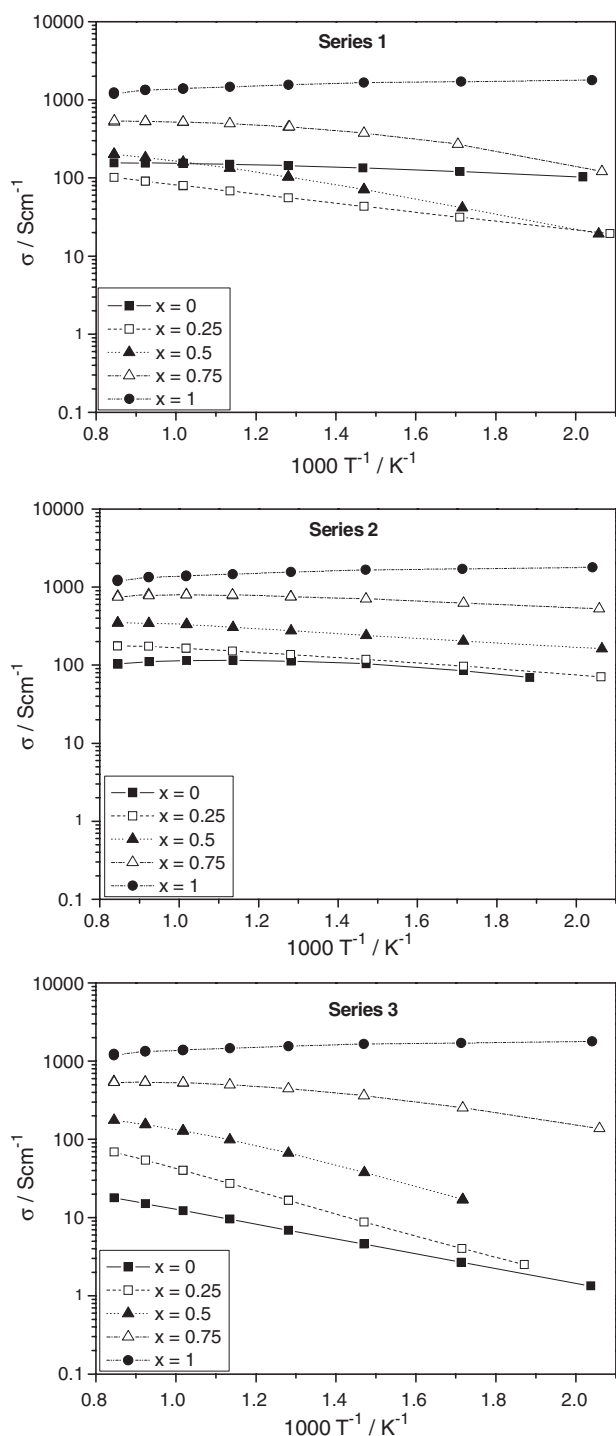


Fig. 3. Dependence of electrical conductivity on inverse temperature of investigated compositions within $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ (series 1), $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ (series 2) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x/2}\text{Fe}_{1-x/2}\text{Co}_x\text{O}_{3-\delta}$ (series 3).

an impurity in $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.125}\text{Fe}_{0.125}\text{Co}_{0.75}\text{O}_{3-\delta}$ at 1100 °C. Furthermore, it was observed that at 900 °C in air all perovskites crystallized in hexagonal structure except $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$, which showed orthorhombic structure.

In general, similar behavior was observed for the samples heat-treated at 1100 °C in air showing a higher degree of

perovskite crystallization. A crystallographic structural transformation was observed for $x=0.25$ in series 3, which was found to crystallize in hexagonal structure at 1100 °C instead of the orthorhombic lattice observed at 900 °C. The reflections of the impurity phases decreased significantly at 1100 °C as shown in Fig. 1. However, these impurities persist in the series 1 and 3 as listed in Table 1. The Co_3O_4 impurity disappeared, whereas $\text{Sr}_2\text{MnO}_{4-6}$ remained in composition $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.125}\text{Fe}_{0.125}\text{Co}_{0.75}\text{O}_{3-\delta}$ or appeared in compositions $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.25}\text{Fe}_{0.25}\text{Co}_{0.5}\text{O}_{3-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.25}\text{Co}_{0.75}\text{O}_{3-\delta}$. All the compositions exhibiting only pure perovskites at 900 °C also remained stable at 1100 and 1300 °C.

3.2. Electrical conductivity

The porosity of the specimens used for DC electrical conductivity measurements varied between 9% and 44%, as shown in Fig. 2 (left), allowing an empirical correction of the conductivity [5].

The corrected electrical conductivity values at 800 °C shown in Fig. 2 (right) vary over a wide range from 15 to 1338 S cm^{-1} and are in good agreement with literature data [6,7]. All compositions exhibited semiconducting behavior except $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$. These materials showed metallic behavior and a transition from semiconducting to metallic behavior, respectively. This can be seen in the series 2 ($x=1$ and $x=0$, respectively) presented in Fig. 3. While studying the dependence of the conductivity on the composition of the series, it is evident that for series 2 and 3 an increase in Co content leads to a steady increase in conductivity, whereas in series 1 this behavior can be observed only beyond $x=0.25$. For all three series, a significant increase in conductivity can be found (up to 1338 S cm^{-1} for $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$) when $x>0.5$. This value is in good agreement with measurements reported in Refs. [6–9]. Small variations can be attributed to the differences in the material synthesis and processing methods adopted by these authors. In general, for all studied compositions, the presented conduc-

Table 2
Activation energy values between 200 and 900 °C for electrical conductivity

Perovskite systems	x	Activation energy (eV)
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ (series 1)	0	0.10
	0.25	0.20
	0.5	0.21
	0.75	0.11
	1	Metallic conductor
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ (series 2)	0	Transition semiconductor/ metallic conductor
	0.25	0.13
	0.5	0.13
	0.75	0.07
	1	Metallic conductor
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x/2}\text{Fe}_{1-x/2}\text{Co}_x\text{O}_{3-\delta}$ (series 3)	0	0.26
	0.25	0.36
	0.5	0.26
	0.75	0.11
	1	Metallic conductor

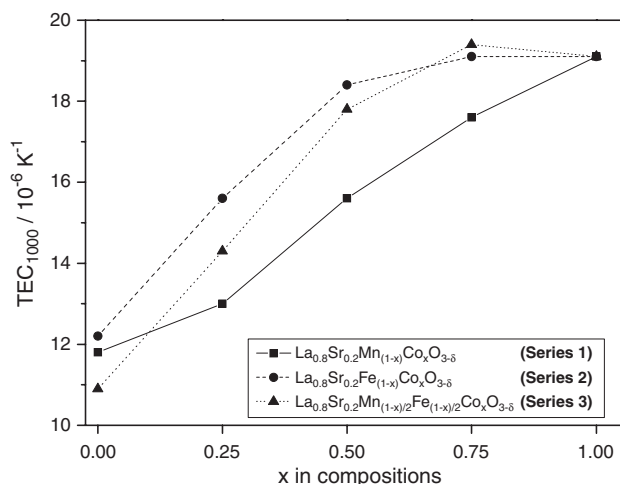


Fig. 4. Thermal expansion coefficients between 30 and 1000 °C of the investigated compositions in series 1, 2 and 3.

tivity values fit very well with the data reported previously [6–13].

The activation energy values calculated from the temperature dependence of the electrical conductivity as listed in Table 2 vary from 0.1 to 0.21 eV for $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ (series 1), 0.07 to 0.13 eV for $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ (series 2) and 0.11 to 0.36 eV for $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x/2}\text{Fe}_{1-x/2}\text{Co}_x\text{O}_{3-\delta}$ (series 3). The activation energy of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (0.1 eV) is in very good agreement with the value of 0.09 eV reported by Kuo et al. [14]. For $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ the activation energy was not calculated as it exhibited metallic electrical conduction from 200 to 900 °C. However, for this composition a low temperature dependence of the electrical conductivity with an activation energy value between 200 and 800 °C of 0.04 eV was reported in Ref. [6]. The value of 0.13 eV obtained for $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ from this measurement agrees well with the value of 0.12 eV reported earlier [6]. The activation energy value for $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ was not calculated, since it exhibited a transition from semiconducting to metallic behavior at 600 °C. However, Tai et al. [6] reported an activation energy of 0.09 eV between 400 and 800 °C.

3.3. Dilatometry

The thermal expansion coefficients (TEC) were determined at temperatures between 30 and 1000 °C in air and are presented in Fig. 4. By increasing the Co content towards $x=1$ an increase in TEC values can be observed similar to the behavior shown in the electrical conductivity measurements. In all series, compositions without Co exhibited low TEC values in a range of

$10.9\text{--}12.3 \times 10^{-6} \text{ K}^{-1}$, whereas for $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.125}\text{Mn}_{0.125}\text{Co}_{0.75}\text{O}_{3-\delta}$ a maximum is reached ($19.4 \times 10^{-6} \text{ K}^{-1}$). The TEC values for $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$, $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ were 19.1×10^{-6} , 11.8×10^{-6} and $12.2 \times 10^{-6} \text{ K}^{-1}$, respectively. It is evident that a given composition in series 2 exhibited higher TEC values than the respective compositions in the other series, except for $x=0.75$. The TEC values of series 1 as reported in Ref. [7] differ from our results and are significantly smaller than the values shown in Fig. 4. The values reported here, however, are in very good agreement with other measurements on lanthanum manganites, [see Ref. [15] and references therein].

4. Conclusions

A uniform synthesis and processing route was applied for all samples in the $\text{La}_{0.8}\text{Sr}_{0.2}(\text{Mn},\text{Fe},\text{Co})\text{O}_{3-\delta}$ system for better comparison of the results. It is clearly shown that the magnitude of the electrical conductivity and thermal expansion of the perovskites investigated in this work are mainly determined by the percentage of Co in the compositions.

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