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Thermoelectric oxide materials based on cobalt perovskites

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Abstract. Perovskites on the basis of $LaCoO_3$ are nowadays regarded as thermoelectric materials with a potential to replace conventional bismuth and tellurium-based semiconductors. In this contribution, we examine in details the effect of multiple metal substitutions on the thermoelectric properties of $LaCoO_3$-based perovskites. Two groups of compositions are studies: $LaCo_{1-2x}Ni_xFe_xO_3$ (x=0.1, 0.25) where both Ni and Fe substitute for Co, and $La_{1-x}Sr_xCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$ ($0\leq x\leq 0.25$) where Sr substitutes for La. This study demonstrates that by a rational choice of the content of strontium, iron and nickel additives it is possible to obtain eco-compatible $LaCoO_3$-based perovskites with desired thermoelectric efficiency.

Keywords: Thermoelectric oxides; cobalt-based perovskites

1. INTRODUCTION

The capability of thermoelectric materials to convert waste heat into electricity determines them as a key source of the “clean” energy of the future [1]. Thermoelectric oxides are nowadays considered as more stable and less toxic materials in comparison with the conventionally used metals and semiconductors, but their thermoelectric efficiency is still lower. The state-of-the-art research is mainly devoted to identify new oxide materials with higher thermoelectric efficiency [1, 2]. Among oxides, three groups of cobaltates can be outlined: Na_xCoO_2 with a layered structure; misfit $Ca_3Co_4O_9$, with similar CoO_2 layers and $LaCoO_3$ with a perovskite structure. $LaCoO_3$ is one of the most interesting as a material with potential application in thermoelectric devices due to its high Seebeck coefficient ($|S|>500$ μV/K at room temperature) [3-5]. The transport properties of $LaCoO_3$ are determined (to a great extent) by the ability of Co^{3+} ions to adopt low-, intermediate- and high-spin configurations in the perovskite structure, leading to an additional spin entropy effect [6,7]. However, the electrical resistivity is high (about 10 Ωcm at room temperature) [8], which lowers the thermoelectric activity ($ZT<0.01$ at T=300 K) [4,7].

Recently we have reported that $LaCoO_3$ perovskite displays an improved thermoelectric efficiency when Co is replaced simultaneously by nickel and iron ions: $LaCo_{1-y}(Ni_{0.5}Fe_{0.5})_yO_3$ [9]. The important feature of the transport properties of single-substituted cobaltates is that the nickel ions give rise to electron delocalization, which is opposite to the effect of the iron ions acting as electron trapping centers [9]. The improvement of the thermoelectric efficiency for double substituted perovskites is achieved by balancing the opposite effects of nickel and iron ions.

In this contribution, we extend our studies and provide new data on the improving the thermoelectric properties of $LaCoO_3$ by multiple substitutions at both La and Co-sites with strontium, nickel and iron ions. Two groups of compositions are studies: $LaCo_{1-2x}Ni_xFe_xO_3$ with x=0.1 where both Ni and Fe substitute for Co, and $La_{1-x}Sr_xCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$, $0\leq x\leq 0.25$ where Sr substitute for La. All perovskites are obtained from freeze-dried citrate precursors at 900 °C. This method is shown to be effective for the preparation of substituted perovskites, where all metal additives are randomly distributed [10, 11]. Structural and morphological characterizations are carried out by powder XRD and SEM analysis. The thermoelectric efficiency of the perovskites is determined by the dimensionless figure of merit, calculated from the independently measured Seebeck coefficient (S), electrical resistivity (ρ) and thermal conductivity (λ).

2. EXPERIMENTAL

A precursor-based method was used for the preparation of $La_{1-x}Sr_xCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$, $LaCo_{1-}$

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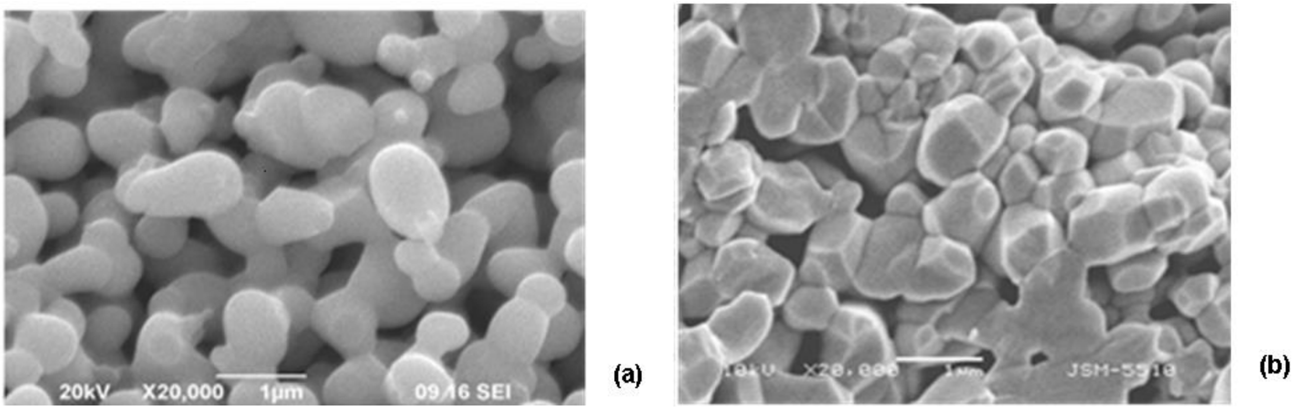

Figure 1. SEM images of the cross section of the pellets consisting of *$LaCoO_3$* (a) and *$LaCo_{0,5}Fe_{0,4}Ni_{0,1}O_3$* (b) sintered at 900 °C for 40h.

$_xNi_xO_3$ and $LaCo_{1-x}Fe_xO_3$ following the procedure described elsewhere [10, 11]. Homogeneous La-Co-Fe-Ni citrate precursors were obtained by freeze-drying of mixed citrate solutions of La-Co-Fe-Ni ions (1M La). The ratio between the components was La:$Co_{1-2x}Fe_xNi_x$:Citric acid = 1:1:10. After stirring, a clear solution was obtained, which was diluted to 0.25M La. The solution was instantly frozen with liquid nitrogen and dried *in vacuum* at -30 °C in Alpha-Christ Freeze-Dryer, leading to the formation of freeze-dried precursors. The thermal decomposition of the citrate-precursors was achieved at 400 °C for 3 h in air. The obtained solid residue was annealed at 900 °C for 40 h in air, then cooled down to room temperature with a rate of 5°/min. The same procedure was used for the synthesis of the samples with following compositions:
$La_{1-x}Sr_xCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$, $LaCo_{1-x}Ni_xO_3$ and $LaCo_{1-x}Fe_xO_3$.

X-ray structural analysis was performed on a Brucker Advance 8 diffractometer with Cu Kα radiation. Step-scan recording for structure refinement by the Rietveld method were carried out using 0.02 °2θ steps of 5s duration. XRD patterns are analyzed by a structural model comprising rhombohedrally distorted perovskite-type structure ($R\bar{3}c$ space group) where La occupies the 6*a* position (0, 0, ¼), Co/Fe/Ni are in the octahedral 6*b* position, and oxygen is in the 18*e* position. In accordance with our previous data [11], the replacement of Co by Ni and Fe led to lattice expansion of the perovskite structure. It is worth to mention that all metal additives (Ni, Fe and Sr) are randomly distributed over the 6*a* and 6*b* positions.

The transport properties were measured on pellets sintered at 900 °C for 40 hours. Pellet density was determined by Archimedes' method. The property was evaluated by comparison with the theoretical density of $LaCoO_3$ (7.299, JCPDS No25-1060). For the pellets with different perovskites compositions the porosity varied between 20 and 25 % despite the Ni, Fe and Ni, Fe content. SEM analysis was also undertaken to analyze the pellet porosity. SEM images of pellets coated with gold were obtained by Zeiss DSM 962 microscope and Philips XL30 scanning electron microscope. Figure 1 shows the porosity of the pellets for unsubstituted and double substituted perovskites. The SEM images demonstrate that well shaped particles fused one to another give rise to the pellet porosity. The close pellet porosities allow us to compare the thermoelectric properties of the perovskites with different level of substitution.

Electrical resistivity (ρ), density and mobility of charge carriers were determined by MMR's Variable temperatures Hall System (k2500-5SLP-SP) using Van der Pauw method over a temperature range from 90K to 600K. The benchtop permanent magnet (0.5T) is used. Thermal conductivity was determined at room temperatures on Thermal Conductivity Analyzer TCi (SETARAM). In order to compare the thermal conductivities of samples having different lappet porosity, the thermal conductivity is normalized to 95% of the theoretical density (λ_t) using the following density correction [2]: $\lambda_t = \lambda(0.95^{1.5})/(1-P)^{1.5}$, where λ is the measured thermal conductivity and P is the fractional porosity of the pellet.

3. RESULTS AND DISCUSSIONS

The multiple substitutions at La and Co sites proceed in the framework of the rhombohedrally distorted perovskite type structure. Lattice parameters for $LaCo_{1-2x}Ni_xFe_xO_3$ and $La_{1-x}Sr_xCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$ are summarized in Table 1. The multiple substitutions at La and Co sites lead to a lattice extensions irrespective of the origin of metal additives.

Table 1. Lattice parameters of $LaCo_{1-2x}Ni_xFe_xO_3$ and $La_{1-x}Sr_xCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$.

Samples	a±0.0001, Å	c±0.0003, Å	V, $Å^3$
$LaCoO_3$	5.4407	13.0914	335.61
$La Co_{0.8}Ni_{0.1}Fe_{0.1}O_3$	5.4532	13.1191	337.86
$LaCo_{0.50}Ni_{0.25}Fe_{0.25}O_3$	5.4737	13.1676	341.67
$La_{0.95}Sr_{0.05}Co_{0.8}Ni_{0.1}Fe_{0.1}O_3$	5.4540	13.1397	338.49
$La_{0.90}Sr_{0.10}Co_{0.8}Ni_{0.1}Fe_{0.1}O_3$	5.4524	13.1536	338.65
$La_{0.75}Sr_{0.25}Co_{0.8}Ni_{0.1}Fe_{0.1}O_3$	5.4488	13.1880	339.09

Transport properties of single-substituted cobaltates have been already studied [2, 12], while the double substituted cobaltates are still not explored. The electrical resistivity (ρ) significantly decreases during the replacement of cobalt by nickel, while the substitution of iron for cobalt leads to an increase in ρ (Table 2). For double substituted oxides $LaCo_{1-2x}Ni_xFe_xO_3$, the electrical resistivity decreases as compared to that of $LaCoO_3$ and it does not depend on the total Ni+Fe content: 0.0722 and 0.0939 Ω.cm for x=0.1 and x=0.25, respectively. This means that when Ni and Fe ions are in equal amounts, their effects are balanced leading to the formation of $LaCo_{1-2x}Ni_xFe_xO_3$ with a resistivity, which is concentration-insensitive despite of the replacement of 50% of Co ions. The reduction in the resistivity is a result from the increase in the carrier density induced by double substitution: from 2-3 x $10^{18}cm^{-3}$ for $LaCoO_3$ to 7-9 x $10^{18}cm^{-3}$ for $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$. The carrier mobility seems to be unchanged during the replacement of the cobalt ions: 1-3 $cm^2/V.s$ for $LaCoO_3$ and 4-6 $cm^2/V.s$ for $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$.

The electrical resistivity of $LaCoO_3$ decreases also when La^{3+} ions were replaced by aliovalent Sr^{2+} ions (Fig. 2). Because the transport properties of $LaCo_{1-x}Ni_xO_3$ and $La_{1-x}Sr_xCoO_3$ are usually interpreted in the same manner [13, 14], there is a need to compare the density of the charge carriers for both $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$ and $La_{1-x}Sr_xCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$ compositions (Fig. 2). As one can be expected, the electrical resistivity decreases with the Sr content (Fig. 2). This decrease is valid in the whole temperature range of measurement: from 250 to 600 K. For $La_{1-x}Sr_xCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$, the density of the charge carriers is higher in comparison with the unsubstituted $LaCoO_3$ and double substituted $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$ (Fig. 2). In addition, Sr^{2+} ions induce a strong increase in the carrier mobility: from 4-6 $cm^2/V.s$ for $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$ to 20-35 $cm^2/V.s$ and 70-80 $cm^2/V.s$ for x=0.1 and x=0.25 (Fig. 2). In the temperature range of 250-600K, the charge density increases slightly. The carrier mobility for unsubstituted $LaCoO_3$ and double substituted $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$ increases with the registration temperature, while all Sr-substitute perovskites display constant carrier mobility in the temperature range of 250 – 600 K. Therefore, the enhanced electrical conductivity for Sr-substituted

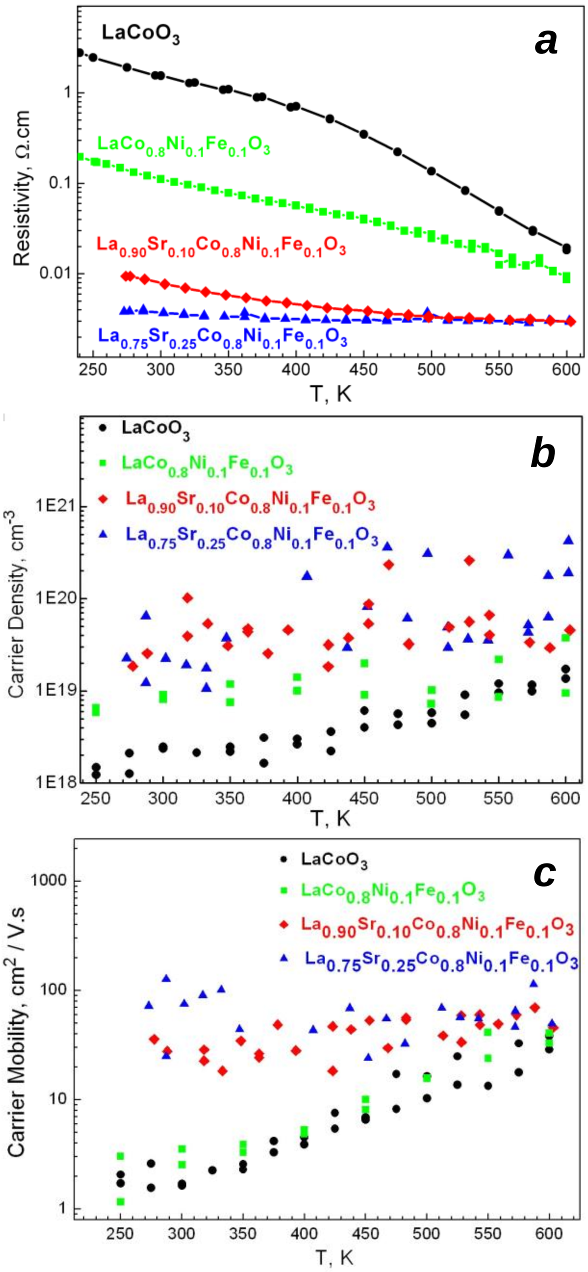

Figure 2 Temperature dependence of the electrical resistivity (a), carrier density (b) and carrier mobility (c) for $LaCoO_3$, $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$ and Sr-substituted $La_{1-x}Sr_xCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$.

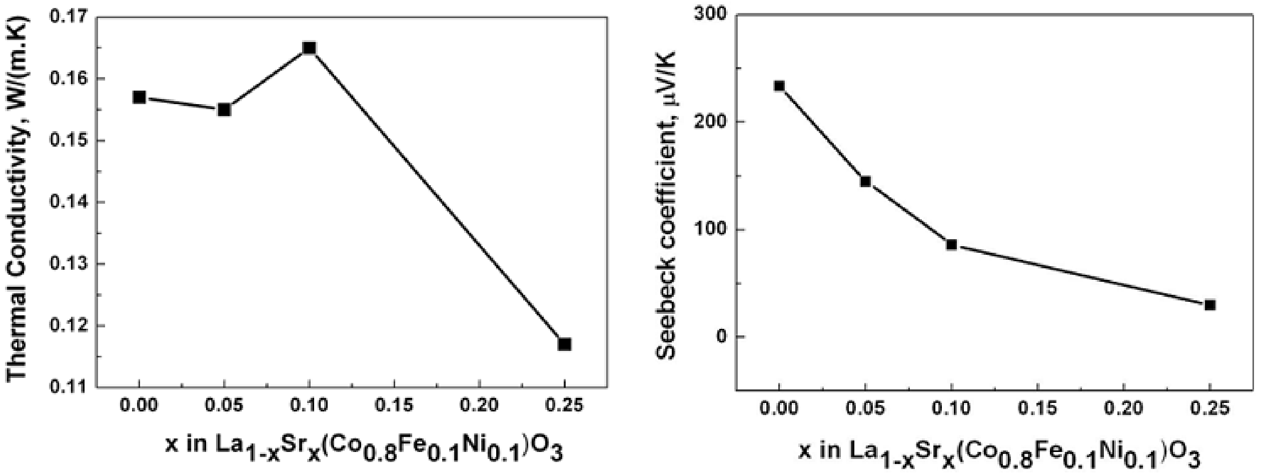

Figure 3. Concentration dependence of the thermal conductivity (left) and Seebeck coefficient (right) for $La_{1-x}Sr_xCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$. (All parameters are measured at 300 K).

Table 2. Electrical resistivity (ρ), thermal conductivity (λ), Seebeck coefficient (S), Power factor ($PF=S^2/\rho$), Figure of merit ($ZT=S^2T/(\rho k_t)$) for single, double and multiple substituted perovskites. (For better comparison, all parameters are measured at 300 K).

Samples	ρ Ω.cm	λ W/m.K	S μV/K	PF μW/K^2.cm	FM
$LaCoO_3$	1.555	0.434	600	0.231	0.015
$LaCo_{0.9}Ni_{0.1}O_3$	0.066	0.425	264	1.056	0.075
$LaCo_{0.9}Fe_{0.1}O_3$	2.549	0.257	599	0.141	0.016
$LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$	0.0722	0.157	234	0.761	0.158
$La_{0.9}Sr_{0.1}Co_{0.8}Ni_{0.1}Fe_{0.1}O_3$	0.0446	0.123	86	0.165	0.040

perovskites can be regarded as a consequence from the increased carrier density and mobility, while the carrier density accounts mainly for the electrical conductivity of Ni,Fe-substituted cobaltates.

The thermal conductivities of the single and double-substituted perovskites are shown in Fig. 3. In general, the thermal conductivity decreases upon increasing the metal content (Ni, Fe and Ni, Fe, respectively). It is shown that the double substitution yields a more significant decrease in the thermal conductivity in comparison with the single substitution (Table 2). The thermal conductivity comprises two contributions that are due to conductive carriers (λ_e) and phonon scattering. If the electron conduction is due to one type of charge carriers only, then λ_e can be calculated by the Wiedemann–Franz law: $\lambda_e = LT/\rho$ (the Lorentz number, L, is $2.45x10^{-8}$ V^2 K^{-2}). It is obvious that the λ_e term increases for Ni-substituted perovskites (3.10^{-4} and 0.015 W/m.K for $LaCo_{1-2x}Fe_xNi_x)O_3$ with x=0.1 and 0.25, respectively), but it remains lower than the total thermal conductivity (0.101 and 0.069 W/m.K, respectively). This means that even in this case the total thermal conductivity is governed by the lattice contribution. As a result, the thermal conductivities of the nickel- and iron-substituted perovskites are close. The dopant-induced decrease in the thermal conductivity of the cobaltates can mainly be explained by the enhanced phonon scattering due to the disordering of Co-Ni or Co-Fe ions in the octahedral 6*b* position (with coordinates 0, 0, 0) of the perovskite structure. This is a consequence of the ionic mismatch of the nickel, iron and cobalt ions. The appearance of Sr in the 6*a* position leads to a further decrease in the thermal conductivity (Fig. 3).

The Seebeck coefficient is strongly dependent on the amount of nickel, iron and strontium dopants (Fig. 3). All perovskite compositions display positive sign of the Seebeck coefficient (*S*), thus indicating that the predominant mobile charge carriers are holes. It is well known that Sr and Ni additives lead to a decrease in the *S*-value, while Fe additives have an opposite effect (Table 2). When Sr, Ni and Fe additives are included together into the perovskite structure, there is a smooth decrease in the *S*-value. It is noticeable that after 50% of Co substitution the sign of *S* remains positive reaching a value of 108 μV/K for $LaCo_{0.5}Ni_{0.25}Fe_{0.25}O_3$.

Based on the Seebeck coefficient and electrical resistivity data, the power factor is estimated: $PF=S^2/\rho$ (Fig. 4). The power factor displays a decrease during the increase in the Sr content. The highest PF is obtained for the single substituted

$LaNi_{0.1}Co_{0.9}O_3$ perovskite (Table 2). The addition of Fe into $LaNi_{0.1}Co_{0.9}O_3$ leads to a decrease in the PF, but it remains higher than that of unsubstituted $LaCoO_3$. This reveals that nickel additives have a positive effect as compared to iron and strontium ones (Table 2, Fig. 4). The observed power factor for multiple substituted cobaltates is lower than the unusually high power factor established for $SrTiO_3$ (20 μW/(K^2.cm) [15,16]. However, the extremely large thermal conductivity of $SrTiO_3$ (about 10 W/m.K) reduces its figure of merit [15, 16].

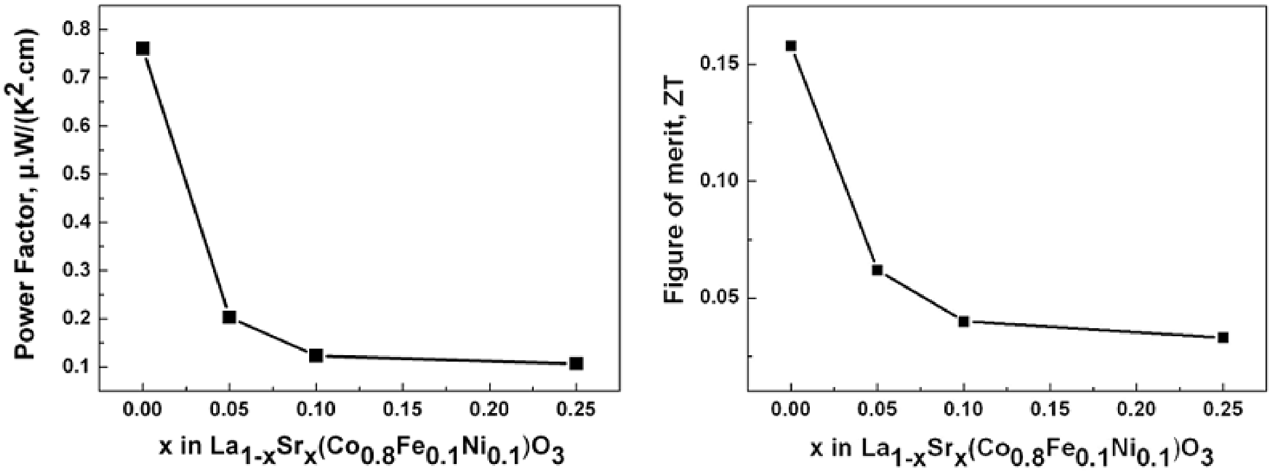

Figure 4. Concentration dependence of the power factor (left) and figure of merit (right) (left) for $La_{1-x}Sr_xCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$. (All parameters are measured at 300 K).

The figures of merit for single- and multiple-substituted perovskites are summarized on Table 2 and Figure 4. The lower level of nickel substitution causes a strong increase in thermoefficiency due to the enhanced electrical conductivity, while iron additives do not have any effect. In comparison with single substituted perovskites, the thermoelectric efficiency strongly increases for double-substituted perovskites. This means that the thermoelectric activity is a result from the synergic effect of the simultaneous appearance of Fe and Ni in the cobalt perovskite structure. The perovskite containing Fe and Ni ions in equal amount exhibits the higher thermoelectric activity. The increased thermoelectric activity can mainly be related with the decreased thermal conductivity for double-substituted perovskites (Fig. 3). The figure of merit is not improved when Sr ions substitutes for La ions (Fig. 4). Comparing the transport properties of Sr, Ni and Fe substituted perovskites, it appears that the perovskite with $LaCo_{0.8}Fe_{0.1}Ni_{0.1}O_3$ composition exhibits best thermoelectric activity with $Z.T=0.16$. This figure of merit is comparable with that reported for $La_{0.92}CoO_{2.93}$ that contains vacancies in both lanthanum and oxygen sites (ZT-value (of about 0.18) [17]. The comparison shows that double-substituted cobaltates, $LaCo_{1-x}(Ni_{0.5}Fe_{0.5})_xO_3$, exhibit a relatively good figure of merit, that makes them interesting as materials with thermoelectric properties.

4. CONCLUSIONS

The thermoelectric activity of $LaCoO_3$-based perovskites is effectively controlled by multiple substitutions at the La- and Co-sites. The highest figure of merit is observed for double substituted perovskites with composition $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$. The improved thermoelectric efficiency is a consequence from the decreased thermal conductivity for double-substituted perovskites. The multiple substituted cobalt perovskites are also of interest as eco-compatible thermoelectric materials since iron and nickel ions are less toxic and cheaper in comparison with cobalt ions. In addition, the structural approach of selective ion substitution can be extended towards other groups of thermoelectric oxide materials.

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ТЕРМОЕЛЕКТРИЧНИ ОКСИДНИ МАТЕРИАЛИ НА ОСНОВА НА КОБАЛТ

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(Резюме)

Перовскитите на основа на $LaCoO_3$ се разглеждат като термоелектрични материали, които имат потенциал да заместят добре известните полупроводници на основата на бисмут и телур. В това съобщение са представени резултатите от наши детайлни изследвания за подобряване на термоелектричните свойства на $LaCoO_3$ чрез многокомпонентно заместване с Ni, Fe и Sr. Две групи съединения са изследвани: $LaCo_{1-2x}Ni_xFe_xO_3$ с x=0.1, където Ni и Fe заместват Co, и $La_{1-x}Sr_xCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$, $0≤x≤0.25$, където Sr замества La. Получените резултати показват, че чрез рационален подбор на количеството на заместителите от Sr, Ni и Fe могат да се получат оксидни материали на основата на $LaCoO_3$ с желаната термоелектрична ефективност и безвредност към околната среда.