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Ba substitution for enhancement of the thermoelectric properties of LaCoO$_3$ ceramics ($0 \leq x \leq 0.75$)

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Ba substitution for enhancement of the thermoelectric properties of LaCoO$_3$ ceramics ($0 \leq x \leq 0.75$)

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Abstract: In the present work, dense perovskite ceramics were successfully prepared from a series of La$_{1-x}$Ba$_x$CoO$_3$ solid solutions in the range of substitution $0 \leq x \leq 0.75$ using solid state reaction and conventional sintering. Structural properties of La$_{1-x}$Ba$_x$CoO$_3$ were systematically investigated and thermoelectric properties were measured in the temperature range of 330 –1000 K. The results show that the thermoelectric properties of Ba-substituted LaCoO$_3$ depend on $x$. Indeed, at 330 K, electrical conductivity presents an optimum value for $x = 0.25$ with a value of $\sigma_{\text{max}} \approx 2.2 \times 10^5$ S·m$^{-1}$ whereas the Seebeck coefficient decreases when $x$ and/or the temperature increases. The Ba-substituted LaCoO$_3$ samples exhibit p-type semiconducting behaviour. The best power factor value found is $3.4 \times 10^{-4}$ W·m$^{-1}$·K$^{-2}$ at 330 K for $x = 0.075$, which is 10% higher than the optimum value measured in La$_{1-x}$Sr$_x$CoO$_3$ for $x = 0.05$. The thermal diffusivity and thermal conductivity increase with increasing temperature and Ba concentration. La$_{1-x}$Ba$_x$CoO$_3$ shows a maximum figure of merit ($ZT = 0.048$) for $x = 0.05$ at 330 K, 25% higher than the best value in La$_{1-x}$Sr$_x$CoO$_3$ compounds.

Keywords: perovskite; Ba-substituted LaCoO$_3$; oxide; thermoelectric; p-type semiconductor

1 Introduction

The efficiency of a thermoelectric material $\eta$ depends on the thermoelectric figure of merit $ZT = S^2\sigma T/\kappa = \text{PF} \cdot T/\kappa$, where $T$ is the absolute temperature, $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa$ is the thermal conductivity, and PF is the power factor. Therefore and in general, efficient thermoelectric material exhibits large absolute $S$, high electrical conductivity (leading to a high PF), and low thermal conductivity.

Perovskite-like lanthanum cobalt oxides LaCoO$_3$ attract much interest since the 1950s with many controversial explanations of their peculiar structural [1,2] and physical properties [3–5]. The physical properties found in these materials are varied, including...
the change in the spin states of cobalt ions, insulator–metal phase transitions as well as various types of orbital, charge, and electric ordering. In this regard, cobalt perovskite oxides are considered as promising thermoelectric materials since the discovery of large S and PF in the metallic oxide Na$_2$CoO$_2$ in 1997 [6] as many other cobalt oxides such as Ca$_2$CoO$_4$ [7–11], Sr$_2$O$_3$CoO$_2$ [12], Bi$_2$SrCoO$_4$-like [13–15], and more recently Ba$_2$Co$_3$O$_{14}$ [16,17] or Na-doped CoO [18].

Indeed, on the contrary to all the other cobalt oxides that present high thermoelectric properties at high temperatures, Androulakis et al. [19] have reported in La$_{1-x}$Sr$_x$CoO$_3$ ($x = 0.05$), the highest thermoelectric properties for an oxide at 300 K (ZT = 0.18). Therefore, Sr substituted LaCoO$_3$ ceramics have been largely studied [20–23] and the optimum value for thermoelectric properties is obtained for $x = 0.05$. Moreover, Bousnina et al. [23] have shown that the substitution can be realized up to $x = 0.8$ without any addition and up to $x = 1$ for an additional substitution of 3% Si for Co.

Calcium and barium substitutions for lanthanum have probably been less studied than the strontium for lanthanum substitution [24–26]. However, in the case of the Ba-substituted LaCoO$_3$, different magnetic and electrical behaviours have been reported for different degrees of substitution [27–29]. Indeed, substitution of La$^{3+}$ with Ba$^{2+}$ leads in enhanced oxide ion conductivity in the samples up to certain Ba content [30]. Furthermore, this substitution improves electrical conductivity of La$_{1-x}$Ba$_x$CoO$_3$ as for Sr-substituted samples. Moreover, as barium is heavier than strontium, a lower thermal conductivity is expected.

Therefore, the aim of this work is to synthesize, sinter, and characterize the thermoelectric properties of dense La$_{1-x}$Ba$_x$CoO$_3$ ceramics.

2 Materials and methods

La$_2$O$_3$ (Sigma Aldrich, purity $\geq 99\%$), Co$_3$O$_4$ (Sigma Aldrich, no specified purity), and BaCO$_3$ (Sigma Aldrich, purity $\geq 99\%$) were used to synthesize La$_{1-x}$Ba$_x$CoO$_3$ ($0 \leq x \leq 0.75$) by conventional solid state reaction. The precursor La$_2$O$_3$ was preheated at 1073 K for 2 h to remove any trace of lanthanum hydroxide (La(OH)$_3$) which may be originated to air hydration. Stoichiometric amounts of the precursors were well mixed for 5 min at 400 rpm in an agate ball mill (Retsch PM 100). The powders were pelletized with a small amount of PVA (5% weight) as binder. To avoid any contamination, the pellets were placed on LaCoO$_3$ previously sintered pellets deposited on zirconia beads in an alumina crucible. They were calcined at 1273 K for 12 h in air with a heating rate of 5 K·min$^{-1}$, and slowly cooled down. This step has been repeated twice after manual grinding. Finally, the calcined samples were pressed into pellets, and sintered for 12 h in air at 1673 K [23].

X-ray diffraction (XRD) was performed at room temperature, on the pellets after sintering, using BRUKER D8 Advance $\theta$/$\theta$ diffractometer equipped with a Linxeye energy-dispersive one-dimensional detector. The data have been recorded, using Cu K$_\alpha$ radiation, from 5° to 85° ($2\theta$) with a step of 0.02° and a counting time of 2 s per step. Rietveld refinement was carried out using Fullprof software [31] to determine the samples lattice parameters.

Microstructure was examined using Zeiss Supra 40 VP Field Emission Gun Scanning Electron Microscope (FEG-SEM) without prior coating of the samples.

Thermoelectric properties of the sintered samples were determined from simultaneous measurement of Seebeck coefficient and electrical conductivity in ZEM-3 equipment (ULVAC Technologies) from 323 to 1000 K. The thermal diffusivity was measured three times using the laser flash technique (Netzsch LFA 457) from 298 to 1000 K in air. The heat capacity of the materials was measured from 298 to 1073 K, using differential scanning calorimetry (Netzsch Pegasus 404 F1), with a heating rate of 20 K·min$^{-1}$ in platinum crucibles with alumina liners in argon atmosphere.

Apparent density of the samples was calculated from the weight and dimensions of the bars cut apparent density from the pellets for ZEM-3 characterization and the theoretical value [32].

3 Results and discussion

The XRD patterns in Fig. 1 can be assigned to the perovskite structure. Pure phase has been obtained without the appearance of impurities over the whole composition range of the solid solution ($0 \leq x \leq 0.75$). For higher Ba contents, samples do not present a cubic perovskite structure anymore. On the contrary to Sr-substituted samples, a 3% substitution of silicon for cobalt does not allow to stabilize the cubic perovskite structure. The XRD patterns of samples after sintering
were analyzed by Rietveld refinement using Fullprof software [31]. The results of the refined structural parameters show a phase transition depending on the Ba concentration. XRD patterns show a gradual transition from rhombohedral to cubic perovskite phase (Fig. 1). For the low values of $x$, this phase transition is mainly manifested by the doubling of the diffraction peaks located at 32°, 40°, 52°, and 68° of $2\theta$. It is clear that the diffraction double peaks reduce to single peaks with increasing barium content, which indicates that a structure phase transition has occurred. Figure 2 presents the examples of a Fullprof software fit of the XRD pattern for representative samples of the two phases, rhombohedral and cubic perovskite. For $0 \leq x < 0.5$, the refinement result confirms the rhombohedral perovskite structure type of the LaCoO$_3$ ($R\bar{3}c$ space group, PDF Card No. 48-0123 [32]). The La$_{0.9}$Ba$_{0.1}$CoO$_3$ sample is displayed in Fig. 2(a) with unit cell parameters of $a_h = 5.440(2)$ Å and $c_h = 13.124(5)$ Å. However, the patterns for the sintered samples with $0.5 \leq x \leq 0.75$ are indexed in a cubic system, similarly to what is observed in SrCoO$_3$ compound ($Pm\bar{3}m$ space group, PDF Card No. 38-1148 [23], Fig. 2(b)). The unit cell parameter is $a = 3.833(2)$ Å for the La$_{0.25}$Ba$_{0.75}$CoO$_3$ sample. These results are consistent with those of Luo and Wang [33]. Indeed, they have detected a structural phase transformation from $R\bar{3}c$ to $Pm\bar{3}m$ at $x = 0.30–0.35$. Finally, as the Ba content increases, peak positions shift to lower $2\theta$ values which are consistent with the substitution of lanthanum cations by larger barium cations, 1.36 and 1.61 Å, respectively [34].
Figure 3 shows the microstructure of La$_{1-x}$Ba$_x$CoO$_3$ pellets examined by FEG-SEM. For $x < 0.5$, it is noted that with increasing Ba content, an increase in grain size is observed. The grain size of these samples is in the range of 20–50 µm. All these samples are dense sintered ceramics, indicating the effectiveness of conventional sintering in preparing such ceramics. These ceramics have high relative densities in the range of 94%–98%.

For $x \geq 0.5$, after the rhombohedral–cubic transition, the samples showed high compactness ($\leq 92\%$). However, a remarkable decrease in grain size was noted ($\leq 15 \mu m$).

Figure 4(a) exhibits the Ba substitution content dependence ($x$) of the electrical conductivity ($\sigma$) of the La$_{1-x}$Ba$_x$CoO$_3$ sample at 330 K. The electrical conductivity $\sigma$ presents an optimum value for $x = 0.25$ with a value of $\sigma_{\text{max}} \approx 2.2 \times 10^5$ S·m$^{-1}$. Indeed, measurements of the electrical conductivity show that the ceramics substituted by Ba display a high electric conductivity at low temperatures. This value is slightly lower than the optimum electrical conductivity in La$_{1-x}$Sr$_x$CoO$_3$, which is $\sigma_{\text{max}} \approx 3 \times 10^5$ S·m$^{-1}$ at 330 K for $x = 0.3$ [23]. However, it is consistent in terms of substitutant content. This is also consistent with Khalil’s data [30] that reported the highest electrical conductivities between room temperature and 573 K for $x = 0.3$ in La$_{1-x}$Ba$_x$CoO$_3$ samples prepared by sol-gel. For $x > 0.25$, $\sigma$ decreases with increasing Ba concentration.

The temperature dependence of $\sigma$ of the La$_{1-x}$Ba$_x$CoO$_3$ sample with $x = 0.05$ from 330 to 1000 K is shown in Fig. 4(b). At lower temperatures, the electrical conductivity increases when temperature increases which is the characteristic of a semiconducting behaviour. Then, $\sigma$ starts decreasing upon higher temperatures, exhibiting an insulator–metal (I–M) transition around 800 K. This behaviour is attributed to closing of charge-transfer gap caused by the expansion of Co-3d and O-2p bandwidths regardless of the spin state of Co$^{3+}$ [35,36]. Similar variation in electrical conductivity as a function of temperature was observed in previous study [37]. Indeed, they found that the La$_{1-x}$Ba$_x$CoO$_3$ samples become metallic at temperatures above 700 K.

At 330 K, $S$ of the La$_{1-x}$Ba$_x$CoO$_3$ sample is plotted as a function of the Ba concentration ($x$) (Fig. 5(a)). The Seebeck coefficient of the La$_{1-x}$Ba$_x$CoO$_3$ sample for $x = 0$ shows a negative value ($-250 \mu V\cdot K^{-1}$), while, it becomes positive for $x > 0$. Then, it can be deduced that the substitution of La$^{3+}$ by Ba$^{2+}$, even at low levels, leads to a change of carrier type. The highest value
(S = 271 µV·K⁻¹) is observed for x = 0.03. Kun et al. [37] found that, for the same Ba content, S exhibits a value close to our value, whereas for lower Ba content (1%), a higher value of S (≈ 400 µV·K⁻¹) was measured. This is similar to the values measured in La₁₋ₓSrₓCoO₃ compounds but for higher substitutant content (x = 0.05) [23].

For x > 0.03, S decreases with increasing Ba concentration. The decrease of S with increasing x shows that the carrier concentration increases as a function of x. This is consistent with the substitution of trivalent La³⁺ cations by divalent Ba²⁺ cations and the increase of electrical conductivity. Furthermore, we notice that for values of x > 0.15, S presents very low value, which indicates the high electrical conductivity of samples. This decrease in S values is expected because additional charge carriers are introduced when the Ba²⁺ substitution rate increases.

Figure 5(b) depicts the temperature dependence of S of the La₁₋ₓBaₓCoO₃ sample with x = 0.05 from 330 to 1000 K. S of the La₁₋ₓBaₓCoO₃ sample shows a positive value over the whole measured temperature range, indicating p-type conduction. However, the value of S roughly decreases with increasing temperature. From 330 to 500 K, the value of S strongly decreases from 194 to 42 µV·K⁻¹. Then, in the range of 500–1000 K, it decreases softly to reach 15 µV·K⁻¹.

By combining S and electrical conductivity, the dependence of PF as a function of the Ba concentration for these samples is shown in Fig. 6. The value of PF increases when Ba concentration tends to the value of 0.075. The best PF value reaches 3.4×10⁻⁴ W·m⁻¹·K⁻² at 330 K for x = 0.075. This value is three times higher than the one reported by Kun et al. [37] (x = 0.05 at 350 K) due to their low density and therefore low electrical conductivity.

For 0.075 ≤ x ≤ 0.75, the value of PF roughly decreases to reach a value of almost zero for x ≥ 0.5. It is important to note that the optimum PF value is 10% higher than the one obtained in La₁₋ₓSrₓCoO₃ compounds [23] and that is obtained for x = 0.075 and 0.05, respectively, whereas both strontium and barium are divalent cations. This clearly emphasizes the influence of other parameters (such as orbital recovery due to changes in the morphology or tilting of octahedra) than the only charge carriers concentration in the transport properties of La or Sr-substituted LaCoO₃ ceramics.

Temperature dependence of κ of the La₁₋ₓBaₓCoO₃ sample with 0 ≤ x ≤ 0.1 from 330 to 1000 K is shown in Fig. 7. It is noted that, for all compositions, as the temperature increases, κ increases to reach a maximum value of 7.53 W·m⁻¹·K⁻¹ for x = 0.1 at 1000 K. Moreover, whatever the temperature, κ increases when the substitution rate increases. Indeed, this increase in κ can be correlated with the increase in...
Fig. 7 Temperature dependence of $\kappa$ of the La$_{1-x}$Ba$_x$CoO$_3$ sample with $x = 0, 0.03, 0.05, 0.075,$ and 0.1.

The electrical conductivity that increases when temperature or Ba content increases. $\kappa$ of La$_{1-x}$Ba$_x$CoO$_3$ sample with $x = 0.05$ is lower than for the sample with the same Sr content probably due to the heavier character of barium compared to strontium. However, when the optimum PF values are at 330 K ($x = 0.05$ and 0.075 for Sr and Ba, respectively), thermal conductivities are pretty similar.

Figure 8 shows the temperature dependence of ZT of the La$_{1-x}$Ba$_x$CoO$_3$ sample with $0 \leq x \leq 0.1$ from 330 to 1000 K. ZT shows a maximum value of 0.048 for $x = 0.05$ at 330 K. It rapidly decreases when the temperature increases. Decrease in ZT as a function of temperature is attributed to both the decrease in $S$ and increase in $\kappa$. Compared to La$_{1-x}$Sr$_x$CoO$_3$ compounds that present the highest ZT of 0.038 for $x = 0.05$, two values in Ba-substituted samples are higher, for $x = 0.075$ (the best PF) and $x = 0.05$. On the contrary to La$_{1-x}$Sr$_x$CoO$_3$ compounds, the sample with the best ZT value is not the one with the highest PF. The ZT value for $x = 0.05$ is similar to the one reported by Kun et al. [37] for the same Ba content, even if the sample made from particles synthesized by sol-gel method is porous.

4 Conclusions

The La$_{1-x}$Ba$_x$CoO$_3$ samples ($0 \leq x \leq 0.75$) have been synthesized by solid state reaction and conventionally sintered. Their structural and thermoelectric properties have been studied in the range of 330–1000 K. After several thermal cycles, pure and dense ceramics are obtained over the whole composition range. XRD characterization shows a structural change from rhombohedral to cubic perovskite phase for $x \geq 0.5$. For $x > 0.75$, even with the addition of silicon, samples do not present a cubic perovskite.

Electrical and thermal properties exhibit strong variations when $x$ varies: the electrical conductivity exhibits an optimum value for $x = 0.25$ ($\sigma_{\text{max}} \approx 2.2 \times 10^5$ S·m$^{-1}$), while $S$ decreases when $x$ and/or temperature increases. The La$_{1-x}$Ba$_x$CoO$_3$ presents a p-type semiconductor behaviour. The value of PF increases to reach $3.4 \times 10^{-4}$ W·m$^{-1}$·K$^{-2}$ at 330 K when $x = 0.075$. This value is 10% higher than the best one obtained in La$_{1-x}$Sr$_x$CoO$_3$ compounds. The lowest $\kappa$ is observed at low temperatures for small $x$ values. Finally, the best thermoelectric properties are observed at low temperatures: the highest ZT value of 0.048 is achieved at 330 K for $x = 0.05$. It is 25% higher than the best ZT value in La$_{1-x}$Sr$_x$CoO$_3$ compounds.

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