Thermoelectric properties of the LaCoO_3 - LaCrO_3 system using a high-throughput combinatorial approach

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Abstract

A combinatorial film of the $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ system was fabricated using the LaCoO_3 and LaCrO_3 targets at the NIST Pulsed Laser Deposition (PLD) facility. As the ionic size of Cr^{3+} is greater than that of Co^{3+} , the unit cell volume of the series increases with increasing x . Using a custom screening tool, the Seebeck coefficient of $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ approaches a measured maximum of 286 $\mu\text{V/K}$, near to the cobalt-rich end of the film library (with $x \approx 0.49$). The resistivity value increases continuously with increasing x . The measured power factor, PF , of this series, which is related to the efficiency of energy conversion, also exhibits a maximum at the composition of $x \approx 0.49$, which corresponds to the maximum value of the Seebeck coefficient. Our results illustrate the efficiency of applying the high-throughput combinatorial technique to study thermoelectric materials.

Keywords: $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ solid solution; thermoelectric properties; combinatorial approach; PLD films; distorted perovskite

1. Introduction

The continuing demands for environmentally friendly energy conversion technologies have led to increased activities in the area of thermoelectric research. The characteristics of efficient thermoelectric materials include high figure of merit, ZT ($ZT = (S^2/\rho\kappa)T$, where S is the Seebeck coefficient, ρ is resistivity, and κ is the total thermal conductivity [1]). The power factor, PF ($PF = S^2/\rho$), which is part of the ZT expression, indicates the efficiency of energy conversion. For high temperature waste heat conversion applications, thermoelectric oxides that have both stability at high temperature and high efficiency for energy conversion applications appear to be promising. Since Funahashi et al. discovered the misfit $\text{Ca}_3\text{Co}_4\text{O}_9$ layered oxide having excellent thermoelectric properties more than a decade ago [2], extensive searches for oxides in both film and powder forms have increased substantially worldwide [3-10].

In recent years, the ABO_3 perovskite phases ('A' refer to atoms at cube corner positions, 'B' at body center position and 'O' at face center positions) have also been found to be potential thermoelectric materials [3, 8-12]. Wang et al. reported that the p -type LaCoO_3 with dopant of Sr and Ca on the La-site yields much improved thermoelectric properties [3]. For example, the ZT value increases to 0.1 at $x = 0.1$ at room temperature (RT). This is one of the highest reported values for oxides at room temperature. Phase equilibrium study of the Ca-La-Co-O system and the solid solution extent of $(\text{La,Ca})\text{CoO}_3$ were reported by Wong-Ng et al. [8]. Theoretical study of the Seebeck coefficient of the LaCrO_3 system was conducted by Marsh and Parris [12]. The importance of the $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ solid solution system is highlighted by its potential applications for heterogeneous catalysis, for energy conversion, as improved cathodes for solid oxide fuel cells, and for automotive pollution control [13-15]. Magnetism and potential magnetic applications have also been explored by Tilset et al. [16].

Preparation and characterization of a solid solution series using the conventional solid state synthesis and measurement techniques are often time-consuming, and the combinatorial approach could be an efficient alternative to locate compositions with optimal properties in a complex material system [17-21]. The goal of this work is to prepare and study the trend of the structure and power factor, PF of the $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ combinatorial films using high throughput synthesis and thermoelectric property screening techniques. In particular, whether any of the solid solution members would have a higher PF value than that of the end members. Our combinatorial approach involves fabricating "film libraries" with continuously varying compositions between two different materials on a substrate, followed by high-throughput screening.

2. Experimental¹

Details of synthesis and measurements are reported as electronic supplementary information (ESI). Deposition of a binary oxide combinatorial library, $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$, was achieved using a

¹ The purpose of identifying the equipment in this article is to specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology.

pulsed laser deposition (PLD) facility. Bulk polycrystalline targets were produced for LaCoO_3 and LaCrO_3 using a sol-gel method. The gel was washed and manually ground. The powder was calcined at 700 °C for 4 h and cooled in a tube furnace with continuous oxygen flow. After calcinations, the fine powder was uniaxially pressed into pellets under a pressure of 1 GPa. The pellets were finally sintered at 1000 °C for 9 h. The polycrystalline LaCoO_3 and LaCrO_3 bulk targets were analyzed by X-ray diffraction (XRD) [22].

The $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ film was deposited on both LaAlO_3 <100> and thermally grown SiO_2 on Si <100> substrates during the same experiment. A LaAlO_3 substrate strip was cut in the <100> direction, and was attached to a silicon wafer using silver paste. The substrate system was heated to 650 °C in a vacuum pressure of less than 10^{-3} Pa. Once the substrate equilibrated at temperature, deposition occurred in an oxygen partial pressure of 8.3 Pa. The surfaces of the targets were struck with 200 mJ of excimer laser KrF ($\lambda = 248$ nm) resulting in a plasma directed towards the inverted substrate. The LaCrO_3 target was directed towards one side of the substrate while the LaCoO_3 target towards the opposite side. The laser was alternately pulsed for 250 pulses on the lanthanum-chromate target and 150 pulses on the lanthanum-cobaltate target at laser frequency rate of 15 Hz for a total of 2645 repeated cycles (Fig 1). The resulting film was annealed for two additional hours at 600 °C under oxygen flow to reduce oxygen vacancies within the film.

The structure of the film was analyzed using a Bruker D8 diffractometer equipped with a three dimensional x-y-z translation stage and a 2D area detector. Using a collimated CuK_α X-ray beam with a ≈ 3 mm² spot size, the film was analyzed at 3.9 mm steps from the Co-rich end to the Cr-rich end of the combinatorial library. This was performed on the LaAlO_3 substrate as well as the adjacent film deposited on a thermally grown silicon oxide layer. At each scan location the counts were measured from $2\theta = 15^\circ$ to $2\theta = 70^\circ$, followed by a χ -integration across the 2-dimensional detector into a 1-dimension diffraction profile.

The Seebeck coefficient was measured across the combinatorial library using a custom NIST screening tool described by Otani et al. [23, 24] and Yan et al. [25, 26]. A two-probe technique was employed. The temperature difference and electric potential were measured 10 times and averaged at each point for three different heater settings. The Seebeck coefficient was calculated using linear least-squares regression of the slope data. The Seebeck coefficient was measured at 3 mm increments across the film from the cobalt rich end towards the chromium rich end. All measurements were performed at RT.

The electrical resistance of the film was measured using a four-probe van der Pauw technique at the same positions where the Seebeck coefficient measurements were performed. The probe was calibrated using a Si reference sample (Four Dimensions 280DI Sheet Resistance Mapping System). Two sets of resistance data were measured and averaged (Table S1, Fig. S1). Since the resistivity of a film can be obtained from $\rho = tR$, where t and R are the thickness and resistance of the film, respectively, one can obtain the trend of resistivity vs. x in $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ by using the average values of two sets of resistance data. The thickness of the $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ film was measured in six regions (Fig. S2a), five of which were estimated using the ellipsometry spectroscopy technique where the spectra were fit with the Lorentz oscillator model consisting of

substrate, film, and surface roughness in the photon energy region of 0.775 eV to 2.0 eV [27]. The 6th region was measured using a Hitachi S4700 scanning electron microscope (SEM) for thickness confirmation.

3. Results and Discussion

The targets LaCoO_3 and LaCrO_3 were confirmed to belong to the distorted perovskite ABO_3 family, having rhombohedral $R\bar{3}c$ structure ($a = 5.4445(2) \text{ \AA}$, $c = 13.0936(6) \text{ \AA}$, $V = 336.13 \text{ \AA}^3$, and $Z = 6$ [28]) and orthorhombic $Pbnm$ structure with a relatively smaller unit cell ($a = 5.508 \text{ \AA}$, $b = 7.791 \text{ \AA}$, $c = 5.484 \text{ \AA}$, $V = 235.33 \text{ \AA}^3$, and $Z = 4$) [29]) (Fig. 2), respectively. As these structures deviate from the ideal cubic ABO_3 structure, they are considered as pseudo-perovskites (Fig. S3). According to Tolochko et al. [29] the structure of the bulk solid solution, $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$, is rhombohedral with $0 \leq x \leq (\approx 0.7)$ and orthorhombic with $x \geq (\approx 0.7)$.

To compare the volume of the solid solution members in $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ using a common basis across the series, the pseudo-cubic perovskite cell volume of the film was estimated. The pseudo-cubic perovskite volumes are the cell volumes divided by the perovskite formula units per cell ($Z=6$ for the rhombohedral cells and $Z=4$ for the orthorhombic cells). As the ionic size of Cr^{3+} is reported to be greater than that of Co^{3+} [30], the literature data indeed show that pseudo-cubic unit cell volume of the series increases with increasing x (Fig. S4) in a near linear relationship [28, 29, 31].

The lattice parameters of the film are apparently influenced by that of the substrate. In all cases the pseudo-cubic perovskite cells were somewhat greater when the XRD profile was collected from film atop the thermally grown amorphous SiO_2 substrate compared to those from the single crystal LaAlO_3 substrate. The difference in lattice parameter is most likely due to strain caused by mismatch in coefficient of thermal expansion (CTE) between the film and the two substrates (LaAlO_3 and SiO_2). The CTE values were reported to be $10 \times 10^{-6}/\text{K}$ for LaAlO_3 [32], and a much smaller value of $0.5 \times 10^{-6}/\text{K}$ to $4.1 \times 10^{-6}/\text{K}$ (average $2.3 \times 10^{-6}/\text{K}$) for SiO_2 [33]. The average CTE value for $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ is $22.5 \times 10^{-6}/\text{K}$ [34]. Therefore, the difference of CTE is much greater between SiO_2 with $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ than that between LaAlO_3 and $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$.

The relationship of the $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ combinatorial film composition (x) to film position was obtained by least-squares fitting of the average pseudo cubic cell volume for each location across the film library with reference to Fig. S4. The results are shown on Fig. 3, whereas the compositional x values are shown on the right hand-side axis. Based on Fig. S3, the symmetry of our $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ film was estimated to be rhombohedral when $x \leq 0.40$, and orthorhombic when $x > 0.40$, which is different from Tolochko et al.'s reported transition point at $x=0.7$ [29]. This difference could be due to the film and substrate strain effect.

A plot of the Seebeck coefficient vs the distance from Co-rich end to Cr-rich end of the library is shown in Fig. 4. The Seebeck Coefficient of the polycrystalline LaCrO_3 target is higher than that of LaCoO_3 target at room temperature and both targets demonstrate a p -type semiconductor behavior. Similar to the bulk counterpart, the Seebeck coefficients measured for LaCrO_3 in the film is also relatively greater than that for LaCoO_3 . The trend of the Seebeck

coefficient across the $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ series suggests that it increases with Cr-doping, with a measured maximum of $286 \mu\text{V/K}$ at $x \approx 0.49$ (or $\text{LaCo}_{0.51}\text{Cr}_{0.49}\text{O}_3$). The actual maximum Seebeck coefficient is estimated at $0.40 \leq x \leq 0.49$. This increase of the Seebeck Coefficient with Cr is similar to that observed by Koc and Anderson [36]. This peak approximately corresponds with the transition between rhombohedral to orthorhombic symmetry at $x \approx 0.40$. The interconnection geometry of the octahedral sites determines the formation of charge carriers through charge disproportionation between adjacent octahedral trivalent cobalt cations, leading to the evolution of electronic properties [37]. For compositions where $x > 0.6$ the Seebeck coefficient measurements had a larger uncertainty (discussed later).

The 6 regions on the film were estimated to have a thickness of 522 nm, 513 nm, 520 nm, 450 nm, 463 nm, and 456 nm, respectively (Fig. S2a). The region that was estimated using a SEM gives the thickness of 450 nm (Fig. S2b). The two independent data sets agree reasonably well with each other. The roughness of the film was estimated to be between 16 nm and 27 nm.

Table 1 summarizes the Seebeck coefficient and the average resistivity data. A general trend is observed. As Cr concentration increases, the resistivity value increases which agrees with that reported by Tolochku [29], and by Anderson [14] who observed that LaCoO_3 has much higher intrinsic conductivity as compare to that of LaCrO_3 . Tolochku et al. further described that the increase in resistivity is moderate at lower concentration Cr, but much faster as the concentration of Cr is substantial, with a maximum at $x=0.8$ [29]. As the resistivity value is rather high beyond the region of $x > 0.6$ in our $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ film, the uncertainty in measuring the electrical voltage and subsequently in measuring the Seebeck coefficient increases.

Combining the Seebeck coefficient data with the resistivity data, a plot of the power factor PF vs x in $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ is shown in Fig. 5. The right axis represents the composition x . The relation of the dopant concentration x and the distance is also shown. The composition of each of the data point is indicated by the open circles. The measured PF reaches a maximum of $2.69 \times 10^{-4} \mu\text{W-K}^{-2}\text{cm}^{-1}$ at $x \approx 0.49$. The actual maximum is estimated to be at $0.40 \leq x \leq 0.49$. This trend parallels the trend of that of the Seebeck coefficient vs x . Therefore, the combinatorial film provides us a trend of the PF values (with an x value range of 0.40 to 0.49) from which samples with optimum properties can be prepared, i.e., via bulk sample synthesis routes.

4. Conclusions

This work illustrates an efficient method to study the trend of structure and power factor as a function of composition of $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$. The highest Seebeck coefficient and PV values of the system in $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ were estimated to be between $x=0.40$ to 0.49 . In the region of $x>0.6$, the resistivity values are very high and the uncertainty of the Seebeck coefficient measurement is much greater. In conclusion, the combinatorial methodology is an efficient technique that can be used to guide bulk sample investigations.

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Table 1. Seebeck Coefficient and Resistivity across the $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ combinatorial film on LaAlO_3 as substrate.

Distance from Co-rich end (mm)	Seebeck Coefficient ($\mu\text{V/K}$)	Resistivity ($\Omega\text{-cm}$)
28.25	67.3	121
31.5	88.7	107
34.5	122.2	199
37.5	171.9	269
40.5	232.8	371
43.5	286.3	305
46.25	208.6	527
49.5	182.0	608
52.5	181.2	736
55.5	208.1	635
58.5	184.4	1280

Figure legend

Fig. 1. Schematic and image for PLD processing of a $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ combinatorial library

Fig. 2. X-ray diffraction patterns of LaCrO_3 and LaCoO_3 bulk targets as prepared by sol-gel method.

Fig. 3. X-ray diffraction results showing the calculated pseudo-cubic perovskite cell volume vs. distance from cobalt rich end of the library. The estimated 'x' in $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ is also given.

Fig. 4. Seebeck coefficient of $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ measured across the combinatorial library and correlated to composition using results for XRD. Uncertainties of measurements are given [35].

Fig. 5. Power Factor PF ($PF=S^2/\rho$), of $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ across the combinatorial library as a function of the distance from Co-rich end (filled circle). The relation of the Cr concentration x and the distance is also shown (empty circle). Uncertainties of measurements are given [35].

Supplementary Material

Thermoelectric properties of the LaCoO_3 - LaCrO_3 system using a high-throughput combinatorial approach

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(I) Synthesis and measurement Details

Synthesis of Targets

Deposition of a binary $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_{3-y}$ combinatorial library was achieved through pulsed laser deposition (PLD). Bulk targets were produced of LaCoO_3 and LaCrO_3 using a sol-gel method. First citric acid and polyethylene glycol were dissolved in deionized water, then $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and either $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to the mix in stoichiometric amounts. Lastly ethylene glycol was added. The mix was then manually stirred until all the precursors were dissolved and a homogenous mix was obtained. Once the mix was homogenous, it was put in a hot stage heated at $\approx 353\text{ K}$ and stirred for 3 h in order to form a gel. The gel was ashed at $500\text{ }^\circ\text{C}$ for 2 hours in a Lindberg/Blue ThermoScientific box furnace. The resulting ash was manually ground for 20 min in a mortar and pestle. The powder was subsequently calcined at 973 K for 4 h using a 10 K/min ramp for heating and cooling in a tube furnace with continuous oxygen flow. After calcinations, the fine powder was uniaxially pressed into pellets under a pressure of 1 GPa for 10 minutes at 298 K . The pellets were finally sintered at 1273 K in a box furnace, using a temperature ramp rate of 10 K/min for heating and a 4 K/min for cooling. The desired sintering temperature was held for 9 h. The targets were analyzed with via X-ray diffraction and indexed to the corresponding powder diffraction files to determine the initial structure.

XRD characterization of film

The structure of the film was analyzed using a Bruker D8 diffractometer equipped with a three dimensional translation stage, and two dimensional area detector. Using a collimated CuK_α X-ray beam with a $\approx 3\text{ mm}^2$ spot size the film was analyzed at 3.9 mm steps from the cobalt rich end to the chromium rich end of the combinatorial library. This was performed on the LaAlO_3 substrate as well as the adjacent film deposited on a thermally grown silicon oxide layer. At each scan location the counts were measured from $2\theta = 15^\circ$ to $2\theta = 70^\circ$, then integrated across the 2 dimensional detector into a single dimension diffraction profile. The resulting peak positions were used to calculate the lattice parameters.

On both the LaAlO_3 and SiO_2/Si substrates, XRD analysis of the film at 15 points across the library both show gradual peak shifting which corresponds to the expected behavior where the lattice parameters increase upon greater chromium concentrations (Fig. S3). To compare the volume of the solid solution members, the pseudo-cubic perovskite cell volumes of the film were estimated. Based on the near-linear volume/composition x relationship in the literature reported bulk $\text{LaCo}_{1-x}\text{Cr}_x\text{O}_3$ phase (Fig. S4), and the possible overlap of substrate peaks with peaks from the film, the 15 points were assumed to have rhombohedral symmetry for simplicity, and the a and c lattice constants and unit cell volume, V , were estimated using the 012 and the 024 peaks, followed by conversion to the pseudo cubic cell volume (Fig. 3).

Seebeck Coefficient measurements

The Seebeck coefficient was measured across the combinatorial library using custom NIST apparatus described in [23-26]. A two-probe technique was employed, where two probes $\approx 2\text{mm}$ apart, each with a $\approx 1\text{mm}^2$ contact area, were placed against the film and a miniature heater was used to create a temperature gradient. A piece of Grafoil[®] ($\approx 1\text{mm}^2$) was placed between the film and each probe as an intermediate which increased the quality of the electrical contact, in addition to increasing the thermal conductivity between the probes and film. The temperature and electric potential were measured 10 times and averaged at each point for three different heater settings. A linear least squares regression of the values results in the Seebeck coefficient, seen as the slope. The Seebeck coefficient was measured at 3 mm increments across the film from the cobalt rich end to the chromium rich end. All measurements were performed at room temperature.

Resistance measurements

The resistance measurements were conducted using the “Four Dimensions 280DI Sheet Resistance Mapping System” (Model # RS 3-0.01, Serial # 8155-019). Further information could be obtained from (http://www.nist.gov/cnst/nanofab/four_dim_280di.cfm). A four-probe (linear probe) technique was used. Each probe has a 1 mm spacing and with a probe radius of 100 μm . The measurement scheme is performed to match the Seebeck coefficient measurement, at positions as close to each other as possible. This was done based on the distance from cobalt rich end such as that shown on Figs. S2a, S2b. Once the position was determined, the four-probe was placed on top of the tape in a vertical manner, while putting the probe inside the tape.

Before sample measurement, the alignment condition of the system/probe was confirmed using a Si reference sample. The first value was 0.1753 ohm/sq. After the 1st measurement, the ‘Si 68’ reference sample was measured to assure correct measurement (0.1751 ohm/sq). A second series of measurements were conducted at the same or in close proximity to the locations of the first set of measurements. After the second measurements, the value was confirmed to be 0.1743 ohm/sq.

Thickness estimation of film

For thickness measurements, the film was divided into six regions (Fig. S3), five of which were estimated using the ellipsometry technique where spectra were fit with the Lorentz oscillator model in the photon energy region of 0.775 eV to 2.0 eV region. The 6th region was measured using a scanning electron microscope (SEM) for confirmation.

Seebeck coefficient and Power Factor uncertainty Estimation

Uncertainty in the measured y-axis data is obtained using the least squares fit for a line [35]:

$$\sigma_y = \sqrt{\frac{1}{N-2} \sum_{i=1}^N (y_i - A - Bx_i)^2} .$$

Uncertainty in the constant B for the expected linear relation $y = A + Bx$, which is the Seebeck coefficient, can then be obtained using the following relation:

$$\sigma_B = \sigma_y \sqrt{\frac{N}{N \sum_{i=1}^N x_i^2 - \left(\sum_{i=1}^N x_i \right)^2}} .$$

The error propagation for the power factor was calculated using the following equation:

$$2\sigma_{PF} = 4(2\sigma_S)^2 + (2\sigma_\rho)^2 .$$

We ignored a negative correlation error term for S^2/ρ , i.e. $-2\sigma_{S^2/\rho} = 0$. While it is safe to assume this term to be zero for independent properties, it is not correct when the measurements of S and ρ share the same probes on the same specimen. Since these two properties are measured at the same temperature, the correlation term is embedded in the data.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5