UNIVERSITY OF TWENTE.



Master's thesis

$\begin{array}{c} {\bf Structural \ engineering \ of \ Ca_3 Co_4 O_9} \\ {\bf thermoelectric \ thin \ films} \end{array}$

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Abstract

Oxide materials offer new possibilities for thermoelectric devices because of their natural abundance, non-toxicity and good performance and therefore they are studied in all their variety, different materials, different structures, different compositions. Big expectations lie in the use of thermoelectric thin films since they can be used on a small as well as on a large scale, so the range of applications is large.

After the first findings with Na_xCoO_2 now the more interesting material is $Ca_3Co_4O_9$ because due to the non-volatility of the Na Na_xCoO_2 materials are not stable in air environment without an extra capping layer.

In this research epitaxial $Ca_3Co_4O_9$ thin films have been grown on two different substrates using pulsed laser deposition. As substrate materials Al_2O_3 and $(La_{0.3}Sr_{0.7})(Al_{0.65}Ta_{0.35})O_3$ (LSAT) are chosen. According to the crystal lattice structure the mismatch between the film and the Al_2O_3 substrate should be small, since they both have hexagonal unit cells with relatively similar lattice parameters. But LSAT has a cubic unit cell, so here there should be a large mismatch between film and substrate.

The structural properties of the different samples show a lot of differences, so on the LSAT substrate the diffraction peaks of the thin film are much lower in intensity as compared to those on the Al_2O_3 substrate. The surface roughness of the thin films on the LSAT substrate is higher and the grains are smaller comparing them with the films on Al_2O_3 . On top of the substrates there is a buffer layer formed before the actual $Ca_3Co_4O_9$ forms, which is different in thickness for both substrate materials.

There has been done a temperature variation for the deposition process and a thickness variation of the thin films. For grown films of 60nm thickness at deposition temperatures from 430 to 850 °C on both substrates there are maxima in the resistivity and the Seebeck coefficient found for 430, 750, and 850 °C, while for 650 °C there is on both substrates the lowest thermoelectric performance. The curves of the resistivity and Seebeck coefficients look the same on both substrates, but on LSAT both values are quite a bit higher than on Al₂O₃ (92.5 μ V/K and 5m Ω cm as the best at 750 °C on Al₂O₃ and 13.3 μ V/K and 21.39m Ω cm on LSAT).

For thickness variation a range of 10 to 120nm has been used at the best performing temperature of 750 °C. With a film thickness of only 10nm no good thermoelectric performance was achieved, which is probably due to the buffer layer between substrate and film. For the other thicknesses there is only slight variation, but on both substrates the film of 90nm thickness has a somewhat worse performance.

Interestingly all samples that performed worse than the others in their measurement series showed a shift to the left in the diffraction $2\theta/\omega$ analysis.

The Seebeck coefficient and resistivity have also been measured at increasing temperature and here it has revealed that the films on LSAT show a stable performance up to 700 °C, while with the Al_2O_3 substrate it is stable only up to 600 °C. At these temperatures the resistivity increases abruptly when cooling the sample back down to room temperature.

The thermal conductivity of both film-substrate combinations has been measured in the US, resulting in 1.2 and 2.1 W/mK respectively for Al_2O_3 and LSAT.

Based on the results obtained in this thesis it is concluded that $Ca_3Co_4O_9$ thin films can play an important role in the application of thermoelectric materials.

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1 Introduction

In 1821 Thomas Seebeck discovered that two different materials at different temperatures brought in contact generate a voltage which is proportional to the temperature difference. The proportionality factor is called the Seebeck coefficient after the discoverer. This effect was the beginning of the field of thermoelectricity. Nowadays the use of electricity reaches larger and larger dimensions. For this reason it is important to find new technologies generating electric energy for minimum cost and as effective as possible. [1]



Figure 1.1: Convert waste heat into electrical energy [2]

Motivation In a lot of industrial processes and exhaust gases waste heat is produced nowadays which can be recovered and converted pollution-free into useful electric power by thermoelectric energy conversion. This could help reduce global warming and climate change issues by maximizing the efficiency of existing energy sources and lower the consumption of fossil fuels. The best performing materials, however, contain toxic elements such as tellurium or antimony,

which oxidize easily when exposed to high temperature air. Using thermoelectric oxides, where nontoxic, naturally abundant, so also cheap elements are involved can enlarge the possible application range, although their thermoelectric properties are worse than that of the previously mentioned elements. Most promising is the application of thermoelectric energy recovery in automobiles, where a lot of waste heat is produced in the engine coolant or exhaust gas, which could be used as electrical energy in the car again. Thermoelectric energy conversion could also improve the efficiency of power plants. A big advantage of thermoelectric devices is also that they are working independently of any moving parts, so they are easy to maintain and the solid-state design makes them reliable and silent. Another advantage lies in the small size which makes them applicable in almost every sector. [3, 4, 5]

State-of-the-art Up to now there has been done a lot of research on thermoelectric materials. After it had been found that $Na_x CoO_2$ offers very good thermoelectric properties the attention has been drawn to $Ca_3Co_4O_9$ because of the high volatility of Na which serves a lot of problems. Ca is much more stable so it could be used much more efficiently and the sample structure would be much more stable. There has been done an analysis of the growth of $Ca_3Co_4O_9$ on four different substrates (LaAlO₃ (LAO), LSAT, $SrTiO_3$ (STO) and Al_2O_3) with different film thicknesses of 40 and 100nm. For LAO and LSAT measurements have been done at both film thicknesses, while on STO and Al_2O_3 only 100nm thick films have been analyzed. On LSAT the Seebeck coefficient decreases with increasing thickness, while the resistivity increases, but on LAO both, the Seebeck coefficient as well as the resistivity decrease with increasing thickness. But in these two materials there is also a large difference in the thickness of the buffer layer. [5] Other aspects of the growth of $Ca_3Co_4O_9$ thin films on Al_2O_3 substrates that have been analyzed are different growth rates (3-10Hz), temperature (550-750 °C), oxygen pressure (0.05-0.6mbar), and fluence $(1.2-1.9 \text{J/cm}^2)$. Since not all materials can be grown at high temperatures, this range is much too small, to give a whole picture of the possibilities of $Ca_3Co_4O_9$ thin films. [6, 7, 8, 9] There has also been done a Seebeck coefficient measurement at varying temperature showing a change in electronic behavior at several temperatures. [10, 11]

This work In this work a strategical analysis of the thermoelectric properties of $Ca_3Co_4O_9$ thin films grown by pulsed laser deposition at different deposition temperatures, in different thicknesses and comparison of these results for two different substrates has been performed. The two different substrates are chosen because of their totally different crystal structures.

2 Thermoelectrics

Thermoelectricity describes the interplay between temperature and electricity. It is used in either the Peltier effect, the Seebeck effect or the Thomson effect. In this thesis the Seebeck effect will be analyzed on different samples, so in the following section more details about the physical processes will be given.



Figure 2.1: Seebeck effect in n-type and p-type material [12]

One end of an either n-type or p-type material is heated, while the temperature at the other site is maintained at a lower temperature. Initially the carriers (electrons or holes, depending if it is a n-type or p-type material) move from the hot to the cold side, since they have a larger moving energy than the ones at the cold side of the conductor, due to the additional heat energy and an electric field is set up across the material. At some point the potential difference that is built up this way, is that large that there is a compensation current, bringing 'cold' electrons back to the hot side to work against the abundance of electrons at the cold side. These diffusion currents create the final voltage, determined by $V = S \cdot \Delta T$, with ΔT the temperature difference between the two sides of the conductor and S the Seebeck coefficient.

Up to now, the best thermoelectric materials are semiconductors, as can be seen in figure 2.2, but why are they so much better than metals?

2.1 Theoretical aspects

To enhance the thermoelectric performance it is important to understand the dependencies of the three variables on the atomic and electronic structure of the material. Therefore, in the



Figure 2.2: Thermopower for different materials [13]

following section a theoretical background on all three of them, Seebeck coefficient, electrical conductivity and thermal conductivity will be provided.

All variables giving a contribution to the figure of merit ZT, the Seebeck coefficient S, the electrical conductivity σ and the electronic thermal conductivity κ_E are determined by the Boltzmann transport equation (BTE):

$$\left(\frac{\mathrm{d}f}{\mathrm{d}t}\right)_{coll} = \frac{\mathrm{d}f}{\mathrm{d}t} + \frac{\mathrm{d}\mathbf{k}}{\mathrm{d}t}\nabla_{\mathbf{k}}f + \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t}\nabla_{\mathbf{r}}f \tag{1}$$

Here t is time, **k** is the wave vector of the electrons, **r** is the position vector and f the nonequilibrium distribution function. The BTE is used to describe the change of a system of particles which arises due to an external force such as a temperature gradient. This perturbation of the system causes a redistribution of the position and momentum of the electron system. By random scattering of the electrons the equilibrium is restored within a relaxation time (τ) and a solution to the BTE can be found. It is then given by the equilibrium distribution function f₀, which at equilibrium obeys the Fermi-Dirac statistics:

$$f_0(E) = \frac{1}{exp((E-\mu)/k_B T) + 1}$$
(2)

with E the energy of the electrons, μ the chemical potential (or Fermi level), k_B the Boltzmann constant and T the temperature of the electronic system. [14] Two important characteristics of the Fermi-Dirac distribution are that far away from the Fermi level there is either a 100% or a 0% chance of finding an electron at this energy level and that its derivative is zero for all values of E except when E is close to the Fermi level. This means for the actual physical process, that in the case of any perturbation (e.g. by an electric field or temperature gradient) only electrons close to the Fermi level react to this disturbance. In other words, only electrons close to the Fermi level contribute to the electrical conduction (and the Seebeck coefficient). So to have a high contribution the density of states should be high around the Fermi level, or for semiconductors, their bandgap should be small enough to allow enough carriers contribute to electrical conduction.

The electronic structure of a material is shown by its electronic band structure. By measuring the distance between the lowest part of the conduction band and the highest part of the valence band, the bandgap of the material can be determined. The curvature of each band is inversely proportional to the effective mass of the charge carriers $m^* = \hbar^2 (d^2 E/d\mathbf{k}^2)^{-1}$. Different bands have a different curvature and thus a different effective mass. To give a complete description of the complete structure the bands are taken individually and the relevant transport coefficients for each band are determined. The coefficients of all single bands are then added up to form the transport coefficients of the material as single band materials. This single band can than be approximated with a parabolic band. Therefore we have a parabolic dispersion relation between E and **k**:

$$E_{3D}(\mathbf{k}) = \frac{\hbar^2}{2} \left(\frac{k_x^2}{m_x^2} + \frac{k_y^2}{m_y^2} + \frac{k_z^2}{m_z^2} \right)$$
(3)

with $k_{x,y,z}$ the electron wave number and $m_{x,y,z}$ the effective mass in the corresponding direction. From this single band model all relevant transport parameters for a certain material can be calculated. [15]

From the dispersion relation we can calculate the corresponding density of states:

$$g(E) = \frac{1}{2\pi^2} \left(\frac{2m_d}{\hbar^2}\right)^{3/2} E^{1/2}, m_d = (m_x m_y m_z)^{1/3}$$
(4)

With these equations in mind all relevant parameters can be determined and by having the understanding of the theory behind the thermoelectric phenomena there can be thought of possible ways to improve the values of the Seebeck coefficient, the electrical conductivity and the thermal conductivity.

2.1.1 Seebeck effect

The Seebeck coefficient can be described as the proportionality factor of the temperature difference and the voltage, but physically it can be seen as the entropy transported with a charge carrier divided by the carrier's charge: S = C/q with C the specific heat and q the charge of the carrier. It is useful to divide the transported energy into two components. The first component is the change of the net entropy of the material due to the addition of a charge carrier. The second component is the ratio of the energy transported in the transfer process and the absolute temperature. Thus, the Seebeck coefficient is the sum of contributions associated with the presence of charge carriers and their motion.

$$S = S_{\text{presence}} + S_{\text{transport}} \tag{5}$$

For derivation of the general description of the Seebeck coefficient, an analysis of the first part contributing to the Seebeck coefficient is sufficient. When there are no interactions of the electrons within the material, we only need to take the change in entropy due to adding of a charge carrier into account. In the ideal situation of n fermion charge carriers distributed among N degenerate states of an energy band, the energy needed to distribute the carriers equivalently is

$$\alpha = -Nk_B[c\ln c + (1-c)\ln(1-c)]$$
(6)

with c = n/N is the carrier concentration. When there is a charge carrier added, the entropy changes, giving us the Seebeck coefficient:

$$qS = k_B \ln[(1-c)/c] \tag{7}$$

An alternative form of this simple expression is obtained when the carrier concentration is expressed in terms of the energy of the electronic energy band, the chemical potential, μ , and the thermal energy, k_BT , via the Fermi function so that $c=1/\exp((E-\mu)/k_BT)+1$:

$$S = (k_B/q)[E - \mu)/k_BT \tag{8}$$

By this, the determinant factor for the Seebeck coefficient is the difference between the average energy of the carriers, which are responsible for conduction, and the Fermi energy (i.e. chemical potential). [14, 15, 16]



Figure 2.3: Bandstructure dependence of thermoelectric energy (top semiconductor, below metal) [17]

In the case of a metal the Fermi energy lies on the same level as the conduction band, so the density of states is symmetric at the Fermi energy and the average conduction energy is close to the Fermi level. For the semiconductor the Fermi level is below the conduction band, so we have an asymmetric density of states at the Fermi level and the average conduction energy is higher than the Fermi level (see figure 2.3). When using this knowledge and equation 8 to determine the Seebeck coefficient of a material, it is clearly visible that for a larger average conduction energy the Seebeck coefficient increases. So this is the reason why semiconductors have a higher Seebeck coefficient than metals and why insulators have a very low Seebeck coefficient.

When increasing the band gap of the semiconductor up to a specific point the average energy of the conduction electrons decreases, so the Seebeck coefficient also decreases. [17]

Grain boundaries can also have a positive influence on the figure of merit, since they can act as a filter for charge carriers with low energies, for which the Seebeck coefficient is negative. This way the contribution of low energy electrons to transport is minimized and the Seebeck coefficient is increased. This mechanism is called electron grain boundary scattering. Although the mobility is lowered, the chance of scattering for low energy electrons is increased. [18]

2.1.2 Electrical conductivity

The electrical conductivity, a measure of how freely charge carriers can move through the lattice crystal of the material, is given by the Drude equation.

$$\sigma = \frac{e^2 \tau n}{m} \tag{9}$$

The relaxation time τ and the mass can here be replaced via the equation for the carrier mobility, $\mu = e\tau/m_e$ with m_e the effective mass and τ the mean scattering time between collisions, so that

$$\sigma = ne\mu \tag{10}$$

2.1.3 Thermal conductivity

After the conduction of electrons now the conduction of heat is investigated. Since the heat is "transported" on two ways through the material, the thermal conductivity is split into two parts, an electronic part and a lattice part:

$$\kappa = \kappa_E + \kappa_L \tag{11}$$

The electronic part is the contribution of the charge carriers also carrying heat and so by their movement conducting heat through the material. The lattice part is the contribution of phonons (lattice vibrations).

Electronic thermal conductivity Since the electronic thermal conductivity depends on the ability of the electrons to move freely through the material it makes sense that κ_E is connected to the mobility and the number of charge carriers. If electrons can move hardly through the crystal lattice without scattering, they will also not conduct heat that easily. So the electronic thermal conductivity is directly interrelated with the electronic conductivity. An increase in carrier concentration or mobility will increase κ_E . The electronic thermal conductivity κ_E can be determined via the Wiedemann-Franz law:

$$\kappa_E = L\sigma T \tag{12}$$

With the Lorentz number given as:

$$L = \frac{\pi^2}{3} \left(\frac{k_B}{e}\right)^2 = 2.45 \cdot 10^{-8} W \Omega K^{-2}.$$
 (13)

the electronic thermal conductivity can then easily be calculated.

Lattice thermal conductivity Heat is also transported through the atomic lattice by phonons (lattice vibrations). Essentially the lattice thermal conductivity is given by:

$$\kappa_L = \nu C L_{ph} \tag{14}$$

where ν is the average phonon velocity, C is the specific heat, and L_{ph} is the phonon mean free path. [16]

2.1.4 Figure of merit

As mentioned in the introduction the figure of merit gives the actual thermoelectric performance of a material, combining all the parameters described above. It is given by

$$ZT = \frac{S^2 \sigma}{\kappa} T,\tag{15}$$

with S the Seebeck coefficient, σ the electrical conductivity and κ the thermal conductivity.

According to the relation to reach a high value for the figure of merit the Seebeck coefficient and the electrical conductivity should reach maximum values and the thermal conductivity minimum value.

As can be seen in figure 2.4, Seebeck coefficient and electrical conductivity have just an opposing trend for different carrier concentration. Too reach the maximum figure of merit the point where both lines intersect has to be chosen. Here it is also visible, that a lowering in electronic thermal conductivity would also result in a decrease in electrical conductivity and thereby in a decrease in the figure of merit.

Further, the dependence of the figure of merit on the carrier concentration can be seen. Due to a high carrier concentration the electric conductivity gets large, but unfortunately the electron thermal conductivity also does so, and the Seebeck coefficient decreases. So only up to a specific point in carrier concentration doping would have a positive influence on the figure of



Figure 2.4: Thermoelectric properties as function of carrier concentration [19]

merit, for too high doping concentrations it gets worse again. The only parameter that could be improved without a negative influence on the other variables is the lattice thermal conductivity.

Another possibility to increase the thermoelectric performance is to look for a temperature at which there are several valence bands at the same level (see figure 2.5), so that there are a number of contributions to the thermoelectric energy. In this case the two valence bands L and Σ converge at a temperature of 500K and we have transport contributions from both bands. [20]

2.2 Thermoelectric materials

Modern thermoelectric research is based on Ioffe's observation in the 1950s [21] that heavily doped semiconductors made the best thermoelectric materials. He made several restrictions for the best thermoelectric behavior. The first one states that the degenerate semiconductors or semimetals with carrier concentrations $n\sim10^{18}-10^{20}$ cm⁻³ make good thermoelectrics because such n values maximize the power factor. Secondly, semiconductors with a bandgap



Figure 2.5: Relative energy of valence bands [20]

 $\Delta \sim 10 k_B T_O$ make good thermoelectric materials, with T_O the operating temperature. Further, a high-symmetry crystal structure is favorable as well as having small eletronegativity difference between the constituent atoms. A low lattice thermal conductivity, as is necessary for a good thermoelectric performance, is often found in materials consisting of heavy elements. [22]

Established thermoelectric materials (those which are employed in commercial applications) can be conveniently divided into three groups with each dependent upon the temperature range of operation. Alloys based on bismuth in combinations with antimony tellurium, and selenium are referred to as low-temperature materials and can be used at temperatures up to around 450K. These are the materials universally employed in thermoelectric refrigeration and have no serious contenders for applications over this temperature regime. The intermediate temperature range up to around 850K is in the regime of materials based on lead-telluride while thermoelements employed at the highest temperatures are fabricated from silicon germanium alloys and operate up to 1300K.

Although the above mentioned materials still remain the cornerstone for commercial applications in thermoelectric generation and refrigeration, significant advances have been made in synthesizing new materials and fabricating material structures with improved thermoelectric performance. Efforts have focused on improving the figure of merit by reducing the lattice thermal conductivity. Two research avenues are currently being pursued. One is a search for a so-called phonon-glass electron-crystal, in which it is proposed that crystal structures containing weakly bound atoms or molecules that rattle within an atomic cage should conduct heat like a glass, but conduct electricity like a crystal. Candidate materials receiving considerable attention are the filled skutterudites and the clathrates. [23]

During the past decade material scientists have been optimistic in the belief that lowdimensional structures such as quantum wells, quantum wires, quantum dots and superlattices



Figure 2.6: Comparison of various thermoelectric materials [22]

will provide a route for achieving a significantly improved thermoelectric figure of merit.

2.2.1 Phonon-glass, Electron-crystal

G.A. Slack and several other researchers [24, 25, 26, 27] defined the chemical characteristics of candidates for a good thermoelectric material as a narrow bandgap in semiconductors $(E_q=10k_BT \text{ or } 0.25eV)$, high-mobility carriers ($\mu=2000cm^2/Vs$) and minimized thermal conductivity. As mentioned before ZT depends via the Seebeck coefficient and the electronic conductivity strongly on the doping level and the chemical composition and can therefore be enhanced by optimizing these two factors. In complex materials this optimization process can pose a large problem since there are several degrees of freedom possible. The best thermoelectric material therefore "would behave as a 'phonon-glass/electron-crystal' (PGEC); that is, it would have the electronic properties of a crystalline material and the thermal properties of an amorphous or glass-like material" [28]. Therefore the mean free paths of the phonons would be as short as possible, that is they are scattered a lot and since phonons are responsible for the thermal conduction, these atomic structures would conduct heat like glass, only for a very low amount. The mean free paths of the electrons on the other hand would be as long as possible, so there would be almost no scattering, as it is the case in a crystalline material, and we would have ideal conditions for electronic conductivity. So there are minimized thermal conductivity and maximized electronic conductivity, leading to a maximized figure of merit.

According to Slack, a maximum figure of merit ZT=4 may be achieved at room temperature if the lattice thermal conductivity of the used material is lowest with approximately 0.25W/(mK)and the carrier mobility is $1800cm^2/(Vs)$. This value has been observed for several materials, so the logical consequence was to search for improvements in the lattice thermal conductivity. Since a decrease in the lattice thermal conductivity makes the electronic thermal conductivity more important, there are only materials with a low enough electronic thermal conductivity taken into account; otherwise this contribution would let increase the total thermal conductivity. It has been figured out, that with materials where the lattice thermal conductivity amounts approximately 60-80% of the total thermal conductivity the highest figure of merit could be reached. The smallest possible value for the thermal conductivity is achieved if the mean free path and the phonon wavelength are of the same order.

The quintessence of the phonon-glass, electron-crystal theory is a weakly bound atom in the material, which is located in a larger atomic cage. It will undergo large vibrations which are not influenced by the surrounding atoms and it is therefore called a 'rattler' or Einstein oscillator. Rattlers interact randomly with the lattice phonons and by this result in intense phonon scattering. Depending on the concentration, mass fraction and frequency of these rattlers, the thermal conductivity can be decreased. [13]

2.3 Devices

The usual form in which thermoelectric devices are designed is a pair of thermoelectric materials, one p-type and one n-type. These two materials are connected at one end, which will be the positive voltage for one material and negative for the other, such that the voltage difference at the other end of the module is the sum of the two thermovoltages. The modules can be connected in series to increase the voltage. An alternative design is called an unileg module using only one type of thermoelectric material (either p-type or n-type). [29]



Figure 2.7: Making use of the Seebeck effect and the Peltier effect [28]

Thermoelectric devices are used either for cooling (Refrigeration mode) or generating a voltage from waste heat (Power generation mode). One possible way to do this is a closed loop with a n-type and a p-type thermoelectric material, where either a current is applied and via the Peltier effect converted to create a temperature gradient along the material or the Seebeck effect is used to transform thermal energy directly into electrical energy (see figure 2.7). Since this conversion of thermal to electric energy is a solid-state process, where no moving parts are involved, it has a longterm stability.

The efficiency of this process, η_{TE} , is given with an equation including the figure of merit and the temperatures of the hot and cold side.

$$\eta_{TE} = \eta_C \cdot \left(\frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_C}{T_H}}\right),\tag{16}$$

Here η_C is the Carnot efficiency, given by $(T_H-T_C)/T_H$ and T_C and T_H are cold and hot temperature respectively, so obviously also the temperature difference has to be as high as possible.



Figure 2.8: Conversion efficiency as function of temperature and Carnot efficiency [15]

The efficiency for different ZT values (see figure 2.8) does not only depend on the figure of merit, but on the values for the hot and cold temperature as well. For a given temperature range there is even a maximum figure of merit, resulting in the highest possible conversion efficiency. [1]

3 Oxide Materials

Cobalt-oxide-based layer-structured cystals including Na_xCoO₂, Ca₃Co₄O₉, and their derivative compounds have been developed as p-type materials having fairly high thermoelectric performance, and the maximum ZT value generated from this compound group has to date reached unity or larger. Additionally, modulated layer cobalt oxides have been found promising as p-type materials. In contrast, the n-type oxide materials so far proposed, such as ZnO:Al and Zn₅In₂O₈, only show rather low figures-of-merit (ZT < 1) and remain to be further improved, or otherwise novel oxide materials have to be explored. STO, and its derivative layered compounds, (SrO)(SrTiO₃)_m (m=integer), have recently been shown to exhibit promising high thermoelectric performance.



Figure 3.1: Progress in thermoelectric oxide materials [22]

Challenges to create novel oxide thermoelectrics have been motivated recently and extensive investigations from various viewpoints of materials design are being carried out. It is especially difficult to control an electronic system and a phonon system simultaneously in a single crystalline field. A complex crystal composed of more than two nanoblocks with different compositions and structural symmetries is considered to be effective to control electron transport and phonon transport separately and hence enhance the total conversion efficiency. Nanostructure control through nanoblock integration would be a promising route for developing novel oxide thermoelectrics. [30]

3.1 Layered Cobaltates

The layered cobaltates are a family of materials consisting of metallic cobalt oxide planes with insulating planes in between. Most materials have the crystal structure ACoO₂, where A can be an element such as Na, Ca, La or even a combination of more than one element such as Bi and Sr. Originally these layered cobaltates were investigated as candidate high T_C superconductors. Surprisingly, it was discovered that Na_xCoO₂ single crystals exhibited a large Seebeck coefficient (100 μ V/K, 300 K) while maintaining a low resistivity, (200 μ Ωcm; 300K) [17]. Add to this a lower than expected thermal conductivity [18] and it is clear that these discoveries sparked interest in the thermoelectric properties of the layered cobaltates. The structure of Ca₃Co₄O₉ is shown in figure 3.2. The origin of the high Seebeck coefficient and the low conductivity will be explained in more detail in subsection 2.

The promising thermoelectric properties of cobaltates have lead to the discovery of several high-ZT materials, most notably $Bi_2Sr_2Co_2O_y$ (zT = 1.1 at 973 K) [19] and Na_xCoO_2 (zT = 1.5 at 800 K) [20]. As no scarce or toxic elements are used in these materials they can provide a viable route towards the use of thermoelectric power generation for the recovery of waste heat.

$3.2 \quad Ca_3Co_4O_9$

Among the p-type oxide thermoelectrics, $Na_x CoO_2$ and $Ca_3Co_4O_9$ are some of the most promising materials. According to literature they both offer high room temperature (RT) thermopower, but also a low resistivity of only several m Ω cm, resulting in a power factor of ~ $50\mu WK^{-2}cm^{-1}$ and $13\mu WK^{-2}cm^{-1}$, respectively. But when working with these oxide materials, there occurs a problem with the Na_xCoO_2 , due to the volatility of the sodium in air. So without some capping layer on top of the material the chemical structure would change with time and the thermoelectric performance would degrade. This is why in this research there has been chosen to investigate the properties of $Ca_3Co_4O_9$, which is stable in air environment.

Ca₃Co₄O₉ is a layered material, consisting of a Ca₂CoO₃ distorted triple rocksalt-like layer (RS), which is sandwiched between two hexagonal CoO₂ cadmium iodide-like layers, building a misfit structure, since the lattice parameters of the two subsystems do not agree along all axes (see figure 3.2). The common lattice values are given with a=4.8339Å, c=10.8436Å and β =98.14°, but along the *b*-axis, we have b₁=2.8238Å for the CoO₂ sublattice and b₂=4.5582Å for the Ca₂CoO₃ sublattice. The thermoelectric properties of bulk Ca₃Co₄O₉ at room temperature are ρ =12mΩcm and S=125 μ V/K.

 $Ca_3Co_4O_9$ is a semiconductor with a bandgap of 0.018eV as can be seen in figure 3.3. [31]

The CoO₂ subsystem is responsible for the electrical conductivity and the high thermoelectric transport, while the rocksalt subsystem is acting as a charge reservoir. The structure of the CoO₂ layer remains nearly unchanged while the thermoelectric power of the different layered cobaltate compounds increases as the thickness of the insulating rocksalt layer increases from 100μ V/K at 300K in L₂ to 140μ V/K at 300K in Pb and Ca doped (Bi₂Sr₂O₄)_x CoO₂. Therefore the insulating rocksalt layer must play a crucial role in the high thermoelectric power of these misfit-layered compounds. Among the different layered cobaltate systems, the Ca₃Co₄O₉ stands out as the only system containing one cation with nominally different oxidation states, namely Co²⁺ in the rocksalt buffer layers (Ca₂CoO₃) and Co⁴⁺ in the octahedral CoO₂ layers,



Figure 3.2: Crystal Structure of $Ca_3Co_4O_9$ [8, 22]

which makes it an ideal system for studying effects such as charge transfer, orbital ordering, and spin-state transitions on the material's thermoelectric behavior. [10] There is significant hole transfer from the rocksalt CoO to the hexagonal CoO_2 layers. This hole transfer increases the mobile hole concentration and breaks the electron-hole symmetry in the CoO_2 layers, thereby enabling the high thermoelectric power in the strongly correlated CoO_2 subsystem. The CoO_2 subsystem is subject to compressive strain in the a-axis direction, and several studies have shown that increasing the compressive strain will further increase the thermoelectric power. In the CoO_2 layers there is a higher concentration of mobile holes, which could explain the p-type thermoelectric behavior of the CoO_2 layers. The CoO layer in the rocksalt Ca_2CoO_3 layer is positively charged, while the hexagonal CoO_2 layer is negatively charged. By preserving the overall charge neutrality of both layers, holes are now transferred from the CoO to the CoO_2 layer, resulting in the high concentration of mobile holes measured in the CoO_2 layer. Such a hole transfer is essential for the thermoelectric effect since it not only provides the necessary mobile charge carriers, but the existence of a half-filled band (or the existence of particle-hole symmetry) will result in a zero thermoelectric power (Seebeck coefficient). The hole transfer will thus remove the orbital degeneracy, thereby explaining the nonzero thermopower in $Ca_3Co_4O_9$. [11] Two different kinds of Co sites that exist in $Ca_3Co_4O_9$ play completely different roles in its thermoelectric behavior, namely to provide charge carriers to the CoO_2 layer and to conduct holes along the CoO_2 layer. The hole transfer from the rocksalt subsystem to the CoO_2 layer and the increase in the mobile hole-state concentration in the CoO_2 layer, suggest that the hole doping of the CoO_2 layers results in an increased density of mobile hole states, which is essential in breaking the particle-hole symmetry of the half-filled Co-band thereby allowing a nonzero



Figure 3.3: Calculated band structures of $Ca_3Co_4O_9$ [31]

thermoelectric power. From this it can be concluded that the transport properties of the CoO_2 layers are governed by itinerant holes. So the hole transfer in $Ca_3Co_4O_9$ plays a crucial role in understanding the atomic-scale mechanisms that govern the high thermoelectric properties in these misfit layered materials. [15]

3.3 Thin films

The atomic structure of $Ca_3Co_4O_9$ thin films is significantly different compared to polycrystalline samples, which has a considerable effect on the thermoelectric properties. A combination of the lattice and symmetry mismatch with the substrate, combined with non-equilibrium growth kinetics, determines the $Ca_3Co_4O_9$ thin film structure. The hexagonal CoO_2 layers of $Ca_3Co_4O_9$ are particularly difficult to stabilize at the initial growth stage on cubic substrates, and as a result a buffer layer of cubic Ca_2CoO_3 can be observed near the substrate [5]. Further, a large number of CoO_2 stacking faults is observed near this buffer layer, which is attributed to the weak interlayer attraction between the layers. The formation of the CoO_2 stacking faults has significant impact on the Seebeck coefficient, acting as phonon scattering sites, and a moderate enhancement in the Seebeck coefficients values on thinner, more disordered films can observed. There seem to be several ways to further increase the thermoelectric properties of $Ca_3Co_4O_9$; while the substrate induced strain does not directly affect the Seebeck coefficient or lattice parameters of $Ca_3Co_4O_9$, the creation of CoO_2 stacking does. Therefore, controlled synthesis of CoO_2 stacking faults within $Ca_3Co_4O_9$ thin films appears to be one method of increasing the Seebeck coefficient without negatively affecting the electrical conductivity. [7]

In contrast to the general bulk material of $Ca_3Co_4O_9$, thin films can be tuned by strain, growing the film on different structured substrates and variation of the growth conditions (temperature, rate, air environment, growth process)

4 Sample fabrication and characterization

In the following paragraph all techniques that have been used for fabrication and analysis of the here presented samples are described. It is divided in two main parts, the fabrication and the characterization, which is again subdivided into structural and electrical properties. All samples have been grown by pulsed laser deposition. The surfaces have been analyzed by atomic force microscopy and their crystal structure by X-ray diffraction. The thin film structure has been investigated by scanning electron microscopy. Afterwards the electronic properties of the samples have been investigated, this means we measured the resistivity and Seebeck coefficient at room temperature as well as at increasing temperature.

4.1 Pulsed laser deposition

The most applicable growth technique for oxide thin films is pulsed laser deposition (PLD). A high energetic laser pulse ablates material from a target to grow on a single crystal substrate. The energy density of the laser can be tuned using a lens outside the system, and the growth of the material can be tuned by changing the temperature of the substrate or the pressure/gas composition in the system. A mask placed into the laser beam outside the system helps to keep the spot on the target homogeneous. The ablated material forms a plasma plume in front of the target and moves towards the substrate due to a pressure gradient. Reaching the surface of the substrate there is some thermally-activated diffusion between substrate and plasma material, resulting in a thin film of ablated material forming on the substrate.

The substrate on which the thin film is to be grown is fixed on a heater block, via which the deposition temperature is controlled. In the system with a given distance this setup is placed just in front of the target, since there the plasma plume will be the most homogeneous when reaching the substrate. The target is mounted in a target stage which can hold up to 5 different targets and by rotating it films of different components can be grown within one deposition process. When coming into the system the laser beam hits the chosen target under an angle of 45° (see complete setup in figure 4.1). To not only use the target at single points during a deposition process, it is scanned 7mm along the horizontal direction, keeping the targets surface more homogeneous and making it also easier to re-prepare the target for new depositions. Previously to the actual deposition process, there is some material ablated from the target to avoid getting impurities in the film.

Besides the above mentioned parameters laser fluence and laser spot size are important parameters to tune the deposition process. In combination with the good values the supersaturation during the deposition pulse as well as subsequently relaxation and kinetic properties of the plasma reaching the substrate can be regulated.

The here presented thin films have been grown with a KrF excimer laser (Lambda Physik



Figure 4.1: Schematic overview of a typical pulsed laser deposition setup [32]

LPX 210) with a wavelength of 248nm and a pulse width of ~25ns. The laser repetition rate as well as the pulse energy are adjustable in a given range of 1 to 100Hz and 0 to 1J, respectively. The laser beam is focused onto the target using a lens with a focal length of about 453mm. The previously mentioned changing of the pressure inside the system in the range of $1 \cdot 10^{-6}$ mbar to $3 \cdot 10^{-1}$ mbar is possible due to two valves and a mass flow (0-40ml/min). For this thesis only oxygen gas was used in the background pressure. The deposition temperature can be chosen in a range up to 900 °C, measured with a K-type thermocouple. The actual deposition conditions are summed up in table 1.

After the deposition the so grown sample was cooled down to room temperature at a rate of $10 \,^{\circ}\text{C/min}$ in atmospheric oxygen environment (P_{O2}=1bar).

Because of the pulsed nature of the pulsed laser deposition process, adsorption and diffusion of the arriving species can occur at two different time scales. During one single pulse, $\sim 3 \cdot 10^{13}$ ion species arrive at the substrate. The typical overall growth rate is 0.2 nm/s which is comparable to other deposition techniques, such as molecular-beam epitaxy. However, the material is only deposited during the short plasma pulse durations (which are typically $500 \mu \text{s}$), leading to much higher species density during the actual deposition. The high density causes a high nucleation density. Because the mean diffusion time exceeds the plasma pulse duration, adatoms diffuse across the surface and find their optimal positions in between the plasma pulses. The high nucleation density and the possibility for diffusion during growth favor layer-by-layer growth. The interplay of the supersaturation and subsequent relaxation determines the growth properties and can be tuned by adjusting the growth parameters.

Material	Al_2O_3	LSAT
Laser Fluence $[J/cm^2]$	4	4
Pulse Energy [mJ]	48	48
Laser Repetition Rate [Hz]	1	1
Mask Position [mm]	803	803
Mask Size [mm ²]	55.9	55.9
Spot Size $[mm^2]$	1.08	1.08
Lens Position [mm]	531	531
Target-Substrate Distance [mm]	506	506
Process Pressure [mbar]	$P_{O_2} = 0.01$	$P_{O_2} = 0.01$
Temperature [°C]	430,600,650,700,750,800,850	430, 650, 750, 850
Film Thickness [nm]	10, 30, 60, 90, 120	10, 30, 60, 90, 120

Table 1: Deposition parameters for Ca₃Co₄O₉

4.2 Sputtering gold contacts

For better electrical contact to the $Ca_3Co_4O_9$ thin film metal contacts are sputtered on the corners of the sample before resistance and Seebeck coefficient measurements. During sputtering Argon ions are accelerated to the metal target and when hitting its surface, atoms from the target are removed which then land on the sample forming a metal layer. The Argon ions are accelerated due to a bias applied to the target. Since the vacuum chamber is kept at constant Argon pressure of 10^{-2} mbar on their way to the target the Argon ions ionize even more argon atoms resulting in a constant stream onto the target, so also a constant stream of metal atoms to the sample.

For our purpose we only need gold contacts at the corners of the sample, so before loading the sample into the chamber a mask is mounted onto the sample with kapton tape covering the surface except for the corners. To make a good contact between the gold contact and the $Ca_3Co_4O_9$ thin film, first there is a (10nm) thin layer of titanium sputtered on the film. On top of that a 100nm thick gold layer is then deposited onto the corners of the sample (see figure 4.2).



Figure 4.2: Gold contacts on the sample after sputtering

4.3 Structural characterization

The as prepared samples were analyzed regarding their surface properties, crystal structure and epitaxial structure by atomic force microscopy, X-ray diffraction and scanning electron microscopy respectively. In the following chapter the general working principles and and ways of analysis will be explained.

4.3.1 Atomic force microscopy

The first analysis of the samples is done by atomic force microscopy (AFM), a technique to investigate the surface characteristics of a sample. A sharp tip follows the topography of the sample and by this images the structure of the surface. The setups that have been used for all measurements in this research are a Veeco Dimension Icon AFM and a Veeco Multimode SPM. In all measurements tapping mode (TM) has been used and they all have been performed at room temperature and ex-situ. In this mode the tip is brought close to the surface (10-100Å) and until it feels a repelling force from the sample. At this position the tip oscillates above the sample with a frequency between 100 to 400kHz. Since the force at the tip has to stay constant, the tip moves up and down above the sample according to changes in the topography, thereby changing the vibrational amplitude. From these variations the surface of the sample can be imaged (see figure 4.3) and the roughness of the surface can be measured.



Figure 4.3: With a constant force between tip and surface the tip traces exactly the surface topography following trajectory B

In figure 4.4 typical surface structures of Al_2O_3 and LSAT can be seen. The Al_2O_3 substrate was annealed for 1 hour at a temperature of $1050 \,^{\circ}$ C, the LSAT substrate for 10 hours at that same temperature. Terraces on both substrates are clearly visible, although on LSAT they are less defined than on Al_2O_3 . For Al_2O_3 they are about 0.25nm high and about 50nm large, while for LSAT they are only 0.1nm high but 500nm large. By this we get a first indication about the miscut angle and the crystal direction of the sample, and thin film growth can be started. When the thin film is deposited the surface of the sample is scanned again and the surfaces of the substrate and the thin film can be compared.



(a) Al₂O₃ substrate $(1 \times 1 \mu m^2)$

(b) LSAT substrate $(2 \times 2 \mu m^2)$

Figure 4.4: Substrates after annealing

4.3.2 X-ray diffraction

The crystal structure of the samples has been analyzed by X-ray diffraction (XRD). The incoming X-ray beam is adjusted on the center of the thin film and then the X-ray source as well as the detector can be rotated around the sample (see also figure 4.5). With this setup not only crystallographic measurements can be done but also optical measurements, e.g. to determine the thickness of the thin film.



Figure 4.5: Schematic overview of a typical X-ray diffraction setup [33]

The mostly done measurement with XRD is the $2\theta/\omega$ scan. In this scan the 2θ angle is scanned and the ω angle is adjusted to exactly half of the scanning angle, so $\omega=\theta$. For optical

measurements the detector is only rotated at low angles to make use of the reflectivity of the sample. The beam is aligned on the optical surface of the sample $(2\theta=0.4^{\circ}, \omega=0.2^{\circ})$ and then the actual scan is performed between $2\theta = 0$ to 8°. For a typical scan result see figure 4.6.



Figure 4.6: Reflectivity measurement of $Ca_3Co_4O_9$ thin film sample to determine the film thickness

The fringes appear due to the different refractive indices of the thin film and the substrate, which is also visible because the film is that thin. When analyzing the angles at which we see the fringes the film thickness can be determined.

The second scanning type is the $2\theta/\omega$ measurement at larger angles (10 to 110°), after alignment of the beam on a substrate peak, since these are much more intense than the film peaks due to the much larger thickness. From this scan we get information about the crystal structure of the sample. This can be easily explained with the help of Bragg's law, the basic working principle of XRD:

$$n\lambda = 2d\sin\theta \tag{17}$$

Here λ is the wavelength of the X-rays, d is the spacing between the crystal planes and θ the angle between the sample and the incoming X-ray beam. Thus, according to Bragg's law we see peaks in the $2\theta/\omega$ scan whenever the wavelength matches twice the distance between two crystallographic planes. Due to the periodicity of the crystal structure of the thin film and the substrate, these peaks should be equidistant for the thin film and the substrate respectively. A typical scan of the Ca₃Co₄O₉ thin film is shown in figure 4.7.

The first visible film peak in this spectrum is the (002) peak of the thin film at $2\theta \approx 16^{\circ}$. Since this scanning technique is an out-of-plane measurement, using Bragg's law we get an indication of the out-of-plane lattice parameter of the grown film (d ≈ 11 Å), which is in consistence with the data from literature (10.8Å).

Another possible scan of the sample is an in-plane map scan, meaning a ϕ -scan with a complete rotation of ω at each ϕ -value. to do this scan the X-ray beam has to be aligned on a plane with additional in-plane component, for this thesis for the map scan of the substrate



Figure 4.7: Typical $2\theta/\omega$ measurement of Ca₃Co₄O₉ thin film sample on Al₂O₃

the (104) plane has been used and for the film the (112) plane. The measured peaks are an indication for the direction of the in-plane crystal axis.

All XRD measurements presented in this thesis have been done on a Bruker D8 and a Panalytical diffractometer with a K α -1 radiation source and a wavelength of 1.54Å.

4.3.3 Scanning electron microscopy

To analyze the growth structure of thin films scanning electron microscopy (SEM) has been done on a Zeiss-1550 HRSEM, operating between 0.3 and 20kV. This energy high tension has to be chosen high enough to provide a good image, but at the same time low enough to prevent charging of the sample.



Figure 4.8: Optics of a general SEM

The structure of the surface of the sample gets visible by an interaction of the electrons in

the sample with an high-energy electron beam of about 10Å in diameter (in figure 4.8 shown in blue), which is scanning the surface. The incoming electrons transfer energy inelastically to the electrons at the sample's surface, and by this these so-called secondary electrons get emitted from the sample onto a detector. At the same time elastically backscattered electrons are also detected and can be used for electron back-scatter diffraction (EBSD). For the purpose SEM has been used in this thesis, EBSD has not been used, since the optical resolution of this technique is too low to observe the expected characteristics. The working distance of the detector is between 4 to 10mm.

The different aspects to be investigated by SEM are the sample uniformity, thickness uniformity, columnar structure and possible grain boundaries.

The presented SEM pictures have been taken at a current of 70pA, an electron high tension of 1.40kV and a working distance of about 3-4mm.

4.4 Electronic properties analysis

The samples, which have been analyzed as described above were then tested for their thermoelectric behavior. This has been done at room temperature as well as increasing temperature for some selected samples. The different setups for these measurements are described in the following sections.

4.4.1 Resistivity at room temperature

The electrical resistivity of the samples is measured with the van der Pauw method, which allows to determine the resistivity of an arbitrarily shaped sample. Measuring the resistance in both horizontal and vertical direction across the sample (see figure 4.9 we get $R_A = V_{43}/I_{12}$ and $R_B = V_{14}/I_{23}$.



Figure 4.9: Resistance measurement at room temperature

From this the van der Pauw equation can be solved to determine the sheet resistance of the sample (\mathbf{R}_S) :

$$e^{-\pi \frac{R_A}{R_S}} + e^{-\pi \frac{R_B}{R_S}} = 1 \tag{18}$$

The resistivity of a flat sample can be easily calculated through: $\rho = R_S d$, with d the thickness of the thin film.

4.4.2 Seebeck coefficient at room temperature

To measure the Seebeck coefficient of the $Ca_3Co_4O_9$ samples, a setup with two thermocouples is used. One of the thermocouples is heated, while the other one stays cold, so that a temperature gradient across the sample arises, which results in an induced voltage (see figure 4.10). A reference for this voltage is made with a junction kept at 0 °C, to be able to determine the actual temperature difference between the two thermocouples out of the voltage difference between V₁ and V₂ (see figure 4.11). Since the alumel lead which is used to measure the induced voltage also gives a contribution to the Seebeck coefficient, this value (+18.5 μ V/K) always has to be subtracted from the determined Seebeck coefficient.



Figure 4.10: Setup for measuring the Seebeck coefficient at room temperature



Figure 4.11: Wire setup for Seebeck measurements



Figure 4.12: Measured Seebeck data with linear fit

The equipment that is used in this setup are three HP34401a digital multimeters to measure the three voltages (V₁, V₂ and V_{Seebeck}), two peltier elements for temperature control and a Keithley 2400 sourcemeter to power them. With a LabView program the peltier elements are brought to several temperature differences (one is heated, the other one cooled) and at 6 different temperature differences the induced voltage is measured. With this setup both measurements, temperature and induced voltage are done at exactly the same point, so we really do know the circumstances of our measurements. Since both measurements are done at exactly the same moment we don't need to wait for some stabilization time that the system is in thermal equilibrium. The error margin for all measurements is 5% of the measured value. This has been determined by doing a measurement of the Seebeck coefficient of a Bi₂Te₃ sample, which is known in literature [34]. By comparing these values the measured data differed from the literature value by ~5%.

4.4.3 Resistivity and Seebeck coefficient at high temperatures

To measure the thermoelectric properties of the sample at high temperatures, it is positioned between two electrodes. One of them is connected to a heater, and the whole setup is surrounded by another furnace. This furnace heats the sample to the desired temperature and when that is reached the heater in the electrode creates a previously determined temperature gradient on the sample. At the front there are two thermocouples on the sample's surface which then measure the two temperatures at the hot and cold side of the sample respectively (see 4.13). At the same time the resistivity is measured with a four-point measurement. A constant current (here 0.1mA has been used) is applied at both ends of the sample and measuring the resulting change in voltage between the two thermocouples we can determine the electrical resistance. The calculation of the resistivity is done within the program. Unfortunately the program can only take a sample thickness of several mm, so the final result has to be corrected for nm.



(a) Schematic overview of the setup for the high temperature measurements



(b) Mounted sample with thermocouples

Figure 4.13: Setup for high temperature Seebeck coefficient and resistivity measurements [35]

The temperature variation has been done between 50 and 600 °C with steps of 25 °C in an environment of 0.1bar O_2 and 1bar He. The used temperature gradient was 50 °C, the applied current 0.1mA and per temperature step there were five measurements done.

5 Results and Discussion

5.1 Working plan

As earlier mentioned there have been grown thin films of $Ca_3O_4O_9$ on a substrate by pulsed laser deposition. To improve the electronic performance of the thin films the deposition conditions have been changed. In the following section the influence of the deposition temperature on the structure of the thin film and the electronic properties is presented.

Since not only the deposition conditions but also the fitting of the film on the substrate may influence the final electronic performance the films have been deposited on two substrates with different crystal structures, Al_2O_3 (sapphire) (0001) and LSAT (001). While Al_2O_3 has a hexagonal structure with the lattice parameters a=4.785Å and c=12.991Å, the LSAT crystal is shaped cubic with a lattice parameter a=3.868Å. Both materials are electrical insulating, so that there is no net contribution to the Seebeck coefficient or resistivity when measuring at the surface of the thin film. A possible disadvantage of the use of an Al_2O_3 substrate may be its high thermal conductivity.

When looking at the above mentioned crystal structure of $Ca_3Co_4O_9$ (see section 3.2) in the first instance one could expect that with its hexagonal crystal structure of the CoO_2 layer it will fit well on the as well hexagonally shaped crystal structure of Al_2O_3 , with lattice parameters close to each other. So it is interesting how the performance will change when the $Ca_3Co_4O_9$ thin film is deposited on LSAT with a not fitting cubic crystal structure.

The differences of the surfaces of the two substrates have been shown in section 4.3.1 (see figure 4.4).

For all room temperature measurements $5 \times 5 \text{mm}^2$ substrates have been used, but for high temperature measurements there have been grown additional samples on $10 \times 5 \text{mm}^2$ substrates.

5.2 Variation in deposition temperature

Several 60nm-samples have been grown on Al_2O_3 substrates at different temperatures between 430 °C and 850 °C. This range has been chosen because of previously measured data of samples where the deposition conditions as pressure, laser fluence and pulse rate had been improved to the best possible results. For the most interesting temperatures the films have also been deposited on LSAT substrates.

5.2.1 Structural characterization

After the deposition the terraces on both substrate materials (see figure 4.4) are not visible anymore, but there are grains on the surface of the sample (see figure 5.1), whose sizes vary for the different deposition temperatures. The roughness of the surface of the complete sample is increased compared to the substrate and varies over the whole deposition temperature range between 1 to 15nm for the films grown on Al_2O_3 and between 5 to 20nm for those grown on LSAT. The grains look completely different for the films on the two different substrates as expected



(a) $Ca_3Co_4O_9$ thin film on Al_2O_3 substrate (b) $Ca_3Co_4O_9$ thin film on LSAT substrate

Figure 5.1: Sample surface after deposition $[3 \times 3\mu m^2]$

according to the fitting of Ca₃Co₄O₉ crystal structure on the substrates crystal structure.

The surface of the thin film grown on LSAT looks completely different than the one of the film grown on Al_2O_3 . The grains are more elongated and smaller and by this the surface of films grown on LSAT is rougher than on Al_2O_3 .

For all samples the XRD $2\theta/\omega$ scan has been done over a 2θ -range of 10 to 110°. The scan shows only peaks belonging to the deposited material and the substrate, so it can be concluded that the grown Ca₃CO₄O₉ films are of good crystal quality. There are no peaks belonging to secondary phases which may have occurred during growth or other unexpected peaks not fitting to the crystal structure of the grown material. The even peaks are much more sharp than the uneven which are only visible for temperatures ≥ 750 °C. Since due to the crystal lattice the (002) peak of the film is the highest in intensity for all grown samples on Al₂O₃ there is zoomed in on this peak to analyze the structure of the samples grown at different temperatures.

The (002) peaks of the samples grown at $650 \,^{\circ}\text{C}$ and $700 \,^{\circ}\text{C}$ are shifted to the left, indicating a larger crystal lattice and a slightly different composition of the thin film. There could be a lower amount of oxygen in the film, or the ratio of the Ca and the Co in the film is different. For the film grown at $430 \,^{\circ}\text{C}$ there is no peak at all visible, increasing the deposition temperature also the film peaks increase, but for temperatures larger than $750 \,^{\circ}\text{C}$ the intensity decreases again. The film peaks of the films grown on LSAT are much lower than the above shown peaks of the



Figure 5.2: 2θ diffraction peaks on Al₂O₃ for different deposition temperatures



Figure 5.3: 2θ diffraction peaks on Al₂O₃ for different temperatures zoom in at Ca₃Co₄O₉ (002)

films on Al_2O_3 , so here only the zoom-in on the highest film-peak is shown. The lower intensity is due to the fact, that the hexagonal crystal structure of the film fits much less on the cubic



Figure 5.4: 2θ diffraction peaks on LSAT for different temperatures zoom in at Ca₃Co₄O₉ (002)

lattice of LSAT than on the as well hexagonal Al_2O_3 .

5.2.2 Investigation of electronic properties

The Seebeck coefficients and resistivity values of the different samples on Al₂O₃ and LSAT are shown in figure 5.5. Beginning with the curve of the thin film on Al₂O₃ substrate it can be seen, that there is no clear trend for increasing or decreasing temperature. At a deposition temperature of 650 °C the Seebeck coefficient reaches its minimum value of 5.5μ V/K and the resistivity its maximum value of 402.1mΩcm. Going just 100 °C higher in deposition temperature we reach the maximum in Seebeck coefficient and the minimum in resistivity for the same film thickness of 60nm (92.5 μ V/K and 5.0mΩcm respectively). Increasing the temperature to 800 °C the Seebeck coefficient decreases and going even higher to 850 °C it increases again (65.2 μ V/K at 800 °C and 77.5 μ V/K at 850 °C). The resistivity behaves in analogy to that, i.e. after the minimum value at 750 °C it increases for 800 °C and decreases again for 850 °C. The most interesting part lies at the left side of the graph, not only at high deposition temperatures a high Seebeck coefficient and a low resistivity can be reached, but also at 430 °C both values are in the same region as compared to 850 °C. This might be an indication that not only the crystallinity determines the thermoelectric behavior, since the XRD showed no peak.

Since there are four interesting points in the curve of the thin film grown on Al₂O₃ (430, 650, 750 and 850 °C) for these values there have also been done samples on LSAT substrates. When comparing the values of these values it is obvious that resistivity as well as Seebeck coefficient are for all samples higher compared to Al₂O₃. But the trend of the measured data is the same



Figure 5.5: Seebeck coefficient and resistivity for different deposition temperatures on Al_2O_3 and LSAT

for both substrate materials, The best values are achieved with the samples grown at 750 °C (92.5μ V/K and $5m\Omega$ cm for Al₂O₃ and 134.3μ V/K and $21.4m\Omega$ cm for LSAT) and the worst with those grown at 650 °C (5.5μ V/K and 402.1m\Omegacm for Al₂O₃ and 42.24μ V/K and $457.4m\Omega$ cm for LSAT). But at the minimum and the maximum growth temperature of 430 and 850 °C there are again reached acceptable values for resistivity as well as Seebeck coefficient on Al₂O₃ and LSAT.

For both the extrema, so the samples of $750 \,^{\circ}\text{C}$ and $650 \,^{\circ}\text{C}$ there have been done comparison samples at exactly the same conditions and they all delivered the same results, confirming the first obtained data was no error in measurement or that something had gone wrong during the deposition.

5.2.3 Discussion

When comparing the above presented results for different samples on Al_2O_3 substrates, with as prepared samples on LSAT substrates, we get very similar shaped curves. But the overall Seebeck coefficient as well as the overall resistivity are higher for all samples on LSAT compared to these on Al_2O_3 . It is remarkable that all samples that showed a shift to the right in the XRD data have a worse electronic performance compared to those without a shift. While the sample grown at 430 °C does not even show a film peak, it still shows a very good electronic behavior. All film peaks of samples grown on Al_2O_3 have a higher intensity than of those grown on LSAT.

For the maximum Seebeck coefficient of the LSAT sample at 750 °C, as well as of the Al_2O_3 sample at 750 °C and the minimum Seebeck coefficient of the one on Al_2O_3 at 650 °C, there have been done a comparison sample at exactly the same conditions, which gave comparable results, indicating the correctness of the data.

While Zhou et al [18] reported an increasing Seebeck coefficient with increasing grain size and a decreasing resistivity, this has only been found for the variation in substrate material, but not for the deposition temperature variation. For well-performing thermoelectric materials a high Seebeck coefficient going along with a low resistivity, as has been found here, is just what is needed. Although the Seebeck value of LSAT samples was much higher than that of Al_2O_3 samples, taking the even higher resistivity in account the Power factor for the Al_2O_3 samples was still larger.

5.3 Variation of film thickness

After the different measurements for varying deposition temperatures it yielded that at 750 °C the best results can be reached. At this temperature there has been done a thickness variation between 10 to 120nm. Since in literature there is a buffer layer mentioned, which grows on the substrate for several nm before the actual material thin film is grown and which may impede the moving electrons for very thin films, resulting in a very high resistivity and low Seebeck coefficient, there have been done additional measurements for the structural characterization. The 90nm thick film has not only been analyzed by AFM and $2\theta/\omega$ measurement with XRD, but also with a ϕ/ω map scan and some SEM characterization.

5.3.1 Structural characterization

AFM characterization (not shown here) indicates a clear trend in the roughness variation for different film thicknesses. While the actual RMS value increases only slightly from 1 to 23nm for all films grown on Al_2O_3 , this happens parallel to the increase in film thickness, so for the thinnest film with 10nm there is the lowest roughness of 0.8nm and the thickest film of 120nm has a RMS value of 23.2nm. Just as with the deposition temperature variation the roughness of films grown on LSAT is higher than of those grown on Al_2O_3 . Here the RMS covers a range of 3.7nm to 30.1nm.



Figure 5.6: 2θ diffraction peaks for different film thicknesses zoom in at Ca₃Co₄O₉ (002)

In the XRD data the highest film peak is again the (002) peak of $Ca_3Co_4O_9$, so in turn there is zoomed in on that to analyze the different samples. The curve of the sample with 90nm film thickness is clearly shifted to the left, just as seen in the previous paragraph with the curves of the samples grown at 650 and 700 °C. In this data series the film of 10nm thickness shows no peak at all. With increasing thickness also the peak intensity increases, but just as with the temperature limit of 750 °C, here the peak intensity decreases again for films thicker than 60nm.

Also we see higher peaks, meaning more intensity, for the films on the Al_2O_3 substrates as compared to those on the LSAT substrates.



Figure 5.7: ϕ/ω map scan of Ca₃Co₄O₉ thin film and Al₂O₃ substrate

To check the in-plane crystal properties of the thin film, there has been done a map scan of the 90nm-sample on Al₂O₂. In the map scan it is clearly visible, that the film is grown epitaxially since we see twelve peaks (twice the six-fold symmetry of Ca₃Co₄O₉) with equal distances (30°) and intensities. From the hexagonal crystal structure of Ca₃Co₄O₉ a six-fold symmetry is expected, but since there are two different ways of fitting on the substrate for the film, both with a relative angle of 15°, due to this we see twelve peaks, each with a distance of 30°.

Also they fit just in the middle of the peaks of the Al_2O_3 substrate (each 120° apart) as can be seen in figure 5.7. The scan on the substrate has been done in the (104) direction and on the film in the (112) direction, since there were the best visible peaks.

For the sample with the Ca₃Co₄O₉ film on LSAT substrate the map scan has not been done, because the peaks in the $2\theta/\omega$ scan were already much lower and so would not have been visible in the ϕ scan, since the film peaks on the Al₂O₃ substrate are already very low compared to the substrate peaks.

The SEM measurement shows clear layers of the 90nm thick film on the Al_2O_3 substrate (see figure 5.8). But there are also parts visible where the growth direction is rotated by 90°. The expected buffer layer is hardly visible, since it is very thin (of about several nm). On LSAT

on the other hand, there is a clear buffer layer, since this one is much thicker than the one on Al_2O_3 , as already had been expected from the literature. This much thicker buffer layer may be an indication for a much higher resistivity of the samples grown on LSAT.



(a) Ca₃Co₄O₉ thin film on Al₂O₃ substrate (corner above shows zoom-in)



⁽b) $Ca_3Co_4O_9$ thin film on LSAT substrate



Since the grains in the samples on Al_2O_3 are much larger than in those on LSAT, again a larger resistivity can be expected for LSAT. The surface of the sample is very well visible as well and confirms the larger roughness of samples grown on LSAT compared to those on Al_2O_3 .

5.3.2 Investigation of electronic properties

Just as in temperature variation the curves for both substrates behave the same, and again, in all cases the values of the LSAT samples are higher than those of Al_2O_3 , resistivity, as well as Seebeck coefficient. In figure 5.9 we can see, that for different film thicknesses between 10 and 120nm, there is a clear decreasing trend for the resistivity. For the thicker films (60 to 120nm) the resistivity is in the same range for all the three sample per substrate material. On Al_2O_3 the resistivity reaches its best value with the 60nm thick film (~5m\Omegacm), while on LSAT the best value is achieved with the sample with the 90nm thick film (~9m\Omegacm). Then it increases again up to 13m\Omegacm for the 120nm thick film on Al_2O_3 and 20mΩcm on LSAT. When making the film 30nm thick there is an abrupt increase in resistivity up to 51mΩcm and 88mΩcm for both substrate materials respectively. For the 10nm thin film the resistivity reaches on both



Figure 5.9: Seebeck coefficient and resistivity for different film thicknesses on Al_2O_3 and LSAT

substrate materials such a high resistivity that is was not possible to make good contact for the Seebeck coefficient measurement (~1.2 Ω cm for the Al₂O₃ substrate and ~7 Ω cm for LSAT). While the resistivity of the 30nm thick films was still somewhat higher than for the thicker films, the Seebeck coefficient is for all samples that could be measured in the same range per substrate material. But on both substrates there is a clear dip for the 90nm thick film. On the Al₂O₃ substrate the Seebeck coefficient lies in the range between 92.5 μ V/K with the 60nm thick film and 102 μ V/K with the 30nm thick film, but the 90nm thick film only reaches a Seebeck coefficient of 78 μ V/K. With the LSAT substrate this dip at 90nm is even better visible. Here the Seebeck coefficients of the 30, 60 and 120nm thick films lie all in the range of 134.3 μ V/K for 60nm and 141.55 μ V/K for 120nm, but at 90nm it only reaches 120.8 μ V/K.

5.3.3 Discussion

Again the maximum value for the Seebeck coefficient (here $134.3\mu V/K$) is reached with the sample grown at 750 °C, which even increases for thicknesses of 30 as well as 120nm compared to that of 60nm. The dip in the curve for different film thicknesses at 90nm is visible on Al₂O₃ as well as on LSAT. Further for both substrate materials the resistivity increases to more than 1Ω cm.

For thin films of 10nm thickness, the resistivity is too high, to measure the Seebeck coefficient with the available equipment. This is expected to be due to the buffer layer, which consists of insulating $Ca_x CoO_2$ according to literature [5].

5.4 Investigation of electronic properties at high temperatures

High-temperature thermoelectric measurements for samples grown on Al_2O_3 at 430 °C, 750 °C and 850 °C have been done and they revealed that also in a broad temperature range the thermoelectric attributes of the 750 °C sample give the best results. For comparison the sample on LSAT has also been measured.



Figure 5.10: Change in Seebeck coefficient and resistivity with increasing temperature

As can be seen in figure 5.10 when increasing the temperature the resistivity of the sample decreases, while the Seebeck coefficient increases. When going back in temperature though, one would expect the numbers to go back to their initial value, but while the Seebeck coefficient does so, the resistivity values always end higher than they started. Only for the first measurements up to $150 \,^{\circ}$ C, also the resistivity was stable. Up to $450 \,^{\circ}$ C environment temperature graph shows increasing resistivity curves per measurement series. At that point when cooling down the sample the resistivity follows a lower curve back to room temperature, so that the resistivity at room temperature after heating up to a temperature of $550 \,^{\circ}$ C and cooling down again is almost as low as at the initial samples starting value. In the last measurement series up to a



Figure 5.11: When the resistivity gets unstable for samples on Al_2O_3 and LSAT

temperature of $600\,^{\circ}$ C the sample gets unstable, since during cooling down there is a sudden increase in resistivity.

On LSAT the resistivity shows a stable variation with increasing temperature, meaning that it reaches back its initial value after cooling down. Here the big jump in resistivity only happens at a temperature of 700 $^{\circ}$ C (see figure 5.11).

The Seebeck coefficient increases for both substrate materials with increasing temperature, but after cooling down it gets back to its initial value for the LSAT as well as Al_2O_3 substrate. Also it stays stable at the abrupt increase in resistivity at high temperature.

6 Conclusion and Recommendation

6.1 Conclusion

Structural engineering of different $Ca_3Co_4O_9$ thin films on two different substrates has been done. The films have been grown at temperatures between 430 and 850 °C and with thicknesses of 10 to 120nm.

When varying the deposition temperature the best results have been achieved with the sample grown at 750 °C, for the Al₂O₃ substrate as well as the LSAT substrate. The Seebeck coefficient of the sample is higher for all films grown on LSAT compared to those grown on Al₂O₃, but since the resistivity is also higher, when taking both parameters together, the thermoelectric power S^2/ρ , used to determine the final ZT, is higher for samples grown on Al₂O₃.

For the thickness variation thin films of 10nm thickness did not deliver any Seebeck coefficient, but for films of 30 to 120nm thickness the thermoelectric properties are all in the same range, except for the film of 90nm thickness. Here for both materials, there is a small decrease in thermoelectric performance, meaning a lower Seebeck coefficient and a higher resistivity. But when combining Seebeck coefficient and resistivity still the sample grown at 750 °C with a thickness of 60nm gives the best result.

Material	Al_2O_3	LSAT
Seebeck coefficient $[\mu V/K]$	92.5	134.4
resistivity $[m\Omega cm]$	5	21.4

Table 2: Best results of 60nm thick Ca₃Co₄O₉ film grown at 750 °C

6.2 Outlook to future research

As a final measurement the thermal conductivity of the here prepared samples has been measured at the University of Illinois (US). But since all electronic characterization described above has been done in-plane and the thermal conductivity has been measured out of plane we cannot combine it to determine the final ZT.

From literature [36] values of the in-plane thermal conductivity for single crystal and bulk $Ca_3Co_4O_9$, and the out-of-plane thermal conductivity for the bulk material are known, so this can be compared. The thermal conductivity of the here prepared samples has been 1.2W/mK for a 100nm thick film on Al₂O₃ and 2.1W/mK for a 100nm thick film on LSAT, all measured at room temperature.

The single crystal and bulk values from literature at room temperature are in-plane 3.5 and 3.2W/mK respectively and out-of-plane for the bulk material ~ 2 W/mK. With increasing temperature the in-plane thermal conductivity decreases so it will be interesting to see how far the already lower thermal conductivity at room temperature on the Al₂O₃ substrate decreases below the single crystal and bulk value.

First measurements of the same as prepared thin films on STO substrates have been done and revealed a high Seebeck coefficient of $132.1 \mu V/K$, so in the range of the results on LSAT, but also a very high resistivity (44m Ω cm).

Since doping a material can improve its thermoelectric performance for some amount, another analysis could be done with the use of doped thin films, replacing either some of the Co or some of the Ca.

Nanostructures give a good thermoelectric performance, so the thin films presented here, could be combined with other materials thin films, such as $Na_x CoO_2$ to build superlattices.

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Bibliography

- Tritt et al. Thermoelectrics: Direct Solar Thermal Energy Conversion. MRS Bulletin, 2008 (33), pp 366-368
- [2] Get in on DOE Thermoelectrics Workshop. http://ehsmanager.blogspot.nl/2009_06_01_archive.html last visited, 02/07/2013
- [3] K. Koumoto, Y. Wang, R. Zhang, A. Kosuga, and R. Funahashi. Oxide Thermoelectric Materials. A Nanostructuring Approach. Annual Review of Materials Research, 2010 (40), pp 363-394
- [4] J.W. Fergus. Oxide materials for high temperature thermoelectric energy conversion. Journal of the European Ceramic Society, 2012 (Volume 32, Issue 3), pp 525-540
- [5] Q. Qiao, A. Gulec, T. Paulauskas, S. Kolesnik, B. Dabrowski, M. Ozdemir, C. Boyraz, D. Mazumdar, A. Gupta, and R.F. Klie. *Effect of substrate on the atomic structure and physical properties of thermoelectric Ca*₃Co₄O₉ thin films. Journal of Physics: Condensed Matter, 2011 (23), 305005 (6pp)
- [6] H.W. Eng, W. Prellier, S. Hbert, D. Grebille, L. Mchin, and B. Mercey. Influence of pulsed laser deposition growth conditions on the thermoelectric properties of Ca₃Co₄O₉ thin films. Journal of Applied Physics, 2005 (97), 013706 (5pp)
- [7] M.G. Kang, KH. Cho, S.M. Oh, J.S. Kim, C.Y. Kang, S. Nahm, and S.J. Yoon. Hightemperature thermoelectric properties of nanostructured Ca₃Co₄O₉ thin films. Applied Physics Letter, 2011 (98), 142102 (3pp)
- [8] T. Sun, J. Ma, Q.Y. Yan, Y.Z. Huang, J.L. Wang, and H.H. Hng. Influence of pulsed laser deposition rate on the microstructure and thermoelectric properties of Ca₃Co₄O₉ thin films. Journal of Crystal Growth, 2009 (311), pp. 4123-4128
- [9] T. Sun, H.H. Hng, Q. Yan, and J. Ma. Effects of Pulsed Laser Deposition Conditions on the Microstructure of Ca₃Co₄O₉ Thin Films. Journal of Electronic Materials, 2010 (39), pp. 1611-1615
- [10] P. Limelette, V. Hardy, P. Auban-Senzier, D. Jrome, D. Flahaut, S. Hbert, R. Frsard, Ch. Simon, J. Noudem, and A. Maignan. *Strongly correlated properties of the thermoelectric cobalt oxide Ca₃Co₄O₉*. Physical Review B, 2005 (71), 233108 (4pp)
- [11] T. Wu, T.A: Tyson, H. Chen, J. Bai, H. Wang, and C. Jaye. A structural change in Ca₃Co₄O₉ associated with enhanced thermoelectric properties. Journal of Physics: Condensed Matter, 2012 (24), 455602 (7pp)

- [12] http://www.mn.uio.no/fysikk/english/research/projects/bate/thermoelectricity/ last visited, 02/07/2013
- [13] D.T. Morelli. Research on New Thermoelectric Materials: from Seeds to Samplings. American Ceramic Society Conference, Daytona Beach, FL, (2008)
- [14] A. Bulusu, and D.G. Walker. Review of electronic transport models for thermoelectric materials. Superlattices and Microstructures, 2008 (44), pp 1-36
- [15] D.M. Rowe. Thermoelectrics handbook, macro to nano. CRC Press, Boca Raton, Florida, 2006
- [16] T.M. Tritt. Thermoelectric Materials: Principles, Structure, Properties, and Applications. Encyclopedia of Materials: Science and Technology, 2002, pp 1-11
- [17] T.D. Sands. Designing Nanocomposite Thermoelectric Materials. http://nanohub.org/resources/383 last visited, 02/07/2013
- [18] Y. Zhou, I. Matsubara, W. Shin, N. Izu, and N. Murayama. Effect of grain size on electric resistivity and thermopower of (Ca_{2.6}Bi_{0.4})Co₄O₉ thin films. Journal of Applied Physics, 2004 (95), pp 625-628
- [19] Z.G. Chen, G. Han, L. Yang, L. Cheng, and J. Zou. Nanostructured thermoelectric materials: Current research and future challenge. Progress in Natural Science: Materials International, 2012 (22), pp 535-549
- [20] Y. Pei, X. Shi, A. LaLonde, H. Wang, L. Chen, and G.J. Snyder. Convergence of electronic bands for high performance bulk thermoelectric. Nature, 2011 (473), pp 66-69
- [21] A.F. Ioffe. Semiconductor Thermoelements and Thermoelectric Cooling. Infosearch Ltd., London, 1957
- [22] J. He, and Y. Liu. Oxide Thermoelectrics: The challenges, progress, and outlook. Journal of Materials Research, 2011 (26), pp 1762-1772
- [23] J. Tervo, A. Manninen, R. Ilola, and H. Hnninen. State-of-the-art of Thermoelectric Materials, Processing, Properties and Applications. VTT Working Papers, 2009, (29pp)
- [24] D.M. Rowe. Handbook of Thermoelectrics. CLC Press, Boca Raton, Florida, 1995
- [25] G.S. Nolas, J.L. Kohn, B.C. Chakoumakos, and G.A. Slack. Glass-Like Heat Conduction in Crystalline Semiconductors. Thermal Conductivity, 1999 (25), pp 122-129
- [26] G.S. Nolas, D.T. Morelli, and T.M. Tritt. SKUTTERUDITES: A Phonon-Glass-Electron Crystal Approach to Advanced Thermoelectric Energy Conversion. Annual Review of Materials Science, 1999 (29), pp 89-116
- [27] G.D. Mahan, and J.O. Sofo. The best thermoelectric. Proceedings of the National Academy of Sciences USA, 1996 (93), pp 7436-7439
- [28] T.M. Tritt, M.A. Subramanian, et al. Thermoelectric Materials, Phenomena, and Applications: A Bird's Eye View. MRS Bulletin, 2006 (31), pp 188-198

- [29] J.W. Fergus. Oxide materials for high temperature thermoelectric energy conversion. Journal of the European Ceramic Society, 2012 (32), pp 525-540
- [30] H. Ohta, K. Sugiura, and K. Koumoto. Recent Progress in Oxide Thermoelectric Materials: p-Type Ca₃Co₄O₉ and n-Type SrTiO₃⁻. Inorganic Chemistry, 2008 (47), pp 8429-8436
- [31] A. Vora-ud, T. Seetawan, and A. Ratchasin. Simulating electronic structure of Ag-doped $Ca_3 CO_4 O_9$ by first principles. Journal of Material Science and Applied Energy, 1012 (1), pp 19-21
- [32] M. Huijben. Interface Engineering for Oxide Electronics. PhD thesis, University of Twente, the Netherlands, 2006
- [33] P. Brinks. *Highly anisotropic transport properties at interfaces of oxides*. Master's thesis, University of Twente, the Netherlands, 2010
- [34] H.H. Hsu, C.H. Cheng, C.H. Yeh, Y.W. Chou, Y.L. Lin, Y.R. Chen, and C.C. Yang. Characteristics of Annealed Bi₂Te₃ for Thin-film Thermoelectric Application. The Electrochemical Society, 2011, Abstract #1815
- [35] Seebeck Coefficient/ Electric Resistance Measuring System. http://www.linseis.com/uploads/media/LSR_Lit_11_2012_01.pdf last visited, 02/07/2013
- [36] R. Funahashi, S. Urata, T. Sano, and M. Kitawaki. Enhancement of thermoelectric figure of merit by incorporation of large single crystals in Ca₃Co₄O₉ bulk materials. Journal of Materials Research, 2003 (18), pp 1646-1651

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Appendix

```
% Resistivity calculation
clear all
                       % Clear memory
clc
                       % Clear command window
delta = 0.0005; % Error limit, initialized to 0
error = 0; % Error detection
iterations = 100; % Number of iterations
[file,path]=uigetfile('*.*','Choose data file'); % Load data file. First two columns
M=load(file); % should contain Ra and Rb. Additional columns no problem
for j=1:length(M)
Ra = M(j, 1);
Rb = M(j,2);
diff = delta+1; % Initialization: diff is set above delta to enter
i = 2; % the while loop. z(1) is calculated and counter i
z(1) = (2*log(2))/(pi*(Ra+Rb)); % is set to 2
while and(i<iterations,not(diff<delta)) % As long as error criterion not met and not
    % last iteration:
y(i)=1/(exp(pi*z(i-1)*Ra))+1/(exp(pi*z(i-1)*Rb));
z(i)=(z(i-1))-(((1-y(i))/pi)/((Ra/(exp(pi*z(i-1)*Ra))+(Rb/(exp(pi*z(i-1)*Rb))))));
diff=((z(i)-z(i-1))/z(i));
i=i+1;
end
\operatorname{Rsc}(j)=1/z(i-1);
if not(i<iterations) % If error criterion not met
error=1;
end
end
if error==1 % Displays message if (no) errors occured
disp('Warning! More iterations required!')
else
disp('Resistivity calculated successfully')
```

end

```
[file,path]=uiputfile('*.*','Choose output file name'); % Save data. First two columns
R = [M(:,1) M(:,2) Rsc']; % are Ra and Rb, third column contains Rsc
%R = [Rsc'];
save(file,'R','-ascii');
```

Abbreviations

AFM	Atomic Force Microscopy
BTE	Boltzmann Transport Equation
EBSD	Electron Back-Scatter Diffraction
η_C	Carnot efficiency
η_{TE}	thermoelectric efficiency
\hbar	reduced Planck constant
κ	thermal conductivity
κ_E	electronic thermal conductivity
κ_L	lattice thermal conductivity
k_B	Boltzmann's constant
L	Lorentz number
LAO	$LaAlO_3$
LSAT	$(La_{0.3}Sr_{0.7})(Al_{0.65}Ta_{0.35})O_3$
Р	Thermopower
PGEC	Phonon-Glass/Electron-Crystal
PLD	Pulsed Laser Deposition
ho	electrical resistivity
\mathbf{RS}	Rock-Salt
σ	electrical conductivity
\mathbf{S}	Seebeck coefficient
SEM	Scanning Electron Microscopy
STO	$ m SrTiO_3$
Т	Temperature
T_C	Temperature at the cold side
T_H	Temperature at the hot side
TM	Tapping Mode
XRD	X-Ray-Diffraction
ZT	figure of merit

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