Formation and Characterization of Periodic Lattice Defects at the Nanometric Length Scale in Calcium-Manganate Thermoelectric Compounds for Energy Harvesting

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# Formation and Characterization of Periodic Lattice Defects at the Nanometric Length Scale in Calcium-Manganate Thermoelectric Compounds for Energy Harvesting Research Thesis

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# List of Symbols and Acronyms

- TE thermoelectric
- ZT figure of merit
- RP Ruddlesden-Popper
- PGEC phonon glass electron crystal
- U umklapp processes
- GB grain boundaries
- PF power factor
- S Seebeck coefficient
- T<sub>D</sub> Debye temperature
- $v_s$ -Sound velocity
- $k_B$  The Boltzmann constant:  $k_B = 1.38 \times 10^{-23} J \cdot K^{-1}$
- h The reduced Planck's constant:  $\hbar = h/2\pi = 1.054 \times 10^{-34} J \cdot s$
- $\omega$  The phonon angular frequency:  $\omega = 10^{12} Hz$
- $\gamma$  The Grüneisen parameter:  $\gamma = 2$
- XRD x-ray diffraction
- SEM scanning electron microscopy
- HRSEM high-resolution scanning electron microscope
- LFA laser flash analysis
- SBA Seebeck Analyze

# 1. Literature review

### 1.1 Thermoelectric Compounds for Energy Harvesting

Energy harvesting is the concept of extracting power from environmental sources such as wind, sunlight, vibrations, shock, and heat. [Harb (2011)] Devices applying energy harvesting will be able to serve environmentally friendly as a renewable energy source or increase the efficiency of sustainable energy resources. The first time a possible way of Energy Harvesting was observed in 1821, when Thomas Johann Seebeck found that within in a closed circuit of two dissimilar metals a current would flow if they're exposed to a temperature gradient, so that heat could directly be converted into electrical power. [Seebeck (1826)]. The thermoelectric (TE) effect was discovered.

It occurs because of charge carriers traveling to regions of higher temperature within a material due to a higher mobility on the wormer side.

In order to describe the quality of the thermoelectric effect in a material the thermopower was defined as the Seebeck coefficient S, which is the amount of Voltage that is created referring to the temperature difference applied within the material, as shown in Eq. (1). [Rowe (2006)]

$$S(T) = \frac{\partial V}{\partial T} \tag{1}$$

Thereby it's possible to define a good TE material by a Seebeck coefficient of 150–250  $\mu V/K$  or higher [Tritt and Subramanian (2006)]. To evaluate performance of a material as a TE Compound it's not only necessary to refer to its Seebeck coefficient, but it's dimensionless thermoelectric figure of merit ZT in total, which is defined by

$$ZT = \frac{S^2 \sigma T}{\kappa} = \frac{PF T}{\kappa}$$
(2)

Whereas  $\sigma$  is the electrical conductivity,  $\kappa$  the total thermal conductivity, T the absolute temperature and PF the Power factor PF=S<sup>2</sup> $\sigma$ .[Koumoto et al. (2013)] Most state-of-the-

art TE materials exhibit a maximum figure of merit of ZT~1-2. [He et al. (2011)]

For power generation n-type and p-type semiconductors are combined form a series of TE couples as seen in Figure 1. The mobile charge carriers diffuse from the hot side to the cold side, when a temperature difference is applied. As for the n-type these charge carriers are electrons and for the p-type they are holes, it's possible to combine them electrically in series and thermally parallel.



**Figure 1: Power Generation using n-type and p-type semiconducting thermoelectric materials.** [Weidenkaff et al. (2008)]

TE generators do not depend on mechanical or chemical conversion processes. Therefore their main advantages are being emission free during operation, noiseless and extremely durable. [Weidenkaff et al. (2008)] The main problem in nearly all of the applications is the rather low efficiency of the processes of energy conversion, as can be seen in Figure 2. The efficiency of the thermoelectric compounds is compared to other common sources of electrical energy and the Carnot level, which marks the maximum possible efficiency.



Figure 2: Power Generation efficacy of TE-materials compared to other common energy sources and the Carnot limit referring to the Heat Source Temperature. The Temperature assumed for the cold side of the TE is 300 K. [Shakouri (2011)]

# **1.2 The Figure of Merit**

The efficiency of TE couple is determined by the figure of merit of both the p-type and the n-type material. A high Figure of merit can be achieved by combining a large electrical conductivity and thermopower with a low thermal conductivity. These properties have the tendency not to be compatible. For example, a good metal has a high electrical conductivity but also a high thermal conductivity (Wiedemann-Franz law). Materials which have high thermopower tend also to have low electrical conductivity.[Rowe (2006)]

Yet all three of them show different ways of dependency on material properties like molar weight, crystal structure, microstructure, porosity or the charge carrier concentration, n, latter is illustrated in Figure 3. [Ohtaki (2010)]



Figure 3: Expectations for doping influence on Power factor, thermal conductivity (split in lattice thermal conductivity and electronic thermal conductivity and the overall Figure of merit. Marked are the optimum doping levels in terms of Power Factor and Z. [Pichanusakorn and Bandaru (2010)]

Figure 3 also makes it obvious why the interest in thermoelectric materials suddenly rised when Semiconductors were found: The highest thermopower is reached when the Charge carrier concentration is in the range that highly doped Semiconductors reach.

Most current applications of thermoelectricity are based on heavily doped Semiconductors. [Rowe (2006)]

#### **1.2.1 Strategies for Enhancing the Figure of Merit**

One way of approaching the problem is to increase the power factor utilizing quantum mechanical principles. There has been some success in the past, for example using materials with strongly correlated electrons, finding thermoelectric anomalies in high-temperature superconductors caused by the proximity of the chemical potential to the Mott-Hubbard gap and heavily doping of semiconductors, like lead telluride, where resonant enhancement of the of density of states due to the impurities leads to a higher power factor.[Rowe (2006)]

Another strategy for enhancing *ZT* is called the *phonon glass–electron crystal strategy*, which will be explained in the following. It is utilizing that the thermal conductivity is only partly determined by electrons transporting the heat (electron thermal conductivity  $\kappa_{el}$ ), but also phonons (lattice thermal conductivity  $\kappa_{ph}$ ) as seen in eq.3.[Cohn et al. (1999); Tritt and Subramanian (2006); Chen (1997); He et al. (2011)]

$$\kappa = \kappa_{ph} + \kappa_{el} \tag{3}$$

The electron thermal conductivity can be determined well by the empirical Wiedemann– Franz law (eq.4) for metals at high temperatures and also for semiconductors if neither electronic density of states nor doping density nor layer thickness in super lattices is changed.[Pichanusakorn and Bandaru (2010)]

$$\kappa_{el} = L \cdot T \cdot \sigma \tag{4}$$

With T being the absolute temperature and  $L=2.44\cdot10^{-8}W\Omega K^{-2}$  being called the Lorenz number and varying slightly depending on Parameters like the temperature and the material.<sup>1</sup>

Thus the dimensionless figure-of-merit can be written as

<sup>&</sup>lt;sup>1</sup> Variations of the Lorenz number can be understood due to the difference in electrical and thermal relaxation times of electrons. An electrical current is created by shifting of the Fermi sphere by  $\delta k$ . A heat current is created, because electrons with a wave vector +k<sub>F</sub> have in average a different Temperature than electrons with a wave vector -k<sub>F</sub>. For the relaxation of an electrical current there are scattering processes with a wavenumber q of the magnitude  $q \approx 2 k_F$  necessary. In contrary for the relaxation of a heat current Wavenumbers with the magnitude of  $q \approx T/\hbar \cdot v_F$  are sufficient, as they move the electrons located near the Fermi-level from high energy levels to low energy levels and the other way round.[Ibach and Lüth (2009); Pichanusakorn and Bandaru (2010)]

$$ZT = \frac{S^2}{L} \left( 1 + \frac{\kappa_{ph}}{\kappa_{el}} \right)^{-1} \tag{5}$$

As the electrons not only infect the thermal conductivity, but also the power factor it's necessary to keep  $\kappa_{el}$  on a high level. That's why making  $\kappa_{ph}$  small compared to  $\kappa_{el}$  is the challenge that the *phonon glass–electron crystal strategy* is trying to solve. [Rowe (2006)]

#### 1.2.2 The Phonon Glass – Electron Crystal Strategy

In order to understand how the quotient  $\frac{\kappa_{ph}}{\kappa_{el}}$  can be increased, it is necessary to understand how electrons and phonons travel through a material. In both cases there are outer fields empowering the particles to travel and scattering events prohibiting them from traveling, so that the overall movements can be described as relaxation process, determined by the relaxation time  $\tau$ .[Ibach and Lüth (2009)]

Now in a glass phonons and electrons are scattered so much, that even when a field is applied, their movements rather resembles a random walk than a transportation process, which leads to both - some of the minimum thermal conductivities and electrical conductivities<sup>2</sup>. In a crystal, however, the distance between scattering processes is a lot wider and therefore conductivities are higher. [Ibach and Lüth (2009)]

The strategy of creating a Phonon Glass – Electron Crystal tries to combine the best of both "worlds" by finding a method of scattering phonons which doesn't scatter the electrons. This is a hard task, because they have most of the scattering mechanisms in common.[Cohn et al. (1999); He et al. (2011); Chen (1997)]

<sup>&</sup>lt;sup>2</sup> Not only the lower mobility due to increased electron scattering, but also lower effective masses (because of broader bands) make glasses electrical isolators.

### **1.3 Decreasing lattice thermal conductivity**

Figure 4 shows as an example how the thermal conductivity of the two modifications  $SiO_2$  glass and  $SiO_2$  crystal differ. As  $SiO_2$  is an electrical isolator it can be assumed that here only the lattice thermal conductivity is crucial.



Figure 4: Thermal conductivity of SiO2 as a function of Temperature. Drown through: crystalline modification (Quarz). Dotted: glass modification.[Ibach and Lüth (2009)]

In the past, the dominant way to reduce the thermal conductivity is through alloying. The mass difference in alloys scatters phonons more than electrons. In recent years, new ideas such as inserting phonon rattlers in cage structures have also been demonstrated to be effective in reducing the lattice thermal conductivity [Lei et al. (2004)]. The pursuit in lowering the lattice thermal conductivity in bulk materials is to approach the so-called minimum thermal conductivity. [Cohn et al. (1999)] New approaches try to reach it trough nanostructuring. [Chen et al. (2000); Weidenkaff (2004); He et al. (2010b); Rowe (2006); Tarkhanyan et al. (2014); He et al. (2011); Lee et al. (2007); Koumoto et al. (2010)]

#### **1.3.1 Fundamentals of Thermal Conductivity**

There are several scattering mechanisms for phonons, such as scattering on boundaries (grain boundaries, interfaces), dislocations, precipitations or other phonons. Each scattering mechanism has its own individual relaxation time  $\tau_i$ . The overall relaxation time  $\tau_t$  can be summed up from the different relaxation times as Matthiessen's rule gives (Equation 6). [Zlatic and Hewson (2013); Ibach and Lüth (2009)]

$$\tau_t^{-1} = \sum_i \tau_i^{-1} \tag{6}$$

Especially interesting are the Phonon-Phonon Scattering Processes. They can be divided in Normal scattering Processes (N) and Umklapp scattering Processes (U). Figure 5 shows the mechanism of both scattering Processes in the Brillion zone.



```
b) Umklapp (U)
```



Figure 5: The Brillion Zone with a) an Normal Phonon-Phonon scattering Process and b) an Umklapp scattering Process.  $q_1$  is the Phonon that is scattered and  $q_2$  and  $q_3$  are each the Phonons that are going out. G is the Transformation Vector. [Ibach and Lüth (2009)]

The phonon symbolized by  $q_1$  is scattered and results in the vectors  $q_2$  and  $q_3$ . In a normal scattering process these together have the same overall impulse as the ingoing one  $q_1$ . If the energy of the ingoing phonon is so high, that  $q_1$  is longer than half the Brillion Zone, there is an equivalent point to the one that  $q_1$  is pointing at in the neighboring Brillion Zone, marked by the transformation vector G. As in a lattice, there is translation

periodicity, the resulting vectors  $q_2$  and  $q_3$  might as well sum up to that equivalent point. If this happens it is called the Umklapp Process. The important feature of the Umklapp Process is, that the direction of the impulse of the outgoing phonons is in the opposite direction of the ingoing. Therefore, they do not contribute to the transportation of the thermal energy anymore. In the contrary, they exhibit it. As Umklapp Processes are thermally activated, their relaxation time is exponentially depending on the temperature (eq. 6).

$$\tau_{U}^{-1} = B\omega^2 e^{-\theta/2T} \tag{7}$$

This is the reason for the decrease of thermal conductivity with the temperature of the crystalline phase as seen in Figure 4. [Ibach and Lüth (2009)]

What makes this process very special is that such a mechanism doesn't occur for electrons. Increasing the Influence of Umklapp Process is possible by shrinking the Brillion-Zone, for example by building a super lattice. [Rowe (2006)].

Super lattice also serve with the advantage of additional scattering processes on the interfaces of the different layers.[Chen et al. (2000)] The relaxation time for these boundaries can be calculated just alike the ones for grain boundaries as shown in equation 8.

$$\tau_B^{-1} = \frac{v_{ph}}{L} \tag{8}$$

#### **1.3.2** The Callaway Model for Thermal Conductivity

In order to calculate the lattice thermal conductivity from the different mentioned relaxation times, the Callaway modal can be applied. It is derived from the Boltzmann equation for relaxation times and works with the Debye-approximation. [Callaway (1959)]

It is commonly used in the field of TE materials [He et al. (2010a); Kim et al. (2008); Wu et al. (2009); He et al. (2010b); Kim et al. (2006); Amouyal (2014)] and determined for

the limit of T adequately larger than  $T_D$  by equation 9. It has been reviewed and improved [Allen (2013); Ma et al. (2014); Holland (1963); He et al. (2010a); Morelli et al. (2002)]

$$\kappa_p(T) = \frac{k_B}{2\pi^2 v_s} \left(\frac{k_B T}{\hbar}\right)^3 \int_0^{T_D/T} \tau_t(x) \frac{x^4 e^x}{(e^x - 1)^2} dx$$
(9)

Where  $\omega$  is the phonon angular frequency,  $\hbar$  is the reduced Planck's constant:  $h/2\pi$ ,  $x \equiv \frac{\hbar\omega}{k_BT}$  and  $\tau_t$  is the equivalent relaxation time.

### **1.4 Oxides as Thermoelectric Materials**

Several strategies for improving the figure of merit led to thermoelectric materials based on more environmentally harmful heavy p-block elements such as Bi, Pb, Sb, or Te exhibiting a maximum figure of merit, ZT, of  $\sim 1-2$  [Flahaut et al. (2006); He et al. (2011)].

However, there are more factors than the Figure of Merit to take into account for application of a thermoelectric material. It should be non toxic, stable at high temperature in air and inexpensive. Inexpensive is of high importance for TE materials, as the price per Watt of the produced electricity is not determined by fuel (the Temperature gradient is for free for energy harvesting applications) but by the price per square of the TE-material itself.[Rowe (2006)]

Oxides are generally considered to be insulators with a bandgap of about 3 eV. In the undoped material the charge carriers are ions and the charge carrier concentration is determined of the ratio of ions per formula unit. In contrary the doped samples are hole or electron-conductors depending on the kind of doping Atoms.

The discovery of the p-type NaCo<sub>2</sub>O<sub>4</sub> single crystal compound with a large thermoelectric power in-plane (100mV/K at 300 K) attracts renewed interest in metal oxide materials.[Terasaki et al. (1997)] Other promising p-type Materials are Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> (for epitaxial film ZT $\approx$ 0.3 at 1000 K) and Bi<sub>2</sub>Sr<sub>2</sub>Co<sub>2</sub>O<sub>9</sub>.[Nan et al. (2002); He et al. (2011);

Weidenkaff et al. (2008)]

Although ZT-values of oxides is still low compared to those of the current state-of-the-art TE materials, oxides are particularly suitable for high temperature power generation in air as they fulfill all the other mentioned criteria. What is missing for application though is a suitable n-type oxide, as their ZT are only a third of the p-type one.[Koumoto et al. (2013)]

It should be mentioned that in metal-oxide materials the phonons dominate thermal conductivity.[Chen et al. (2000)]

### **1.5 Ruddlesden Popper Phases**

CaMnO<sub>3</sub> is one of the most prominent n-type thermoelectric oxides with a reported maximum ZT~0.3 for CaMn<sub>0.98</sub>Nb<sub>0.02</sub>O<sub>3,7</sub> at 1000 K making it a typical choice when designing an all-oxide thermoelectric generator [Bocher et al. (2008)]. Its TE properties with substitution for Ca and Mn separately have been widely investigated [Wang et al. (2008); Bocher et al. (2008); Ohtaki et al. (1995); Xu et al. (2004); Flahaut et al. (2006)].CaMnO<sub>3</sub> possesses Perovskite structure, which can be modulated with a microstructure of inserted CaO Rock-Salt (RS) layers. They are called the homologous Ruddlesden Popper series of CaO(CaMnO<sub>3</sub>)<sub>m</sub>. The m=infinity (inf.,  $\infty$ ) composition does not exhibit multilayered structure. The m=1 composition, in contrary, exhibits the highest possible number of layers. The layered structure is build with a smaller Brillion zone and the shortest possible distance in between the interfaces in the real space. The crystallographic information of these two compositions as well as some compositions in between appears in Table 1.

Sample	m	Crystal structure	Space group	Number of RS- layers
CaMnO <sub>3</sub>	inf	Orthorhombic	Pnma	none
$Ca_4Mn_3O_{10}$	3	Tetragonal	I4/mmm	every 3 perovskite cells
Ca <sub>3</sub> Mn <sub>2</sub> O <sub>7</sub>	2	Tetragonal	I4/mmm	every 2 perovskite cells
Ca <sub>2</sub> MnO <sub>4</sub>	1	Tetragonal	I4/mmm	maximum

Table 1: Room temperature crystallographic data for the  $CaO(CaMnO_3)_m$ -compounds with m=1, 2, 3 and m= $\infty$ .

### **1.6 The Influence of Athmosphere**

It is well established that the oxygen content in  $CaMnO_{3-\delta}$  can be varied over a broad range. Therefore, thermoelectric measurements on identical samples with different oxygen partial pressure can lead to significantly different results and temperature dependences. [Schrade et al. (2014)]

It was found the basis of thermogravimetric (TG) measurements that the defect properties of CaMnO<sub>3- $\delta$ </sub> can be described by two chemical reactions: The filling of oxygen vacancies accompanied by a oxidation of Mn-sites (eq. 10) and the thermal excitation of electronic charge carriers across the band-gap (eq. 11). [Goldyreva et al. (2012)] These reactions are formulated In the Kröger-Vink-notation: [Goldyreva et al. (2012)]

$$\frac{1}{2}O_2(g) + v_0^{"} + 2Mn_{Mn}^{/} = O_0^x + 2Mn_{Mn}^x$$
(10)

$$2Mn_{Mn}^{x} = Mn_{Mn}^{\prime} + Mn_{Mn}^{\cdot}$$
(11)

The reaction enthalpies of both reactions depend on the structural state of the Calcium Manganate.[Goldyreva et al. (2012)]

The Influence of the oxygen partial pressure on undoped  $CaMnO_{3-\delta}$  at high temperatures on electrical conductivity and Seebeck coefficient have recently been investigated by Schrade et. al..[Schrade et al. (2014)] In that research the highest power factor was determined to 1.81 WK<sup>-2</sup>cm<sup>-1</sup> at 900 °C and for an oxygen partial pressure of 1 atm. Higher temperatures and lower  $p_{O2}$  lead to a significant reduction of the power factor (Figure 6).[Schrade et al. (2014)]



Figure 6: Dependency of (b) electrical conductivity and (c) Seebeck coefficient ( $\alpha$ ) of the oxygen partial pressure for undoped CaMnO<sub>3- $\delta$ </sub>. [Schrade et al. (2014)]

Schrade et. al. postulate that "this behavior can be explained by a conduction process in  $CaMnO_{3-\delta}$  at high temperatures via strongly interacting small polarons. The mutual Coulomb repulsion of these polarons quickly reduces the mobility once charge carriers are introduced into the system" [Schrade et al. (2014)]

It is known, that  $CaMnO_{3-\delta}$  undergoes a phase change from orthorhombic to tetragonal and finally to cubic when varying the oxygen partial pressure in the range from 1 to  $10^{-4}$ atm. The oxygen partial pressure may also affect the stacking of the Perovskite – Rock salt layers.

### **1.7 Research Goals**

It is imported to develop an n-type thermoelectric oxide with an increased figure of merit. The goal is to increase ZT of  $CaMnO_3$  further by nanostructuring. It is hypothesized, that the layered structure of Ruddlesden Popper phases can lead to an increased phonon scattering, thereby reducing the lattice component of thermal conductivity. This is, eventually, expected to therefore enhances ZT. Further improvement should be obtained by increasing the charge carrier concentration by doping, which should lead to a higher power factor.

This thesis is based on the former work of Graff and Amouyal, who performed thermoelectric measurements on the Ruddlesden Popper series of  $CaO(CaMnO_3)_m$  with m=1, 2, 3, 4,  $\infty$  and La- and Nb-doping. They were able to show that the thermal conductivity of these oxides can be manipulated by altering the density of the CaO/(CaMnO<sub>3</sub>)<sub>m</sub> interfaces, but not enhance the ZT. They suggest to increase ZT by the chosen doping conditions.[Graff and Amouyal (2014)]

In this work I will repeat the sample preparation and analysis of the m=1 and m= $\infty$  compounds in order to examine new research directions within this topic, and to proceed with selected directions. Therefore, the results will be compared to Graff's constantly. In this case it is always referring to the Master theses "Effects of lattice defects on thermoelectric properties of calcium-manganite compounds for energy harvesting applications" which was submitted by Ayelet Graff in September 2014 to the Technion – Israel Institute of Technology.

It should be noted that in the present study we, first, determined the materials' bulk densities more accurately than in Graff's work applying the Archimedes Principle; second, we extended the temperature range to 1273 K, which is considerably higher than in Graff's work, and approaches the linmit of the LFA apparatus. Also, some measurement conditions have been changed in order to investigate their influence on the results.

# 2. Experimental and analytical methods

This chapter explains first how the specimen were prepared (2.1) and afterwards how they were analyzed (2.2). Analyzing Systems were X-ray diffraction (2.2.1), scanning

electron Microscopy (SEM) (2.2.2, 2.2.3), Archimedes density measurements (2.2.4) Netzsch SBA-458 system (SBA) (2.2.5) and Netzsch *Microprobe* LFA-457 system (LFA) (2.2.6).

# 2.1 Sample preparation

The samples produced were undoped CaO(CaMnO<sub>3</sub>)<sub>m</sub>, La-doped CaO(Ca<sub>1-x</sub>La<sub>x</sub>MnO<sub>3</sub>)<sub>m</sub> and Nb-doped CaO(CaMn<sub>1-x</sub>Nb<sub>x</sub>O<sub>3</sub>)<sub>m</sub> with x=0.4. Of each kind the two fractions m=1 and m= $\infty$  were aimed to be synthesized. The pure oxide powders used in stoichiometric ratio as well as information about them (as far as available) can be found in Table 2.

Oxide powder	Manufacturer	Major impurities (>0.01 %)
CaCO <sub>3</sub>	Merck KGaA	SO <sub>4</sub> (<0.03 %), Mg (<0.02 %), Na (<0.2 %), and
		Sr (<0.1 %)
MnO <sub>2</sub>	Baker Co	Cl (<0.01 %), NO <sub>3</sub> (<0.05 %), SO <sub>4</sub> (<0.05 %), and
		Fe (<0.03 %)
La <sub>2</sub> O <sub>3</sub>		
Nb <sub>2</sub> O <sub>5</sub>		

Table 2: Information about oxide Powders used for specimen characterization.

After mixing the powders at room-temperature, grinding them and applying uniaxial pressing of 700 MPa, specimens were sintered: at first 24 hours 900°C, than, after repeated grinding and pressing after each step at increasing temperatures for 24 h each. The whole procedure is performed in Air-atmosphere. The further temperature steps were 1050, 1200, 1300, 1350 and 1400°C. Each compositions, had its characteristic highest sintering temperature, following the routing Graff applied successfully for the sample preparation in the past. Before the final sintering process each of the powders was pressed uniaxial at 700 MPa into at least two bars ( $2 \times 2 \times 12.5$  mm) and three discs (diameter 12.5 mm, thickness 2 mm) as greenbodys. An overview of the proceeded temperature steps for the different samples can be found in Table 3.

	m	T 1	T 2	Т3	T 4	Т 5	T 6	Τ7
Undoped	1	900	1050	1200	1300	1400	1400	
	$\infty$	900	1050	1200	1300	1300		
Nb-dobed	1	900	1050	1200	1300	1350		
	$\infty$	900	1050	1200	1300	1350		
La-doped	1	900	1050	1200	1300	1300	1400	1400
	x	900	1050	1200	1300	1300		

Table 3: Sintering Steps 1 to 7 for each Compound. All the temperature Steps were applied for 24 hours. In between the steps specimen were grinded and pressed. Fat printing indicates greenbody shaping.

### 2.2 Analysis

This section provides all details about the performed experimental work. Figure 7Figure 7: Working procedure. Dark blue: Experimental method. Light blue: produced Data. gives an overview of the performed measurements and the hereby determined properties.



Figure 7: Working procedure. Dark blue: Experimental method. Light blue: produced Data.

#### 2.2.1 X-Ray Diffraction (XRD)

XRD measurements were carried out using a Rikagu MiniFlex X-Ray Diffractometer with an angular resolution of 0.02°, located at the Material Science Department,

Technion, applying Cu-K  $\alpha$  radiation at the angular range of 2  $\theta$  = 10-60 °. The data was collected by angular scanning with 0.02 ° steps. The intensity peaks were compared to a database in order to find out weather the phases that were aimed for have been successfully produced. A quotient q of the highest unidentified peaks intensity I<sub>2</sub> and the highest identified peaks intensity I<sub>max</sub> was build for describing the pureness of the phases (eq. 12).

$$q = \frac{I_?}{I_{max}} \cdot 100 \tag{12}$$

#### 2.2.2 Scanning Electron Microscopy (SEM)

The Zeiss Ultra Plus high-resolution scanning electron microscope (HR-SEM) was used for taking surface images. It's equipped with a field emission gun and was operated at 5 keV. Additionally, the fracture of the m=1 undoped before and after the LFA measurement was observed by the environmental Quanta 200, which is equipped with a Wolfram emission gun, was operated at 20 keV. Both of the microscopes are located at the Materials Science & Engineering Department, and are equipped with a secondary electron (SE) detector and a back scattered electron (BSE) detector.

#### **2.2.3 SEM Picture Analysis**

The SEM pictures with a magnification of 1000 were analyzed using Gwyddion $\bigcirc$ . Average grain diameter was measured by counting the amount of grain boundaries crossed by horizontal lines and divided by the sum of their length, which was about 6 mm. Open porosity was analyzed by masking the pores in the surface images and using the masks' surface fraction. Closed porosity can only be analyzed by the surface fraction of the pores in the pictures of the specimen fraction, which was only taken for m=1 undoped Specimen.

#### 2.2.4 Archimedes Density and Porosity Measurements

The Archimedes principle determines density by the weight of a sample and the volume of liquid it is displacing when being submerged. The Procedure for Archimedes Measurements was adapted from the ASTM C373- 14a standard, except for the boiling of the specimen in distilled water, because boiling caused so many fractions to the specimen that they were destroyed. Also this standard is made for heavy tiles. As the specimen weight is 0.2g to 0.5g standard ASTM B962- 14 was used in terms of accuracy. Table 4 summarizes the achieved values per measurement. Of each kind, two or three different Specimen underwent the procedure each twice, so that error and standard derivation of the results could be determined.

с с	
Variable	Definition
D	Dry specimen weight
S	Weight of specimen immersed in water

Table 4: Values directly measured by Archimedes Principle.

M W(T)

Now Bulk Density B, density without open porosity B\*, total porosity P, closed porosity  $P_{cl}$  and open porosity  $P_{op}$  can be calculated following the equations 13 - 17.

$$B = \frac{D * W}{M - S} \tag{13}$$

Weight of specimen after immersing and surface cleaning

Water Density (Temperature)

$$B^* = \frac{D * W}{D - S} \tag{14}$$

$$P = \left(1 - \left[\frac{B_{av}}{D_{theo}}\right]\right) \cdot 100 \tag{15}$$

$$P_{cl} = \left(1 - \left[\frac{B^*_{av}}{D_{theo}}\right]\right) \cdot 100 \tag{16}$$

$$P_{op} = P - P_{cl} \tag{17}$$

#### 2.2.5 Electrical Conductivity and Thermopower Measurements

Both electrical conductivity and thermopower measurements were simultaneously performed by the Netzsch SBA-458 system. The sample holder is enabled to be heated

differently on both sides of the bar shaped sample, which is contacted on each side by a thermocouple and an electrical contact. Within the temperature range from room temperature up to 750 °C, the sample is equally heated to the programmed temperature steps with a distance of 100 K in between them, when measuring  $\Delta V$  for electrical conductivity. Subsequently, it undergoes a temperature gradient  $\Delta T$  in a range from -5 K to +5 K around the set temperature from the one side to the other during the measurement of  $\Delta V$  for the Seebeck coefficient. In order to avoid oxidation of the contacts at high temperatures it is mandatory to perform the measurements under flowing, high-purity Argon-atmosphere.

The sheet resistivity of a sample is determined by Smits' and Valdes' method called "linear four terminal arrangement". Applying their theories the sheet resistivity for the present configuration, ( $s_1=s_3=1.5$  mm, and  $s_2=7.8$  mm) is given by Eq. (18). [Smits (1958)]

$$\rho = \frac{\Delta V}{I} \frac{2\pi}{\left(\frac{1}{s_1} - \frac{1}{s_1 + s_2}\right)}$$
(18)

Electron scattering on the specimen surface is automatically considered by the SBA-458 utilizing finite element analysis for calculating the specimen dimension specific scattering factors  $\delta_i$  and calculating a corrected expression for resistivity  $\rho_{final}$  from the measured resistivity  $\rho$  (Equation 19, 20).

$$\delta_i = \sum A_n \cdot e^{-i/t_n} \tag{19}$$

$$\rho_{final} = \frac{\rho}{\delta_x \cdot \delta_y \cdot \delta_z} \tag{20}$$

Where i stands for either the thickness x, width y or length z.

The Seebeck coefficient is calculated using eq. (21), given the Seebeck coefficient of the connecting material in between the reference temperature point and the two sides of the sample ( $S_B$ ).

$$S - S_B = \lim_{\Delta T \to 0} \frac{\Delta V}{\Delta T}$$
(21)

### 2.2.6 Thermal Conductivity Measurements

The thermal conductivity measurements were performed by the Netzsch *Microprobe* LFA-457 system (LFA), which actually measures the thermal diffusivity of disc-shaped specimen. Later on thermal conductivity can be calculated by equation 21. The LFA working principle is sketched in Figure 8.



Figure 8: Working principle of the Laser Flash Analysis method (LFA) indicating the direction for the photon radiation.

The laser (here: 18.5 J/pulse Nd-YAG laser system) gives a pulse of about 500 $\mu$ s duration, which is absorbed by the specimen. Coating the specimens' surfaces with carbon before the measurement ensures the immediate absorption. The absorbed heat has to diffuse through the whole thickness d of the specimen. Afterwards, a radiation thermometer (here: indium-antimonide detector) measures the increase of temperature on the other side of the specimen depending on the time that passed by after the laser pulse. The material can be characterized by the time t<sub>50</sub> after which the thermal signal reaches 50% of its maximum intensity.

The furnace has ben programmed to heat from room temperature to 1000 °C and stop at set points every 100 K for 5 shots of laser pulses on each specimen. Repeating the shots is especially necessary for high temperatures as reliability of  $t_{50}$  might be questionable and needs to be supervised. Using the average  $t_{50}$ , thermal diffusivity can be calculated applying equation 22.

$$\alpha(T) = 0.1388 \cdot \frac{d^2}{t_{0.5}};\tag{22}$$

Three specimens can be located on a horizontal rotating table, so that they are heated at the same time and alternately measured after rotating in between. Two vacancies were always filled with specimen and one with an Al<sub>2</sub>O<sub>3</sub>-reference. The reference was needed for simultaneous temperature-dependent heat capacity determination.

The materials' thermal conductivity  $\kappa$  can now be calculated by the measured thermal diffusivity  $\alpha$ , the specific heat of the reference,  $c_p$ , and the bulk density B found by the Archimedes principle [Rowe (2006)]:

$$\kappa(T) = \alpha(T) \cdot B \cdot C_p(T) \tag{23}$$

Table 5 gives an overview of the performed LFA measurements. If not mentioned otherwise, measurements have been performed in Argon atmosphere for compatibility with the SBA measurements.

The influence of several measuring conditions was investigated: Some specimen have been measured a couple of times to find out whether there is some change within the material during the process of the measurement itself. Measurements in air atmosphere should provide us with the influence of Oxygen partial pressure on the results. An m=1 undoped specimen with a lower porosity has also been measured.
		$1^{st}$	2 <sup>nd</sup>	3 <sup>rd</sup>	Measured under special
	m	Measurement	Measurement	Measurement	conditions
Undoped	1	$\checkmark$	$\checkmark$	$\checkmark$	Twice in Air Atmosphere,
					double pressed specimen
	$\infty$				
Nb-	1				
dobed	x				
La-	1				Twice in Air Atmosphere
doped	$\infty$				

Table 5: Overview of performed LFA Measurements.

# **3. Results and Discussion**

As formation of all the specimen was successful (Figure 9), this chapter first displays the experimental results and draws some connection between them (3.1). Following, calculations based on the data in 3.1 are proceeded (3.2). Starting with the power factor (3.2.1), followed by the Figure of merit (3.2.2) and the thermal lattice conductivity

(3.2.3).



Figure 9: Successfully produced disc-shaped specimen of all kinds after the SEM image taking. The fractures appeared after detaching the specimen from the graphite tape used to stick the specimen onto the specimen holder and indicate how different the mechanical stability of the specimen seems to be.

## **3.1 Experimental Results and their Discussion**

First, the X-ray diffraction results enable phase identification (3.1.1) followed by the scanning electron microscopy images (3.1.2) and their analysis in terms of the grain size and porosity (3.1.2.1. and 3.1.2.2) compared to the porosity values achieved by Archimedes principle (3.1.3). In the following sections trends of electrical conductivity (3.1.4), thermopower (3.1.5), and thermal conductivity measurements (3.1.6) depending on the doping (3.1.6.1), amount of layers (3.1.6.2), and measuring conditions (3.1.6.3) are shown.

### **3.1.1 X-ray Diffraction (XRD) Analysis**

Comparing the peaks to the databases it can be seen that all the different kinds of phases were produced successfully: For m=inf periodicity they fit the orthorhombic crystal structure having the Pnma space group symmetry (JCPDS number: 040078030) and for m=1 periodicity they fit the tetragonal crystal structure having the I4/mmm space group symmetry (JCPDS number 040067894). Unidentyfied peaks were small and didn't fit any

of the other possible produced or startig phases: The factor q was found to range in between 0.5 and three Percent (see section 6.1) wich indacates a sufficient purity.

## 3.1.2 Scanning Electron Microscopy (SEM) Analysis

We performed SEM analysis for the entire specimen in different magnifications using SE and BSE-detectors. Figure 10 gives an overview of the microstructure that could be observed for the different compounds, looking at the disc shaped specimens' surface.



Figure 10: HR-SEM micrographs of specimen discs' surfaces. a-d, f Magnification 5000. e Magnification 50. a, b BSE detector, c-f SE detector.

All of them show a small amount of almost circular pores and grains, which are bordering each other. This microstructure is typical for ceramics in the ultimate (third) stage of sintering.[Telle (2003)] The doped m=1 and the undoped m=inf surfaces show a high number of surface cracks. This correlates with the low mechanical stability experienced for these specimen.

Zooming in, growth steps can be recognized for all components at some points. Figure 11 gives an example for this observation. They are driven by surface energy anisotropy, and

presumably grow in surface diffusion mechanism, as described by Kossel and Stranski. [Kossel (1934)]



Figure 11: HR-SEM micrograph of specimen discs' surface. Composition m=inf, undoped. Magnification 34 000. SE detector.

#### 3.1.2.a Grain Size Analysis

The grain boundaries of all specimens are clearly visible due to thermal etching of the external surfaces taking place during the sintering process, as seen in Figure 10. The average grain diameter measured is 55  $\mu$ m, varying in between 40  $\mu$ m ± 1  $\mu$ m for m=1, Nb-doped and 88  $\mu$ m ± 5  $\mu$ m for m=1 undoped. This Length is considerably large compared to the phonon mean free path.. We, therefore, neglect the effect of phonon scattering by grain boundaries is very small compared to the perovskite/RS multilayering.. A bulk diagram of all the results can be found in chapter 6.2.

#### **3.1.2.b** Porosity Analysis

Masking of the pores was successfully processed (Figure 12) and open porosity determined. The results of this procedure can be found in chapter Archimedes principle (3.1.3).



Figure 12: HR-SEM micrographs of the discs surface composition m=inf, Nb-doped. Magnification 1000. a: original picture, b: masked pores. red Area: Mask.

Filling the histogram data of the pore diameters given by Gwiddion into it log-normal grid reveals, that all compounds exhibit log-normal-like distribution of pore diameter. Regarding the shape of the pores, it can be observed that they are curved convexly, which means that they will shrink for further sintering.

## 3.1.3 Archimedes Density and Porosity

The Archimedes principle enabled the accurate determination of B and B\*, as can be found in section 6.3 in detail. B will be used for the calculation of the thermal conductivity in the following. Calculation of the porosity revealed, that a major part of the porosity is open porosity, as can be seen in Figure 13: Comparing Bulk Porosity and closed Porosity determined by Archimedes Principle for all compositions. because the open porosity is the difference between bulk porosity and open porosity.



Figure 13: Comparing Bulk Porosity and closed Porosity determined by Archimedes Principle for all compositions.

The vales for open porosity determined by the two different methods Archimedes and SEM-picture analysis show a discrepancy for the compositions m=1 doped and m=inf undoped (Figure 14). These are exactly the compositions for which lots of cracks were observed. These cracks will contribute to the open porosity in reality, but not, if only the optical surface fraction is taken into account. This is why the Archimedes principle can be trusted to serve with accurate results better than the analysis of the SEM pictures.



Figure 14: Comparing open Porosity result from SEM picture analysis and Archimedes principle for all compositions.

## **3.1.4. Electrical Conductivity**

Over all composites an temperature ranges electrical conductivity was found to vary in magnitude from 0.1 Scm<sup>-1</sup> and 100 Scm<sup>-1</sup>, All these values are significantly low compared to other oxide thermoelectric materials, like the p-type NaCo2O4 with about 5000 Scm<sup>-1</sup>[Terasaki et al. (1997)]. The highest conductivities have been found for m=inf doped compounds at high temperature.

The dependency of the temperature indicates for all compounds conduction in the exhaustion range, except for the m=inf undoped composition, which has found to be intrinsic in the investigated temperature range.

The layered structure leads to a decrease of electrical conductivity of about two orders of magnitudes. This means that the internal interfaces not only scatter the phonons, as aimed for, but also the electrons and therefore decrease their mean free path, too. The decreasing effect is stronger for low temperatures and becomes less as temperature increases.

Both kinds of doing atoms have almost the same effects on the conductivity: For m=inf the undoped specimen is observed to have a conductivity, that is 1-2 orders of magnitudes lower than those of the doped ones, which is expected. Conversely, the values measured for m=1 undoped are greater than for the doped compounds. The SBA measurement for this specimen has been repeated in order to confirm the deviation, as can be seen in Figure 15. It is not likely that the specimen has been swapped, because the Seebeck coefficient measured accordingly turned out both time as expected. It's also the only one that is not in good accordance to the results that were found by Graff (cf. section 6. 4). As the synthesis was not repeated, it is seems likely that there was some error in preparation.



Figure 15: Electrical conductivity for the m=1 specimen plotted logarithmical depending on the temperature.

## 3.1.5 Seebeck coefficient

As expected, due to their n-type nature all samples exhibit negative S-values (Figure 16). The magnitude ranges from -500 to -100  $\mu$ VK<sup>-1</sup> which is equivalent (even slightly higher) to other oxide thermoelectric materials and the same as reported previously for the same materials [Flahaut et al. (2006); Ohtaki (2010); Bocher et al. (2008)]. The highest absolute values of thermopower have been found for m=1 undoped compounds, directly followed by the m= $\infty$  undoped ones at room temperature. Both decrease with temperature, in absolute values. This is related to its low carrier concentration and semiconductor behavior. The doping leads to a clear decrease of the absolute S value, which is in agreement with the increase of the charge carrier concentration. Dopant identity has almost no or little effect on thermopower, as S only depends on the concentration, and not of the nature of the charge carrier.



Figure 16: Seebeck coefficient for all compounds depending on the temperature.

For the undoped specimens the layered structure leads to an increase of thermopower, for the doped ones the effect is reversed. At higher temperatures, the effects of doping and layered structure vanish: For 750 °C all components show a similar thermopower roughly around  $S\approx-200 \ \mu V K^{-1}$ .

All values are in good accordance to Graff's findings. Only the m= $\infty$  undoped specimen were observed to have higher S., than found by Graff. (cf. section 6.4)

## **3.1.6 Thermal Conductivity**

The magnitude of thermal conductivities ranges from 0.5 to 3  $Wm^{-1}K^{-1}$  which is in accordance with the literature values for this material [Bocher et al. (2008)] and Graff's values, too.

It was possible to decrease the thermal conductivity by inserting the layered structure into the Material. That means the goal of decreasing  $\kappa$  by nanostructuring was reached. As an example at low temperatures thermal conductivity of the Nb-doped compounds was decreased to about one third of the m= $\infty$  type. The lowest thermal conductivities achieved by this method (m= $\infty$ , undoped) are close to the minimum thermal conductivity  $\kappa_{min}$ .  $\kappa_{min}$ was defined by Slack as the lowest achieveable thermal conductivity. This is the case when the mean free path is essentially limited and has the length of the interatomic distance between the atoms within the crystal. It's size is  $\kappa_{\min} \approx 0.25 - 0.5 \text{ Wm}^{-1}\text{K}^{-1}$ [Cohn et al. (1999); Tritt and Subramanian (2006)]. (cf. Section 6.5)

#### 3.1.6.a Thermal Conductivity in Comparison to Results fond by Graff

Trying to determine the influence of the doping atoms on thermal conductivity, a major discrepancy of the results from this study and Graff's is undeniable, as can be seen in Figure 17.



Figure 17: Comparing thermal conductivities for the over the Temperature (note a, c is in  $^{\circ}C$  and b, d is in K) a) measured in this study, m=1 compounds ; b) measured by Graff, m=1 compounds; c) measured in this study, m= $\infty$  compounds; d) measured by Graff, m= $\infty$  compounds. Black: undoped, Blue: La-doped. Red: Nb-doped.

Even though the magnitude found is the same, it can be easily seen, that neither the development of  $\kappa$  over the temperature, nor the trend depending on the doping is the same. Whereas it was found now, that doping leads to an incense of  $\kappa$ , in Graff's study the thermal conductivity of the undoped specimen lies mostly in the middle of the thermal conductivity of the La-doped and the Nb-doped specimen. Actually, it was hoped the doping atoms would not change or maybe even decrease lattice thermal conductivity, as it can be observed for solid solutions for example in PbTe [Tritt and Subramanian (2006)]or acting as scattering centers .[Lo et al. (2012)]. It can be suspected that electronic injection by dopants contribute to thermal conductivity, which opposes to the trend of scattering, but that might not be the whole explanation, as the calculated  $\kappa_e$  is very small for doped and undoped Specimen alike (compare section 2.3.2).Another explanation could be, that alloying changes lattice periodicity.

#### **3.1.6.b Heat Capacity and Reliability of Results**

As the results in thermal conductivity seem to be quite incomparable to Graff's the directly measured values, the thermal diffusivity, was compared instead (Figure 18). They are found to show a more similar temperature depended progress.



Figure 18: Thermal Diffusivity as a function of Temperature. Filled squares stand for the new measurements, empty circles stand for Graff's measurements. Black: undoped, Blue: La-doped. Red: Nb-doped.

For calculating the thermal conductivity from these diffusivity values applying  $\kappa(T) = \alpha(T) \cdot P \cdot C_p(T)$  the indirectly determined heat capacity and the by Archimedes Principle determined density have to be taken into account. Calculating thermal conductivity with Graff's diffusivity values and the Cp-data and density of this study, similar trends were found (Figure 19): Now both show highest  $\kappa$  for the La-doped and lowest for the undoped as well as the rising trend with increasing temperature.



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Figure 19: Thermal conductivity calculated with the heat capacity and density found in this theses as a function of the temperature. Filled squares stand for the new measurements, empty circles stand for Graff's diffusivity data as basis. Black: undoped, Blue: La-doped. Red: Nb-doped.

Density measurements have been performed by Graff only by measuring the dimensions of the sample and the weight. The Archimedes procedure provides a far better accuracy and is the preferable version. The main discrepancy though is due to the different  $c_p$ -curves that were found. The  $c_p$ -values used for calculations are plotted in Figure 20. Also the  $c_p$ -curves measured by Ekaterina Zoubenko and Liza Nuzman for the undoped m=1 and m= $\infty$  compositions at the same LFA machine are plotted there. It can be seen that all the curves vary in the form of their dependency of the temperature. All the single  $c_p$ -measurements obtained in this thesis and by Graff can be found in section 6.6.



Figure 20: Heat capacity as a function of the temperature. Red: Average of all the heat capacity measurements of this theses, this values are used for thermal conductivity calculations. Green: A single heat capacity curve measured by Graff that was used example wise for her thermal conductivity calculations. Blue: Two single heat capacities measured by K&L.

Taking into account that  $c_p$ -measurements are made indirectly, and are not supposed to be 100% repetitive the results seen in Figure 20 are in good accordance and also fit to literature values as found in [Srivastava and Gaur (2009)].

As it cannot be decided which  $c_p$ -values are the most accurate ones, in the following it will just be continued to work with the newly obtained data. The comparison that has been made example wise here for m=1 can be found in section 6.6 for m= $\infty$ , La-doped and Nb-doped Specimen.

#### 3.1.6.c Influence of Rock-Salt Layers

As already mentioned the most remarkable observation is the decrease of thermal conductivity when rock-salt layers are introduced, as can be seen in Figure 21.



Figure 21: thermal Conductivity as a function of the temperature a) La-doped; b) Nb-doped. pink: m=1. Black:  $m=\infty$ .

What also can be observed is that this effect vanishes for temperatures over 600-700 °C. This temperature area hasn't been observed by Graff: This is a new and very interesting observation, that will be discussed in the following.

## 3.1.7 Influence of Measuring Conditions on Thermal Diffusivity

The Interest in how different measuring conditions change the results in thermal diffusivity led to a series of experiments. In this chapter we are discussing the influence of atmosphere, porosity of the specimen and repeated LFA measurement. Please note, that here no changing influence of the heat capacity is taking place, as we are plotting the thermal diffusivity directly as it was measured.

#### 3.1.7.a Atmosphere

All LFA measurements have been carried out in Argon atmosphere in order to make them comparable to the SBA-measurements. Latter can currently only be operated under exclusion of oxygen, but the LFA can also operate in air atmosphere. As explained in section 1.5 the oxygen partial pressure has been found to have a big influence on the power factor of undoped m= $\infty$  specimen due to polaron interaction, so it is not far of imagination, that there might be some change to the thermal conductivity, too. Figure 22

shows the difference between the measurement in air- and Argon atmosphere for the m=1 undoped and La-doped specimen.



Figure 22: Thermal Diffusivity as a function f the temperature. a) La-doped; b) undoped. Purple: in Argon atmosphere. Green: in Air atmosphere. Dark green: first measurement. Light Green: Second measurement of the same specimen in the same conditions.

It can be observed for both kinds of specimen, that there is an increase of thermal conductivity in Air atmosphere. Whereas the increase is only small, but constant, for the La-doped specimen, thermal diffusivity rises almost four times at room temperature for the undoped specimen, but the effect vanishes slowly with increasing Temperatures. Changes can be due to the change of the O-concentration or changes in the stacking of the layers and therefore can vary for different compounds.

#### **3.1.7.b** Porosity

One specimen of the m=1, undoped composition didn't have a very good shape and was again grinded and pressed into a disc before the last sintering step of 24 hours was repeated. It turned out to have just about the same B\* (density without open porosity), but B (bulk density) was doubled. This means that the open porosity must have decreased immensely, almost disappeared during the process. Even though this change is not really explainable other than by chance, it is interesting to see the changes in thermal diffusivity, that it caused (Figure 23).



Figure 23: Thermal Diffusivity as a function of the Temperature. Purple: normal m=1 undoped sample. Dark red: reshaped m=1 undoped sample.

In contrary to Graff's forecast that the defect number density of the pores is too low to have a noteworthy influence on thermal conductivity, it can be seen that the elimination of open porosity leads to a quadruplicating of thermal conductivity values, at least at low temperatures. That doesn't necessarily have to mean that the pores actually decrease thermal conductivity. It can also mean that the measuring process is changed by the quality of the specimen surface and the changes occur because that.

#### **3.1.7.c Repeated Measurement**

For almost all samples thermal conductivity sample have been repeated at leased once (section 6.7) and all of them show similar trends to the example wise shown m=1 undoped specimen introduced in Figure 24.



Figure 24: Thermal Diffusivity as a function of the Temperature. All measurements carried out under the same conditions with the same sample. Purple: First measurement. Azure: Second measurement. Dark blue: third measurement.

For lower temperatures thermal diffusivity occurs to be lower after the first measurement, however for about 600 °C and higher it occurs to be higher. The third measurement is almost accurately the same as the second, which insures that there is a change in the specimen caused by the LFA measurement and no random changes or insecurities of the measurement procedure.

There are several mechanisms that can lead to this kind of change that will be discussed in the following. Further sintering of the specimen due to the temperature treatment during the LFA measurement seems to be quite unreasonable, as the specimen was treated for 24 hours at 1400 °C before and during the LFA heating process it reaches only as far as 1000 °C for a short period of time. In comparison this should not have a negotiable influence.

The possibility of a reaction of the carbon coating with the specimen has been discarded after DSC measurements of m=1 and m= $\infty$  undoped specimen, each once uncoated and coated: The curves didn't show any difference while heating just exactly with the same temperature process the specimen were undergoing during a LFA measurement (section 6.6.3).

Finally SEM micrographs of the fraction surface of a unmeasured specimen and the three times measured specimen were taken. The results are shown in Figure 25.

a) Before





Figure 25: Quanta SEM Micrographs of the fracture surface of specimen discs composition m=1 undoped. SEdetector. Magnification 3000. a: before any measurements were performed on this specimen, b: after three LFAmeasurements have been performed.

It seems like the porosity level or the shape haven't really changed (so no further sintering), but were the unmeasured specimen broke with a very smooth surface, the specimen with the LFA history broke at its grain boundaries. It can be hypothesized that there is some segregation of impurities on the grain boundaries, which changes the scattering mechanisms and also the fracture behavior. But this is unlikely, for the same reason as the additional sintering: The temperature and time frame are considerable low.

What should also be taken into account is the reducing atmosphere: CaMnO<sub>3</sub> is kinetically stable upon reduction only below ~500 °C [Schrade et al. (2014)], but the measurement went far above. Reduction wouldn't explain though why there are similar changes for the Specimen measured in Air, too. But coarsening of voids, which join to microcracks that cleave the grains, might.

## **3.2 Calculations and Discussion**

In this section the Results from 3.1 are utilized to calculate the power factor (3.2.1), the figure of merit (3.2.2) and the lattice thermal conductivity as a fraction of the measured

thermal conductivity (3.2.3). The results are discussed in terms of doping and RS-layer influence.

### **3.2.1 Power Factor**

The Power Factor was calculated as defined by Equation 2 and is plotted for all compositions in Figure 26. It defines the combined influence of the electrical conductivity and the Seebeck coefficient. The highest PF is obtained for the m=inf Ladoped specimen. The relation of the specimen towards each other is mainly dominated by the electrical conductivity: All the trends are the same. They also fit the literature values. [Lan et al. (2009); Wang et al. (2009)] except for the m=1 undoped specimen, that is found to have an considerable higher PF than expected, due to the high  $\sigma$ , that was measured.



Figure 26: logarithmic plotted Power Factor as a Function of the Temperature for all compositions. Pink: m=inf. Grey: m=1. Dark: undoped. Medium: La-doped. Light: Nb-doped.

### **3.2.2 Figure of Merit, ZT**

The figure of merit was calculated as defined by Equation 2 and is plotted for all compositions in Figure 27. The highest figure of merit, 0.15, is reached for the m=1 undoped specimen at 700 °C. It is the composition with the extraordinary and unexplained high electrical conductivities and one of the lowest thermal conductivities. For the lower temperatures the composition with the highest power factor, m= $\infty$  Ladoped, exhibits the highest ZT (at 700 °C 0.12. Graff: 0.095). These Vales are more reliable than the ones for m=1 undoped. Nb-doping here turns out to be a little bit less effective (at 700 °C 0.07. Graff: 0.1). The trends and relations in between the samples are similar to the trends of electrical conductivity the most: The layered structure of the RP-phases were able to decrease thermal conductivity by phonon scattering, but also decreased electrical conductivity by electron scattering, which leads to the overall effect, that the doped m=1 compounds have the lowest ZT values.



Figure 27: Figure of Merit plotted as a function of temperature. Pink: m=inf. Grey: m=1. Dark: undoped. Medium: la-doped. Light: Nb-doped.

In the literature it is a ZT of 0.1 reported for 6 at.% La-doping at 1000K [Wang et al. (2009)], which is slightly lower than our results for 4 at.% La-doping (0.12 at 1000K) and slightly higher than the results found by Graff (0.095). In case of Nb-doing for a similar solid state reaction manufacturing process a ZT value at 1060K of 0.16 (m= $\infty$ , 2% Nb) [Bocher et al. (2008)]can be found, which is higher than what we can support (0.07). About a third of the highest value reported for n-type TE-Materials at the same Temperature range (0.33 for Y-doped In<sub>2</sub>O<sub>3</sub>-ZnO) was reached. [Ohtaki (2010)]

## **3.2.3 Lattice Thermal Conductivity**

The thermal conductivity can be divided in lattice and electronic thermal conductivity, which is realised in this case by determining the electronic thermal cnductivity through the Wiedeman-Franz-Law (eq.4).



Figure 28: log. plotted thermal conductivity as a function of the temperature. a) m=1 undoped. b)  $m=\infty$  Ladoped. Filled circles: Total thermal conductivity. Empty triangles tip up: electronic thermal conductivity. Empty triangles tip down: lattice thermal conductivity.

The thermal conductivity is mainly determined by the lattice thermal conductivity. The electronic thermal conductivity makes an insignificant fraction of the overall thermal conductivity. For the La-doped Specimen it's two magnitudes higher, what can be easily explained by the increased number of charge carriers that contribute to the transport of thermal energy.

In Figure 29 it becomes very obvious how successfully the goal of decreasing lattice thermal conductivity was reached. It looks actually very similar to the thermal conductivity of SiO<sub>2</sub> glass and crystal shown in section 1.2.2, Figure 4. Whereas for the overall thermal conductivity the decreasing effect of the Rock-Salt layers has vanished for lower temperatures, this effect is here not observable anymore, except for a slight decrease of  $\kappa_e$  at higher temperatures. This means it was an effect of charge carrier injection that led to the narrowing of the curves. Unfortunately electrical conductivity could not be measured up to a temperature of 1000 °C, where the trend became very obvious, so that it cannot be approved, that the lattice thermal conductivity also stays constant for these high temperatures.



Figure 29: Lattice thermal conductivity as a function of the temperature. Pink: m=inf. Grey: m=1. Dark: undoped. Medium: la-doped. Light: Nb-doped.

Another effect that can be observed in Figure 29 is that the increase of thermal conductivity with doping is not only an effect of an increased number of charge carriers, which contribute to the transport of thermal energy, but apparently doping increase

somehow the phonon mean-free-paths. Lattice thermal conductivity was expected to stay constant or possibly decrease due to scattering on impurities (section 1.2.1). An explanation for the anomaly can be that alloying can change lattice periodicity.

In order to confirm the quality of separation the correlation in between the ZT and the quotient of thermal and electrical thermal conductivity is utilized (eq 5) in Figure 30.



Figure 30: Figure of Merit and the quotient of electron and phonon thermal conductivity as a function of the temperature for all compositions. Pink: m=inf. Grey: m=1. Dark: undoped. Medium: la-doped. Light: Nb-doped.

The Graphs of the figure of Merit and the Quotient look very similar, which confirms the possibility of separating the thermal conductivity with the introduced method. The difference for m=1 undoped can be explained by the exceptionally high Seebeck coefficient for this composition or simply due to the lack of validity of the electrical conductivity found for this composition.

# 4. Summary, Conclusions, and Recommendations for Further Research

Ruddlesden-Popper phases of CaO(CaMnO<sub>3</sub>)<sub>m</sub> with m=1 and m= $\infty$  have been produced successfully in the three types doped, 4% La-doped and 4% Nb-doped, as confirmed by X-Ray diffraction. The greatest ZT-values were obtained for m=1 undoped (0.15), m= $\infty$  La-doped (0.12) and m= $\infty$  Nb-doped (0.07) at 1000 K. The m= $\infty$  doped results are typical

for calcium-manganite compounds and similar to Graff's results, but still low compared to the highest ZT-values which were obtained for other n-type Oxide TE-materials by nano compositions (0.6 - 0.7).[He et al. (2011)]

It has been approved, that it is possible to decrease the lattice thermal conductivity by scattering phonons on Rock-Salt layer interfaces in the  $CaO(CaMnO_3)_m$  system. However, at the same time electron scattering increased too, so that the Figure of Merit was finally reduced by the procedure. Doping was shown to improve electrical conductivity as expected, but also increased lattice thermal conductivity, which is not explainable yet.

La-doping turned out to be more effective than Nb-doping for the m=1 specimen, but less effective for  $m=\infty$ . This non-conformity can also not be explained by the performed characterizations.

In order to solve these two problems, attempts have been made to prepare some TEM samples and should be further continued in the future. TEM micrographs can hopefully [Kim et al. (1990)]show how the doping atoms fit into the crystal lattice exactly and how they are distributed in the microstructure. For example, whether they prefer to occupy Ca-places in the perovskite or in the rock-salt phase or both equally. DFT calculations can also help with this task.

The current way of doping, mixing, grinding and diffusion during the sintering for putting additives into solid solution has been shown to occasionally cause irregular contribution or small unreacted grains. [Schubert and Petzow (1988)] If TEM analyses should show that this happens in some of our samples, Sol-Gel processes or coprecipitation processes can lead to further improvement. [Kim et al. (1990)]

Interestingly, the compositions that showed cracked surfaces on the SEM pictures and a big discrepancy in open porosity for the two procedures Archimedes principle and SEM picture analysis are the ones that exhibit low Figure of Merits. This suggests that the preparation procedure and the thereby obtained mechanical cohesion of the specimen have a negotiable influence of the thermoelectric quality.

Also for such low-density specimens, large deviations in porosity levels are to be expected. This is a possible reason why complete correspondence to Graff's results, could not be obtained. For better repeatability it's necessary to reach porosity levels close to the theoretical one. This will also enable to gain higher conductivities. Possible solutions for better preparation methods are SPS or hot-pressing

Another improvement can be done by employing "chimie douce" for the powders before sintering, which was applied by Bocher et. al successfully and led to a doubling of ZT for Nb-doped CaMnO<sub>3</sub>. The preparation method of "chimie douce" requires to put Ca(NO<sub>3</sub>)<sub>2</sub>  $\cdot$ 4H<sub>2</sub>Oand Mn(NO<sub>3</sub>)<sub>2</sub>  $\cdot$ 4H<sub>2</sub>O into solution for homogenization before producing the complex precursors by stepwise calcination.[Bocher et al. (2008)]

The Influence of the oxygen partial pressure was not incorporated enough in this thesis, even though it became obvious from literature research for m=inf undoped specimen (section 1.5) and changes in thermal diffusivity (section 3.1.6.a) that it influences all obtained data: The power factor will most likely increase and thermal conductivity could increase in air atmosphere.[Schrade et al. (2014)] also it might influence the stacking of the layers and the crystal structure. That means that for application in air atmosphere the Figure of Merit might change. For further research it would be helpful to change the physical measuring conditions for the SBA and LFA in order to be able to determine the power factor also for determined oxygen partial pressures and find out about the decencies of the thermoelectric properties also for the layered specimen.

Discrepancies in the thermal diffusivity for the repeated measurement were found but could not be fully explained yet. A detailed characterization of the specimen before and after the measurement including nano- and microstructure, as well as surface analysis will help understanding the changes within the specimen. This is a point of interest because it might restrict the field of application of the material, if there are corrosive changes within it at certain atmosphere and temperature conditions.

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# 6 Appendix

This chapter is attached to the theses as it contains all the results and information which are not necessary for the understanding or the reading process, but are necessary to deliver for the sufficiency of the results. Structure-wise it is build parallel to chapter 3.1.

## 6.1 X-ray Diffraction (XRD) Analysis

Table 6: Quotient of Intensity of the biggest Impurity peak and biggest identified peak for all compositions.

	m	q=I/I <sub>max</sub> [%]
Undoned	1	1.5
Chuopeu	00	1.6
Nb-doped	1	1.6
Tu-uopeu	00	0.5
La-doned	1	3.0
La-uopcu	$\infty$	2.4

## 6.2 Scanning electron microscopy Electron Microscopy (SEM) Analysis



Figure 31: Grain Size determined by SEM-Picture. Blue: m=∞. Red: m=1. Error bar: standard derivation.

## **6.3 Archimedes Density and Porosity**



Figure 32: Density without open Porosity. Blue: m=10. Red: m=1. Error bar: Gauss error



Figure 33: Bulk Density. Blue: m=∞. Red: m=1. Error bar: Gauss error.



Figure 34: Petrol: Bulk Porosity. Brown: closed Porosity. Error Bar: Gauss error.

## **6.4 Electrical Conducticity**



Figure 35: Electrical conductivity as a function of the Temperature. m=∞. Influence of doping: Black: undoped. Blue: la-doped. Red: Nb-doped.



Figure 36: Graff. Electrical conductivity as a function of the Temperature.  $m=\infty$ . Influence of doping: Black: undoped. Blue: la-doped. Red: Nb-doped.



Figure 37: Electrical conductivity as a function of the Temperature. m=1. Influence of doping: Black: undoped (measured twice). Blue: la-doped. Red: Nb-doped.



Figure 38: Graff. Electrical conductivity as a function of the Temperature. m=1. Influence of doping: Black: undoped. Blue: la-doped. Red: Nb-doped.



Figure 39: Electrical conductivity as a function of the Temperature. Nb-doped. Influence of RS-layers: Pink:  $m=\infty$ . Black: m=1.



Figure 40: Graff. Electrical conductivity as a function of the Temperature. Nb-doped. Influence of RS-layers: Red:  $m=\infty$ . Black: m=1.


Figure 41: Electrical conductivity as a function of the Temperature. La-doped. Influence of RS-layers: Pink:  $m=\infty$ . Black: m=1.



Figure 42: Graff. Electrical conductivity as a function of the Temperature. La-doped. Influence of RS-layers: Red:  $m=\infty$ . Black: m=1.

## 6.5 Seebeck Coefficient



Figure 43: Seebeck coefficient as a function of the Temperature. m=1. Influence of doping: Black: undoped. Blue: Ladoped. Red: Nb-doped.



Figure 44: Graff. Seebeck coefficient as a function of the Temperature. m=1. Influence of doping: Black: undoped. Blue: La-doped. Red: Nb-doped.



Figure 45: Seebeck coefficient as a function of the Temperature. m=∞. Influence of doping: Black: undoped. Blue: Ladoped. Red: Nb-doped.



Figure 46: Graff. Seebeck coefficient as a function of the Temperature.  $m=\infty$ . Influence of doping: Black: undoped. Blue: La-doped. Red: Nb-doped.



Figure 47: Seebeck coefficient as a function of the Temperature. La-doped. Influence of RS-layers: Pink: m=∞. Black: m=1.



Figure 48: Graff. Seebeck coefficient as a function of the Temperature. La-doped. Influence of RS-layers: Red:  $m=\infty$ . Black: m=1.



Figure 49: Seebeck coefficient as a function of the Temperature. Nb-doped. Influence of RS-layers: Pink: m=∞. Black: m=1.



Figure 50: Graff. Seebeck coefficient as a function of the Temperature. Nb-doped. Influence of RS-layers: Red: m=∞. Black: m=1.

# 6.6 Thermal Conductivity



Figure 51: Range of all thermal conductivities measured for all the compounds over the whole Temperature Range.

### 6.6.1 Heat Capacity



Figure 52: All heat capacity Values measured as a function of the temperature. Pink and black: Directly measured. Orange: Average of all measurements, that was used for thermal conductivity calculation.



Figure 53: Graff. Heat capacity as a function of the temperature. Selected measurements. m=5, Nb-doped was selected for thermal conductivity calculations.

#### 6.6.2 New Calculation of Graff's Results



Figure 54: Thermal conductivity as a function of the Temperature. m=1. Doping influence: Black: undoped. Blue: Ladoped. Red: Nb-doped.



Figure 55: Graff. Thermal conductivity as a function of the Temperature. m=1. Doping influence: Black: undoped. Blue: La-doped. Red: Nb-doped.



Figure 56: Graff + New. Thermal Diffusivity as a function of the Temperature. m=1. Doping influence: Black: undoped. Blue: La-doped. Red: Nb-doped. Filled: new. Empty: Graff.



Figure 57: Graff (New  $c_p$  and B) + New. Thermal conductivity as a function of the Temperature. m=1. Doping influence: Black: undoped. Blue: La-doped. Red: Nb-doped. Filled: New. Empty: Graff (New  $c_p$  and B).



Figure 58: Thermal conductivity as a function of the Temperature. m=inf. Doping influence: Black: undoped. Blue: La-doped. Red: Nb-doped.



Figure 59: Graff. Thermal conductivity as a function of the Temperature.  $m=\infty$ . Doping influence: Black: undoped. Blue: La-doped. Red: Nb-doped.



Figure 60: Graff + New. Thermal Diffusivity as a function of the Temperature.  $m=\infty$ . Doping influence: Black: undoped. Blue: La-doped. Red: Nb-doped. Filled: new. Empty: Graff.



Figure 61: Graff (New  $c_p$  and B) + New. Thermal conductivity as a function of the Temperature.  $m=\infty$ . Doping influence: Black: undoped. Blue: La-doped. Red: Nb-doped. Filled: New. Empty: Graff (New  $c_p$  and B).



Figure 62: Thermal conductivity as a function of the Temperature. La-doped. RS-layer influence: Pink: m=inf. Black: m=1.



Figure 63: Graff. Thermal conductivity as a function of the Temperature. La-doped. RS-layer influence: Pink:  $m=\infty$ . Black: m=1.



Figure 64: Graff + New. Thermal Diffusivity as a function of the Temperature. La-doped. RS-layer influence Pink:  $m=\infty$ . Black: m=1. Filled: new. Empty: Graff.



Figure 65: Graff (New  $c_p$  and B) + New. Thermal conductivity as a function of the Temperature. La-doped. RS-layer influence Pink:  $m=\infty$ . Black: m=1. Filled: new. Empty: Graff.



Figure 66: Thermal conductivity as a function of the Temperature. Nb-doped. RS-layer influence: Pink: m=inf. Black: m=1.



Figure 67: Graff. Thermal conductivity as a function of the Temperature. Nb-doped. RS-layer influence: Pink: m=inf. Black: m=1.



Figure 68: Graff + New. Thermal Diffusivity as a function of the Temperature. La-doped. RS-layer influence Pink:  $m=\infty$ . Black: m=1. Filled: new. Empty: Graff.



 $\label{eq:Figure 69: Graff (New \ c_p \ and \ B) + New. \ Thermal \ conductivity \ as \ a \ function \ of \ the \ Temperature. \ Nb-doped. \ RS-layer \ influence \ Pink: \ m=\infty. \ Black: \ m=1. \ Filled: \ new. \ Empty: \ Graff.$ 

6.6.3 Influence of Measuring Conditions on Thermal Diffusivity



Figure 70: Thermal diffusivity as a function of the temperature. m=1, La-doped. Measurement repeated three times for the same specimen. Purple: 1<sup>st</sup> time- Blue: 2<sup>nd</sup> time. Azure: 3<sup>rd</sup> time. Arrows: Guidance for the Ayes.



Figure 71: Thermal diffusivity as a function of the temperature.  $m=\infty$ , Nb-doped and  $m=\infty$ , undoped. Measurement repeated two times for the same specimen. Purple: C undoped. Pink:  $2^{nd}$  time  $m=\infty$ , undoped. Dark Azure:  $m=\infty$ , Nb-doped Azure:  $2^{rd}$  time  $m=\infty$ , Nb-doped. Arrows: Guidance for the Ayes.



Figure 72: Thermal diffusivity as a function of the temperature. m=1, undoped. Purple: First measurement in Argonatmosphere. Green: Measurement in air-atmosphere.



Figure 73: Thermal diffusivity as a function of the temperature. m=1, La-doped. Purple: First measurement in Argonatmosphere. Green: Measurement in air-atmosphere.

#### 6.6.4 DSC Measurement



Figure 74: Heat flow, measured by the DSC, as a function of temperature. m=1, undoped (red) and  $m=\infty$  undoped (blue) each once coated (light) and once uncoated (dark).