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Growth and thermoelectric properties of CaMnO_3 -based thin films

Erik Ekström

Thin Film Physics Division
Department of Physics, Chemistry and Biology (IFM)
Linköping University, SE-581 83 Linköping, Sweden
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Abstract

The field of thermoelectrics started in early 19th century. Since the discovery of the Seebeck effect and the Peltier effect, thermoelectric modules have found their way into, mostly, niche applications such as radioisotope thermoelectric generators on space missions. Thermoelectric modules can also be used for cooling, utilizing the Peltier effect.

Thermoelectrics are promising materials due to the operation nature of the modules. That is, they have no moving parts, no exhaust, long lifetime without maintenance, features that make them attractive for many applications. Despite these promising properties, thermoelectric modules are mostly used in niche applications. The main reason for this is conventional modules with the highest efficiency are commonly made of expensive and/or rare elements which prevents mass production.

To tackle this problem, new materials are investigated to find a module that can be made widely available. Oxides are one possibility, where an added benefit is that they are chemically stable even at elevated temperature. The perovskite CaMnO_3 is one of the more promising oxides, with elements that are abundant on earth and cheap. The material does suffer from low electrical conductivity which results in a low electrical conductivity and efficiency. A substantial effort has been put in to increase the efficiency of CaMnO_3 , but it still needs improvement.

In my thesis, I have investigated the CaMnO_3 system. CaMnO_3 was synthesized using co-reactive RF-magnetron sputtering and post annealing. The synthesis method is already known but has not been used for deposition of perovskites. I have also demonstrated that this synthesis method can be used to dope CaMnO_3 with niobium at appropriate levels for enhancing the efficiency.

Preface

This licentiate thesis is part of my PhD studies in the Energy Materials unit in the Thin Film Physics Division at the Department of Physics, Chemistry, and Biology (IFM), at Linköping University.

I am grateful for the financial support from Swedish Foundation for Strategic Research (Future Research Leaders grant to my supervisor Per Eklund) and the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU No. 2009 00971). The European Research Council, the Swedish Research Council, and the Knut and Alice Wallenberg Foundation are also acknowledged for their financial support to co-workers that has been highly involved in the project. I also acknowledge ÅForsk and Kungliga Vetenskapsakademien (KVA) for financial support to conferences and travel costs and CeNano for financially supporting my collaboration with the Theoretical Physics group at IFM.

During the course of research underlying this thesis, I was enrolled in *Agora Materiae*, a multidisciplinary doctoral program at Linköping University, Sweden.

Populärvetenskaplig Sammanfattning

Med dagens utveckling av teknologi ökar behovet av elektricitet. Många teknologier är små saker som behöver egna energikällor t.ex. sensorer. Dessa kan sitta på människokroppen, i datorer, i olika industrier och andra miljöer. Det de har gemensamt är att alla behöver en tillförlitlig kraftkälla som i många fall behöver fungera utan något underhåll samt ta lite plats.

Ett annat problem i samhället är det stora slöseriet med energi i form av spillvärme, det vill säga en oönskad restprodukt, från i stort sett alla processer. Denna värme är i många fall helt outnyttjad och om man kunde ta till vara på denna värme skulle effektiviteten av många processer kunna ökas.

Jag har undersökt material som skulle kunna lösa dessa problem, nämligen termoelektriska material. Sådana material har förmågan att omvandla värme till elektricitet och det som driver denna förmåga är Seebeck-effekten, uppkallad efter Thomas Seebeck som upptäckte den i början av 1820-talet. De fungerar genom att materialet har en varm och en kall sida. På den varma sidan rör sig elektronerna snabbare än på den kalla sidan. Denna skillnad resulterar i att fler snabba elektroner kommer röra sig mot den kalla sidan än tvärt om och en ström/spänning har skapats i materialet. Ju bättre materialet är på att upprätthålla värmeskillnaden, leda elektricitet samt har hög Seebeck-koefficient, desto högre verkningsgrad har materialet som termoelektriskt material. Tyvärr är det få material som leder värme dåligt och elektricitet bra samt har hög Seebeck-koefficient och därför är många material ineffektiva som termoelektriska material.

Jag har tillverkat kalcium-mangan-oxid (CaMnO_3) filmer genom en sputtringsprocess och förbättrat dess termoelektriska egenskaper genom att byta ut små mängder mangan mot niob (Nb). Effekten av detta är att det finns flera fria elektroner som ökar den elektriska ledningsförmågan hos CaMnO_3 filmerna vilket i sin tur förbättrar dess termoelektriska egenskaper.

Jag har också fördjupat mig i tekniken röntgendiffraktion (x-ray diffraction, XRD). Denna teknik är ett kraftfullt verktyg i materialforskning för att mäta avstånd mellan atomplan i kristallina material. Genom att mäta avstånden mellan atomplanen går det att analysera strukturen, hur atomerna är arrangerade, samt i viss utsträckning bestämma vilka element som finns i materialet.

List of Included Papers

Paper I

Thermoelectric properties and formation of CaMnO_3 thin films by annealing $(\text{Ca}_{0.5}\text{Mn}_{0.5})\text{O}$ films grown on Al_2O_3 substrates.

Authors: E. Ekström, A. le Febvrier, F. Eriksson, P. Eklund and B. Paul.

Manuscript in final preparation.

Author's contribution:

I performed XRD measurements, summarised and analysed the data, and wrote the manuscript.

Paper II

Growth, characterization, and thermoelectric properties of $\text{Ca}(\text{Mn}_{1-x}\text{Nb}_x)\text{O}_3$.

Authors: E. Ekström, A. le Febvrier, F. Bourgeois, B. Lundqvist, J. Klarbring, S. I. Simak, F. Eriksson, B. Paul, and P. Eklund.

In manuscript.

Author's contribution:

I planned the study and coordinated the experiments. I performed all depositions and all the XRD, SEM, EDX, Seebeck coefficient and four-point probe measurement. I wrote the manuscript.

Acknowledgment

First of all, I would like to thank **Per Eklund** for giving me the opportunity to perform my PhD studies in the energy materials group. His input and suggesting throughout my thesis are invaluable for me.

Fredrik Eriksson, one of my co-supervisors, has been particularly helpful in my work to deepen my knowledge in the field of x-ray diffraction.

Biplab Paul, also one of my co-supervisors, was the one to introduce me to sputtering and CaMnO_3 . I am also thankful for the many ideas he has on future and ongoing projects.

My colleague **Arnaud le Febvrier** has helped me a lot with my daily work giving small, but valuable, tips on how to do all kind of various science related things, such as analysis, experiment design and so on.

During my studies, I have had a CeNano collaboration with **Johan Klarbring**. He has been a helpful co-worker who has been a good help for understanding and making calculations on the CaMnO_3 system. Without his work, I would not know as much as I do today.

I thank the **9 o'clock coffee group**, even though we are fewer than we used to be, I still enjoy the discussions and breaks.

There are many more that I would like to mention, but the list would be too long, but I thank all my other **collaborators** and **colleagues** in the **Thin Film Physics Division**, and **IFM**.

I thank all my **friends** and my **family** for helping me take my mind off work on my free time.

Last but not least, my wife **Hanna Ekström** deserves my thanks for being supportive during my studies.

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1 INTRODUCTION AND RESEARCH QUESTION

The field of thermoelectrics started in 1821 with the rediscovery of the Seebeck effect by Thomas Johann Seebeck.¹⁻⁴ The effect was originally discovered by Alessandro Volta in 1794⁵ but received no attention at the time. The effect observed by Seebeck was small and little research was performed in the field until the 1950s when improved thermoelectric materials were synthesized from compound semiconductors.¹ A breakthrough in the thermoelectric field was achieved when the first radioisotope thermoelectric generator was used in the first space mission, Transit IV-A, in 1961.¹ Nevertheless, we are still not seeing thermoelectric technology taking a large role in power generation, even after its successes in remote power generation. This is mainly due to low efficiency and the fact that the best materials are tellurides for low- to mid-range applications and Si-Ge for high temperature applications.⁶ Tellurides are not suitable for mass production because they are toxic, expensive and, the biggest problem, rare on earth.⁷ Si-Ge working temperature range is in a range where there are very few applications.^{8,9}

Today's society is heavily reliant on electricity and the demand is predicted to increase.¹⁰ Researchers are looking into many different solutions to produce cheap and renewable energy that has low impact on the environment. Another way to tackle this problem is to increase the efficiency of all technologies. More than 70 % of the world's energy consumption is lost due to heat.¹¹ Part of it could be recovered using thermoelectric modules, which can generate electrical power from a heat gradient across them.

Thermoelectric modules are not only useful for converting heat to energy or vice versa. They can also be used as the working material for other applications, e.g. as a thermocouple which measures the temperature, cold trap¹² in ultra-high vacuum systems and hydrogen gas sensors¹³ where a reaction on the surface of the sensor generates heat which can be correlated with the amount of hydrogen in the air.

A thermoelectric material is characterised by a high Seebeck coefficient, high electrical conductivity and low thermal conductivity. These demands on material properties do not naturally draw oxides to mind, but they gained interest in the 1990's¹⁴ when some oxides, e.g. $\text{In}_2\text{O}_3\text{-SnO}_2$ and alloyed CaMnO_3 , were discovered to have good thermoelectrical properties. Thermoelectrics overall have had an increase in interest in the last 15-20 years, which is due to improved synthesis methods, allowing researchers to control the materials on the nano to atomic level. Other contributions to the increased interest is the possibility to model complex materials and also characterize them experimentally.¹⁵

Because of above mentioned limitations of today's conventional thermoelectric materials, and benefits of using oxides, many oxides have been researched for thermoelectric applications. Out of these, most are p-type, with n-type materials in general performing worse. To make an all oxide module viable, the n-type material has to be improved.

Motivated by this general background, the research question investigated in this thesis is how to produce oxides of the perovskite type using co-sputtering combined with post synthesis annealing with special attention to the n-type calcium manganite (CaMnO_3). I have also shown that it is possible to introduce small amounts of niobium (Nb) in the system which is known to increase the electrical conductivity.

Additionally, part of my PhD studies is to specialize in x-ray measurement techniques. As a part of this I am involved in the education of other researchers for the operation of the department's diffractometers and for the evaluation of measured x-ray data. I have also been engaged in wide-angle x-ray scattering measurements at the synchrotron radiation facility Petra III in Hamburg. To reflect this work, a chapter is devoted to basic theory about x-rays, with a focus on x-ray diffraction.

2 BACKGROUND ON CaMnO_3

2.1 HISTORY OF OXIDES FOR THERMOELECTRICS

The research on oxides as candidates for thermoelectric materials gained momentum in the late 1990's, for instance, Na_xCoO_2 in 1997¹⁶ and $\text{Ca}_3\text{Co}_4\text{O}_9$ in 2000.¹⁷ Many other oxides, such as layered cobalt oxides (Ca_xCoO_2 , CaCo_2O_5 , and the other above mentioned), layered oxychalcogenides (BiCuSeO), ZnO , In_2O_3 , perovskite oxides (SrTiO_3 , CaMnO_3) to name a few,^{6,7,14,18} have been researched since.

The p-type oxides are the best performing so far with reported dimensionless figure of merit (ZT) of 1.1 at 923 K for doped BiCuSeO ¹⁹ and 0.5 at 1000 K for $\text{Ca}_3\text{Co}_4\text{O}_9$.²⁰ The ZT depends on the Seebeck effect, electrical conductivity, absolute temperature and thermal conductivity and is explained more in detail in chapter 7. There is therefore a need to develop n-type thermoelectric oxides that has similar ZT as the p-type oxides. As of now, the ZT for n-type oxides typically does not reach above 0.35 at around 1000 K.^{21,22} The focus on this paper is on CaMnO_3 which is a well-known perovskite studied for its magnetic properties, but research on thermoelectric properties and their enhancement is not as well explored. Nevertheless, there are studies performed mainly on the effect of alloying CaMnO_3 with the purpose to substitute on either the A (Ca) or B (Mn) site.

2.2 THE MATERIAL SYSTEM CaMnO_3

In this thesis, the slightly distorted perovskite CaMnO_3 is studied. It has been studied in detail because of its magnetic properties before attention for its thermoelectric properties was paid, starting in 1995.²³ After research started, on its thermoelectric properties, several attempts has been made to improve the ZT of CaMnO_3 . Most commonly by doping on the A or B site, or more recently co-doping.

The synthesis method used in this thesis consist of a two-step approach where (Ca,Mn)O, figure 2.1 (a), was grown on M-plane sapphire using RF magnetron reactive co-sputtering from elemental Ca and Mn targets. The as deposited films were annealed to induce a phase transformation to CaMnO_3 , figure 2.1 (b). The formed CaMnO_3 is in a slightly distorted perovskite phase with space group Pnma. The distortions are commonly described by tilts of the MnO_6 octahedra as seen in figure 2.1 (b).

Fig. 2.1. Structure of (Ca,Mn)O (a) and CaMnO_3 (b).

The most common synthesis method of CaMnO_3 is a solid state reaction, but there are studies where other synthesis methods are explored, such as; a gas phase reaction synthesis,²⁴ chemical coprecipitation method,^{25,26} glycine–nitrate synthesis,^{27,28} electrostatic spray deposition,²⁹ and soft chemistry synthesis.^{30,31} Many of these synthesis techniques have proven successful for synthesising CaMnO_3 with improved ZT compared to the solid state reaction method. One common nominator is denser films or finer grain-structure.

Previous research reports thermoelectric properties as the following:

- resistivity 20-0.12 Ωcm .³²⁻³⁴
- Seebeck coefficient -200 to -550 μVK^{-1} .^{23,33-35}

- thermal conductivity 2.8-4.1 Wm⁻¹K⁻¹.^{23,32,34,35}

The resistivity, compared to conventional thermoelectric materials, is the main issue for this material. A substantial effort has been made to decrease the resistivity by alloying the material on either the Ca or Mn site, or both. Example of tested elements on the Ca site are La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Bi³⁶⁻⁴¹ and Mo, Ru, Nb, Ta, W and Si^{33,34,42-45} on the Mn site. Wang et. al. concluded that the size and weight difference between the Ca²⁺ and alloyant (X³⁺) plays a role on the thermoelectric properties. The conductivity is governed by polaron hopping in the Mn⁴⁺-O-Mn⁴⁺ structure. By introducing X³⁺, Mn³⁺ is formed and the Mn³⁺-O-Mn⁴⁺ framework has a lowered resistivity. In the process, the Seebeck coefficient is lowered due to increased amount of charge carriers. The thermal conductivity is insensitive to carrier concentration as the largest contribution is from the lattice vibrations. Therefore, the conductivity is sensitive to both distortion in the lattice and weight differences of atoms. To lower the conductivity the alloyant should be larger/smaller than the parent element and heavier/lighter, where mass difference is the dominating factor.

A few attempts to alloy on both the Ca²⁺ and Mn⁴⁺ site at the same time has been done. However, so far, the results have not improved compared to single alloying.⁴⁶⁻⁵¹

3 PHYSICAL VAPOUR DEPOSITION

Physical vapour deposition (PVD) covers a wide variety of deposition techniques, e.g. cathodic arc deposition, evaporative deposition, pulsed laser deposition and sputtering. All PVD techniques generally use a condensed material which is turned into vapour and transported to a substrate where it condenses. This chapter will focus on sputtering as it is the technique used in the thesis.

3.1 VACUUM SYSTEM

A high vacuum system is essential for PVD. The vacuum is not only needed for a clean environment, it is also needed for ignition, at relatively low voltage (100-1000 V), of the plasma^a. The vacuum system often consists of two chambers, one main chamber for the process and the other (load-lock chamber) for loading and unloading samples into the main chamber. The chambers also have different instruments connected to them, e.g. pressure gauges, vacuum pumps, gas analysers and more. The vacuum chamber used in this thesis is described in detail elsewhere⁵² and a picture of it is shown in figure 3.1.

3.2 SPUTTERING

The sputtering process used in this work is called reactive radio frequency magnetron sputtering. To explain how this works, I will split this subchapter into 4 sections about DC sputtering, magnetron sputtering, reactive sputtering, and finally radio frequency (RF) sputtering.

^a Plasma is one of the four states of matter and, probably, the most common in the universe. Ionised gas(es), charged ions and free electrons make up the plasma. The plasma is quasineutral, meaning the plasma is positively or negatively charged at micro-scale but neutral at the macro-scale.

Fig. 3.1. Picture of the PVD system used. Photo by the author.

3.2.1 DC Sputtering

The PVD process requires a vacuum where a gas is inserted, typically argon (Ar). This gas is turned into a plasma by applying voltage between the cathode and anode. Stray electrons are accelerated towards the anode (substrate) and collisions with the gas produces ions and electrons by electron impact ionisation, eq. 3.1.⁵³

This in turn creates more collisions and a cascade of these events is the mechanism behind the plasma ignition. As an added effect the created ions are accelerated towards the cathode (target material) where the impact knocks out both the target material and more electrons which further feeds the plasma. The sputtered material moves in straight lines and collides with constituents in the plasma, the rate of collisions depends on the mean free path of the sputtered

material, and finally hits the chamber walls or, a small percent, hits the substrate where the film develops.

The sputtering technique used in early sputtering is called diode sputtering. It has the benefit of sputtering from the whole target whereas magnetron sputtering does not, explained in next sub-chapter. However, it has some significant drawbacks which results in magnetron sputtering as the preferred technique today. The sputtering rate is much lower compared to magnetron sputtering. Typically a few 100 Å/min for metals with diode sputtering compared to up to μm/min for some metals using magnetron sputtering.⁵³ The reason for the increase in sputtering rate is explained in the next chapter.

3.2.2 Magnetron Sputtering

The magnets in magnetron sputtering are put behind the target material. In a lab system, they are typically cylindrical and most commonly placed in an outer circle with one magnet, or solid piece of iron, in the middle as demonstrated in figure 3.2 (a). The central magnet and outer magnets have opposing poles creating a magnetic field as visualized in figure 3.2 (b) and (c). The effect of this magnetic field is that electrons are confined close to the target which in turn enhances the plasma density. The densification of the plasma greatly enhances the sputtering rate and forms a race track on the target. This means that more material will be sputtered away than for diode sputtering and a lower operating sputtering gas pressure is achievable, increasing the chance for the sputtered species to reach the substrate while also retaining more of its original energy. All these effects result in a high deposition rate and faster film growth. The magnets are often configured in an unbalanced type II mode, where the middle magnet is weaker than the other ones, shown in figure 3.2 (b). The reversed configuration (type I) is shown in 3.2 (c). Type II configuration is more common because this allow some electrons to escape the magnetic field of the magnetron and move closer to the substrate where they can ionise sputtering gas atoms. By applying a bias voltage to the substrate, these ions can be

attracted to the growing film surface to stimulate the adatom mobility and hence the microstructural evolution of the film.

Fig. 3.2. Schematic view of magnetron top view (a) and a slice of the magnetron and the formed magnetic field from type II configuration (b) and type I configuration (c).

3.2.3 Reactive Sputtering

For reactive sputtering, a mixture of Ar and O₂ gas was used in the present work. Other common reactive gases are N₂, C₂H₂ and CH₄ used for deposition of nitrides and carbides, respectively. The addition of O₂ allows the direct deposition of the desired oxide film on the substrate. However, the presence of reactive gas in the chamber drastically reduces the sputtering rate due to so called poisoning of the target. The target readily reacts with the reactive gas, forming an electrically insulating layer on the target surface, which dramatically reduces the sputtering rate. The relation between poisoning of a Ca target and O₂ flow was studied by investigating the target voltage as a function of O₂ flow, as shown in figure 3.3.

Fig. 3.3. Poisoning study on Ca target.

At O_2 flow below 0.5 sccm the target is in metallic mode. Above 0.5 sccm, the target undergoes a rapid change to poisoned mode, as due to the complete oxidation of target surface. This results in steep change of target voltage to a saturated value. However, with further reduction of O_2 flow the decrease in target voltage does not follow the same path as before, resulting in hysteresis as seen in figure 3.3. The challenge with reactive sputtering is to control the stoichiometry of the film. Sputtering in the transition region, generally, results in high quality films with high sputtering rates. This is not possible in our system as the process is unstable and the target is easily poisoned. Small fluctuations of O_2 flow can result in target poisoning, and the recovery of the target to metallic mode becomes impossible without reducing the oxygen flow. However, in industrial applications, the use of feedback control system enables the process to be stable in the transition region.

3.2.4 Radio Frequency Sputtering

Radio frequency (RF) is a sputtering technique where, instead of a DC current, an alternating current (AC) is used. If a frequency of a few MHz is used the electrons is moving back and forth as described below and 13.56 MHz is a reserved frequency for AC sputtering. At low frequencies, roughly below 1 MHz, the ions have enough time to DC sputter for each half cycle meaning that the target and

substrates alternate between being a cathode and an anode which is unwanted during sputtering. The AC prevents charge build-up on the target and is therefore commonly used when sputtering from isolating targets. To understand the mechanisms of RF sputtering, it is important to remember that the plasma consists of free electrons and ions, and electrons are much more mobile (lighter) than ions. That means electrons readily response to an AC. The fast electrons move back and forth with the AC frequency and this movement causes collisions as described in 3.2.1. Therefore, the plasma does not depend on electrons generated from the ion bombardments on the target to stay ignited. The fast movement of electrons also facilitates the self-biasing^b, leading to ion bombardment everywhere. This is, however, not a problem because the whole chamber acts as an anode and the size difference between the target (cathode) and the rest of the chamber (anode) is large, i.e., the energy on the anode is divided over a large area which leads to minimal sputtering from the substrate/growing film.

Despite the advantages, RF sputtering has some drawbacks, it requires expensive equipment, the sputtering rate is low, and it can be difficult to stay in the desired sputtering regime.

3.3 FILM GROWTH

The microstructural evolution during film growth is very important since it highly affects the end results of the film, e.g. its mechanical, electrical and optical properties. There are three different stages of the film growth:

1. Condensation and nucleation
2. Coalescence
3. Continuous growth

^b Self-biasing occurs because electrons are faster than ions. This results in more electrons hitting the target, walls, substrate and basically everywhere than ions do. This generates a negative potential called bias or self-bias in this case.

In the first step, the adatoms condensate on the surface and either the adatoms recombine with the gas or diffuses on the surface and merges with other adatoms/clusters and eventually forms a stable nucleus, figure 3.4.

Fig. 3.4. Adatom recombination and nucleation and different growth modes.

The second step is coalescence, where the islands merge together forming larger islands until the surface is completely covered. During this process, adatoms can land on the islands or on the exposed surface. There are three growth modes that can occur, Volmer-Weber, Frank-van der Merwe and Stranski-Krastanov, depending on the energy of the adatoms, bonding energies and the diffusion barriers. If the tension between adatom and substrate is high compared to adatom and adatom, the resulting growth mode is Volmer-Weber, meaning 3D growth of the islands. If the case is reversed the film is grown layer by layer as in the Frank-van der Merwe mode. The last mode, Stranski-Krastanov, is somewhere in between the two extremes. The growth is in layer by layer mode until a critical energy is built up due to substrate-film lattice mismatch and 3D growth begins. The energy of the adatoms can be controlled by the deposition temperature, sputtering gas pressure, and/or the ion bombardment by adjusting the applied substrate bias voltage. Figure 3.5 (structure zone diagram of Anders) illustrates the effect of an

increasing homologous temperature^c and increasing kinetic energy of arriving species on the microstructure of the film.^{54,55} At low temperatures, the film is grown in a hit and stick mode where little or no diffusion occurs, and the resulting film is amorphous and under-dense. As the substrate is thermally energised, the adatoms can diffuse and form stationary grains in relation to the substrate (zone T). Competing growth occurs and the final film is structured with a preferred orientation. In zone II, sufficient energy is provided to the grains to migrate, where minimization of energy is the driving force, and thus single crystals can be formed.

Fig. 3.5. Microstructural evolution as a function of the homologous temperature and kinetic energy of arriving particles. From ref. ⁵⁵ © Elsevier B.V., reproduced with permission.

^c Homologous temperature is the temperature of a material divided by its melting temperature in Kelvin.

3.4 PHASE TRANSFORMATIONS

The phase of a system is governed by the Gibbs free energy (G). Basically, the system strives to lower its global Gibbs free energy. An example of a phase change can be described by figure 3.6. The system is in metastable state 1 and needs a certain energy, G_e , to overcome an energy barrier for the phase transformation to state 3 to occur.⁵⁶ In state 3, the total energy is minimised, leading to the formation of a more stable material. The added energy is commonly, but not necessarily, from heating the material.

Fig. 3.6. Example of a Gibbs free energy curve for a system with different energy states.

There are other reasons for phase transformations as well. For the transformation of $(\text{Ca,Mn})\text{O}$ to CaMnO_3 in this thesis, the added oxygen is the key component. It is unlikely that the material would change to the perovskite phase without surplus oxygen, as can be understood as the material goes from 50 % to 60 % oxygen. It is also common for oxides to lose oxygen during annealing, which adds another level of complexity to the phase diagram. Take the CaMnO_3 system as an example. It is believed that it undergoes two phase transitions during annealing between 800°C and 1000°C. The first transition, to tetragonal phase, occurs at around 896°C, and the second, to the cubic phase, at 913°C.⁵⁷ The exact temperature varies with, among other things, the oxygen deficiency. Another possibility is described in ref⁵⁸, where the material undergoes a phase transition

from orthorhombic (the perovskite phase) to the cubic crystal structure.

4 THEORY ON X-RAYS

4.1 INTRODUCTION AND BACKGROUND

A part of my PhD is to specialise in the field of x-rays, with an emphasis on diffraction. This chapter is, therefore, more extensive than the other theory chapters, and will cover x-ray generation, x-ray interaction with matter (absorption, scattering and diffraction), x-ray optics, and several different x-ray techniques.

Wilhelm Conrad Röntgen is credited for his work on the subject, as the discoverer of x-rays in 1895, and won the Nobel Prize in 1901. X-rays are electromagnetic radiation with a wavelength on the order of 0.01 to 10 nm, corresponding to energies of about 100 eV to 100 keV. This wavelength is on the same order as the atomic distances in crystals, which give them unique properties for structural characterization of crystalline materials which will be shown in this chapter.

4.2 X-RAY INTERACTION WITH MATTER

X-rays interact with matter in many ways. All are, however, not interesting in this context and are therefore not described. The interactions covered in this chapter are: absorption, scattering and refraction.

4.2.1 Absorption

Photoionisation is the main contribution to the absorption of x-rays in matter. As x-rays propagate through a material, core electrons can absorb the x-ray energy and be excited to a higher electronic state or be expelled from the material. This interaction causes energy losses of the x-ray radiation which follows Beer-Lambert law:

$$I(x) = I_0 e^{-\mu x} \quad 4.1$$

where $I(x)$, I_0 , μ and x are the intensity at depth x , initial intensity, linear absorption coefficient, and the distance travelled inside the

material, respectively. The linear absorption coefficient, μ , depends on both the material and wavelength/energy of the photon and can be calculated using eq. 4.2.

$$\mu = \frac{N_0 \rho_m \sigma_a}{A} \quad 4.2$$

where N_0 , ρ_m , σ_a and A are Avogadro's number, mass density, absorption cross section and atomic weight, respectively. The material dependence in eq. 4.1 is obvious, but the photon energy not so. σ_a depends on both the atomic number and the photon energy and varies several orders of magnitude with energy of photon and binding energy of electrons in different shells.⁵⁹ This strong relation is utilized in x-ray absorption near edge structure (XANES) measurements.

4.2.2 Scattering

I will only consider elastic scattering (Thomson scattering) in this section because it is the most interesting scattering mechanism for x-ray characterization techniques. The reason inelastic scattering (Compton scattering) is of less importance for this thesis is that it does not contribute to Bragg peaks due to change in wavelength/energy. Instead, it is detected as a background noise.

In the case of elastic scattering the incoming x-rays have an oscillating electric field perpendicular to the traveling direction. This field interacts with the electrons in the material and causes them to oscillate at the same frequency as the incoming x-rays. The oscillations of the electron create an electric field which scatters the x-rays and this is called Thomson scattering.⁶⁰ The scattered intensity is described by eq. 4.3 for an unpolarized x-ray beam:

$$I = I_0 \frac{r_e}{r^2} \left(\frac{1 - \sin^2 2\theta}{2} \right) \quad 4.3$$

were I_0 , r_e , r , θ are the intensity of the incident beam, the classical electron radius, distance from the scattering centre, and angle of scattering, respectively, as seen in figure 4.1.

Fig. 4.1. Coherent scattering on an electron.

4.2.3 Refraction

Refraction is commonly used in visible light applications and is described by Snell's law, eq. 4.4 and figure 4.2.

$$n_1 \sin \theta_1 = n_2 \sin \theta_2 \quad 4.4$$

Fig. 4.2. Schematic view of refraction.

There is, however, an important difference between visible light and x-rays. The index of refraction (n) is negative and close to unity for wavelengths in the x-ray region. This means that the x-rays only weakly refract at interfaces between different media making lenses ineffective as focusing optics. Another limiting factor is the high absorption of x-rays. Lenses can, even with these limiting factors, be used. The lens is inverted, that is, the lens is in vacuum and the surrounding material is a low absorption material. The percent reflected is also very low for x-rays because the index of refraction is close to unity, which makes mirrors ineffective (with the exception at low angles (see chapter 4.5.3)).

4.3 CRYSTAL STRUCTURES

A crystal can be defined as a basis (set of atoms) in an infinitely repeating three-dimensional lattice structure. The simplest case, a cubic lattice with one atom as the basis, is illustrated in 2D in figure 4.3.

Fig. 4.3. Illustration how a base with a lattice describe a crystal.

Because of the intrinsic nature of a crystal, the infinite repetition of the lattice, it is possible to define a unit cell made up of three vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ which, by translation of integers m_1 , m_2 and m_3 can describe the whole crystal. A unit cell can be either primitive or non-primitive. The distinction between them is that a primitive unit cell only contains one lattice point while non-primitive contains more than one. Figure 4.4 illustrate how a face centred cubic (FCC) cell (a) can be explained with a primitive cell (b). The primitive cell is much more cumbersome and harder to work with and therefore the FCC variant is used instead.

In total, there are 14 so-called Bravais lattices in three dimensions obtained by coupling the 7 crystal systems with slightly different lattice atomic arrangements. As an example, the cubic system has three different possible atomic arrangements; primitive, body-centered and base-centered. Each Bravais lattice refers to a distinct lattice type and describe the possible translational symmetries in a periodic crystal.⁶¹

Fig. 4.4. The FCC cell (a) and the primitive version of the same (b).

Now we have a tool to describe what a crystal is and the structure it possesses. William Miller developed the Miller indices (hkl) which describes planes and directions in the crystal structure. Miller indices are integers which are reciprocal values of the real space distances. The plane in figure 4.5 (a) intercepts a at 1, b at infinity and c at infinity. The reciprocal of this gives $h=1$, $k=0$ and $l=0$, and the plane is denoted as the (100) plane. If the plane is instead at $a=1/2$, b at infinity and c at infinity the corresponding Miller indices are (200) . This way of describing planes avoid the use of infinity and fractions.

Fig. 4.5. Illustrating the (100) (a) and (200) (b) plane.

When x-rays are incident on a material they can be scattered off the atomic planes. The scattered x-rays from different atomic planes can interfere constructively if Bragg's law is fulfilled (eq. 4.4), as illustrated in figure 4.6. Thus, by using x-ray diffraction the distance between atomic planes in a crystal can be measured.

$$2d \sin \theta = n\lambda \quad 4.4$$

Here d , θ , λ and n are the atomic plane spacing, the angle between sample and incident x-rays, wavelength and integer.

Fig. 4.6. Illustration of Bragg's law.

It turns out that it is not only Bragg's law that needs to be fulfilled for constructive interference and a diffraction peak to appear in an XRD measurement, also the so-called structure factor (F) plays a major role. It is defined as:

$$F = \sum_j f_j \exp(-i\mathbf{G} \cdot \mathbf{r}_j) \quad 4.5$$

where f_j , $\mathbf{G}$ and $\mathbf{r}$ are the atomic form factor, reciprocal lattice vector and distance vector to atom j ,⁶¹ and it takes into account the internal distribution of atoms in the unit cell and describes the amplitude and phase of a wave diffracted from a crystal lattice. The reciprocal lattice vector is equal to:

$$\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 \quad 4.6$$

where $\mathbf{b}_i$ are axis vectors in the reciprocal lattice. The reciprocal lattice vector is related to d in the following way:

$$d = \frac{2\pi}{|\mathbf{G}|} \quad 4.7$$

Multiplying a reciprocal lattice vector with a real space lattice vector has the following relation:

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij} \quad 4.8$$

Where the delta function is 1 when $i = j$ and otherwise 0. Using this relation, it can be understood that eq. 4.5. can be rewritten to:

$$F = \sum_j f_j \exp(-i2\pi(hx_j + ky_j + lz_j)) \quad 4.9$$

where h , k and l are the miller indices and x , y and z are the atomic positions of the base. For example, the FCC has atoms at position $(0,0,0)$, $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ and which results in the following form factor:

$$F = f(1 + \exp(-i\pi(h + k)) + \exp(-i\pi(h + l)) + \exp(-i\pi(k + l))) \quad 4.10$$

From this it is clear that some hkl combination will result in $F=0$, which means 0 intensity (a forbidden reflection), even though Bragg's law is fulfilled.

4.4 LABORATORY X-RAY DIFFRACTOMETER

4.4.1 X-ray Generation in lab-scale instruments

X-rays are generated in x-ray tubes, schematically illustrated in figure 4.7. The thermionic emission of electrons from the tungsten filament are accelerated to the anode target. As the high energy electrons strikes the target two types of x-rays are generated. One part is from the continuous deceleration of electrons (generating the Bremsstrahlung continuum) and the other is the ionisation process. The ionisation process is when a core shell electron is excited, the excited electron falls back to the core shell and energy in the form of characteristic x-rays are released. Commonly a copper anode is used as the x-ray source and the two processes earlier described generate an x-ray spectrum as shown in figure 4.8. The generated x-rays exit the x-ray tube through a beryllium window. The production of x-rays is inefficient (typically less than 1%) and most of the energy from the electrons is transformed to heat and the x-ray tube is therefore cooled with water.

Fig. 4.8. Schematic drawing of an x-ray tube.

Fig. 4.9. Image of intensity of characteristic x-rays, Bremsstrahlung radiation and cut-off wavelength of the Ni-filter.

4.4.2 Optics

X-ray optics can be split into two different sections, conditioning and selective optics. Conditioning optics are focusing the beam while selective optics cuts off intensity to lower the divergence. Mirrors and capillary lenses are conditioning optics, while slits, masks, filters, crystals, and parallel plate collimators are selective in nature.

4.4.2.1 Slits

Slits are simple optics where a small rectangular opening is used which selects which part of the beam can pass. Typically, a slit on the incident path is used to select the divergence of the beam, here care should be taken to make sure the x-rays are confined to the sample dimensions. To determine the 2θ resolution, a receiving slit is used before the detector, this influences the instrumental peak broadening. To reduce the background from air scattering and other stray x-rays an anti-scatter slit is commonly used on either side of the sample. The divergence perpendicular to the x-rays is limited by the use of Soller slits which are several plates stacked together which only accept x-rays with an angle depending on the spacing and length of the plates. A mask can also be used to limit the width of the x-ray beam to reduce artefacts from the holder.

4.4.2.2 *Filter*

A filter is typically used on either side of the sample in order to produce monochromatic x-rays. The filter is made of a material that has an absorption edge between the characteristic peaks of K_{β} and K_{α} (see figure 4.9). Typically, this material has atomic number $Z-1$ if the source (target) material has atomic number Z . For this reason, a Ni-filter is used in conjunction with a Cu source and blocks x-rays with energies higher than $Cu-K_{\alpha}$. This effectively removes the $Cu-K_{\beta}$ radiation at the cost of about half the intensity of the $Cu-K_{\alpha}$.

4.4.2.3 *Crystal Optics*

An alternative to produce monochromatic radiation is to use a set of single-crystals. The monochromator works by diffracting only the wavelength that obey Bragg's law for the particular atomic plane spacing of the monochromator crystal. The same devices can be used before the detector for the examination of the direction of diffracted x-rays and they are then called crystal analysers.

4.4.2.4 *Parallel Plate Collimator*

The use of a parallel plate collimator is similar to that of Soller slits, but they are rotated 90° to be parallel with the scattering plane. The benefit of using parallel plate collimators is that not only does the optics limit the divergence it only let parallel x-rays pass. The parallel plate collimator determines the resolution of the diffraction angle in the experiment.

4.4.2.5 *Mirror Optics*

An x-ray mirror is used to collect divergent x-rays from the x-ray tube and make them parallel and directed towards the sample. A mirror is therefore very different for x-rays compared to visible light. An x-ray mirror consists of a multilayer stack with alternating high and low refractive index materials. The stacks get thicker and thicker and the interfaces must be extremely smooth which make them hard to manufacture.

The mirror reflects all x-ray wavelengths to give a high intensity on the sample, but it does not make the x-rays monochromatic. For this

reason, sometimes, mirrors are combined with crystals, so called hybrid mirrors, to achieve a monochromatic high intensity beam.

4.4.2.6 Capillary Optics

Capillary optics have a similar role as the mirror but are used when the same beam divergence is required in all directions, not only in the scattering plane.

Instead of having a multilayered mirror the x-rays are guided through thin capillaries which produce a parallel circular beam.

4.5 MEASUREMENT TECHNIQUES

4.5.1 Phase Analysis $\theta/2\theta$ Measurements

The most common measurement technique is the $\theta/2\theta$ measurement. It is used to identify the phases of the material and gives information of plains parallel to the surface. It is a symmetrical measurement where the incident angle and diffracted angle is equal throughout the measurement. When the x-rays interfere constructively, i.e. when Bragg's law is fulfilled, and the structure factor is non-zero, a diffraction peak will appear in the diffractogram.

Fig 4.10. $\theta/2\theta$ diffractogram.

The measured peak profile is a convolution of the sample broadening and the intrinsic instrumental broadening which depends on the chosen x-ray optics. An example on this measurement can be seen in figure 4.10.

The position of the peaks gives information about the atomic plane spacings, which is related to the crystal structure. Peak broadening can be related to the grain size and microstrain, while peak shifts can be attributed to e.g. stoichiometry changes (elements) and macroscopic stresses in the material.

4.5.2 GIXRD

Grazing incidence x-ray diffraction (GIXRD) is similar to $\theta/2\theta$ with the difference that the incidence angle is fixed within a few degrees. This allows the x-rays to be confined to a few hundred nm instead of a few μm in depth. This is especially useful for thin film measurements where the film can be a few nm thick only. The drawback is, however, that the measured planes are not in the same direction but will change continuously during the measurement.

4.5.3 XRR

X-ray reflectivity (XRR) is conceptually different. It does not rely on diffraction, instead the x-rays are reflected at the interfaces between two different media with different x-ray optical properties. The reflected x-rays interfere constructively if Bragg's modified law is fulfilled:

$$2D \sin \theta \sqrt{1 + \frac{\eta^2 - 1}{\sin^2 \theta}} = m\lambda \quad 4.11$$

where D , η and m is the film thickness, complex refractive index of the material and the reflection order (integer), respectively.

Fig. 4.11. Illustration of an XRR measurement.

Fig. 4.12. Example of an XRR graph.

Figure 4.12 shows a typical reflectivity profile when performing an x-ray reflectivity measurement of a thin film. At low angles, as a result of a refractive index below unity for x-rays, total external reflection occurs and at the critical angle, which is related to the electron density, the reflected intensity drops. The observed oscillations beyond the critical angle are called Kiessig fringes and the distance between two maxima (or minima) is determined by the thickness of the sample. This measurement has few limits: the film should be thinner than about 100 nm, the surface and interfaces should be smooth enough to give specular reflection of the x-rays, and there should be a sufficient x-ray optical contrast between the film and the substrate, i.e. they can not have too similar refractive indices.

4.5.4 Pole Figure

A pole figure is a measurement where the orientation of a particular atomic plane is mapped out with respect to the sample orientation. In this measurement the incident and diffracted beam angles are kept constant, set to a specific plane spacing, while the sample is rotating 360° in ϕ during the measurement, this is repeated for several ψ tilts up to 85° . Figure 4.13 shows a representative pole figure, where the poles give information about the orientation of the investigated planes. Combining pole figures from the film and the substrate can be used to determine the epitaxial relationship between the film and the substrate.

Fig. 4.13. Example of a pole figure.

5 STRUCTURAL AND COMPOSITIONAL CHARACTERIZATION

5.1 SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy (SEM) is an imaging technique where an electron beam is used to scan the surface. The incident electrons generate several different species. The ones commonly used for imaging are the backscattered electrons (BSE) and the secondary electrons (SE). The BSE are the electrons from the incident beam that have been backscattered due to interaction with the specimen. The probability to create a BSE is higher for heavier elements and is therefore useful for imaging composition. The SE are electrons from the specimen that have been knocked out due to interaction with the incident electron beam. The SE are insensitive to composition but are useful for topographical imaging as they originate from the first few nm of the specimen.⁶²

5.2 TRANSMISSION ELECTRON MICROSCOPY

Transmission electron microscopy (TEM) is similar to SEM in the sense that an electron beam is used in both cases to analyse the sample. They are, however, probing different length scales and TEM is working in transmission mode. SEM has a spatial resolution in the nm region while TEM can image individual atoms. TEM requires special film preparation because the specimen has to be electron transparent. It is also possible to use TEM to do electron diffraction which, similar to XRD and electron backscatter diffraction (EBSD) in SEM, can reveal the structure of the sample. The drawback with TEM is that it requires rigorous preparation of the specimen and that only local information is possible to extract from the sample, and this might not represent the whole sample.

5.3 X-RAY PHOTOELECTRON SPECTROSCOPY

X-ray photoelectron spectroscopy (XPS) is an elemental analysis technique where the sample is irradiated with an x-ray beam which excites core shell electrons above the vacuum level, meaning leaving the material. The excited electrons are measured, both in quantity and kinetic energy. The kinetic energy (E_k) depends on the energy of the x-ray radiation ($h\nu$), binding energy of the electrons (E_b) and work function of the detector (ϕ) as shown in eq. 5.1.

$$E_k = h\nu - E_b - \phi \quad 5.1$$

The binding energy is characteristic for elements and therefore the elements in the material can be determined, and the number of electrons collected can be used for quantification.

XPS can also be used to analyse the chemical state and bonding of the atoms. For instance, different valence states of an element will have different binding energy and therefore, XPS, is sensitive to the chemical state of the atoms. XPS can also be used to do depth profiles for the above-mentioned analysis. This is performed by using a sputtering gun to remove a few nm of material to reveal a surface deeper in the material to be analysed.

5.4 ENERGY DISPERSIVE X-RAY SPECTROSCOPY

Energy dispersive x-ray spectroscopy (EDS) is performed in a SEM. The incident electrons can, as previously mentioned, knock out electrons from the atoms. This leaves an empty state which gets filled by an electron in an outer shell. This process yields characteristic x-rays with energies unique to the difference in energy level of the different shells in each atom. The energy can also be released by the emission of an Auger electron.⁶² The probability for the Auger effect is higher for lighter elements and the Auger electron can be analysed to get information about the elements and its surroundings. This process is schematically described in figure 5.1.

The characteristic x-rays are collected in a detector which detects both the energy and the number of x-rays.

Fig. 5.1. Schematic illustration of characteristic x-rays and Auger electron generation.

6 ELECTRICAL AND THERMAL CHARACTERISATION

6.1 FOUR-POINT PROBE

Four-point probe is used to measure the resistivity of a sample. It consists of four probes on a line as in figure 6.1. The outer probes drive a current and the two inner probes measure the voltage difference. The reason for using four sensors is to avoid errors from contact and lead resistance.

Fig. 6.1. Schematic top view(a) and side view (b).

The resistivity (ρ) can be calculated using eq. 6.1

$$\rho = \rho_s t = \frac{V}{I} t \frac{d}{s} C' * F \left(\frac{t}{s} \right) \quad 6.1$$

where ρ_s , t , V , I , d , s , C' and F are the sheet resistance, film thickness, measured voltage, induced current, sample width, distance between tips, correction factor for finite sample width, and correction factor for sample thickness, respectively. The correction factors depend on the sample geometry, which are described elsewhere.⁶³ The correction factors are both close to theoretical values for infinitely thin and infinitely wide sample ($F \approx 1$ and $\frac{d}{s} C' \approx \frac{\pi}{\ln 2}$) and eq. 6.2. can be used.

$$\rho = \rho_s t = \frac{V}{I} t \frac{\pi}{\ln 2} \quad 6.2$$

6.2 SEEBECK MEASUREMENTS

Figure 6.2 shows a measurement scheme of the Seebeck coefficient. Two thermocouples are mounted on the sample. They measure both the temperature difference and voltage difference. An electrical current is passed through the sample for the measurement of electrical resistivity simultaneously with Seebeck coefficient in a single measurement run.

Fig. 6.2. Schematic view of a Seebeck measurement setup.

6.3 THERMAL CONDUCTIVITY MEASUREMENT

Determining the thermal conductivity experimentally of thin films is a nontrivial task. The measurement must determine the thermal conductivity of a thin film accurately while influenced by the much thicker substrate which it is deposited on. Two common techniques are 3ω method and thermoreflectance.⁶⁴ Thermoreflectance is used in this thesis and utilize the change in reflectance with temperature. A measurement setup is shown in figure 6.3, where a pumping laser heats up a spot on the specimen and a probing laser measures how the refractive index changes as the specimen cools down. A nm thick metallic layer is commonly deposited on the films which absorbs the energy deposited by the laser.

Fig. 6.3. Schematic view of a thermal conductivity measurement setup.

7 THERMOELECTRICS

A thermoelectric material has the ability to generate electricity when a temperature gradient is applied over the material, or vice versa. A module consists of n- and p-type materials connected in series as seen in figure 7.1. The charge carriers on the hot side move faster than on the cold side. This results in a net diffusion of charge carriers to the colder side, generating a current. Thus, thermoelectric power generation does not involve any moving macroscopic parts. Thus, it requires minimum maintenance and can reliably work over years and is therefore useful for remote applications, such as off-grid power generation and space missions.

Fig. 7.1. Schematic image of a thermoelectric module.

The efficiency is related to the dimensionless figure of merit ZT , eq. 7.1

$$ZT = \frac{\sigma S^2}{\kappa} T \quad 7.1$$

where σ , S , κ and T are the electrical conductivity, Seebeck coefficient, thermal conductivity, and absolute temperature, respectively. S of degenerate semiconductors is inversely related to charge carrier concentration following the expression 7.2, whereas σ is linearly related to carrier concentration following the expression 7.3. The thermal conductivity consists of a phonon (lattice) part and an electronic part, eq. 7.4. In thermoelectric materials, the

contribution from phonons to thermal conductivity is usually dominant over electronic contribution.

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3} \quad 7.2$$

$$\sigma = en\mu \quad 7.3$$

$$\kappa = \kappa_e + \kappa_p \quad 7.4$$

$$\kappa_e = L\sigma T \quad 7.5$$

Finding new materials with high ZT or improving existing ones has been a challenge for many years, and still is. The reason is that the different components that determines the ZT are correlated as seen in the above equations. By improving one component another is at the same time made worse. A common way to increase the ZT is by doping which increase the number of charge carriers (n). This increases σ , but S will at the same time decrease and an optimal doping level is found as seen in figure 7.2.¹⁵

Fig. 7.2. The relation between carrier concentration and ZT, S , σ and κ is shown. From ref. ¹⁵ © Nature Publishing group, reproduced with permission.

Take note that there are two different optima in the above graph. Between carrier concentration 10^{19} and 10^{20} cm^{-3} , the ZT is optimized, while the power factor ($S^2\sigma$) is optimized at 10^{20} cm^{-3} .

Both maxima are of importance. Maximizing the efficiency is not always as important as maximising the power output.

Another approach to increase the ZT is by grain boundary tailoring. The electrons have in general much shorter mean free path than phonons. By making a material with grains larger than the mean free path of electrons and in the range of phonons the scattering of phonons can be increased while the electrons are almost unaffected.⁴⁴ There are other approaches with the same basic idea, to scatter phonons, e.g. doping with heavy atoms or induce dislocations to act as a scattering centre and by making multilayers which can scatter phonons.

8 CONCLUDING REMARKS AND FUTURE WORK

I have shown in paper I that it is possible to synthesis CaMnO_3 by a two-step approach. The synthesis method used where co-sputtering using RF reactive magnetron sputtering with a post annealing step. Growth on different faces of Al_2O_3 substrates (C-cut, M-cut and R-cut) were investigated. M-cut Al_2O_3 is suggested to be used out of the three investigated because the resulting power factor (PF) is the highest. The PF measured at 500 °C were $10 \mu\text{V/mK}^2$, $45 \mu\text{V/mK}^2$ and $23 \mu\text{V/mK}^2$ for C-cut, M-cut and R-cut, respectively. The XRD and TEM analysis indicated that the film grown on M-cut Al_2O_3 had the best crystal quality which is connected to lower defect density and higher conductivity which was the main contribution to the difference in PF in this study. The influence of annealing temperature was also investigated and it was seen that a temperature of 550 °C is needed to form CaMnO_3 . Secondary orientation formation is present at all temperatures and are more pronounced at higher temperatures.

In paper II the CaMnO_3 film where alloyed with a few percent Nb ($\text{CaMn}_{1-x}\text{Nb}_x\text{O}_3$, $x = 0-0.10$). M-cut Al_2O_3 substrate was used based on previous study in paper I. It was found that the addition of Nb increased the film quality of both as-deposited films and annealed ones. The PF is also enhanced 8 times for Nb content $x = 0.04$ to $21.6 \mu\text{V/mK}^2$ at RT compared to $2.7 \mu\text{V/mK}^2$ pure CaMnO_3 . This increase in PF is attributed to the increase in carrier concentration which increases the electron conductivity while decreasing the Seebeck coefficient. The increase in electrical conductivity outweighs the decrease in Seebeck coefficient as seen in the increase in PF. A decrease in thermal conductivity was also observed with increasing Nb content. This can be connected to lattice distortion, point defects and possibly grain size differences. Further investigation in the matter is needed to determine the main contribution for the reduction in thermal conductivity.

The field of oxide thin films is vast, and they are not only interesting for thermoelectric applications. A fast-growing field is van der Waals oxide epitaxy.^{65,66} It has been demonstrated that several different oxides can be grown heteroepitaxially on mica by van der Waals bonds. The benefit of van der Waals epitaxy (vdWE) is that the film can be grown strain free retaining the bulk lattice parameters even at large lattice mismatch.⁶⁷ Moreover, mica is also flexible, transparent and isolating which makes it ideal as a substrate. The weak bonding between substrate and film suggest that removal of the film is possible. All these mentioned characteristics of mica opens up possibilities for many applications within electronics, wearable devices and more.

I plan to explore the possibilities to directly grow oxides with vdWE on mica using PVD. The first step is to learn how to grow simpler (cubic structured) oxides. To be able to grow CaMnO_3 using this approach the annealing step must be avoided and therefor a method for directly grow CaMnO_3 using PVD also needs to be developed. There are many more oxides that are interesting to investigate for this method and this is an exciting project to start up.

In addition to above mention projects, the CaMnO_3 is still interesting to explore. The effect of grain size tailoring for reducing the thermal conductivity while keeping the electrical conductivity high is interesting. The reason for this lies in the difference in mean free path between phonons and electrons. Another interesting aspect to investigate is the effect of Nb doping on the electron structure.

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Paper I

Thermoelectric properties and formation of CaMnO_3 thin films by annealing $(\text{Ca}_{0.5}\text{Mn}_{0.5})\text{O}$ films grown on Al_2O_3 substrates.

Authors: E. Ekström, A. le Febvrier, F. Eriksson, P. Eklund and B. Paul.

In manuscript.

Paper II

Growth, characterization, and thermoelectric properties of $\text{Ca}(\text{Mn}_{1-x}\text{Nb}_x)\text{O}_3$.

Authors: E. Ekström, A. le Febvrier, F. Bourgeois, B. Lundqvist, J. Klarbring, S. I. Simak, F. Eriksson, B. Paul, and P. Eklund.

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