

THERMOELECTRIC MATERIALS BASED ON ZnO

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Doctoral Dissertation

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MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA
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TERMOELEKTRIČNI MATERIALI NA OSNOVI ZnO

Doktorska disertacija

Supervisor: Prof. Dr. Slavko Bernik

Ljubljana, Slovenia, June 2017

To my mum.

Acknowledgments

First, I would like to thank Prof. Slavko Bernik for the supervision, guidance and encouragement during my PhD studies. His patience, unselfish help and a thoughtful word made every problem much smaller. I am grateful for many fruitful discussions and all the advice, which helped me gain knowledge in the field of solid state chemistry of zinc oxide. Thank you, Slavko!!

Also, I would like to thank Matejka Podlogar for all the help through the years with every issue I had in the lab, answering all my stupid questions and always having an encouraging and thoughtful word when it seemed that everything in the experiment or elsewhere just went in the wrong direction. Thank you Matejka again and I hope our paths will still cross in the future, at least for a coffee!

A huge gratitude goes to Emmanuel Guilmeau for giving me the opportunity to do a part of research work in the CRISMAT laboratory in Caen, France. It was an amazing experience for me, being able to work in one of the best laboratories for thermoelectrics research in Europe. Your dedication to research work strongly motivated me, and all the encouraging and thoughtful words always helped me through every issue I had. I will never forget your unselfish act of renting me your Toyota car, which took me all around Normandy through weekends. Merci beaucoup Manu!!

Special thanks goes to Aleksander Rečnik and Nina Daneu for their help with the TEM analysis and sharing their knowledge about the zinc oxide!

I cannot express how grateful I am that I did my PhD studies in the K7 group, where I had the chance to work with so many talented people. Thank you all! Thanks to the people I shared the office with: (in alphabetical order) Luka Kelhar, Luka Suhadolnik, Martin Topole, and Sandra Drev. A big thank you goes to the entire “thermoelectric crew” at K7, Mojca Presečnik, Marja Jerič and Rok Rudež!! Thank you guys for all the fruitful discussions, advice and help in the lab.

A huge thanks goes to my “library office” team (in alphabetical order) Martina Lorenzetti, Milivoj Plodinec, Nadežda Stankovič, Shahid Arshad. I will never forget our “scaffold talks” ☺ and numerous scientific discussions during our lunches. Thank you for the support and courageous words all the time. If I quote Martina: *“We learned together, we suffered together and most of all, we have had such a great time I will remember it forever!”*

During my stay at the CRISMAT laboratory, I have to thank so many people which always helped me, no matter what the problem was. Thanks to Pablo Diaz Chao, Nhi Truong, Marine Beaumale, Elisa Tofoni, Etienne Savary, Romain Heuguet, Tristan Barbier, Raghavendra Nunna and to professor Sylvain Marinel for their unselfish help. Special thanks goes to Jérôme Lecourt for his help in the laboratory and encouragement with the French language; Merci JeJe!! Thanks also to Sylwia Wronkowska, Borislava Petkova, Aga Kaczmarczyk and Ana Jovanovska, whom I met at the French class, for all the great memories!

Thanks to my dear friends, especially Maja Gutman Levstik, Snježana Miletič, Maja Pečar and Lucija Kos for all the support throughout the years!

Finally, I would like to thank my family; mum, brother and sis, thank you for always being there for me! To my dear boyfriend Elvis and our son Martin for their love, patience and support during the long working hours. Hvala!!!

Abstract

The rapid development and globalization in the 21st century are still mainly powered by the fossil fuels with the negative environmental impact and limited natural resources. A large and re-usable energy source is the “waste heat” and its harvesting is possible with the thermoelectric generators, which have the ability to transform heat into an electric potential through the Seebeck effect. Oxide-based materials are very suitable for the high-temperature applications due to their good chemical and temperature stabilities in air. The ZnO - In₂O₃ system with the series of the Zn_kIn₂O_{k+3}-type homologous phases with a superlattice structure offers an excellent platform for tailoring the thermoelectric properties of the n-type ZnO-based ceramics.

At first, this PhD study was focused on the formation mechanism of the homologous phases in the (ZnO)_kIn₂O₃ polycrystalline ceramics and its influence on the sintering, microstructure development and thermoelectric properties. Results indicate the homologous phase formation at temperatures above 1000 °C and its strong relation to the local Zn-to-In ratios in the starting powder mixture. Accordingly, in the compositions with high addition of In₂O₃ (k=5) the equilibrium homologous phase Zn₅In₂O₈ forms directly and the growth of plate-like grains is uniform due to soon reached compositional homogeneity. At lower additions of In₂O₃ (k=11, and 18) the Zn₅In₂O₈ and Zn₇In₂O₁₀ phases are formed in In₂O₃-rich areas and grow on expense of the high k phases formed in the In₂O₃-deprived regions till the composition of the equilibrium homologous phase for starting k value is not reached, which requires longer sintering times at higher temperatures. Exaggerated grain growth manifests in these samples as long as compositional homogeneity is not reached through all the sample. Hence, their grain size is larger in comparison to the sample k = 5. It also showed that a higher degree of structural and compositional homogeneity results in better thermoelectric characteristics of the (ZnO)_kIn₂O₃ ceramics.

The study of Al-doping, contrary to previous literature reports, clearly showed that Al substitutes In on its both primary sites in the Zn₅(In_{1-x}Al_x)₂O₈ homologous phase, the octahedral sites in the basal-plane inversion boundaries and the trigonal bi-pyramidal sites in the zig-zag inversion boundaries. This results in a linearly increased shrinkage of the unit cell with the increasing additions of Al, decreased charge carrier concentration and effects on their mobility, resulting in reduced electrical conductivity and just slightly decreased ZT values.

Preparation of the (ZnO)_kIn₂O₃-based ceramics requires long sintering times at high temperatures. Hence, their processing was studied using the microwaves sintering (MW) and the field assisted sintering (FAST) as fast and energy efficient methods. The initial heating in MW sintering was caused by the more effective In₂O₃ coupling with MW, transferring the heat to the less effective MW absorber ZnO. It resulted in the formation of the Zn_kIn₂O_{k+3} homologous phases and well densified ceramics with thermoelectric properties akin to the conventionally sintered samples, however at about 70% lower input of energy. The FAST process resulted in the strongly enhanced sintering and formation of the Zn_kIn₂O_{k+3} homologous phases; i.e. the Zn₅In₂O₈ phase formed already after 5 minutes at 1000 °C, while conventional sintering required 22 h at 1200 °C. Furthermore, the applied pressure together with the electric field resulted in modest texturing and 50 % higher electrical conductivity in comparison to the conventional samples.

Povzetek

Hitri razvoj in globalizacija sta v 21. stoletju še vedno podprta s fosilnimi gorivi, ki imajo negativen vpliv na okolje, njihovi naravni viri pa so omejeni. Velik vir energije lahko predstavlja odpadna toplota, ki jo je mogoče izkoriščati s pomočjo termoelektričnih generatorjev, ki transformirajo temperaturni gradient v električni potencial s t. i. Seebeckovim efektom. Materiali na osnovi oksidov so primerni za visokotemperaturne aplikacije, in sicer zaradi njihove dobre kemične in temperaturne stabilnosti na zraku. Sistem $\text{ZnO} - \text{In}_2\text{O}_3$ s serijo superstrukturnih homolognih faz $\text{Zn}_k\text{In}_{k+3}\text{O}_{k+3}$ predstavlja odlično platformo za nadaljnjo optimizacijo termoelektričnih lastnosti keramike tipa n na osnovi ZnO .

V doktorski disertaciji sem se najprej osredotočala na študij procesov nastajanja homolognih faz v sistemu $(\text{ZnO})_k\text{In}_2\text{O}_3$ keramike in njihov vpliv na sintranje, razvoj mikrostrukture in termoelektrične lastnosti. Rezultati kažejo na formiranje homolognih faz pri temperaturah nad 1000°C , na proces njihovega nastajanja pa močno vpliva lokalno razmerje med Zn in In (Zn/In) v izhodni zmesi prahov. Glede na to v sestavah z visokim dodatkom In_2O_3 ($k = 5$) ravnovesna homologna sestava $\text{Zn}_5\text{In}_2\text{O}_8$ nastane direktno, rast ploščicastih zrn faze pa je enakomerna, ker je homogenost kemijske sestave v celotnem vzorcu dosežena hitro. Nasprotno pri nižjih dodatkih In_2O_3 ($k = 11$ in 18), v področjih bogatih z In_2O_3 , nastaneta fazi $\text{Zn}_5\text{In}_2\text{O}_8$ in $\text{Zn}_7\text{In}_2\text{O}_{10}$ in rasteta na račun faz z visokim k , ki nastanejo v področjih s primanjkljajem In_2O_3 , dokler ne nastane ravnotežna fazna sestava za začetne k vrednosti, kar zahteva dolgo sintranje na visokih temperaturah. V teh vzorcih lahko opazimo pretirano rast zrn, vse dokler ni dosežena homogenost sestave v celotnem vzorcu. Zaradi tega je velikost zrn v teh vzorcih večja kot v vzorcu s $k = 5$. Rezultati so pokazali, da se višja stopnja urejenosti strukture in sestave odraža tudi v boljših termoelektričnih lastnostih keramike $(\text{ZnO})_k\text{In}_2\text{O}_3$.

Študija dopiranja z Al je v nasprotju s prejšnjimi literaturnimi poročili jasno pokazala, da se Al vgrajuje na mesta In na obeh primarnih mestih v homologni fazi $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$, na oktaedrskih mestih v inverznih mejah vzdolž bazalnih ravnin in na trigonalnih bipiramidalnih mestih v cik-cak inverznih mejah. To se odraža v linearnem večanju skrčka osnovne celice z naraščajočimi dodatki Al, zmanjšano koncentracijo nosilcev naboja in vplivom na njihovo mobilnost, kar povzroči nižjo električno prevodnost in le manjše znižanje vrednosti ZT.

Priprava keramike $(\text{ZnO})_k\text{In}_2\text{O}_3$ zahteva dolgo sintranje na visokih temperaturah, zato sem študirala možnosti njene izdelave z mikrovalovnim sintranjem (MW) in sintranjem v električnem polju (FAST). Začetno segrevanje pri MW sintranju je bilo povzročeno z učinkovitim odzivom In_2O_3 na MW polje in prenosom generirane toplote na slabše odzivni ZnO . Ob približno 70 % manjši porabi energije je izdelana keramika s sestavo homolognih faz $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ imela visoko gostoto, podobno kot pri konvencionalno sintranih vzorcih. FAST procesiranje se je izkazalo z bistveno pospešenim sintranjem in formiranjem homolognih faz $\text{Zn}_k\text{In}_2\text{O}_{k+3}$, tako da je faza $\text{Zn}_5\text{In}_2\text{O}_8$ nastala že po 5 min na 1000°C , medtem ko je pri konvencionalnem sintranju potrebno 22 ur pri 1200°C . Električno polje je skupaj s pritiskom prispevalo k zmernemu teksturiranju keramike in za 50 % izboljšani električni prevodnosti v primerjavi s konvencionalnimi vzorci.

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Abbreviations

AZO	...	Al - doped ZnO
CS	...	Conventional sintering
CS-F	...	Conventional sintering-fast
DC	...	Direct current
DFT	...	Density functional theory
DSC	...	Differential scanning calorimetry
DTA	...	Differential thermal analysis
EDXS	...	Energy dispersive X-ray spectroscopy
EM	...	Electro-magnetic
FAST	...	Field assisted sintering
FFT	...	Fast Fourier transform
HAADF	...	High-angle annular dark-field
HRTEM	...	High resolution transmission microscopy
IB	...	Inversion boundary
IPS	...	International Postgraduate School
JSI	...	Jožef Stefan Institute
LFA	...	Laser flash analysis
MW	...	Microwave
PGEC	...	“Phonon-glass, electron-crystal”
PPMS	...	Physical properties measurements system
SEM	...	Scanning electron microscopy
SPS	...	Spark plasma sintering
TE	...	Thermoelectricity
TEM	...	Transmission electron microscopy
XRD	...	X-ray diffraction
YSZ	...	Yttrium stabilized zirconia
ZT	...	Dimensionless figure of merit

Symbols

C_p	...	Heat capacity
C_v	...	Total heat capacity
dT/dx	...	Temperature gradient
e	...	Elementary charge
E	...	Electric field
E_y	...	Hall field
h	...	Planck constant
H	...	Magnetic field
I	...	Current
J	...	Current density
kb	...	Boltzmann constant
L	...	Lorentz number
m^*	...	Effective mass of charge carriers
n	...	Carrier concentration
P	...	Power factor
q	...	Heat current
S	...	Seebeck coefficient
T	...	Temperature
t	...	Time
TC	...	Temperature – cold side
TH	...	Temperature – hot side
U	...	Voltage
V_H	...	Hall voltage
Z	...	Figure of merit
ZT	...	Dimensionless figure of merit
α	...	Thermal diffusivity
ΔT	...	Temperature difference
ε	...	permittivity
ε^*	...	Complex permittivity
ε'	...	Real part of the complex permittivity
ε''	...	Imaginary part of complex permittivity
ε_0	...	Permittivity in air
η (%)	...	Efficiency
μ	...	Magnetic permeability

μ	...	Carrier mobility
μT	...	Thomson coefficient
ν	...	Phonon group velocity
π	...	Peltier coefficient
ρ	...	Density
σ	...	Electrical conductivity
τ	...	Relaxation time
l_{phon}	...	Phonon mean free path for phonon-phonon scattering
l_{def}	...	Phonon mean free path for defect scattering
l_{gb}	...	Phonon mean free path for grain boundary scattering
ω	...	Angular frequency
κ	...	Thermal conductivity
κ_e	...	Electronic thermal conductivity
κ_l	...	Lattice thermal conductivity

Chapter 1

Introduction

1.1 Preface

Rapid development and globalization in the 21st century were followed by a huge population growth and enormous rise in the consumption per capita. The worldwide economy is still mainly powered by fossil fuels with the negative environmental impact and limited natural resources. To tackle these problematics, EU action plans and governmental policies are focusing further economy development on the sustainable resource management and “*circular economy strategy*” with “*closing the loop*” of product/source lifecycles through greater recycling and re-use. A large and re-usable energy source is the “waste heat” generated during many industrial processes and household actions. The waste heat harvesting is possible with the thermoelectric generators, which have the ability to transform heat into an electric potential. They are usually composed of two semiconductors, p- and n-type, which are connected into a series to form a device. The research in thermoelectric materials is increasing since the discovery of bismuth telluride in 1954 by Goldsmid [1] and expanded enormously in mid 1990s with the era of nanomaterials and nanostructuring, which greatly enhanced the efficiency of thermoelectric materials.

1.2 Thermoelectric Effects

The term *thermoelectric effect* consists of the Seebeck effect, Peltier effect and Thomson effect. They can be used to generate electricity under temperature gradient, to create temperature gradient by an electrical current, and to cool or heat a current-carrying conductor with a temperature gradient, respectively.

The thermoelectric phenomena already have a long history since its first discovery in 1821 by T. J. Seebeck. He originally assembled a circuit made of two different metals and heated up one metal junction to create a temperature difference along the circuit [2] (Figure 1.1). As a result, the compass needle, placed in the vicinity of a closed circuit, showed a slight deflection from its initial position. However, he believed that it is due to the magnetism induced by the temperature difference and related it to the Earth’s magnetic field. Later, H.C. Oersted connected this observation with his research about magnetism induction in current carriers and correctly explained that the magnitude of the magnetic needle deflection (induced voltage, U) is proportional to the temperature difference between junctions (ΔT) and named it as a Seebeck effect or thermopower (S) (1.1).

$$U = S \Delta T \quad (1.1)$$

It is the magnitude of an induced thermoelectric voltage in response of a temperature current across the material (1.2) [3]. If there is a temperature gradient between two different conductors, it produces a voltage of several microvolts per Kelvin difference. Typical values of the Seebeck coefficient are for a good thermoelectric material in hundreds of $\mu\text{V}/\text{K}$. It is negative for n-type (electrons conduction) thermoelectric materials and positive for p-type (conduction by “holes”) material.

$$S = \frac{\Delta U}{\Delta T} \quad (1.2)$$

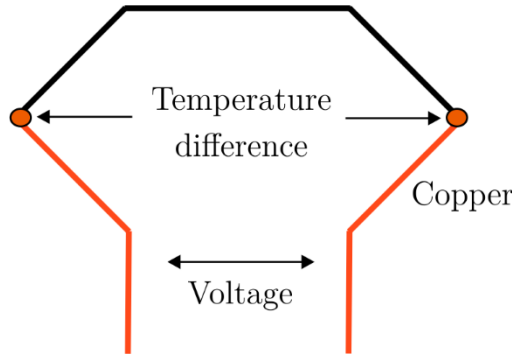


Figure 1.1: Schematic presentation of the thermocouple used by Seebeck in his experiments (re-drawn from ref. [4]).

A decade later after the T. J. Seebeck discovery, in 1834, J. C. A. Peltier reported the complementary effect, when he observed temperature changes in the junctions between dissimilar conductors during the applied current. Four years later, Lenz experimentally presented that this effect is dependent on the current direction; heat can be either removed from a junction to freeze water into ice and by reversing the current, heat is generated and ice is melted.

The Peltier effect is determined as a heat current (q) per unit of charge (I) through a material (1.3) and the proportional constant is called the Peltier coefficient (π). It is the transfer of heat from one side to another in the presence of current. The direction of heat current (hot-cold side) depends on the direction of the electrical current [3].

$$\pi I = q \quad (1.3)$$

The interdependency of Seebeck and Peltier effect was recognized by W. Thomson in 1855, who described the relationship among both effects through the thermodynamic theory. His theory also predicted the presence of a third thermoelectric effect in a homogeneous conductor. Today, this effect is known as the Thomson effect and describes the heating or cooling of a current – carrying conductor in a temperature gradient. Any current carrying conductor with a temperature difference between two points will either absorb or emit heat. If a current density J is passed through a homogeneous conductor, the heat production q per unit volume is (1.4)

$$q = \rho J^2 - \mu J \frac{dT}{dx} \quad (1.4)$$

where ρ is the resistivity of the material, dT/dx is the temperature gradient along the wire and μ is the Thomson coefficient.

1.3 Thermoelectric Modules

Thermoelectric device is built up of many thermoelectric couples of n-type and p-type conducting elements connected electrically in series and thermally in parallel (Figure 1.2).

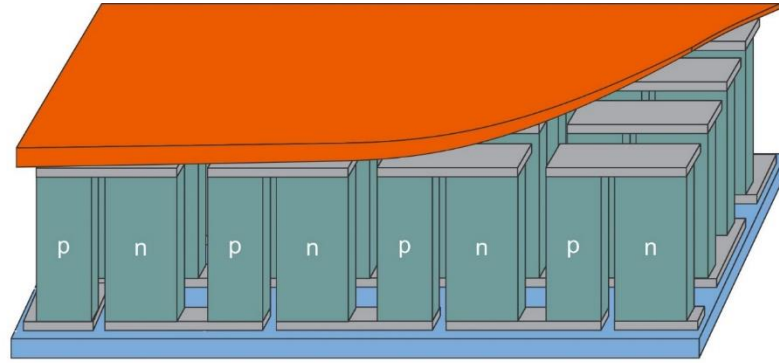


Figure 1.2: The simple thermoelectric module based on p-n type thermoelectric materials.

The basic thermoelectric couples (Figure 1.3, Figure 1.4) are sandwiched between ceramic plates with high thermal conductivity and low electrical conductivity, constructing a basic module. These modules are later arranged in different geometries, like cascade, to build up an actual thermoelectric device. The widely commercially available are Peltier coolers (Figure 1.4), which usually operate below room temperature and have a rather simple design [5]. However, the energy harvesting systems are operating at a much higher temperature and require the effective heat sink design to provide a stable temperature gradient for the effective heat to electricity conversion.

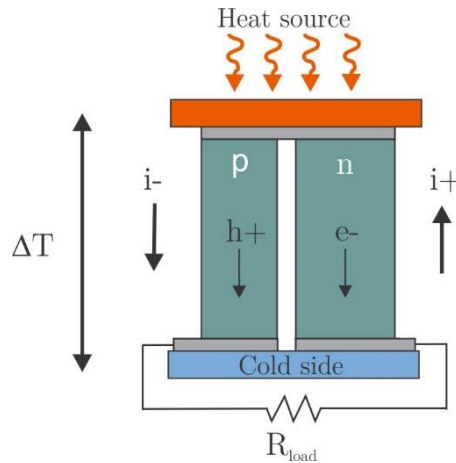


Figure 1.3: Schematic presentation of a generator based on the Seebeck effect.

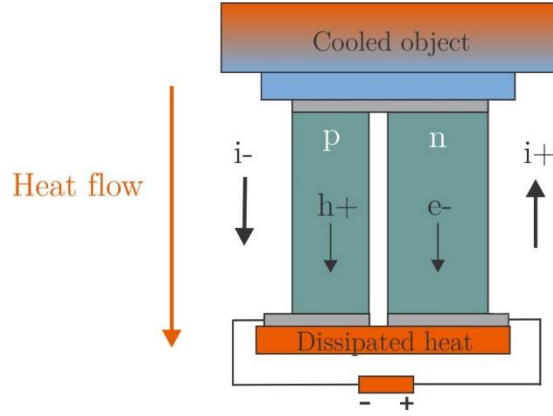


Figure 1.4: Schematic presentation of the Peltier cooler.

The available thermoelectric devices based on the Peltier coolers are widely used where high reliability and stringent temperature control is needed, mainly for cooling electronics. The thermoelectric generators are the main power source in deep space explorations, where they proved extremely good reliability on Voyager 1 and 2 missions, and were afterwards applied on many NASA missions to the Moon and Mars. Other applications, as heat harvesting on exhaust systems, are still not economically viable [6] and are not planned to be applied commercially in the near future.

1.4 Thermoelectric Figure of Merit and Efficiency

To get a good thermoelectric material for the effective electricity generation, we need to play with several conflicting and interdependent parameters. The most important are connected in a dimensionless figure of merit ZT , which was defined by Altenkirch with the following equation (1.5)

$$ZT = \frac{S^2 \sigma}{\kappa} \quad (1.5)$$

where S is the Seebeck coefficient, T stands for the absolute temperature (K), σ is electrical conductivity and κ is the thermal conductivity. So, in order to get high ZT values, there should be a high Seebeck coefficient, high electrical conductivity and low thermal conductivity.

Sometimes the figure of merit Z is described by the power factor divided by the thermal conductivity as seen in equation (1.6).

$$Z = \frac{P}{\kappa} \quad (1.6)$$

The power factor is then defined as (1.7)

$$P = \sigma S^2 \quad (1.7)$$

For a thermoelectric device, not only high ZT of materials and high dimensionless figure of merit of a complete device ($\overline{ZT}$) are enough, but also the actual thermal to electrical conversion efficiency. The maximum theoretical efficiency (η) for conversion of heat transferred from T_H (hot side) to the T_C (cold side) through a device with a defined figure of merit ($\overline{ZT}$) is given by (1.8)

$$\eta(\%) = 100 \left(\frac{T_H - T_C}{T_H} \right) * \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \left(\frac{T_H}{T_C} \right)} \quad (1.8)$$

Materials/devices with higher ZT values will therefore possess better efficiency. However, the efficiency is also largely dependent on the temperature gradient between the hot and the cold side, as presented in Figure 1.5. Thermoelectric generator with a high temperature gradient will have better conversion efficiency and vice versa. This highlights the fact that the high ZT values are meaningless, if the thermoelectric device is not well constructed to provide large temperature gradient and consequently, efficiency. Even more, stable materials with lower ZT values than their over-doped and non-stable relatives, can still be a material of choice for a proper thermoelectric device. Consequently, the goals in the thermoelectric materials design and improvement should be based on optimizing properties which do not deteriorate the material stability.

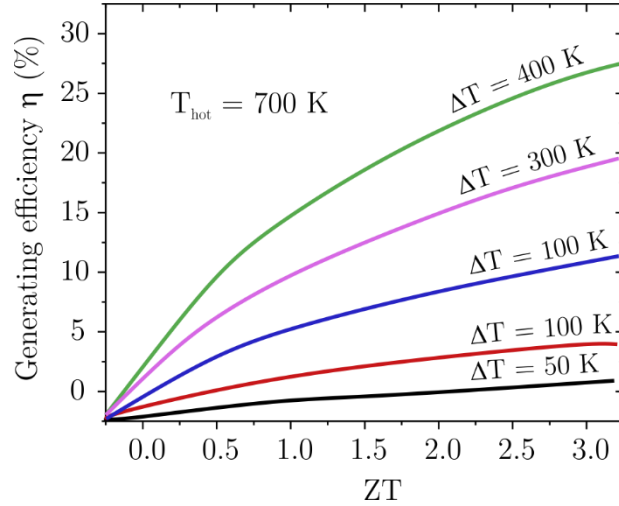


Figure 1.5: Efficiency of a thermoelectric device in dependence to its ZT at different temperature gradients (ΔT) (redrawn from ref. Zhang, 2015 [7]).

1.5 Tailoring TE Properties

In order to optimize the ZT value, we need to increase the electrical conductivity and Seebeck coefficient and decrease the thermal conductivity. These three characteristics are dependent on the interrelated material properties and the change in one parameter can be reflected in the other two, as presented in Figure 1.6. Therefore, during every parameter optimization, all properties should be observed and every improvement should be critically evaluated through the ZT increase. Nevertheless, to improve these three quantities, we need to have a deep knowledge of their physical background and factors which determine their value. These will be described in the next chapters with definitions of the Seebeck coefficient, electrical and thermal conductivity together with proposed ways for their improvement.

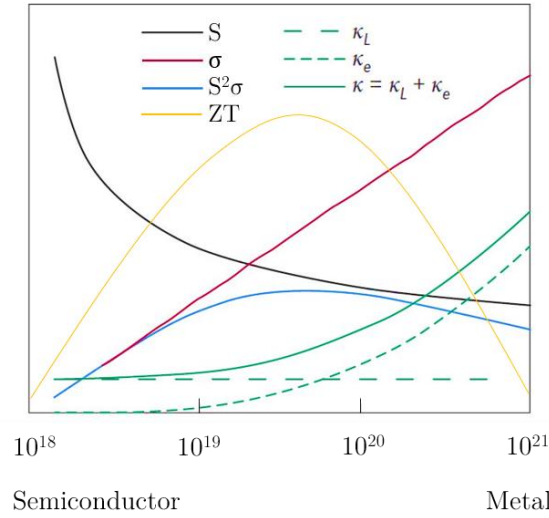


Figure 1.6: Seebeck coefficient, electrical conductivity, power factor, thermal conductivity, electron thermal conductivity and lattice thermal conductivity as a function of material carrier concentration (semiconductor-metal) (adapted from ref. [8]).

1.5.1 Seebeck coefficient & electrical conductivity

Seebeck coefficient and electrical conductivity are strongly interrelated, therefore they will be described together in the same chapter.

The Seebeck coefficient is for metals and degenerate semiconductors with parabolic band and energy-independent scattering approximation, proportional to the effective mass of charge carriers (m^*) and inversely proportional to the carrier concentration (n). This is presented in equation derived from the Mott formula (1.9), where k_B is the Boltzmann constant, h is the Planck constant and e is the elementary charge.

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3} \quad (1.9)$$

There is another important factor, carrier mobility μ , which defines how fast the charge carrier can move through a material under the applied electric field. It is directly related to the carrier concentration and τ , the relaxation time or time between subsequent collisions of charge carriers by defects (1.10).

$$\mu = \frac{e\tau}{m^*} \quad (1.10)$$

The mobility values are directly connected to the electrical conductivity (σ) through the expression (1.11)

$$\sigma = ne\mu \quad (1.11)$$

Electrical conductivity is an intrinsic property of materials which defines the ability to transport the electric charge through the material. It is directly dependent on the carrier concentration and strongly interrelates with the Seebeck coefficient. Materials with low carrier concentration possessing short relaxation/scattering times and high effective mass will have low carrier mobility and also high Seebeck coefficient. However, low carrier mobility results in low electrical conductivity, and therefore a compromise must be found

among the charge carrier concentration, their effective mass and mobility values to maximize Seebeck and not to deteriorate the electrical conductivity.

1.5.2 Thermal conductivity

The thermal conductivity is one of the key material design parameters which directly determines the thermoelectric device performance. It is the intrinsic property of a material which relates to its heat conduction ability. Thermal conductivity in crystals mainly derives from two sources. First, from electrons or holes (κ_e), and second, from phonons (κ_l) which are travelling through the lattice (1.12).

$$\kappa = \kappa_e + \kappa_l \quad (1.12)$$

The contribution of electronic thermal conductivity κ_e and lattice thermal conductivity κ_l has a different ratio for insulators, semiconductors or metals, because of the different band gap structure and the charge carrier density for these three materials, as presented in Figure 1.7.

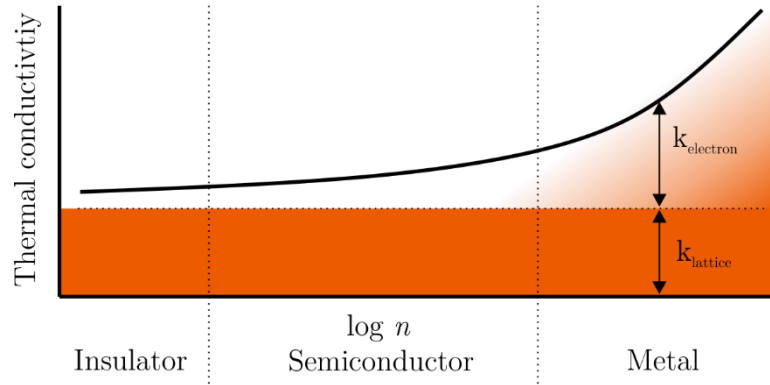


Figure 1.7: Thermal conductivity dependence on material properties (insulator-metal) based on the carrier concentration difference (re-drawn from ref. [9]).

Contribution of charge carriers κ_e to the total thermal conduction is not negligible in the case of heavily doped semiconductors, as common thermoelectric materials are. Since their behavior is closer to metals, the Wiedemann – Franz law could be used for the evaluation of the electronic contribution to the thermal conductivity. The Wiedemann – Franz law (1.13) states that all metals have the same electronic thermal conductivity to electrical conductivity ratio, and this ratio is proportional to the absolute temperature.

$$\frac{\kappa_e}{\sigma} = LT \quad (1.13)$$

The proportionally constant L is known as the Lorentz number (1.14).

$$L_0 = \frac{\kappa_e}{\sigma T} = \frac{\pi^2 k_B^2}{3e^2} \quad (1.14)$$

The value of the Lorentz number for metals and degenerate semiconductors, L_0 , is $2.4453 \times 10^{-8} \text{ W}\cdot\Omega/\text{K}^2$.

The main part of the total thermal conductivity for degenerate semiconductors is the lattice thermal conductivity κ_l , where heat is transported by phonons. They are represented

as lattice vibrations, which are translated through the lattice with waves. The lattice thermal conductivity mechanism was proposed by Callaway [10] as

$$\kappa_l = \frac{1}{3} \int C_v(\omega) v(\omega) l(\omega) \quad (1.15)$$

where C_v is the total heat capacity, v is the phonon group velocity, l the phonon mean free path and ω is the phonon frequency. Traditionally, the low lattice thermal conductivity is based on low C_v and v , achieved by a selection of materials with a large unit cell and loosely bonded heavy elements. These assumptions are based on the principle of the two phonon frequency modes which exist in a crystal or solid material, named as optical and acoustic phonons. They are defined by the number of atoms in a unit cell (N) through the approximation by Debye “*no. of phonon frequencies = $3N$* ”. The number of acoustic branches is always three, regardless the amount of atoms in a unit cell, and the rest are the optical modes. Thus, in a large unit cell, a higher amount of optical branches will be present and they will highly interact with the acoustic ones. These are considered as the main heat carriers due to their high phonon group velocity and the distortion of their propagation will immediately lead to the decrease in the thermal conductivity.

In the presence of impurities or imperfections in a crystal lattice, phonon waves scatter. Therefore, the last parameter, phonon mean free path l , is usually tailored by the introduction of defects into a crystal structure of the chosen material. The scattering of phonons in principle changes the nature (momentum) of the phonon waves. Consequently, they lost their group velocity and heat conduction through the crystal lattice is weaker. If there are scattering processes present, the phonon mean free path is the summation of the free path of phonon-phonon, defects and grain boundaries scattering (1.16).

$$l = \frac{1}{l_{phon} + l_{def} + l_{gb}} \quad (1.16)$$

There are two types of phonon-phonon scattering, normal (N process) and Umklapp (U process) [11]. The Umklapp scattering dominates over other scattering processes in the high temperature region and is exhibited in the T^{-1} curve shape of the thermal conductivity. Measuring thermal conductivity with the increasing temperature reflects the dominant phonon scattering processes at a certain temperature range. At low temperatures, the thermal conductivity is mostly governed by the grain boundary scattering. As the temperature increases, the wavelength decreases and hence, phonons are scattered by defects and impurities in the crystal lattice. At even higher temperatures, Umklapp or phonon-phonon scattering dominates over all.

Therefore, the approaches in the material's design to lower the thermal conductivity should be based on all scale hierarchical structures in a single sample to cover the whole range of temperature dependent scattering processes. This concept has been named proven in practice and named as the panoscopic approach [12], based on the grain boundary engineering, nano-inclusions, point or line defects and the superstructure introduction, presented graphically in Figure 1.8.

Nevertheless, as this approach is highly beneficial for decreasing the thermal conductivity, it inevitably affects the electrical conductivity and Seebeck coefficient through the increased scattering of charge carriers. Therefore, to tackle their interdependency, the compromise must be found with the previously addressed approach in 1995 stated as “Phonon glass, electron crystal” (PGEC) introduced by Slack [13]. He stated that good thermoelectric materials should have the thermal conductivity behavior as a glassy material and on the other hand, the electrical conductivity and Seebeck

coefficient as a perfect crystalline material. Following this principle and guidelines above, many recent improvements in the field of thermoelectric materials were made.

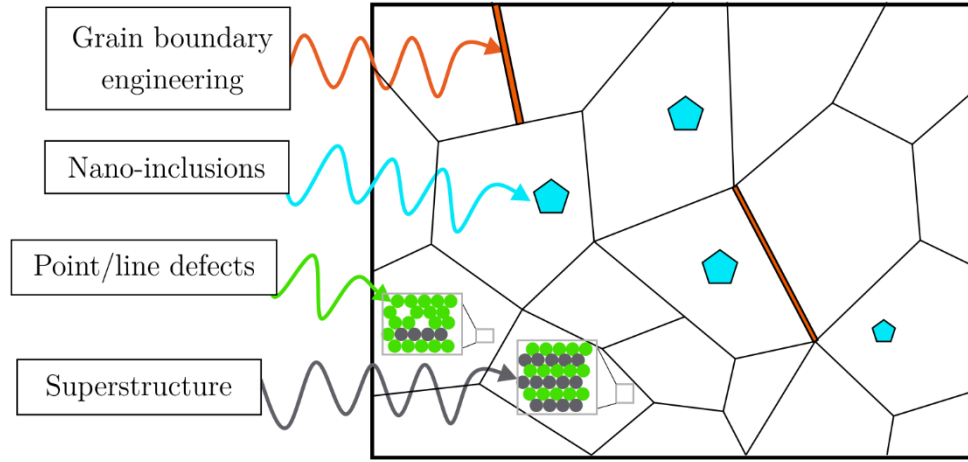


Figure 1.8: Various strategies for increasing phonon scattering in order to decrease the lattice thermal conductivity.

All those approaches are presented in the next chapters through the state of the art thermoelectric materials and their development since the “boom” in thermoelectrics research in 1950s.

1.6 Thermoelectric Materials

The first thermoelectric materials, used in the early experiments by Seebeck, Peltier and Thomson, were based on alloys of PbS, chalcogenide minerals group, cobalt arsenide and zinc antimonide. Later, Becquerel and Haken were exploring particularly ZnSb, CdSb, and Sb_2Te_2 , Bi_2Te_3 , SnTe and PbTe [14]. As nicely presented in Figure 1.9, the modern thermoelectric materials research increased in the middle of the century. At that time, Ioffe and Goldsmid boosted the thermoelectric performance of PbTe and Bi_2Te_3 [1, 15] through alloying with isostructural and isoelectronic relatives, such as PbSe and Sb_2Te_2 , resulting in a large reduction of the thermal conductivity and no significant deterioration of the electronic properties. The other broadly investigated compound since that time is SiGe [16–18], which was widely used in the deep-space missions as a main power supply source. The superior thermoelectric properties and stability of SiGe alloys is proven by Voyager 1 and 2 missions, which are already operative for almost 40 years [19].

For almost half a century, the isostructural alloying was the only effective approach for the thermoelectric materials design. The turning point in the 90s was the idea of Hicks and Dresselhaus [20] with nano-structuration and utilization of the quantum-well superstructures for improvement of the thermoelectric properties. The emerging era of nanotechnology and several technological breakthroughs have confirmed their theoretical predictions in several reports of PbTe/ $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ [21], $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ [22] and SiGe enhancements with nanostructures [23].

In the further years, the revolutionary idea was presented by Slack about “phonon glass – electron crystal” behavior for a good thermoelectric material. Generally, there are two groups of materials following this principle, the clathrates and the skutterudites. These are the “cage compounds” that exhibit low thermal conductivity due to the rattling effect of the trapped atoms/molecules inside the cage [24] and the good electron conduction enabled by the cage itself. The clathrates consist of groups of 13 and 14 elements as “host” atoms

and the cations from group 1 and 2 as “guests”. For the thermoelectric applications mainly the silicide and germanide clathrates are investigated. The highest ZT values were observed in the single crystals of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$, as 1.35 at 900 K [25] and 0.7 at 870 K for their bulk version [26]. The bulk n-type clathrates have ZT of 0.72 at 800 K for $\text{Sr}_8\text{Ga}_{1.5}\text{In}_{0.5}\text{Ge}_{30}$ compound and for the p-type $\text{Ba}_8\text{Ga}_{16}\text{Al}_3\text{Ge}_{27}$, the ZT is 0.61 at 760 K [27].

The other PGEC materials are filled skutterudites, with a general formula RM_4X_{12} where R is La, Ce, Pr Nd, Eu; M is Fe, Ru, Os; and X is a pnictogen P, Ar, or Sb [28]. The most investigated are antimony based compounds, CoSb_3 [29] [30], which have a high Seebeck coefficient (200 $\mu\text{V/K}$), but also a high thermal conductivity (9 W/mK). To improve the final ZT values, modifications of the crystal structure through filling voids with guest “rattling” atoms (R-s in the formulation above) were performed [24, 31-34]. This decreased the thermal conductivity enormously and improved their ZT to values around 1 at 800 K. However, skutterudites are having issues with the thermal stability, due to the sublimation of Sb and material degradation [35, 36] and this slightly hinders their commercial application.

The group of chalcogenides is also widely investigated and it includes selenides, tellurides and sulphides. Especially tellurides, with the most known Bi_2Te_3 , are recognized as a promising thermoelectric material since the first experiments in thermoelectricity. However, the era of nanostructuring largely boosted their performance to ZT 1.4 at 373 K [37] (Figure 9). Selenides and sulphides are other two chalcogenides, which reached attention due to their low-cost and outstanding thermoelectric properties [38, 39] for usage in the low and mid temperature range. Selenides have the reported ZT levels of 2.6 in the SnSe orthorhombic single crystals along b-axis [40], due to ultra-low thermal conductivity around 0.3 W/mK. This was followed by numerous studies of single- and polycrystalline SnSe , however, even with doping, much smaller ZT values around 1 were obtained [41, 42] [43]. Recent reports address this inconsistent trend [44] and estimate the source of the problematics in the measurement of the intrinsic thermal conductivity in the SnSe single crystal. The newest study reports significantly higher thermal conductivity [45] and re-opens a strong debate about the necessity of careful measurement and evaluating all influencing factors on the final thermoelectric properties [46]. Beside the most known SnSe , other thermoelectrics from this group are Cu_2Se with ZT values from 1 to 2 [47] [48, 49], In-Se [50]. However, despite the gigantesque ZT values presented in Figure 9, copper selenides have not been applied in a commercial device, probably due to the known issues with stability under applied current [51]. Among the group of chalcogenides, sulfides are claimed to be more stable and are intensively investigated due to their low cost [52]. The most researched are TiS_2 [53-58] $\text{Cu}_{1.8}\text{S}$ [59], SnS_2 [60], LaS_y [61], PbS [12]. The highest ZT values of 1.7 were reported for $\text{Cu}_{1.8}\text{S}$ [62], however the diffusivity of Cu under applied current remains a big issue for the commercial application. The panoscopic approach in PbS and PbSe materials reported high ZT values due to the all scale hierarchical structures in a single sample, effectively lowered the thermal conductivity and resulted in ZT of around 1.5, which is among the highest reported so far (Figure 1.9).

The tetrahedrites are natural earth abundant sulfo-salts minerals with the general chemical composition $\text{A}_{12}\text{B}_4\text{S}_{13}$, where A is mostly Cu or other elements, such as Zn, Fe, Ag, Hg, Pb, Ni and Co, and B corresponds to Sb or As. They have a complex crystal structure, leading to the intrinsically low thermal conductivity. With the additional co-doping, the best ZT values in this system are from 0.6 to 1.1 at around 600-700 K in several reports [63-68]. One of their main benefits is the possibility to use natural tetrahedrite minerals in the material synthesis [69, 70] and led to one of the first commercial applications of thermoelectric generators (Alphabet energy).

Half Heusler alloys [71, 72] with the compositions XNiSn and XCoSb ($\text{X} = \text{Ti, Zr}$ or Hf) are generally considered as thermoelectric materials [73, 74]. As seen in Figure 1.9, their performance reached ZT values of around 1, with still a lot of room for improvement.

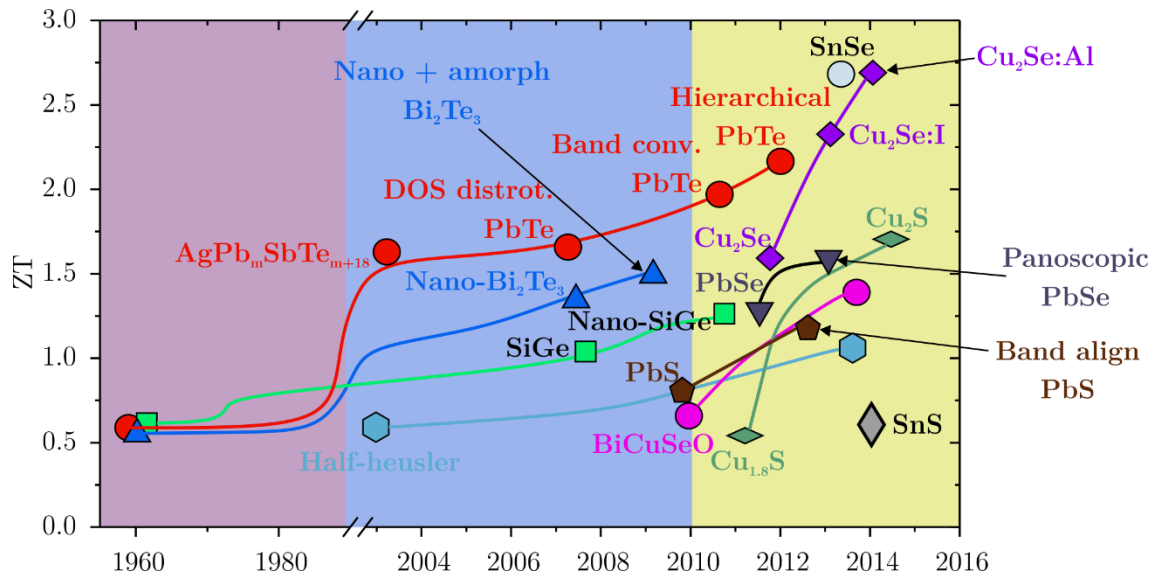


Figure 1.9: The increase in ZT values for the most studied thermoelectric materials in the last 50 years (redrawn from [7]).

Despite all the superior facts, the relative abundance of the constituent elements governs the final commercial applicability of a certain thermoelectric material. As nicely seen in Figure 1.10, many elements, which are indispensable like Bi, Sb and especially Te, have a low abundance and can be in a high risk for the supply shortcuts. This issue together with the general problematics of stability in intermetallics spread the research to other possible thermoelectric materials.

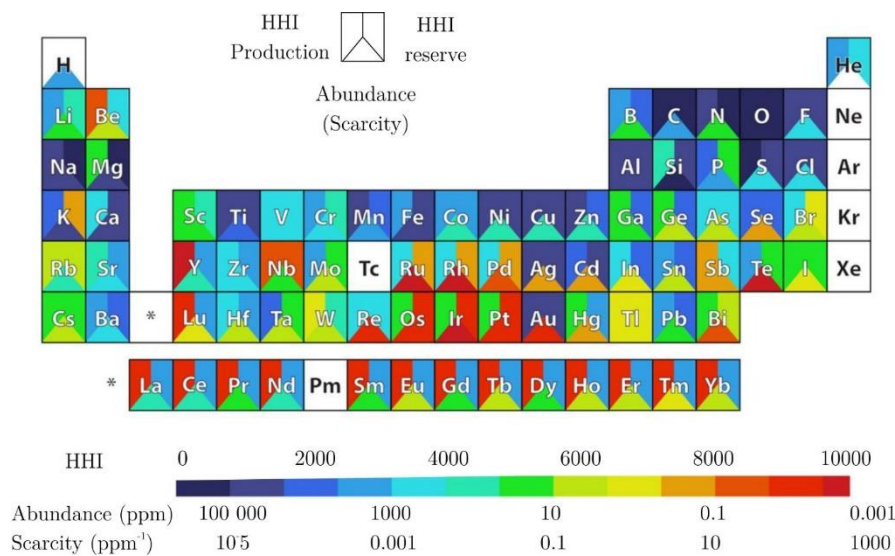


Figure 1.10: Resource considerations from USGS statistics in 2011. (HHI – Herfindahl – Hirschman index, a commonly accepted measure of market concentration calculated from the geological data and geopolitical data (adopted from ref. [75].)

1.7 Oxide Thermoelectric Materials

Oxide thermoelectric materials caught the attention after the discovery of a large thermoelectric effect in a layered cobaltate by Teresaki [76] and Funahashi [77]. The main advantage of oxides in comparison to the intermetallics was considered their low price and a good temperature stability, which make them very promising also for the thermoelectric applications at high temperatures, up to about 1000 K. The field of oxide thermoelectric materials is since then growing and many other oxide materials were intensively investigated [78-81]. So far, cobaltates exhibited the largest ZT values reported among the p-type oxide materials. On the side of n-type materials, focus is put on the doped SrTiO_3 , CaMnO_3 from the perovskite family, ZnO-doped and In_2O_3 doped thermoelectric materials.

The layered cobaltate series includes NaCo_2O_4 , $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Bi}_2\text{Sr}_3\text{Co}_2\text{O}_9$. While NaCo_2O_4 is known to be highly unstable and sensitive to the atmospheric conditions (humidity)[82], the $\text{Ca}_3\text{Co}_4\text{O}_9$ does not have these issues and is much more promising for the further optimization of the thermoelectric properties. These are strongly related to its misfit layered structure composed of CoO_2 layers of the CdI_2 type structure, which are ensuring the good electrical conductivity, and the rock salt type layer of Ca_2CoO_3 , acting as an insulator (Figure 1.11) [83]. The mismatch and the weak connection among these layers is enhancing the phonon scattering and is resulting in the reduced thermal conductivity. Consequently, they have a large anisotropy in thermoelectric properties (i.e. electrical conductivity along a-b plane is about 5-times higher than in the c direction) and possess the ZT values of 0.87 at 1000 °C along the layers in the a-b planes of a single crystal [84]. In the polycrystalline $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramics with distinct plate-like morphology of grains, the best reported ZT values are varying depending on the rate of texturing and microstructural optimization (density, grain size) and are from 0.1 up to 0.31 [85].

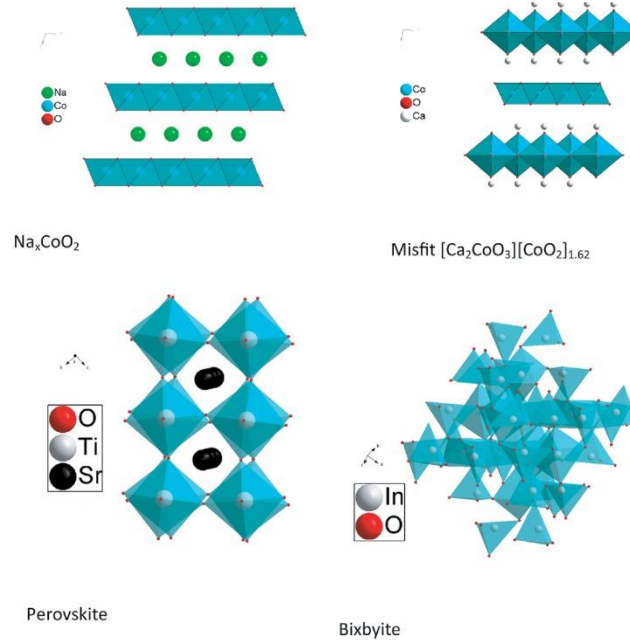


Figure 1.11: Structures of the best thermoelectric oxides, Na_xCoO_2 , misfits, perovskites, and bixbyites [80].

The n-type thermoelectric materials from the perovskite group (Figure 1.11) are represented by the general formula ABO_3 and the most known are SrTiO_3 and CaMnO_3 .

The SrTiO_3 which is in un-doped state behaving as an insulator and becomes an n-type semiconductor upon doping with higher valence ions. The most studied dopants are La, targeting Sr sites, and/or Nb at Ti sites [86], resulting in the best reported ZT values of 0.35 at 1000 °C for 10% Nb-doped SrTiO_3 polycrystalline ceramics [87]. Another pathway for improving the ZT values is the induction of the natural superlattice structure of Ruddlesden-Popper (RP) $(\text{SrO})(\text{SrTiO}_3)_n$ phase [88]. This structure consists of perovskite layers separated by SrO layers [89] and despite effectively lowering thermal conductivity, have not resulted in the improved ZT values above 0.14 at 1000 K.

The best results in the group of perovskite manganites, CaMnO_3 , are made with the Nb^{5+} doping through the *chimie douce* synthesis, resulting in the twinned microstructure and nano-sized crystallites, both effectively decreasing the thermal conductivity. This leads to the $\text{ZT} = 0.32$ at 1060 for 2 % doped CaMnO_3 polycrystalline ceramics [90].

The In_2O_3 series is based on the bixbyite structure (Figure 1.11) and presents maximum ZT values in polycrystalline ceramics for Ga doped samples of about 0.30 at 700 °C [81, 91, 92].

1.7.1 ZnO-based thermoelectric materials

ZnO is a n-type semiconductor with a wide band gap of 3.37 eV at room temperature and interesting properties being also piezoelectric, pyroelectric, bio-safe and biocompatible. Hence, it is already widely used in various technological applications such as varistors in overvoltage protection, piezoelectric devices, optoelectronics, sensors, catalyst and biomedical sciences [93].

1.7.1.1 Crystal structure of ZnO

ZnO is naturally mostly occurring as zincite mineral, crystallizing in the hexagonal wurtzite-type structure. Each anion is surrounded by four cations at the corners of a tetrahedral, and vice versa, as schematically presented in Figure 1.12a. The tetrahedral coordination is a consequence of sp^3 covalent bonding nature among Zn^{2+} and O^{2-} ions. The wurtzite structure has a hexagonal unit cell and belongs to the space group $\text{P6}_3\text{mc}$ in Hermann-Mauguin notation. The structure is non-centrosymmetric and exhibits crystallographic polarity, which is indicated by the orientation of tetrahedrons (Figure 1.12b). The positive $[0001]$ direction points from the face of the O plane to the Zn plane, along the c axis, perpendicular to the (0001) basal planes. These directions are very important, because they determine the growth, defect generation and also some physical properties [94].

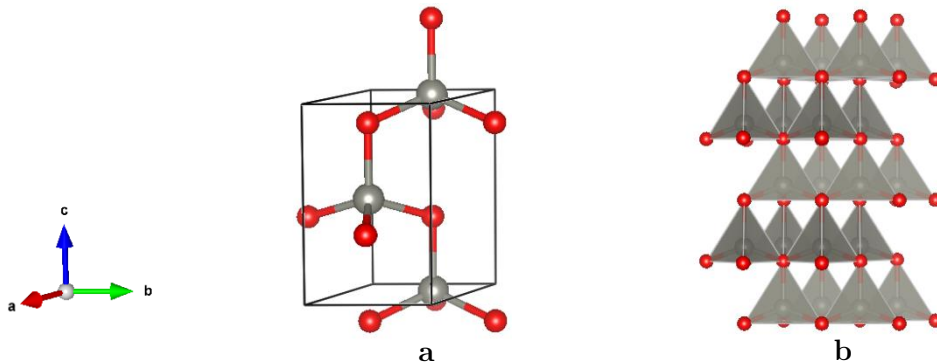


Figure 1.12: The ZnO wurtzite structure viewed along the a axis. (a) Schematic representation of the Zn-O bonding in tetrahedral coordination and (b) the non-

centrosymmetric hexagonal wurtzite structure. (Grey spheres represent Zn and red spheres represent O atoms (re-drawn in VESTA software from [95]).

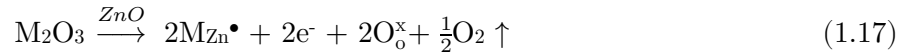
1.7.1.2 Thermoelectric properties

As a thermoelectric material, pure ZnO is not so good; its electrical conductivity is much too low in the range of 10 S/cm and the thermal conductivity is much too high of about 40 W/mK at room temperature due to the non-complex wurtzite structure [96]. Nevertheless, the Seebeck coefficient is around 400 $\mu\text{V/K}$ and through the introduction of dopants to increase the charge carrier concentration, accompanied by the induction of microstructural and structural modifications to decrease the thermal conductivity, the final ZT values could be effectively improved.

For the increase of the thermoelectric properties, ZnO was doped with various dopants such as oxides of In, Ga, Fe, Al, Sn, Ti and Ni [97-102], which is presented below.

1.7.1.3 ZnO doped with 3^+ dopants

Doping of ZnO with 3^+ metallic oxides such as Al, Ga and Fe is described by the following expression (1.17):



All these dopants enter the regular sites of Zn in the crystal lattice of ZnO. As a result, there are free electrons in the system, providing larger charge carrier density and consequently higher electrical conductivity.

The paper from Tsubota et al. [103] for Al-doped ZnO (AZO) was among the first that reported the high electrical conductivity of 1000 S/cm and consequently good power factors of $15 \times 10^{-4} \text{ W/mK}^2$ at 1000 °C. This was attributed to the high carrier mobility and increase in the carrier concentrations. However, the thermal conductivity remained high, at values of around 5 W/mK at 1000 °C, which summed up in the final ZT values of 0.30. Different strategies were employed for the effective decrease of the thermal conductivity in order to improve the final ZT values. In the case of polycrystalline ceramics, it is the decrease in the grain size and processing from nano-powders or usage of hot-pressing [104] or FAST/SPS sintering [105-108]. One of the possible strategies is also the introduction of a second nanophase, and in the case of Al-doping, the formation of a secondary ZnAl_2O_4 spinel phase is quite common and can be effectively tailored for that purpose [10, 103, 109, 110]. The measurements of a single spinel phase ZnAl_2O_4 revealed that the compound has high electrical resistivity [103] and it strongly scatters phonons. Since its presence is hard to avoid even at less than 2 % of Al-doping due to the particle agglomeration, the research went further to effectively use its presence for lowering the thermal conductivity [97]. The samples were prepared from ZnO nano-powders processed by the sol-gel method [97, 110] or chemical co-deposition method [111]. They showed improved properties in contrast to the samples prepared by the conventional mixing of oxide powders due to the better distribution of nano-precipitates of the spinel phase which resulted in decreased thermal conductivity as a result of phonon scattering at the grain boundaries. The thermal conductivity was lowered to 2 W/mK and the resultant ZT of 0.44 was reported at 1000 K [97].

Some reports [100] are also about the additional co-doping of AZO with transition metal oxides of Fe, Ni and Sm, however, despite the improvement in the electrical conductivity,

the thermal conductivity has not been lowered effectively, therefore the ZT values were around 0.12 at 1073 K.

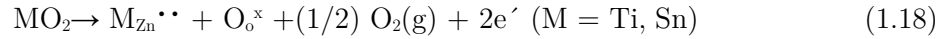
The best ZT values for ZnO-based ceramics were reported for a combination of Al and Ga doping, which exhibit ZT values of about 0.47 at 1000 K [112]. Co-doping of Al and Ga and formation of the $\text{Zn}_{0.96}\text{Al}_{0.02}\text{Ga}_{0.02}\text{O}$ resulted also in a “granular texture” with nanoprecipitates of spinel secondary phases. Nevertheless, recent reports regarding the Ga-doped ZnO revealed a formation of $(\text{ZnO})_k\text{Ga}_2\text{O}_3$ ($k \geq 9$) phase possessing a complex structure composed of IBs, which effectively blocks the phonon transport and contributes to the decrease in the thermal conductivity [113]. Our recent study of low Ga-doped ZnO ceramics with the composition $\text{Zn}_{1-x}\text{Ga}_x\text{O}_{1+x/2}$ showed that already for $x=0.01$ nonperiodic 2D defects are formed. These head-to-head inversion twin (h-IT) boundaries and tail-to-tail inversion boundaries (t-IB) are responsible for strong phonon scattering and hence noticeably reduced thermal conductivity of Ga:ZnO bulk compounds, while maintaining relatively good electrical conductivity [114].

1.7.1.4 Ni-doped ZnO

The Ni-doped ZnO ceramics resulted in the formation of $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ ($x \leq 0.06$) solid solution and the studies [101, 115] revealed the ZT values of 0.09 at 1000 K. It is important to mention that a presence of a secondary cubic phase (NiO_{ss}) was detected, however, the thermal conductivity was not effectively lowered below the desired 5 W/mK at 1000 K.

1.7.1.5 Sn and Ti-doped ZnO

According to reports [109, 116], doping with both TiO_2 and SnO_2 results in the formation of $\text{Zn}_{1-x}\text{Ti}_x\text{O}_4$ or $\text{Zn}_{1-x}\text{Sn}_x\text{O}_4$ solid solutions in the wurtzite structure as a consequence of substituting Ti^{4+} or Sn^{4+} for Zn^{2+} , which is described by a following reaction (1.18):



It shows that doping results in increased concentration of the charge carriers (electrons) in material, however, the formation of cubic spinel phases, Zn_2TiO_4 and Zn_2SnO_4 was also observed, mainly at the grain boundaries. For the additions larger than 1 mol %, the electrical conductivity was negatively affected by the amount of the spinel phase. The final ZT values are 0.09 at 1000 K.

1.7.2 $(\text{ZnO})_k\text{In}_2\text{O}_3$ system

Like in the intermetallic-based TE materials, the research in the oxide-based thermoelectrics is nowadays oriented towards nano-structuring (embedded nanoparticles, nanostructured defects, nano-grain sizes) for enhanced phonon scattering and the reduction of the thermal conductivity [117]. Multiple planar defects (i.e., inversion boundaries or IBs) can be introduced into the wurtzite-type ZnO by adding In_2O_3 . The formed phases belong to the $(\text{ZnO})_k\text{In}_2\text{O}_3$ homologous series and have been widely studied due to their potential as a transparent conducting oxide and a high temperature thermoelectric material. Their main advantages are; good chemical and structural stability in air atmosphere at high temperatures, their wide band gap governs the progressive increase of the Seebeck coefficient to high temperature range, and they possess a low thermal conductivity due to their natural superlattice structure [118].

1.7.2.1 Structure

The first report in 1967 from Kasper et al. demonstrated the formation of homologous phases $(\text{ZnO})_k\text{In}_2\text{O}_3$ with k values from 2-5 and 7 in the temperature range from 1100 °C - 1400 °C [119] with the layered structures close to the wurtzite structure. Nevertheless, he has not observed the spinel phase in this system, and its presence has not been confirmed in any report until nowadays due to its high calculated formation energies and favorable configuration entropy for $(\text{ZnO})_k\text{In}_2\text{O}_3$ homologous phases at high temperatures [120]. Further reports from Kimizuka et al. [121] expanded the number of possible phases to $k \leq 15$ at until 1350 °C. Afterwards, the phase diagram was obtained over the temperature range of 1100 °C – 1400 °C by Moriga et al. [122]. In the phase diagram, the system of $(\text{ZnO})_k\text{In}_2\text{O}_3$ is presented as a series of compounds with the formula $\text{Zn}_k\text{In}_2\text{O}_{k+3}$, as shown in Figure 1.13 [123]. At 1100 °C only two compounds are stable, the $\text{Zn}_5\text{In}_2\text{O}_8$ and $\text{Zn}_7\text{In}_2\text{O}_{10}$, however, the number of stable compounds towards ZnO-rich part of the diagram is increasing with the rising temperature (Figure 1.13).

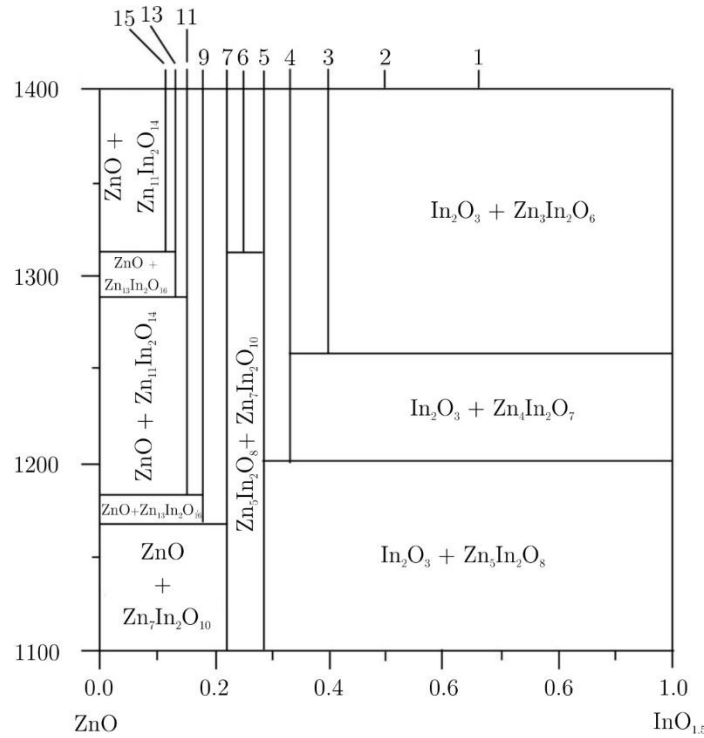


Figure 1.13: The phase diagram of $(\text{ZnO})_k\text{In}_2\text{O}_3$ system (adapted from [123]).

ZnO and In_2O_3 forms a series of complex structures [119] with phases composed of ZnO slabs interleaved with faults [124] creating a natural superlattice structure [125]. Particularly, the system has a polytypoid structure consisting of $(\text{Zn}/\text{In})\text{O}$ slabs separated by single edge sharing InO_2^- octahedral layers, acting as inversion boundaries (Figure 1.14). Therefore another polarity inversion is formed by the fivefold coordinated In and Zn atoms inside $(\text{Zn}/\text{In})\text{O}$ slabs creating a zig-zag pattern [126]. The crystallographic system differs with k ; odd k values belong to the $R\bar{3}m$ space group and even to $P6_3\text{mmm}$. The particular k in the $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ homologous phase is defined by a number of “ ZnO ” layers (d) sandwiched between InO_2^- octahedral layers along the basal planes (0001) according to the formulation $d = k+1$ Figure 1.14.

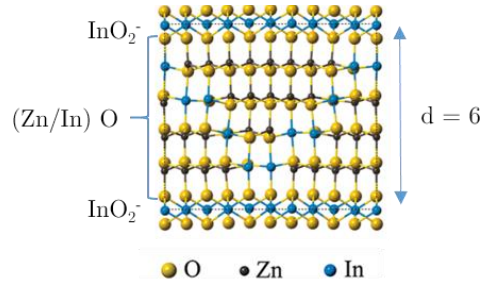


Figure 1.14: Superlattice structure of the $\text{Zn}_5\text{In}_2\text{O}_8$ phase (adapted from [127]).

The formation of these two types of planar defects takes place through diffusion of the In^{3+} ions into the wurtzite structure of ZnO [128]. Diffusion mechanism is dependent on the concentration of indium ions; at lower concentrations they are incorporated on Zn sites, creating a vacancy on Zn site, but at higher concentrations, In-ions are forming a series of planar defects along the c-axis of a hexagonal wurtzite structure [125]. At elevated temperatures, the evaporation of Zn with the formation of Zn-vacancies (V_{Zn}) becomes larger and triggers the system's charge deficiency. As a consequence, the increased diffusion of In-ions starts to compensate the charge balance. This mechanism, presented in Figure 1.15, is named as internal diffusion mechanism and is governed by the local charge deficiency [128]. Simultaneous diffusion along basal planes is controlled by the Zn vacancy diffusion and positioning of In^{3+} in octahedral cavity. This triggers shift in adjacent wurtzite layer which favors tail to tail orientations of tetrahedrons. Therefore, on sides of the octahedrons polarity is inverted. This charge deficiency mechanism propagates through the whole grain, until it exits on the grain boundaries.

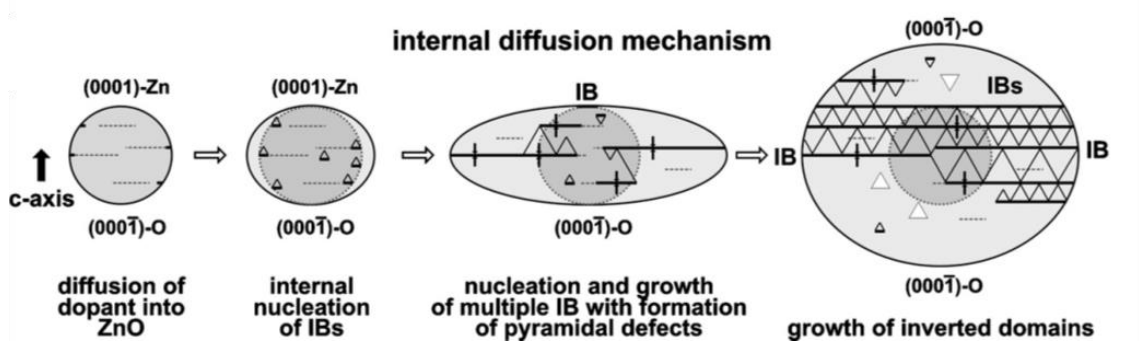


Figure 1.15: Internal diffusion mechanism of In incorporation into the ZnO -wurtzite lattice through formation of inversion boundaries [128].

As a consequence of the In diffusion into the ZnO wurtzite structure, the extremely long sintering times are reported with the increasing amount of ZnO in the composition [121]. Therefore, the most investigated compounds in the system $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ are $k = 3, 5, 7, 9$ due to their lower formation temperature and shorter sintering times. They are usually prepared by mixing the powders in proper amounts, pressed into pellets and then sintered at temperatures from $1100\text{ }^\circ\text{C}$ to $1550\text{ }^\circ\text{C}$ from 2 h up to three to seven days [129, 130].

To study the physical properties, the single crystals of $(\text{ZnO})_5\text{In}_2\text{O}_3$ were grown by a flux method with PbF_2 as a flux media at $1150\text{ }^\circ\text{C}$ for 2 h [131]. The obtained single crystals were plate-like and they had a large anisotropy in the measured electrical conductivity. It was approximately three-times higher in the in-plane direction (along basal planes) than along the c-axis (out of plane)[132]. The basic principles of conduction mechanisms are based on the InO_2^- layers, which are stacked along the a - b plane, acting as charge carrier

sources and at the same time also the main conduction path. The expected electronic properties are somewhere between the parent oxides, ZnO and In_2O_3 , with approaching to those of ZnO with the increasing k values. Dominant defect mechanism in this system depends on the crystal structure and cation composition [133][133]. Therefore, electrical conductivity mechanisms are strongly correlated with the structure of homologous series and are controlled by the k values.

1.7.2.2 Thermoelectric properties

The first report about the thermoelectric properties of the homologous series $(\text{ZnO})_k\text{In}_2\text{O}_3$ ($k = 5, 7, 9$) from Ohta et al. [129] revealed reasonably good thermoelectric properties of “reaction-sintered” powders at 1823 K for 2 h in air atmosphere. The thermal conductivity was below 5 W/mK for all three studied compositions and the ZT of 0.1 was observed for $k = 5$ composition and was almost linearly decreasing with k values.

Due to the plate-like grain shape and anisotropy in the thermoelectric properties, ceramics was also prepared with the so-called “*reactive templated grain growth*” to induce texturing and to improve the ZT values [134, 135]. Samples with $k = 5$ and 9 were prepared from plate-like precursor of ZnO ($\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2$) and In_2O_3 mixture, and afterwards tape casted in order to align grains along their long axis. When dried, stacked, pressed to form a pellet and heated up to 1423 K for 6 h to obtain a homologous phase, additionally pressed and then sintered at 1823 K for 2 h in air. The observed ZT values were 0.18 at 1073 K.

To further improve the ZT values, the co-doping was employed and it was shown that isovalent and/or heterovalent dopant ions can be introduced into the $(\text{ZnO})_k\text{In}_2\text{O}_3$ superlattice structure to obtain a series of $(\text{ZnO})_k(\text{In}_{1-x}\text{M}_x)\text{O}_3$ compounds ($\text{M} = \text{metal ion}$) [136, 137]. Substitution of Zn and/or In with ions of Al, Mg, Co, Y and Fe [138, 139], Ca [140], in general resulted in a decrease of the electrical and thermal conductivities, which was attributed to the lattice distortion due to the incorporation of dopants on the IBs in the basal-plane InO_2^- layers. Furthermore, with their increasing amount, the charge-carrier concentration decreased, which resulted in an increase of the carrier mobility, especially in the case of Co and Y. However, only doping with Y in amounts up to $x = 0.01$ was reported to result in a slightly increased electrical conductivity, and hence improved ZT values to 0.13.

The combination of Y doping with the utilization of the “*reactive templated grain growth*” resulted in the best reported ZT values in this system of about 0.33 at 1073 K. Nevertheless, the textured samples had a very low density (below 90 %) and therefore the thermal conductivity was additionally lowered in comparison to the conventionally sintered samples.

Chapter 2

Aims and Hypothesis

2.1 Description of the Problem

The growing governmental and public awareness of the environmental problems in recent years led to the intensive research of re-use and recycling of the available resources. One of the possible sources of electrical energy is hidden in the waste heat, which can be harvested and re-used effectively with the thermoelectric modules to produce electricity. These types of materials have long been overlooked, until the breakthrough of the nanotechnology field in the middle 90's. Afterwards, the research in thermoelectric materials spread from the well-known Bi_2Te_3 , PbTe -based materials to skutterudites, silicides, other chalcogenides (selenides, sulphides) and clatrates. Due to the issues of thermal stability in all these materials in the high temperature region, the field of oxide thermoelectric materials developed as a low cost alternative.

The n-type thermoelectric material based on $(\text{ZnO})_k\text{In}_2\text{O}_3$ homologous phases with a general formula of $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ and ordered system of In-based defects with a superlattice structure offered an excellent platform for additional tailoring of the thermoelectric properties. Their structure consists of $(\text{Zn}/\text{In})\text{O}$ slabs separated by single edge sharing InO_2^- octahedral layers, creating a natural superlattice structure. The particular k in the $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ homologous phase is defined by a number of “ZnO” layers (d) sandwiched between InO_2^- octahedral layers along the basal planes (0001) according to the formulation $d = k+1$. The phases are formed through the diffusion of In^{3+} ions into the wurtzite structure of ZnO along the basal and pyramidal planes, requiring extremely long times and temperatures for the ZnO-rich compositions (k values above 15). Furthermore, grains predominantly grow along basal planes and develop a plate-like morphology. Only two compounds are considered stable at 1100 °C with an ordered array of defects, these are $\text{Zn}_5\text{In}_2\text{O}_8$ and $\text{Zn}_7\text{In}_2\text{O}_{10}$. Nevertheless, with the increasing sintering temperature and time, the number of stable compounds towards ZnO-rich part of the diagram is increasing. Therefore, the most investigated compounds in the system $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ are $k = 3, 5, 7, 9$ due to their lower formation temperature and short sintering times. In most of the presented studies, the processes of the homologous phase formations and their influence on the grain growth and microstructure development were not analysed and discussed at all, even if they could largely affect the thermoelectric properties. The composition, hence local ZnO to In_2O_3 ratio, in the early phase development could highly influence the further microstructural evolution, especially considering the diffusion based phase formation and anisotropic growth of grains along basal plane In-based defects.

The previously reported thermoelectric characteristics showed the highest ZT for the undoped samples of around 0.1 for $k = 5$ at 1000 K, and a general decrease with the increasing k values. The ZT values for $k = 5$ are still considered too low for the effective waste heat harvesting, and furthermore, this compound also possesses a huge amount of

the expensive In_2O_3 , therefore, the system is currently not commercially attractive at all. To improve it, the co-doping was employed and it was shown that isovalent dopant ions can be introduced into the $(\text{ZnO})_k\text{In}_2\text{O}_3$ superlattice structure to obtain a series of $(\text{ZnO})_k(\text{In}_{1-x}\text{M}_x)\text{O}_3$ compounds (M = metal ion). Nevertheless, the actual incorporation sites of the 3^+ ions inside the $(\text{ZnO})_k\text{InMO}_3$ system and their influence on the TE properties have not been addressed properly so far.

At last, as described above, the conventional synthesis is time consuming, and takes days or even weeks to synthesise the ZnO-rich homologous phase. Till today, there were almost no alternative sintering pathways proposed for this system in order to decrease costs and make the material more applicable for the commercial usage.

2.2 Aims and Goals of the Dissertation

This dissertation is addressing the problematics of the thermoelectric material design in the $(\text{ZnO})_k\text{In}_2\text{O}_3$ system based on the detailed phase composition analysis, microstructural and structural characteristics in order to optimize the thermoelectric performance and reduce the processing costs.

The aim of this dissertation is to systematically study the phase formation, microstructure development and resulting thermoelectric characteristics for ceramics with the compositions of $(\text{ZnO})_k\text{In}_2\text{O}_3$ for $k \geq 5$ through the solid-state processing of the oxide powders in the temperature range from 900 °C to 1500 °C. By resolving the complex processes of homologous phase formation, their effect on the grain growth and the microstructure development, and consequently, thermoelectric properties could be better explained also for higher k phases.

Even more, since the formation of the planar defects defines the plate-like morphology, this gives the possibility for tailoring a microstructure through texturing. This again confirmed the importance of a microstructure optimisation for the improvement of the TE characteristics of ceramics in the $(\text{ZnO})_k\text{In}_2\text{O}_3$ system.

The co-doping with isovalent dopant ions into the $(\text{ZnO})_k\text{In}_2\text{O}_3$ superlattice structure forms a series of $(\text{ZnO})_k(\text{In}_{1-x}\text{M}_x)\text{O}_3$ compounds (M = metal ion). The actual incorporation sites of the 3^+ ions inside the $(\text{ZnO})_k\text{InMO}_3$ system and their influence on the TE properties should be properly addressed. Therefore, the doping with alumina and its effects on the phase composition, structure and charge carrier concentration will be studied and the particular role of alumina dopant will be explained.

Finally, the optimization of the synthesis and sintering time for the homologous phase formation with the alternative methods, based on different heat transfer mechanisms, such as microwave or filed assisted sintering, will be studied and their benefits will be evaluated.

Chapter 3

Synthesis and Characterization Methods

3.1 Organization of the Experimental Work

The experimental work was focused on the principles of the solid-state synthesis, combined with the novel techniques for improving the sintering procedure in the $(\text{ZnO})_k\text{In}_2\text{O}_3$ system. They are explained in the following paragraphs, from the basic solid-state sintering conditions to the electromagnetic (EM) waves assisted processes; microwave sintering and pulsed electric current sintering (PECS). Afterwards, the physical principles and used methods for the material's thermoelectric characterization are presented.

3.2 Sintering

Sintering is a process of consolidating powder compacts by the application of thermal energy. It basically consists of two interconnected phenomena, densification and grain growth, resulting in a particular microstructure for the selected composition. Since the microstructure with the grain size and density largely influences the physical properties of materials, it is crucial to evaluate all critical factors influencing its evolution and appearance in order to obtain the desired properties.

In this PhD study, I used several different techniques, described below, to perform and enhance the sintering process.

3.2.1 Solid-state sintering

Samples following the basic formula $(\text{ZnO})_k\text{In}_2\text{O}_3$ were prepared from as-purchased powders of ZnO (Grillo Zinkoxide, GmbH, Pharma 4, > 99.9 %) and In_2O_3 (Alfa Aesar, 99.9 % metals basis, 325-mesh powder). The stoichiometric powder mixtures were homogenized in a planetary ball mill with ethanol as a milling media in a polyethylene milling vial and YZT grinding balls for 1 h. The obtained mixture was then dried at 80 °C and sieved through the 500 µm mesh sieve, uniaxially shaped into pellets with the diameter of 13 mm and 2 g weight and further additionally isostatically pressed at 750 MPa to obtain pellets with a green density of around 60 %. Pellets were put in a cold furnace and heated to the target temperature by 5 °C/min. After the sintering time expired, the furnace was cooled down by the same rate as in the heating-up.

3.2.2 Microwave sintering

The microwave sintering was performed on pellets prepared by the same protocol as for the solid-state sintering. However, further processing details, especially heating rate, were dependent on the nature of the EM interaction with the material. Therefore, here we give a short explanation of the sintering mechanism under the microwave EM field, the equipment and the experimental setup.

Microwaves are EM waves with wavelengths ranging from 1 m to 1 mm and corresponding frequencies among 0.3 and 300 GHz. The widely applied frequencies in material science are 915 MHz and 2.45 GHz. The first experiments of processing ceramics by microwave heating were over 60 years ago and since then, the research field has grown, especially in the last decade. There are many benefits in comparison with the conventional sintering regarding the less consumed energy and shortened processing time. In conventional sintering, thermal energy is transferred to the material through convection, conduction and radiation from the surfaces of the material. On the other hand, microwaves are directly interacting with the material, therefore heat is generated through its whole volume. This results in the rapid and uniform heating in contrast to the conventional sintering, where the fast heating rates are producing thermal gradients inside the material.

The heat generation inside the material is a complex set of phenomena. Since the microwave radiation has electric (E) and magnetic (H) field components, they agitate the orientation, position and movement of dipoles, free electrons, domain walls and electron spins during microwaves passing through material. Thus, the material's interaction with MW depends on its dielectric and magnetic properties and can be described by the Maxwell's equations for electromagnetic field propagation (3.1, 3.2, 3.3, 3.4).

$$\nabla \times E = j\mu\omega H \quad (3.1)$$

$$\nabla \times E = -j\omega\epsilon_0\epsilon^* E \quad (3.2)$$

$$\nabla \bullet (\epsilon E) = 0 \quad (3.3)$$

$$\nabla \bullet H = 0 \quad (3.4)$$

E and H are electric and magnetic fields, ϵ_0 is the permittivity in air, ϵ^* is the complex permittivity, ϵ is the permittivity, μ is the magnetic permeability, ω is the angular frequency of microwaves and j is the imaginary unit. The complex permittivity (ϵ^*) is the parameter, which describes the heat generation in a non-magnetic material during the interaction with MW and is described as (3.5)

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (3.5)$$

The ϵ' is the real part of the complex permittivity and is also called the dielectric constant, whereas ϵ'' is the imaginary part and represents the ability of the material to dissipate the microwave energy and is named the dielectric loss factor. Both parts of the microwave field, the electric and magnetic components, are interacting with dipole position and movement, free electrons, domain walls and electron spins. The heat generated in a non-magnetic ceramic material is mainly affected by the electric component of the electromagnetic spectra and is generated by the dipolar and conduction losses. The propagating electric field causes oscillation of charged particles and dipole reorganization, which is creating lattice vibrations and generates the heat.

Microwaves interact with a certain material in dependence of the dielectric loss factor ϵ'' as presented in Figure 3.1. Materials with a small ϵ'' , like quartz, are transparent for microwave radiation and do not heat up. With the increasing dielectric loss factor, the materials are “microwave receptive” and heat up by the passing microwave field. The most known and used in the household microwave ovens is the microwave interaction with water molecules. Nevertheless, materials in this range are also ceramics, semiconductors and polymers. The highest values of loss factor are typical for metals, which reflect microwaves and do not heat up.

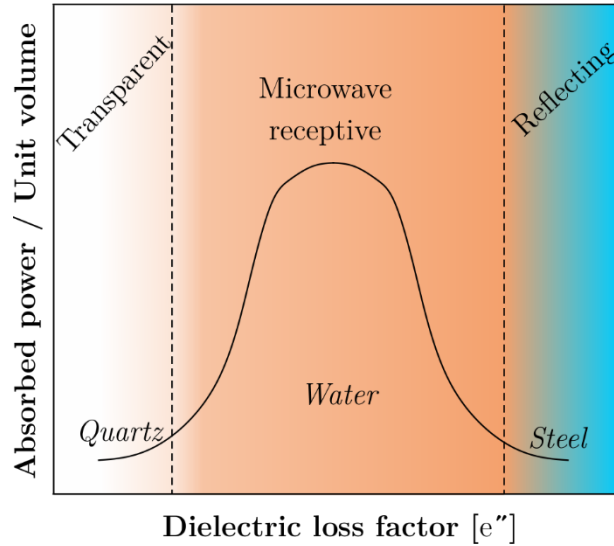


Figure 3.1: The absorbed power per unit volume in dependence of the dielectric loss factor.

The used microwave furnace system (Figure 3.2) was based on a 2.45 GHz microwave generator (SAIREM GMP 20 KSM, France) delivering a variable power up to 2 kW along a standard WR340 rectangular twist and a waveguide (86.36 x 43.18 mm) that conducts microwaves to the TE₁₀p single mode cavity. Cavity modes were tuned by adjusting the length of the coupling iris and the short-circuit piston to maximize the electric (E) or magnetic (H) microwave field in the central cavity position. The system was also equipped with a water-cooled applicator for the absorption of reflected microwaves, which are adjusted with a short-circuit piston to maximize the absorption in the sample during synthesis. In the series of experiments presented in the dissertation, the cavity was tuned in order to maximize E - field. The sample was positioned in an alumina-silicate box (Fiberfrax® - Duraboard®), which is transparent for microwaves and provides a good thermal insulation for the sample by reducing the thermal radiation from its surface (Figure 3.3). The box has a cavity for the pellet and a cover with perforation for the temperature monitoring with pyrometer (Ircon, Modline® 5, 350–2000 °C), which is connected to the computer through ModView Software®.

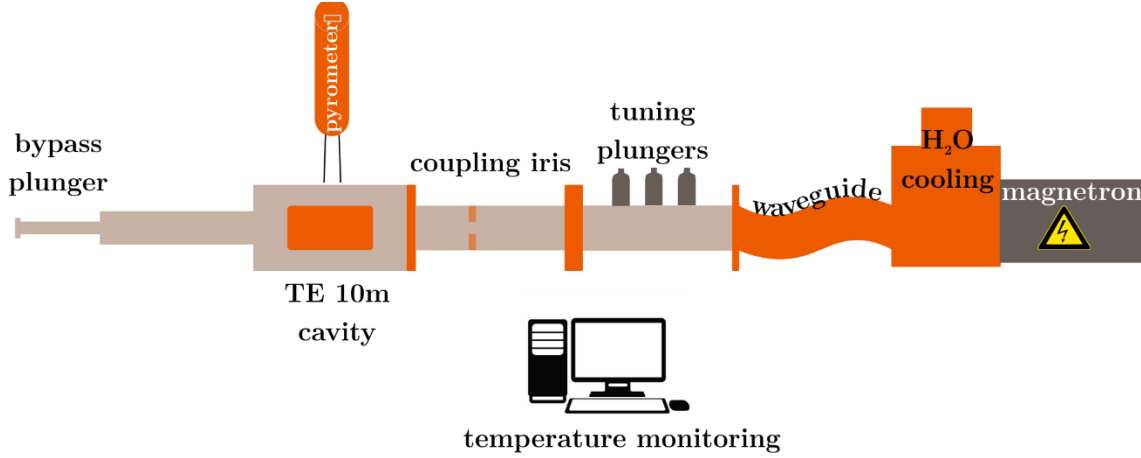


Figure 3.2: The “single mode” microwave furnace system model used in experiments.

The microwave sintering was performed in three different experiment configurations, as presented in Figure 3.3. They include sintering without susceptor and with different variations of the alumina susceptor. The purpose of the alumina susceptor is to minimize heat loss from the surface, contributing to the temperature stability and in some cases providing the heat when the studied samples do not couple well MW. In the first configuration (A), no susceptor was used, implying the direct microwave heating. Second (B), as a basis alumina support was used below the pellet to decrease the thermal losses from the contact with the insulating box. Third configuration (C) was made with the cylindrical alumina crucible, providing the bottom and side shield for the sample. The last two configurations are termed as a “hybrid heating” and are considered as combinations of MW and conventional heating.

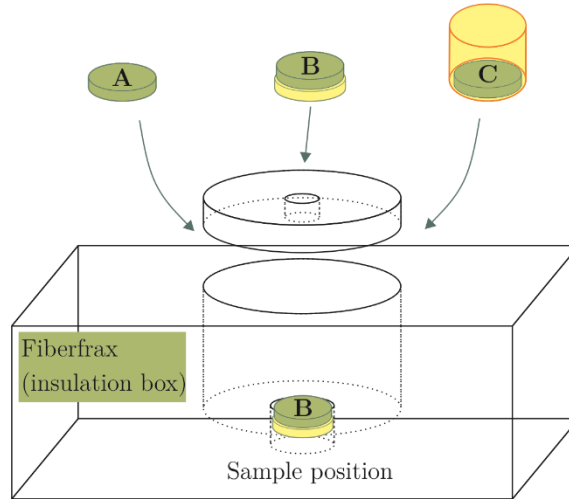


Figure 3.3: Schematics of three different experimental configurations in MW sintering.

The insulating box with the sample in all three experiment variations (Figure 12) was put in the center of the microwave cavity and aligned with the pyrometer axis to ensure precise temperature monitoring. Experimental conditions at the beginning were set on the 200 W power output and pure *E*-field configuration. The resonance was manually tuned with the three stubs and the temperature was monitored by the step adjusting of the incident power. Through the experiment, the power was increased approximately every 100 °C for 20 W to ensure the homogeneous temperature rise. Three target temperatures were

chosen, 1300 °C, 1400 °C and 1500 °C for 10 min, 20 min and 1 h duration time at each sintering temperature. After the dwell time elapsed, the microwave power was shut down immediately and the sample was cooled down naturally.

3.2.3 Field assisted sintering (FAST)

In the field of ceramic processing, FAST represents an effective method to fabricate dense fine grained materials in a severely reduced processing time in comparison to conventional techniques. The sintering is promoted by discharging gaps between powder particles with on-off electrical energy and “*Joule heating*” from the graphite mold by an electrical current [141]. FAST furnace consists of water cooled punches acting as electrodes and also as uniaxial pressure applicators in a reaction chamber evacuated during procedure. It has a pulsed dc current generator, pressure application, z-axis position and temperature regulators.

The FAST sintering was performed on a DR SINTER, SPS-615 model (SPS SYNTEX, Japan). The pre-reacted powder (at 1150 °C/ 2h) was put into the graphite mold and pressed inside the FAST furnace with the initial pressure of 50 MPa. The sintering condition with the applied dc current was set on the ratio of 12 (on) and 2 (off) current times. Sintering ramp was controlled with the ratio of 100 °C/min until 900 °C and further with 50 °C or 25 °C until the target temperature (1000 - 1200 °C). Maximum applied current was up to 1400 A with the voltage of 3.5 V. The holding time at the target temperature was set from 2 to 10 min and then the furnace (dc current) was turned off to cool naturally with the assistance of a water cooling system. The details of every experiment are presented in Chapter 8.

3.3 Characterization Methods

3.3.1 Thermal analysis (DTA, DSC)

The thermal analysis, DTA (differential thermal analysis) and DSC (differential scanning calorimetry) were performed on NETZSCH STA 449 C/6/G Jupiter – QMS 403 C (Netzsch, GmbH, Germany) up to a temperature of 1350 °C with a heating rate of 20 K/min.

The DSC was used to determine the heat capacity, C_p , and to investigate the reaction enthalpies, their nature (endothermic/exothermic) and propagation with the increasing temperature. For compositions made with a mixture of oxides and nitrates, DTA and DSC were used to check if all nitrates were already removed from the powder mixture.

3.3.2 Powder X-Ray diffraction

Phases from homologous series were identified by powder X-ray diffraction at room temperature, utilizing Cu - K α radiation, with diffractometer PANalytical X'Pert (PRO MPD, Almelo, The Netherlands). The measurement angle (2θ) was from 10° – 80° with the step size 0.033 ° per 1 s.

3.3.3 Thermoelectric parameters measurements

3.3.3.1 Commercial system ZEM 3

Samples were additionally cut in rods with a length from 8 till 10 mm and a cross section of 2 x 2 mm for Seebeck coefficient and electrical conductivity measurements. These were investigated with a commercial ZEM 3 device (ULVAC Technologies, Inc, Methuen, MA,

USA) in a partial helium pressure. The schematic of the ZEM 3 device with a mounted sample is presented in Figure 3.4. This system operates at the so-called “small ΔT ” or “differential method”, where the Seebeck coefficient is given exclusively by the ratio of the electrical potential (ΔV) at the temperature difference ΔT . The simultaneous measurement of the Seebeck coefficient and electrical resistivity is controlled by the computer with a programmed schedule for every measurement. The sample of prismatic or cylindrical shape is put in position between upper and lower blocks inside the heating furnace chamber, which is afterwards evacuated and partially filled with helium up to 0.1 bar pressure. The furnace heats the whole sample to a certain temperature and then the heater in the lower block induces the programmed temperature gradient. In our set of experiments, we used a 20 °C, 30 °C and 40 °C temperature difference. The Seebeck coefficient is measured by determining the upper and lower temperatures (T_1 and T_2) with the thermocouples pressed against the side of sample and measurement of the voltage drop (ΔV) at the same points.

Electric resistance is measured by the DC four-terminal method where a constant current (I) is applied to the upper and lower surface and then the voltage drop (ΔV) among two side thermocouples is determined by subtracting the thermo-electromotive force (dE), measured on these two thermocouples.

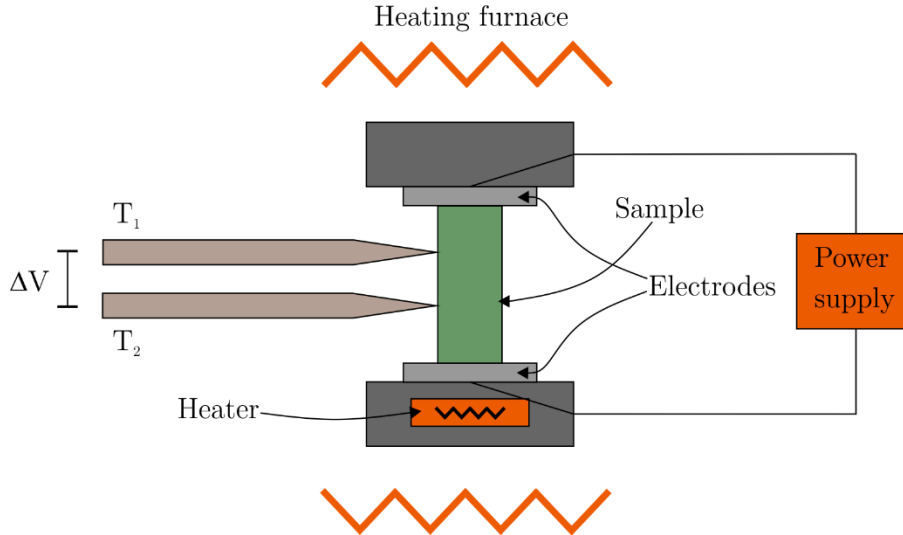


Figure 3.4: The ZEM3 scheme with a mounted sample for temperature dependent measurements of the electrical resistivity and Seebeck coefficient.

3.3.3.2 Laser flash analysis (LFA)

For the thermal diffusivity measurements, squares of 6 x 6 mm and 1 mm thick were cut from the same pellet and measured in air with the laser flash technique (NETZSCH, LFA 457 MicroFlash, Netzsch, GmbH, Germany) without any additional carbon coating. The schematic of the laser flash apparatus is presented in Figure 3.5. The sample is mounted on a holder, which is located inside a furnace. The temperature programme is set at certain temperature points for the measurement of thermal conductivity. After the temperature reaches the defined temperature, a laser pulse is ejected and the absorbed energy heats up the sample. The relative temperature increase is measured on the top of the sample as a function of time by an IR detector. The thermal diffusivity is then calculated by software according to obtained data and equation (3.6):

$$\alpha = 0.1388 \frac{I^2}{t_{0.5}} \quad (3.6)$$

where I is the sample thickness and $t_{0.5}$ is the time at 50 % of the temperature increase. The thermal diffusivity was at every temperature point measured three-times and the average value of these three measurements was calculated and used for the thermal conductivity calculations according to the formula (3.7).

$$\kappa = C_p * \rho * \alpha \quad (3.7)$$

where C_p is heat capacity, ρ is density and α is thermal diffusivity.

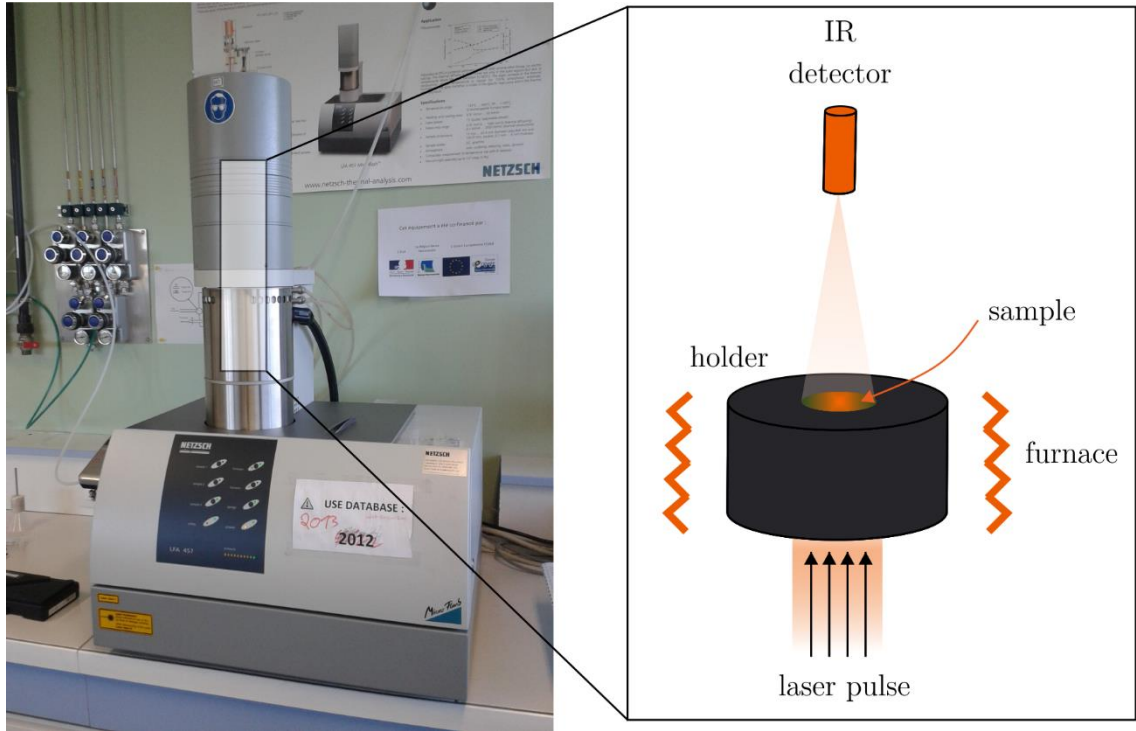


Figure 3.5: Laser flash apparatus and schematics of the thermal diffusivity measurement.

3.3.3.3 Physical properties measurement system (PPMS)

Samples were cut and polished to squares of 3 mm with approximately 0.2-0.3 mm thickness for Hall effect measurements (charge carrier concentration & mobility) in PPMS (Quantum design, USA). The Hall effect is a phenomenon occurring in a current carrying conductor when it is placed in a magnetic field perpendicular to the direction of the electric current. The charge carriers are affected by the magnetic field and their deflection gave rise to an electric field (potential), which is perpendicular to both, electric current and magnetic field. The Hall effect is defined as the ratio of the induced electric field to the product of the current density and the applied magnetic field. During the experiment, the measured quantity is the potential difference across the sample, the Hall voltage, which is related to the Hall field by equation (3.8):

$$V_H = - \int_0^W E_y dy = -E_y W \quad (3.8)$$

where E_y is the Hall field, W is the width in the y direction.

The samples for measurements were mounted with a resin on a glass and then In contacts were applied on their corners. Finally, the In contacts were connected to wires on the PPMS holder. Measurements were performed in the magnetic field in the range 7000 to -7000 Oe. The charge carriers were calculated from the linear function slope according to the formula (3.9):

$$V_H = - \frac{IB}{nte} \quad (3.9)$$

where I is the current, B is the magnetic field, t is the thickness, e is the elementary charge and n is the charge carrier density, in our case of electrons (n-type conductor).

3.3.4 Electron microscopy

Perfectly plane samples were thermally etched at 1250 °C for approximately 10 min and coated with carbon for the microstructure analysis. This was performed on scanning electron microscopes (SEM) JSM-5800 (JEOL, Tokyo, Japan) and Zeiss Supra 55 (Jena, Germany).

Transmission electron microscopy (TEM) studies were carried out in a JEM-2010F and a JEM-ARM200F with a CFEG and Cs probe corrector (Jeol, Tokyo, Japan). Samples for the TEM analysis were prepared according to the standard procedure, including mechanical thinning, polishing, dimpling and ion milling (Model RES 010, Bal-Tec AG, Balzers, Liechtenstein) until perforation of the sample occurred.

Chapter 4

Phase Formation, Microstructure Development and Thermoelectric Properties of $(\text{ZnO})_k\text{In}_2\text{O}_3$ Ceramics

In this chapter the paper [142] entitled “*Phase formation, microstructure development and thermoelectric properties of $(\text{ZnO})_k\text{In}_2\text{O}_3$ ceramics*” by Mateja Košir, Matejka Podlogar, Nina Daneu, Aleksander Rečnik, Emmanuel Guilmeau and Slavko Bernik is presented. For this article, the author of this thesis performed sample preparation, solid-state sintering, XRD sample preparation, polishing and thermal etching of samples, SEM observations, sample preparation for TEM, thermoelectric measurements, processing and interpretation of the obtained data (except TEM).

The purpose of this article was to study the phase formation and its influence on the microstructural evolution and thermoelectric properties in the $(\text{ZnO})_k\text{In}_2\text{O}_3$ system. The samples with the compositions $(\text{ZnO})_k\text{In}_2\text{O}_3$ ($k = 5, 11$ and 18) were prepared by the classic ceramic procedure from powder mixtures of ZnO and In_2O_3 and sintered at temperatures from 900°C to 1500°C . Their phase composition and microstructure were studied by DSC, XRD, SEM and TEM analysis and the thermoelectric properties were measured. Results indicated that the homologous phase formation started at temperatures above 1000°C and was determined by the initial distribution of In_2O_3 in the starting mixture with ZnO and, consequently, the local ZnO-to- In_2O_3 ratio. In the composition with $k = 5$, the amount of added In_2O_3 was sufficient for the proper ZnO-to- In_2O_3 ratio, which enabled the uniform formation of the equilibrium homologous phase $\text{Zn}_5\text{In}_2\text{O}_8$ and resulted in the homogeneous grain growth. In the compositions with a much lower content of In_2O_3 , the local ZnO-to- In_2O_3 ratio facilitated an initial formation of the lower k $\text{Zn}_5\text{In}_2\text{O}_8$ and $\text{Zn}_7\text{In}_2\text{O}_{10}$ phases in In-rich areas and the higher k $\text{Zn}_k\text{In}_2\text{O}_{3+k}$ phases for $k > 9$ towards pure ZnO ($k \rightarrow \infty$) in the In-depleted regions. Consequently, the equilibrium homologous phase for the starting high- k composition was formed only after the extensive diffusion of Zn-ions from grains of higher- k phases to the grains with lower- k phases, requiring higher sintering temperatures and longer sintering times. Therefore, the exaggerated growth of grains with a higher content of In_2O_3 was observed in these samples as long as the compositional homogeneity is not established. Thus, grain size in the samples with $k = 11$ and 18 was much larger than in the sample with $k = 5$. In general, the TE characteristics decreased with an increasing k value in relation to the density of the In-planar defects. However, the ZT of the samples with $k = 11$ and $k = 18$ after sintering at 1500°C was significantly increased, reaching values surprisingly close to the sample with $k = 5$, which could be attributed to the improved compositional homogeneity and a much larger grain size.

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Abstract

The (ZnO)_kIn₂O₃ system is interesting for applications in the fields of thermoelectrics and opto-electronics. In this study we resolve the complex homologous phase evolution with increasing temperature in polycrystalline ceramics for $k = 5, 11$ and 18 and its influence on the microstructural development and thermoelectric properties. The phase formation at temperatures above $1000\text{ }^{\circ}\text{C}$ is influenced by the local ZnO-to-In₂O₃ ratio in the starting-powder mixture. While the Zn₅In₂O₈ equilibrium phase for $k = 5$ is formed directly after sintering at $1200\text{ }^{\circ}\text{C}$, the formation of the $k = 11$ and $k = 18$ equilibrium phases proceeds at higher temperatures by diffusion between the initially formed phases, the lower k Zn₅In₂O₈ / Zn₇In₂O₁₀ and the higher k Zn_kIn₂O_{k+3} ($9 < k < \infty$). Such phase formation affects the sintering and grain growth, and consequently, with the degree of structural and compositional homogeneity, also the thermoelectric characteristics of the (ZnO)_kIn₂O₃ ceramics.

Key words: zinc oxide; indium (III) oxide; homologous phases; microstructure; thermoelectric properties.

4.1 Introduction

Worldwide energy production is mainly based on fossil fuels and the demand for this energy continues to grow. Ecological awareness and the principles of sustainable development stimulate the efficient use of energy and the development of alternative technologies to exploit renewable energy sources. There is a large potential for the harvesting of waste heat, which represents almost 70 % of all the primary energy that is produced. This is possible with the use of thermoelectric (TE) materials, which enable the direct conversion of waste heat into electricity [8, 143]. The characteristics of thermoelectric materials are expressed using the dimensionless figure of merit (ZT), defined as $ZT = (S^2\sigma / \kappa)T$, where S is the Seebeck coefficient (thermopower), σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature. The requirements for high ZT values consist of a reasonably good electrical conductivity, a high Seebeck coefficient and a low thermal conductivity.

State-of-the-art ZT values are achieved with alloys of Bi, Te, Se, Pb and Sn [8, 144], silicides [145, 146], clathrates [147, 148], skutterudites [30, 149], all reaching a ZT of 1 or higher. Unfortunately, their use is limited, because some of them contain toxic elements and most of them are unsuitable for high-temperature applications in air. This opens up an opportunity for oxide-based materials, which are produced generally from abundantly available source materials that are non-toxic.[78, 79, 96, 150]. In the past decade, after the discovery of a large thermoelectric power of 100 V/K at 300 K in NaCo₂O₄ single crystals [76], a great deal of attention was devoted to investigations of semiconducting oxides for TE applications. Among the p-type polycrystalline oxide materials, layered cobaltates currently exhibit the largest ZT values of up to 0.5 at temperatures of $800\text{--}1000\text{ K}$ [77, 83-85, 151]. With the n-type materials, the focus is on SrTiO₃, CaMnO₃, In₂O₃ and ZnO, all with high Seebeck coefficients (S), while the other two parameters important for a high ZT value, the electrical conductivity and the thermal conductivity, need to be improved significantly for them to become technologically attractive [81, 87, 91, 152-154]. For example, polycrystalline ZnO exhibits electrical conductivities of the order of 10 S/cm , Seebeck coefficients of about -400 V/K , and thermal conductivities of around 40 W/mK at room temperature [96]. These properties are not sufficient for effective thermoelectric applications; the electrical conductivity is much too low and the thermal conductivity is too high. The introduction of dopants to increase the carrier concentration, such as Al³⁺, Fe³⁺, Ga³⁺, Mg²⁺, Ni²⁺, results in an increased electrical conductivity, accompanied by a

partially reduced thermal conductivity and finally in an improved ZT with maximum values of 0.4 around 1000 K for Al-doped ZnO [97-102]. The proper doping with a combination of Al and Ga [112] showed the best ZT values for polycrystalline ZnO of about 0.47 at 1000 K. Like in intermetallic-based TE materials, the research in oxide-based thermoelectrics is nowadays oriented towards nano-structuring (embedded nanoparticles, nanostructured defects, nano-grain sizes) for enhanced phonon scattering and the reduction of thermal conductivity [117]. Multiple planar defects (i.e., inversion boundaries or IBs) can be introduced into the wurtzite-type ZnO by adding In_2O_3 . The formation of such planar defects takes place through the mechanism of internal diffusion and is driven by a local charge deficiency, initiated by the Zn vacancies as preferential sites for the incorporation of In^{3+} ions into the wurtzite structure of ZnO [128]. Their ordering leads to the formation of the homologous $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ -type phases [123, 155] that offer an interesting platform for tailoring the TE properties; the planar defects are structural barriers for phonon transport and quantum-confinement pathways for electron transport due to the strongly correlated electron system of planar defects [129, 156, 157].

Phase relations in polycrystalline ceramics for compositions with Zn-to-In ratios from 1 to 15 in the temperature range from 1100 °C to 1400 °C were studied by Moriga *et al.* [123]. According to their report, only two phases are stable at 1100 °C: the $\text{Zn}_5\text{In}_2\text{O}_8$ and the $\text{Zn}_7\text{In}_2\text{O}_{10}$. With an increasing temperature, the phases for higher k are formed, and at about 1320 °C, the $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ phases for $k \leq 15$ are stable. The thermoelectric characteristics were mainly studied for the homologous phase with $k = 5$, which showed the highest ZT of around 0.1 at 1000 K, and less for homologous phases with higher k -values up to 9 [118, 129, 134, 158]. The TE characteristics of ceramics in the $(\text{ZnO})_k\text{In}_2\text{O}_3$ system were also studied for compositions with values of $k > 9$ towards pure ZnO and confirmed the declining of the TE performance (*i.e.*, ZT value) with a decreasing density of the In-rich planar defects in accordance with the smaller addition of In_2O_3 in relation to the higher k -value [157, 159]. However, in these studies, the processes of homologous phase formations with their influence on the grain growth and microstructure development were not analysed and discussed.

In this work we systematically studied the phase formation, microstructure development and resulting thermoelectric characteristics for ceramics with the compositions $(\text{ZnO})_k\text{In}_2\text{O}_3$ for k -values of 5, 11 and 18, by solid-state processing of the oxide powders in the temperature range from 900 °C to 1500 °C. We found that the formation of the homologous $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ -type phases starts at temperatures above 1000 °C and is strongly affected by the distribution of the In_2O_3 in the mixture with ZnO and the local ZnO-to- In_2O_3 ratio. By resolving the complex processes of homologous phase formation we were able to explain their effect on the grain growth and the microstructure development. We also showed how the thermoelectric properties are influenced by the structural and compositional homogeneity of the $(\text{ZnO})_k\text{In}_2\text{O}_3$ ceramics.

4.2 Experimental

The samples with compositions $(\text{ZnO})_k\text{In}_2\text{O}_3$ for $k = 5, 11$, and 18 were prepared from powders of ZnO (Grillo Zinkoxide, GmbH, Pharma 4, > 99.9 %) and In_2O_3 (Alfa Aesar, 99.9 % metals basis, 325-mesh powder) in accordance with the classic ceramic procedure. The powder size distribution was measured with a laser particle size analyser (Model LA-920, Horiba). Powder mixtures of the ZnO and the In_2O_3 with mean grain sizes of 0.45 μm and 2 μm , respectively (Fig. S1), were mixed with absolute ethanol in a polyethylene vial, homogenized in a planetary ball mill for 1 h, and afterwards dried at 80 °C. The obtained powder mixtures were uniaxially pressed into pellets with diameters of 10–20 mm and

heights of about 1–2 mm, followed by cold isostatic pressing under a pressure of 280 MPa with a 30 s holding time. The thermal behaviour of the starting powder mixtures was analysed using TG/DSC methods (NETZSCH STA 449 C/6/G Jupiter – QMS 403 C, Netzsch, GmbH, Germany) up to a temperature of 1350 °C with a heating rate of 20 K/min. Densification of the samples was analysed up to 1400 °C at a heating rate of 10 K/min, using a heating-stage microscope (Ernst Leitz GmbH, Wetzlar, Germany). The samples were sintered uncovered in air in the temperature range from 900 °C to 1500 °C, from 2 h up to several days, depending on their densification rate. The densities of the samples were measured using Archimedes' principle (DENSITEC®, Metar Sa, Rossens, Switzerland). The phase composition of the sintered samples was analysed using powder X-ray diffraction (XRD) analysis (diffractometer PANalytical X'Pert PRO MPD, Almelo, The Netherlands) in the range 20–80° with a step size of 0.04° and 1 s time per step. The cross-sections of the samples, un-etched and thermally etched, were examined using scanning electron microscopes (SEM; JSM-5800, JSM 7600F, JEOL, Tokyo, Japan) equipped with energy-dispersive X-ray spectrometers (EDS; Link ISIS 300, Oxford Instruments Ltd., Oxford shire, U.K.) for compositional analyses of the observed phases. The structural characteristics of the samples were analysed using a transmission electron microscope (TEM; Jeol JEM-2010F, Tokyo, Japan). Samples for the TEM analysis were prepared according to the standard procedure, including mechanical thinning, polishing, dimpling and ion milling (Model RES 010, Bal-Tec AG, Balzers, Liechtenstein) until perforation of the sample occurred.

The samples for the Seebeck coefficient and electrical conductivity measurements were cut into bars with lengths from 8 to 10 mm and cross-sections of about $2 \times 2 \text{ mm}^2$. The measurements were performed on a commercial ZEM 3 device (ULVAC-RIKO, Yokohama, Japan) in a partial helium atmosphere. For the thermal diffusivity measurements, squares of $6 \times 6 \text{ mm}^2$ and 1 mm thick were cut from the same pellet of the samples and measured in air with a laser flash (NETZSCH, LFA 457 MicroFlash, Netzsch, GmbH, Germany). The thermal conductivity was calculated from the heat capacity (C_p), density (ρ) and thermal diffusivity (α), according to the expression $k = C_p \cdot \rho \cdot \alpha$. The estimated measurements uncertainties are 6 % for the Seebeck coefficient, 8 % for the electrical conductivity, 11 % for the thermal conductivity and 17 % for the final figure of merit, ZT ; they are in agreement with the reported uncertainties determined from round robin measurements on skutterudites [160].

4.3 Results and Discussion

4.3.1 Homologous phase formation

The densification characteristics of the pure ZnO and the (ZnO)_kIn₂O₃ samples for $k = 5$, 11 and 18 are shown in Figure 4.1a. In the pure ZnO, the onset of sintering is at about 650 °C and the slope of the sintering curve indicates a relatively fast sintering rate at around 900 °C. With the addition of In₂O₃, the onset of the sintering is shifted towards higher temperatures, which then slowly decreases with the increasing content of In₂O₃ (lower values of k). While for the compositions with $k = 5$ the onset of sintering is as high as ~810 °C, this temperature decreases to ~735 °C for $k = 11$ and to ~670 °C for the composition with $k = 18$. For all the compositions with an In₂O₃ addition, the sintering rate is significantly slower than that of the pure ZnO.

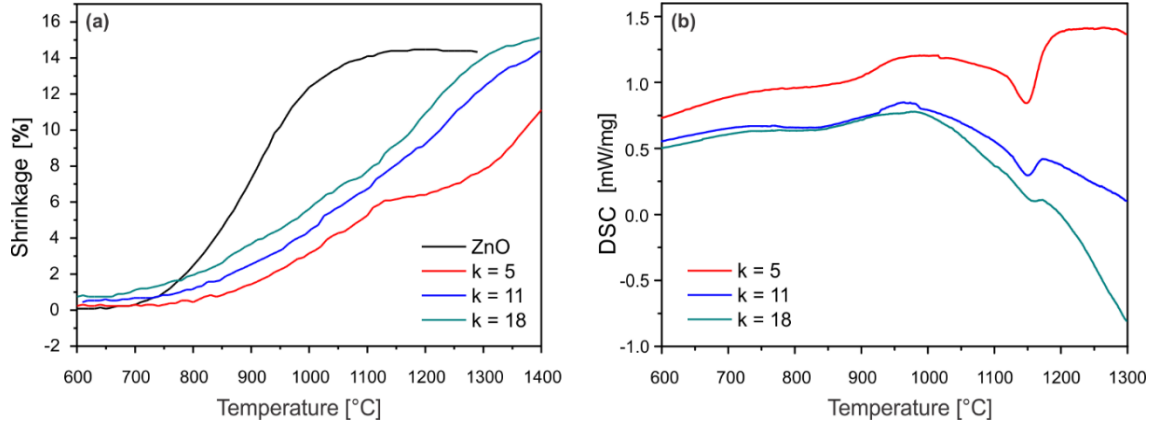


Figure 4.1: a) Sintering curves and b) DSC analyses for pure ZnO sample and the samples with the composition $(\text{ZnO})_k\text{In}_2\text{O}_3$ ($k = 5, 11$ and 18).

In the pure ZnO, the sintering is completed at ~ 1130 °C with a relative shrinkage of about 14 % (Figure 4.1a). Similar shrinkage is also obtained for the samples with $k = 18$ and 11 at temperatures above 1300 °C, while the end of the sintering is approaching 1400 °C. Whereas for the $k = 5$ sample, the sintering is not completed at 1400 °C, the shrinkage is at about 12 % and the sintering curve indicates a tendency for further densification. In this sample, a shoulder in the sintering curve is present at 1150 °C. In the samples with $k = 11$ and 18 , only a slight deviation in the sintering curves could be observed in the range between 1000 °C and 1200 °C.

The DSC analysis (Figure 4.1b) showed the onset of the solid-state reaction at 1000 °C, followed by an endothermic peak between 1100 °C and 1200 °C; its intensity decreased with increasing k . The solid-state reaction can be assigned to the diffusion of the In_2O_3 into the ZnO [128, 161, 162] and the formation of structurally ordered $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ -type homologous phases within the wurtzite-type ZnO [155]. While in the sample with $k = 5$ this process is completed by 1200 °C, the DSC curves of the samples with higher k values indicate a continuation of the reaction at higher temperatures. These results also comply with the results of the sintering behaviour (Figure 4.1a); the distinct shoulder at 1150 °C in the sintering curve for $k = 5$ can be associated with the formation of $\text{Zn}_5\text{In}_2\text{O}_8$, while for $k = 11$ and 18 with a lower quantity of In_2O_3 , the solid-state reaction is much less pronounced and only slightly indicated in their sintering curves.

The XRD patterns of the samples with compositions for $k = 5, 11$ and 18 sintered at temperatures in the range from 900 °C to 1500 °C for 2 h are shown in Figure 4.2 and for 22 h in Fig. S2 in the supporting data. After sintering at 900 °C only the starting oxides were present. The formation of the $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ homologous phases was observed in the XRD patterns after sintering at 1100 °C, as expected from the results of the sintering behaviour and the DSC analysis. The sintering of the composition $k = 5$ at 1100 °C for 2 h resulted in the formation of the $\text{Zn}_5\text{In}_2\text{O}_8$ (JC PDF 00-020-1440) and $\text{Zn}_7\text{In}_2\text{O}_{10}$ (JC PDF 00-020-1441) phases, with a small amount of In_2O_3 still present. Some In_2O_3 was also detected in the sample after sintering for 5 h, while after prolonged sintering for 22 h (Fig. S2), the XRD analysis showed only the $\text{Zn}_5\text{In}_2\text{O}_8$ phase. However, when the sintering temperature was raised to 1200 °C, the $\text{Zn}_5\text{In}_2\text{O}_8$ was obtained already after 2h. The higher sintering temperature of 1300 °C resulted in sharper and narrower XRD peaks, indicating a further compositional homogenization and ordering of the $\text{Zn}_5\text{In}_2\text{O}_8$ homologous phase.

In the sample with $k = 11$, sintered at 1100 °C for 2 h, the XRD analysis showed the presence of $\text{Zn}_5\text{In}_2\text{O}_8$ and $\text{Zn}_7\text{In}_2\text{O}_{10}$ phases together with other higher- k phases towards pure ZnO. After sintering at 1200 °C (2h), a series of phases for k from 9 to 15 could be identified

in the XRD pattern (Fig. 2), and traces of Zn₅In₂O₈ are still present. With the temperature increasing to 1300 °C, the Zn₁₁In₂O₁₄ phase was mainly present; however, the width of its XRD peaks indicates that the structure is not fully ordered at this point. The $k = 18$ sample, sintered at 1100 °C (2 h), is composed mainly of the ZnO, Zn₅In₂O₈ and Zn₇In₂O₁₀ phases. However, multiple peaks around 2-theta 35° indicate the presence of various Zn_kIn₂O_{k+3} phases for $k > 7$ towards the pure ZnO. With increasing sintering temperature, the amount of ZnO-rich phases decreased. In the sample sintered at 1200 °C the phases from Zn₉In₂O₁₂ to Zn₁₅In₂O₁₈ were determined, but the possible presence of higher Zn_kIn₂O_{k+3} phases could not be excluded. After sintering at 1300 °C (2h) the XRD peaks are narrower and indicate the presence of homologous phases with $k \geq 15$. Only after a much longer sintering time of 22 h at 1300 °C did the sample mostly contain the homologous phases expected in terms of the targeted composition, i.e., the Zn₁₇In₂O₂₀ and Zn₁₉In₂O₂₂ phases [123]; however, wide peaks still indicate the possible presence of other k phases.

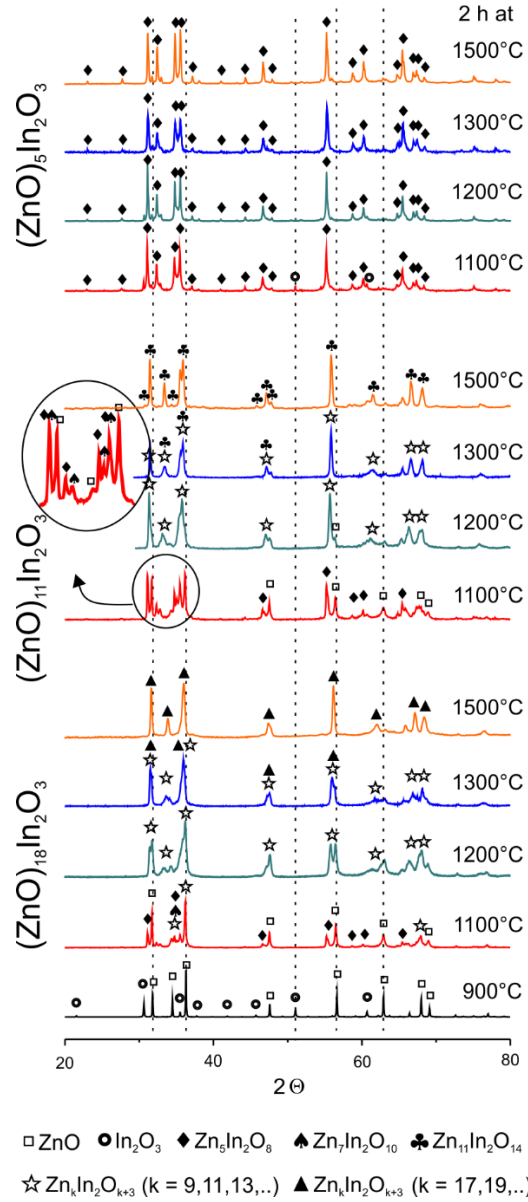


Figure 4.2: XRD patterns of the samples (ZnO)_kIn₂O₃ ($k = 5, 11$ and 18) sintered for 2 h at different temperatures.

To clarify the results of the XRD analysis, the HRTEM analysis of the selected samples for $k = 5, 11$ and 18 , sintered at different temperatures, were made (Figure 4.3 and Fig. S3). Even the sample for $k = 18$ contains grains that are densely populated with In-rich basal-plane defects, as shown in Figure 4.3a. At a higher resolution, a partially ordered defect texture is revealed in all the grains (Figure 4.3b). In some parts of the grains the defects adopt different k -sequences, starting from $k = 9$, including wide sections with no particular order. Sequences with the highest k -distance show a wavy contrast due to the formation of pyramidal defects that are compensating for the polarity inversion between adjacent basal-plane IBs [126, 127, 136, 163]. HRTEM images (Figure 4.3c and e) with the corresponding FFT patterns (Figure 4.3d and f) show the non-periodic and periodic nature of the samples. Such a structural disorder can explain the erroneous identification of different homologous phases and the widening of the peaks in the XRD patterns. If it were to possess the equilibrium homologous phase, represented by the nominal formula $\text{Zn}_k\text{In}_2\text{O}_{k+3}$, it should have periodically spaced In-rich planar defects (IBs) at a distance characteristic for the phase given as $d = k+1$ [121, 126, 127, 136, 163, 164], where d is a number of ZnO layers between two In-rich planar defects, as observed in the case of the sample with $k = 5$ (Fig. S3). However, the composition $k = 18$ (Figure 4.3) sintered at 1300°C for 2 h showed disordered planar defects with d -values ranging from 9 to 45, and even over 100, that varied from grain to grain. Similar non-periodic layers were also observed after a prolonged sintering for 22 h; however, with an increasing sintering temperature and time, more and more sequences displayed d -values corresponding to the starting k -value, which was also expressed in the XRD pattern with sharper (narrower) peaks of a single homologous phase.

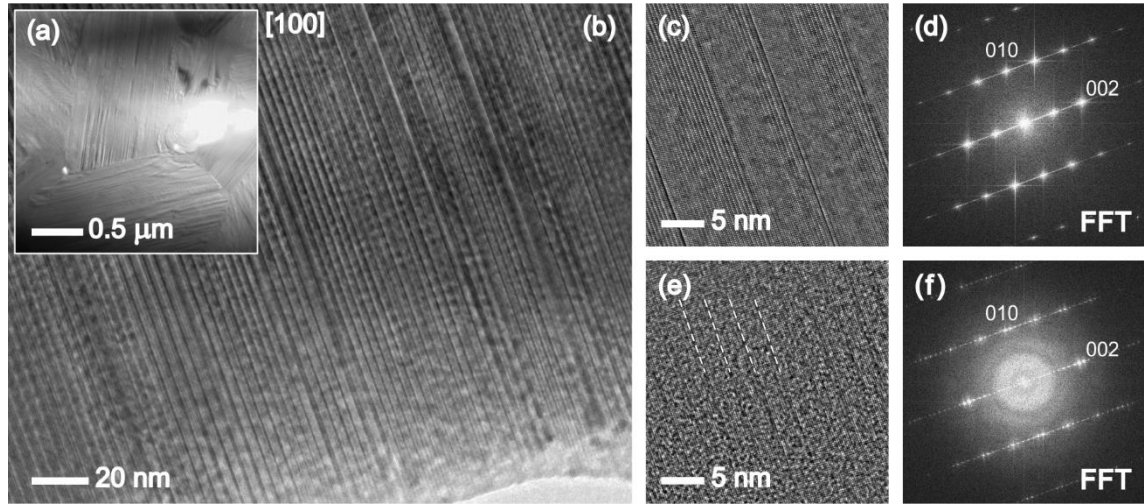


Figure 4.3: TEM study of a sample with $k = 18$, at 1300°C for 2 h (a) Low-resolution TEM image of $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ grains displaying characteristic lamellar texture due to disordered planar defects in the ZnO basal planes. (b) A close up in the $[100]$ zone axis, showing partially ordered short sequences interrupted by disordered longer sequence layers (c) HRTEM image of the disordered layer sequence and its corresponding (d) FFT pattern showing only ZnO reflections with diffuse lines connecting $(0nl)_n = 0,1,2,\dots$ reflections. (e) HRTEM image of ordered $(\text{Zn}_9\text{In}_2\text{O}_{12})$ section with (f) FFT pattern displaying sharp super-periodic reflections along $(0nl)$.

4.3.2 Microstructural evolution

Microstructural analyses of the samples (Figure 4.4) confirmed the results of the XRD analysis that Zn_kIn₂O_{k+3}-type homologous phases start to form at temperatures above 1000 °C. At 1100 °C, the Zn₅In₂O₈ and the Zn₇In₂O₁₀ are formed first (Figure 4.2) in all the compositions, regardless of the amount of In₂O₃ added to the ZnO (*k* value). In compositions with a low amount of In₂O₃ (*k* = 11, 18), homologous phases for *k* ≥ 9 towards pure ZnO are also formed. The amount of various formed phases is different and dependent on the *k* values. Accordingly, for compositions with *k* = 5, a corresponding equilibrium homologous phase Zn₅In₂O₈ is already obtained at 1100 °C; however, only after 22 h of sintering, while at 1200 °C it is obtained after 2 h (Figure 4.2). The formation of the homologous phases for *k* = 11 and 18 (i.e., a smaller amount of In₂O₃) proceeds at the expense of the initially formed Zn₅In₂O₈ phase and the Zn_kIn₂O_{3+k} phases for *k* > 9 towards pure ZnO (*k* → ∞). The results indicated that the larger is the *k* of the starting composition, the higher is the temperature and the longer are the sintering times that are required to obtain an equilibrium homologous phase for that *k*.

The observed formation sequence of the homologous phases indicated that the initial distribution of the In₂O₃ in the matrix powder of the ZnO, and hence, the local ZnO-to-In₂O₃ ratio, likely has a key role. For higher amounts of In₂O₃, there is everywhere more or less enough available In³⁺ locally to the ZnO for the formation of the low-*k* phases like Zn₅In₂O₈ and Zn₇In₂O₁₀ at temperatures sufficient for the diffusion of the In³⁺ into the ZnO. In the compositions with higher *k* values, smaller amounts of added In₂O₃ are likely non-uniformly distributed in the ZnO, even more because it is much coarser than the ZnO powder (Fig. S1). Hence, locally the composition could be either in excess or deficit in In₂O₃ to ZnO regarding the starting nominal composition. Consequently, in the initial stage, at temperatures above 1100 °C, low-*k* phases and very-high-*k* phases towards pure ZnO are formed. Thus, the equilibrium homologous phase for the starting high-*k* composition is formed only after extensive diffusion of the Zn-ions from grains of higher-*k* phases to grains of lower-*k* phases, which is driven by the local differences among the grains in chemical potential, and requires a sufficiently high sintering temperature and time. We can assume that in the case of a perfectly homogeneous distribution of the In₂O₃ in the powder mixture with ZnO, so that locally the ratio of ZnO-to-In₂O₃ is everywhere equal to the *k* of the starting composition, the equilibrium Zn_kIn₂O_{k+3} homologous phase would be formed directly, regardless the *k* value. The high-*k* phases would be obtained already at lower sintering temperatures, similarly to the low-*k* phases like Zn₅In₂O₈.

Relating the results of the DSC (Figure 4.1a), XRD (Figure 4.2) and microstructure analysis (Figure 4.4) with the observed sintering characteristics (Fig. 1b), we can see that for the samples with lower *k* values in which the homologous phase Zn_kIn₂O_{k+3} of the corresponding starting composition is formed faster, the sintering curve is shifted to higher temperatures. In general, the sintering process starts first and is followed by the grain growth. In the case of the (ZnO)_kIn₂O₃ samples, a larger amount of In₂O₃ at the grain boundaries hinders the diffusion and hence the sintering; it proceeds in the shadow of the diffusion of In³⁺ into the ZnO wurtzite structure as long as the In₂O₃ is not sufficiently removed from the grain boundaries to allow the inter-granular diffusion of the Zn ions. Thus, it could be expected that the complexity of these processes, which eventually lead to the equilibrium Zn_kIn₂O_{k+3} homologous phases for the starting *k* values, has a major effect on the grain growth and microstructure development as well.

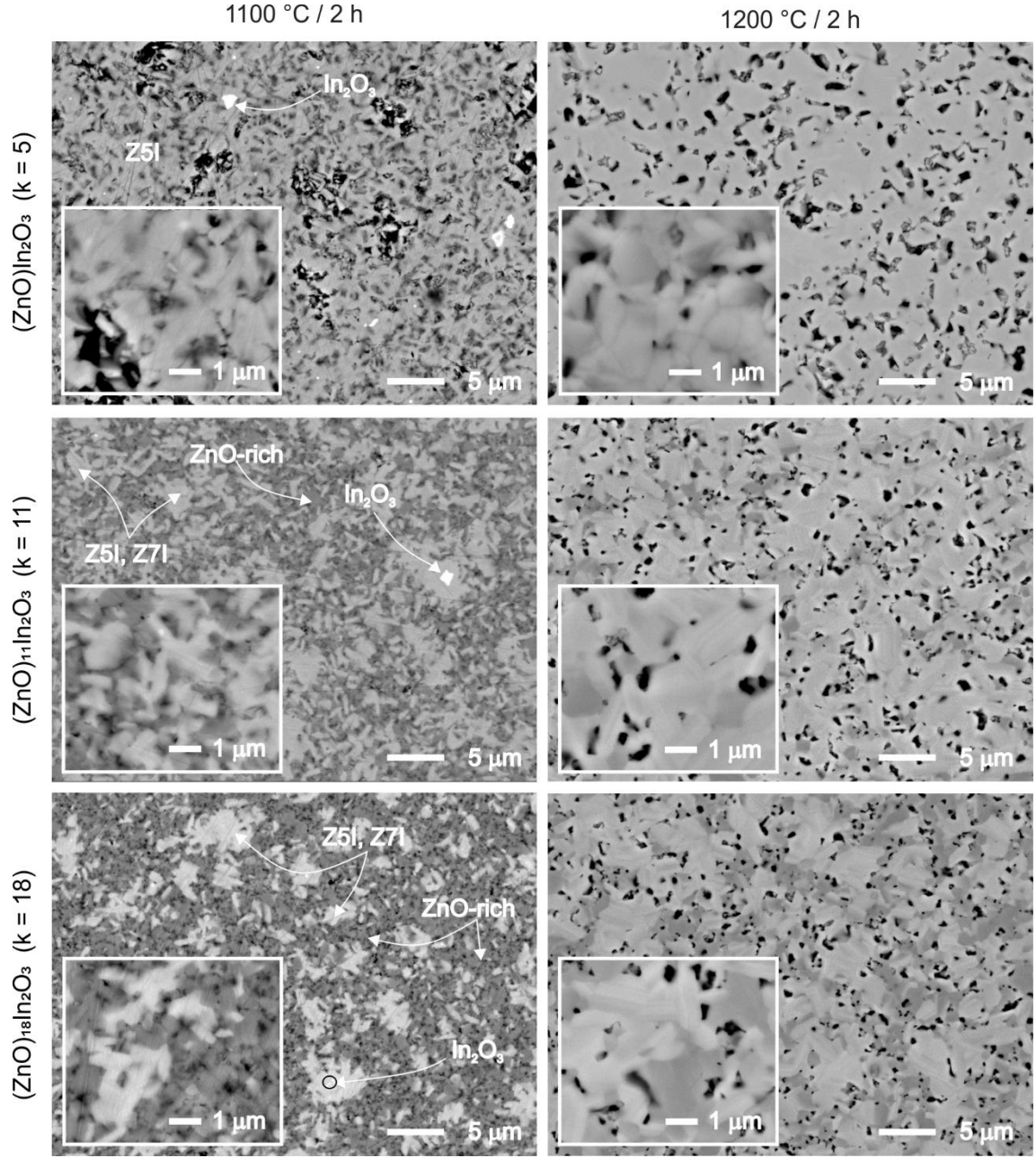


Figure 4.4: The microstructures (BSE images) of the samples $(\text{ZnO})_k\text{In}_2\text{O}_3$ ($k = 5, 11, 18$) sintered for 2 h at 1100 °C and 1200°C.

Figure 4.5 presents etched microstructures of the samples that clearly show the morphology of the grains. The observed anisotropic, plate-like morphology is a result of the homologous phase formation through an internal diffusion mechanism [128], which endorses the preferential growth of the grains in the direction of the IBs. The so-called head-to-head configuration of the multiple inversion boundaries inevitably results in grains with $(000\bar{1})$ oxygen-terminated surfaces, known to have the lowest growth potential among the ZnO planes [165]. Therefore, the preferential growth in the direction of the IBs and the development of the plate-like morphology of the $(\text{ZnO})_k\text{In}_2\text{O}_3$ grains are additionally promoted. Accordingly, in the $k = 5$ sample after sintering at 1100 °C for 2 h, plate-like grains with lengths up to about 2 μm of $\text{Zn}_5\text{In}_2\text{O}_8$ are already present with some traces of the unreacted In_2O_3 (Figure 4.4). With a higher sintering temperature and longer sintering

times, the $\text{Zn}_5\text{In}_2\text{O}_8$ grains become larger with a uniform size distribution, while still preserving their plate-like morphology; they have a size of about 3 μm after sintering at 1200 $^\circ\text{C}$, about 3–4 μm after 2 h and about 5–8 μm after 22 h of sintering at 1300 $^\circ\text{C}$ (Figure 4.5). This showed that the somewhat uniform formation of the $\text{Zn}_5\text{In}_2\text{O}_8$ phase in the sample with $k = 5$ also resulted in a rather homogeneous growth of the plate-like grains at 1100 $^\circ\text{C}$, when it starts to form, and also at higher sintering temperatures. The random growth in all directions of such plate-like grains can give an additional explanation for the characteristic sintering curve of the sample $k = 5$ (Figure 4.1). Although the density increases with the temperature and time of sintering (Table 4.1), random growth of the plate-like grains unavoidably preserves a certain degree of intra-granular porosity that is also observed in Figure 4.4 and Figure 4.5.

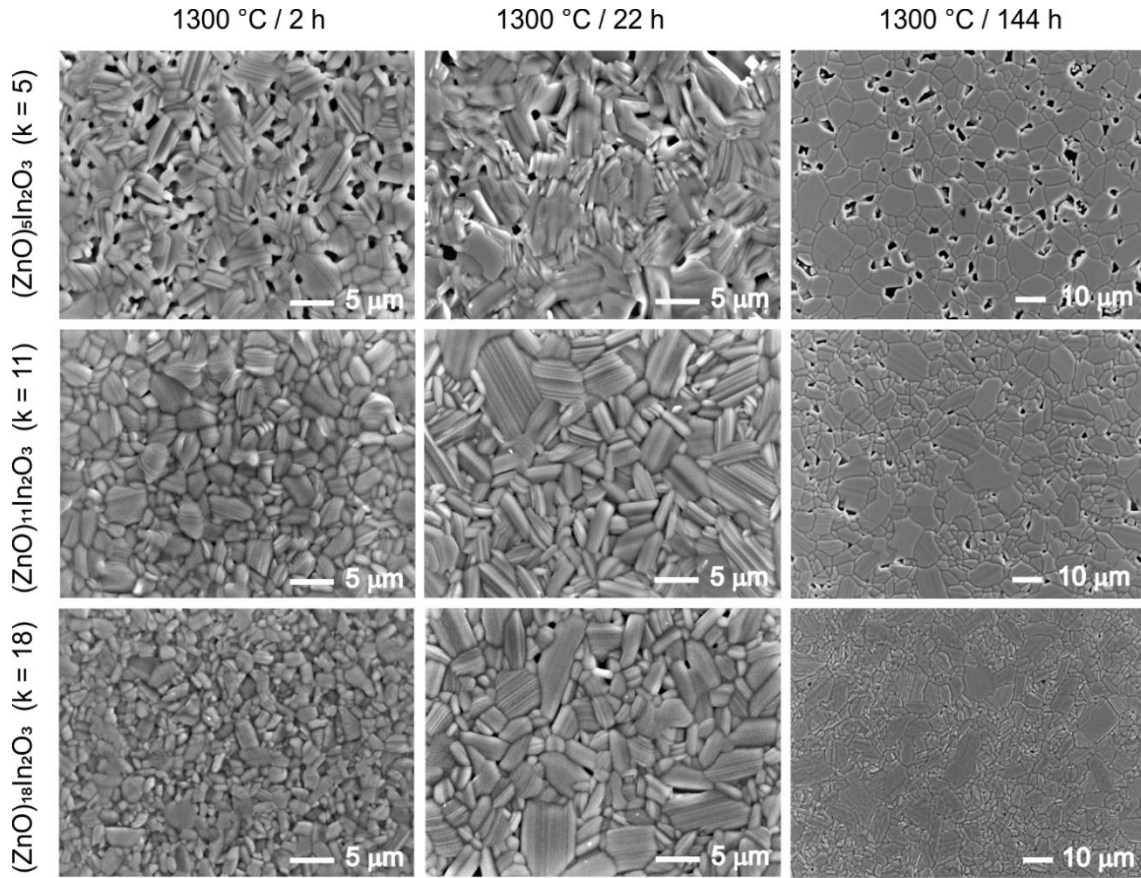


Figure 4.5: The micrographs of the thermally etched samples $(\text{ZnO})_k\text{In}_2\text{O}_3$ ($k = 5, 11, 18$) sintered at 1300 $^\circ\text{C}$ for 2 h, 22 h and 144 h.

In the samples with compositions $k = 11$ and 18, grain growth is determined by the $\text{Zn}_5\text{In}_2\text{O}_8$ and $\text{Zn}_7\text{In}_2\text{O}_{10}$ phases, which are formed as a result of the local In-enrichment. In their microstructures after sintered at 1100 $^\circ\text{C}$ (Figure 4.4), larger and bright plate-like grains of the $\text{Zn}_5\text{In}_2\text{O}_8$ and $\text{Zn}_7\text{In}_2\text{O}_{10}$ phases are clearly distinct from the smaller dark grains of the high- k compositions towards pure ZnO. While in the sample $k = 11$ the $\text{Zn}_5\text{In}_2\text{O}_8$ and $\text{Zn}_7\text{In}_2\text{O}_{10}$ phases are present in larger amounts than in the $k = 18$ sample, this is opposite to the high- k phases towards pure ZnO. With a longer sintering time and a higher sintering temperature, larger grains of the $\text{Zn}_5\text{In}_2\text{O}_8$ and $\text{Zn}_7\text{In}_2\text{O}_{10}$ phases are growing at the expense of the phases with $7 < k < \infty$ values. Their preferential growth is also driven by the differences in the chemical potential among the grains with a different content of

In and a tendency of the system to reach a thermodynamically stable state with a uniform chemical composition. Accordingly, during the growth, the composition of the grains is steadily changing towards an equilibrium homologous phase for the starting k value (*i.e.*, $\text{Zn}_{11}\text{In}_2\text{O}_{14}$ and $\text{Zn}_{17}\text{In}_2\text{O}_{20}/\text{Zn}_{19}\text{In}_2\text{O}_{22}$). In the sample for $k = 11$, the grains of $\text{Zn}_5\text{In}_2\text{O}_8$ and $\text{Zn}_7\text{In}_2\text{O}_{10}$ are initially formed in a noticeably larger amount, and their composition is closer to the equilibrium $\text{Zn}_{11}\text{In}_2\text{O}_{14}$ phase than in the sample for $k = 18$. Hence, at a certain sintering temperature, in the $k = 11$ sample, the equilibrium $\text{Zn}_{11}\text{In}_2\text{O}_{14}$ phase is reached faster than the equilibrium $\text{Zn}_{17}\text{In}_2\text{O}_{20}$ and $\text{Zn}_{19}\text{In}_2\text{O}_{22}$ homologous phases in the sample $k = 18$. Once the equilibrium composition is reached, the grain growth is slowed.

Table 4.1: Densities of the $(\text{ZnO})_k\text{In}_2\text{O}_3$ ($k = 5, 11, 18$) samples sintered at different temperatures.

Sample series	$k = 5$ [g/cm ³]/ Rel. %	$k = 11$ [g/cm ³]/ Rel. %	$k = 18$ [g/cm ³]/ Rel. %
1200 °C / 2 h	4.70 / 77 %	5.50 / 93 %	5.40 / 95 %
1200 °C / 22 h	4.84 / 79 %	5.60 / 94 %	5.58 / 98 %
1300 °C / 2 h	5.52 / 90 %	5.52 / 93 %	5.54 / 98 %
1300 °C / 22 h	5.73 / 94%	5.73 / 97%	5.40/ 95%
1500 °C / 2 h	5.60 / 91%	5.69 / 96%	5.56 / 98%

The $k = 11$ sample sintered at 1300 °C for 2 h has slightly larger grains (Figure 4.5) than the $k = 5$ sample, with an otherwise very similar microstructure in which the equilibrium composition is achieved even faster. However, the $k = 18$ sample has, in general, a smaller grain size. The EDS analysis showed that larger grains have compositions with lower k values ($k < 18$), while for smaller grains, the k values are > 18 . Prolonged sintering at 1300 °C for 22 h resulted in similar microstructures (Figure 4.5) of the samples $k = 5$, $k = 11$ and $k = 18$ with similar sizes and shapes of the grains. In the samples with $k = 5$ and $k = 11$, the grains reached the composition of the equilibrium homologous phase sometime within the first 2 h of sintering, so that afterwards their growth is slowed and proceeds in accordance with the Ostwald ripening. However, in the sample with $k = 18$ the grain takes more time, sometime within the 22 h of sintering, to achieve the equilibrium composition near the $\text{Zn}_{17}\text{In}_2\text{O}_{20}/\text{Zn}_{19}\text{In}_2\text{O}_{22}$ homologous phases. Afterwards, the growth in the $k = 18$ sample also proceeds by the Ostwald ripening mechanism and the sample had a similar microstructure as the samples $k = 5$ and $k = 11$ after 22 h of sintering. Much longer sintering at 1300 °C for 144 h (Figure 4.5) revealed interesting differences among the samples in regard to their grain size; while the $k = 5$ sample had quite a uniform grain size, the exaggerated grain growth of some grains can be observed in $k = 11$ and $k = 18$ samples, which resulted in much larger grains of up to 20 μm , surrounded by fine grains of a few μm . Such grain growth behaviour is likely a consequence of the remaining compositional inhomogeneities in the samples $k = 11$ and $k = 18$. In the sample with $k = 5$ all the grains have a similar composition close to the $\text{Zn}_5\text{In}_2\text{O}_8$ homologous phase and growth in accordance to the Ostwald ripening mechanism leads to a quite uniform increase in their size with thickening for a more isotropic shape. In the $k = 11$ and $k = 18$ samples some grains still vary in their composition from their equilibrium $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ homologous phase, having a k either lower (rich in In_2O_3) or higher (depleted in In_2O_3 content), and the In-rich grains grow exaggeratedly.

4.3.3 Thermoelectric properties

In a view of the detailed study of the formation of the $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ homologous phases and microstructure evolution, we analysed the thermoelectric characteristics of the samples with the starting composition $(\text{ZnO})_k\text{In}_2\text{O}_3$ ($k = 5, 11, 18$), sintered at 1300 °C for 22 h and at 1500 °C for 2 h. The samples sintered at 1300 °C for 2 h had such a high electrical resistivity that we were not able to measure them on the commercial ZEM3 device. In general, it confirmed that the starting composition for the k value, which determines the homologous phase and the density of planar defects, has a major impact on the thermoelectric properties. However, the firing temperature and time effects the phase composition and compositional homogeneity, and the size of grains, which are also expressed in the obtained thermoelectric characteristics of the sample with a certain starting composition.

The electrical conductivity and the Seebeck coefficient of the samples are presented in Figure 4.6a and Figure 4.6b. The samples sintered at 1300 °C have quite a constant electrical conductivity in the temperature range from 50 °C to 700 °C; the highest of about 85 S/cm was found for the $k = 5$ sample, while the samples with $k = 11$ and 18 had quite similar and noticeably lower values of about 22 S/cm. The samples have similar microstructures and grain sizes. Therefore, the differences are evidently related to the density of the In_{Zn} planar defect in the present $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ homologous phases; a higher density of defects related to a lower k resulted in a higher σ . Accordingly, the sample for $k = 5$ has a lower Seebeck coefficient than the other two samples with a higher k . It steadily increases with temperature from about -100 $\mu\text{V/K}$ at 50 °C to about -150 $\mu\text{V/K}$ at 700 °C. The samples with a higher k have uniformly higher S -values across the whole temperature range, the $k = 11$ sample for about -47 $\mu\text{V/K}$ and the $k = 18$ sample for about -60 $\mu\text{V/K}$. Nevertheless, their S -values are still much lower in comparison to the S value of the pure ZnO (-335 $\mu\text{V/K}$).

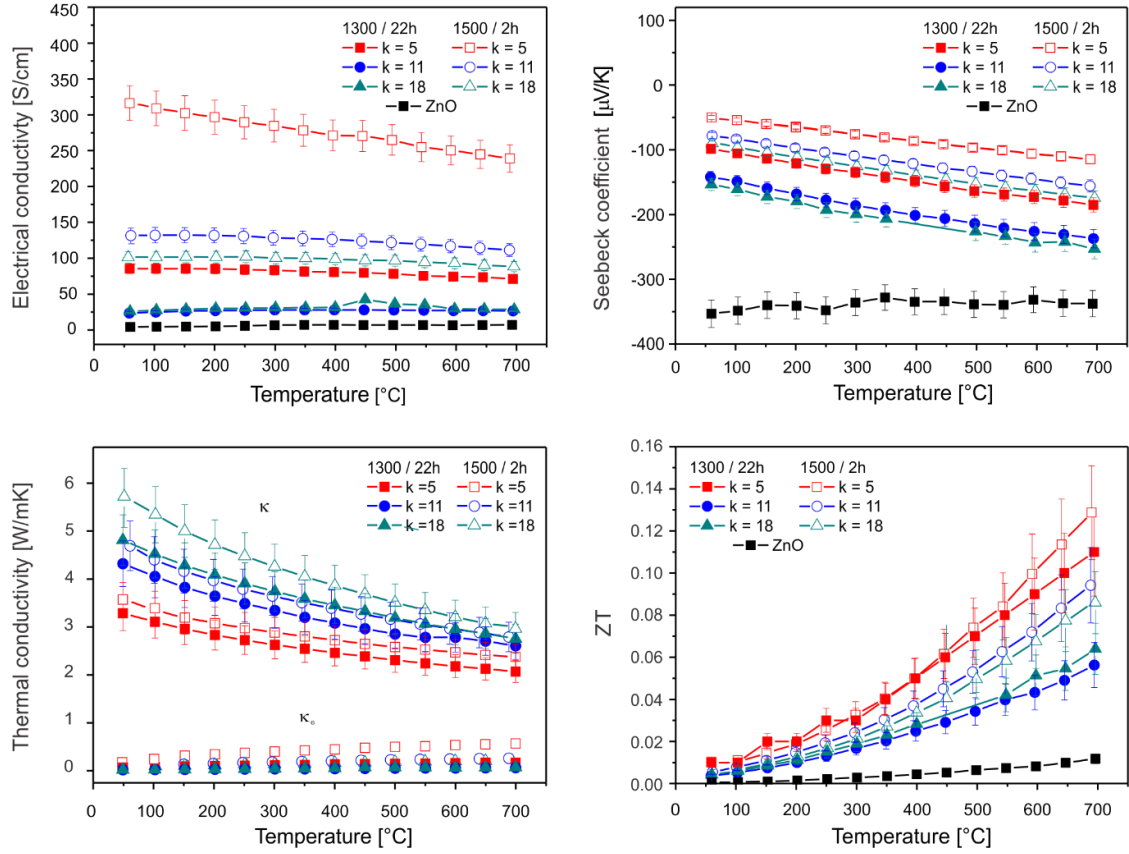


Figure 4.6: The temperature-dependent measurements of (a) electrical conductivity, (b) Seebeck coefficient, (c) thermal conductivity, and (d) ZT of the samples $(\text{ZnO})_k\text{In}_2\text{O}_3$ ($k = 5, 11, 18$) sintered at 1300 °C for 22 h and at 1500 °C for 2 h. The thermal conductivity of pristine ZnO is not shown because it is too high and is out of the range presented here on the graph.

The samples sintered at 1500 °C showed a similar trend for the electrical conductivity σ and the Seebeck coefficient as the samples sintered at 1300 °C (Figure 4.6a and b); however, with noticeably higher values and lower S values. The $k = 5$ samples have of ~ 250 S/cm, the $k = 11$ sample ~ 110 S/cm and the $k = 18$ sample ~ 90 S/cm at 700 °C. This could be attributed to the increased grain size (i.e., a reduced number of grain boundaries) at a higher sintering temperature, which on average increased from about 5 μm to more than 20 μm (Figure 4.5, Fig. 4S). Also, the samples sintered at 1500 °C have a better compositional homogeneity of the equilibrium homologous $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ phase than the samples sintered at 1300 °C, with smaller variations in the composition among the grains, which can also contribute to the higher σ . This is especially evident in the samples with $k = 11$ and $k = 18$; they have the same σ after sintering at 1300 °C, while the difference in the σ reflecting their compositional differences in k was expressed only after sintering at 1500 °C. The Seebeck coefficient is uniformly increasing in the temperature range from 50 °C to 700 °C in all three samples: in the $k = 5$ from -50 $\mu\text{V/K}$ to -110 $\mu\text{V/K}$, in the $k = 11$ from -80 $\mu\text{V/K}$ to -155 $\mu\text{V/K}$ and in the sample $k = 18$ from -93 $\mu\text{V/K}$ to -170 $\mu\text{V/K}$. In general, the Seebeck coefficients of the samples sintered at 1500 °C are at least two times lower than in the samples sintered at 1300 °C.

The thermal conductivities (κ) of the samples are presented in Figure 4.6c. While the pure ZnO has a high κ of about 40 W/mK, the values for the (ZnO)_kIn₂O₃ samples are below 5 W/mK at about 50 °C and plunge below 3 W/mK at about 700 °C, where pure ZnO has a thermal conductivity of 7.5 W/mK. In agreement with previous reports for samples with compositions $k \leq 9$ [129, 157], our study shows that the κ is lowered with an increasing content of In₂O₃ in Zn_kIn₂O_{k+3} (*i.e.*, lower k values) that have a higher density of planar defects. However, when comparing the samples with the same composition, the one sintered at higher temperature has a higher κ , and the difference is larger between the samples having a composition with a higher k value. In order to explain that difference and the effects of the composition, structure and microstructure on the thermal conductivity, we must consider that the total thermal conductivity (κ) is the sum of the lattice (κ_l) and electronic (κ_e) contributions in accordance with the equation $\kappa = \kappa_e + \kappa_l$. The electronic (κ_e) part of the thermal conductivity was calculated using a Wiedemann-Franz law according to the formula $\kappa_e = \sigma L_0 T$, ($L_0 = 2.45 \times 10^{-8}$). The obtained values for κ_e are presented in Figure 4.6c. In the samples sintered at 1300 °C, the κ_e is similar for the compositions $k = 11$ and 18 and slightly larger for the sample $k = 5$, and steadily increases with an increasing temperature. Even though the total thermal conductivity κ decreases with temperature, κ_e still represents a minor contribution to it in the samples $k = 11$ and 18 (*i.e.* 2-3 %) at temperatures above 700 °C, while in the sample for $k = 5$ with the lowest κ the κ_e accounts already for approximately 8 %. However, the strongly increased electrical conductivity of the samples sintered at 1500 °C is also expressed in the increased electronic part of the thermal conductivity κ_e , and is especially significant in the $k = 5$ sample, contributing close to 25 % of the total κ in comparison to less than 10 % in the samples with compositions $k = 11$ and 18. In general, the increase in the thermal conductivity κ of the samples sintered at 1300 °C compared to the samples sintered at 1500 °C could be mainly assigned to the contribution of the electronic part κ_e , while the lattice thermal conductivities κ_l are rather constant. Nonetheless, regardless of the composition and the sintering temperature, κ_l mainly determines the total thermal conductivity of the samples. The noticeably lower κ_l of the sample $k = 5$ in comparison to the samples $k = 11$ and 18 could be explained by the higher density of the planar defects, which defines the narrow phonon mean free path. Larger differences in the total thermal conductivity κ of the samples in the lower temperature range of measurements, expressed more in the samples sintered at 1500 °C, could also result from the observed differences in their density.

The ZT values of the samples are given in Figure 4.6d. In all the samples the ZT value steadily increases with temperature. The highest ZT values of about 0.12 at temperatures of 700 °C were obtained in the samples with the composition $k = 5$. The sample sintered at 1500 °C had a slightly increased ZT in comparison to the one sintered at 1300 °C. In the compositions $k = 11$ and 18, the increase in the ZT from the sample sintered at lower temperature to the sample sintered at higher temperature were noticeably larger, in the range from 0.02 to 0.04. Such an increase in ZT between the samples with the same composition sintered at lower and higher temperatures resulted from the structural and microstructural differences (Figure 4.5). In the sample with a higher addition of In₂O₃ (*i.e.*, $k = 5$) the equilibrium homologous phase is formed at a lower sintering temperature and in a shorter sintering time than in the samples with a lower addition of In₂O₃ ($k = 11$ and 18). Hence, for $k = 5$ the differences in the structural and compositional homogeneity between the sample sintered at a lower temperature and one sintered at a higher temperature are rather small, which led to only a slightly higher ZT for the sample sintered at 1500 °C due to the larger grain size (Fig. 6). For $k = 11$ and 18, the homogeneity of the grains is improved with the sintering temperature, which results in their increased ZT values. Accordingly, the samples with $k = 11$ and 18 had a much lower ZT in comparison

to the sample with $k = 5$ after sintering at 1300 °C, while after sintering at 1500 °C the differences in their ZT values were rather small, below 0.1. Such a result was rather surprising and could be explained by the exaggerated grain growth in these two samples, acting beneficially mostly on the electrical conductivity and resulting in higher ZT values.

4.4 Conclusions

In this work the formation of complex homologous phases in the $(\text{ZnO})_k\text{In}_2\text{O}_3$ system with an influence on the grain growth, microstructural evolution and consequently the thermoelectric properties of ceramics is explained. The samples with the compositions $(\text{ZnO})_k\text{In}_2\text{O}_3$ ($k = 5, 11$ and 18) were prepared by the classic ceramic procedure from powder mixtures of ZnO and In_2O_3 and sintered at temperatures from 900 °C to 1500 °C. The sintering of the In_2O_3 -doped ZnO ceramics is hindered by the presence of In_2O_3 at the grain boundaries, more in the compositions with a larger amount of In_2O_3 ; it proceeds in the shadow of the diffusion of In^{3+} into the wurtzite-type ZnO, which leads to the formation of the multiple planar defects and the homologous phases, as long as the In_2O_3 is not sufficiently removed from the grain boundaries to allow the intergranular diffusion of the Zn-ions. The homologous phase formation starts at temperatures above 1000 °C and is substantially determined by the initial distribution of In_2O_3 in the starting mixture with ZnO and consequently the local ZnO-to- In_2O_3 ratio. In the composition with $k = 5$, the amount of added In_2O_3 is sufficient for the ZnO-to- In_2O_3 ratio to be close to 5 at relatively short-range localities in the starting powder mixture, which enable the uniform formation of the equilibrium homologous phase $\text{Zn}_5\text{In}_2\text{O}_8$ at lower temperatures than for the homologous phase formation and with shorter sintering times. As a consequence of this soon-reached compositional homogeneity and hence the similar composition of the grains, the grain growth in the sample with $k = 5$ is quite uniform, regardless of the sintering temperature. In the compositions with a much lower content of In_2O_3 (i.e., high $k = 11$ and 18 values), the local ZnO-to- In_2O_3 ratio facilitates an initial formation of the lower k $\text{Zn}_5\text{In}_2\text{O}_8$ and $\text{Zn}_7\text{In}_2\text{O}_{10}$ phases in In-rich areas and the higher k $\text{Zn}_k\text{In}_2\text{O}_{3+k}$ phases for $k > 9$ towards pure ZnO ($k \rightarrow \infty$) in the In-depleted regions. Consequently, the equilibrium homologous phase for the starting high- k composition is formed only after the extensive diffusion of Zn-ions from grains of higher- k phases to the grains of lower- k phases, which require higher sintering temperatures and longer sintering times when the starting k -value is higher. Consequently, the exaggerated growth of grains with a higher content of In_2O_3 is manifested in these samples as long as the compositional homogeneity of the equilibrium homologous phase for the starting k -value is not established in the whole ceramic. Hence, after sintering under conditions ensuring ceramics with a uniform composition of the equilibrium homologous phase for the starting k value (i.e., high temperature), grains in the samples with $k = 11$ and 18 are much larger than in the sample with $k = 5$.

The thermoelectric characteristics of the $(\text{ZnO})_k\text{In}_2\text{O}_3$ ceramics are influenced by the observed phase formation and microstructure development with respect to their structural and compositional homogeneity. In general, the TE characteristics decrease with an increasing k value in relation to the density of the In-planar defects. The ceramics with $k = 5$ had similar ZT values after sintering at 1300 °C and 1500 °C (i.e., 0.12 at 700 °C). However, the ZT of the samples with $k = 11$ and $k = 18$ after sintering at 1500 °C significantly increased, reaching values surprisingly close to the sample with $k = 5$, which can be attributed to the improved compositional homogeneity and a much larger grain size.

Acknowledgements

This work was supported by the Slovenian Research Agency (Young researcher programme: PR-04363 and Project grant L2-4192). Part of work was done in CRISMAT Laboratoire (Caen, France) with funding from Slovene Human Resources Development and Scholarship Fund (Contract No. 11012-12/2013). Special gratitude to Marjeta Maček Kržmanc for performing DSC analysis, to Pablo Diaz Chao for useful instructions about the ZEM3 device, and to Jérôme Lecourt for the LFA device training.

Chapter 5

Microstructure and Thermoelectric Characteristics of the $(\text{ZnO})_k \text{In}_2\text{O}_3$ - Based Ceramics ($k = 5$ and 11)

In this chapter the paper entitled “*Microstructure and thermoelectric characteristics of $(\text{ZnO})_k \text{In}_2\text{O}_3$ ceramics*” by Slavko Bernik, Mateja Košir and Emmanuel Guilmeau is presented. For this article the author of this thesis performed sample preparation, solid-state sintering, XRD sample preparation, polishing and thermal etching of samples, SEM observations, analysis, processing and interpretation of the obtained data.

In this paper, the pre-reacted $(\text{ZnO})_k \text{In}_2\text{O}_3$ phases were used to induce the possible microstructure texturing in order to improve the thermoelectric properties. The $(\text{ZnO})_k \text{In}_2\text{O}_3$ -based ceramic for $k = 5$ and $k = 11$ was prepared by a classic ceramic procedure and sintering at 1500 °C. Either a fresh powder mixture of ZnO and In_2O_3 was used, or a mixture of ZnO and In_2O_3 to which pre-reacted powder with a well-defined plate-like grains of the $(\text{ZnO})_k \text{In}_2\text{O}_3$ homologous phase was added.

In the case of a fresh mixture of ZnO and In_2O_3 , the process of the phase formation was controlled by the uniformity of the distribution of the In_2O_3 powder, determining the local ZnO-to- In_2O_3 ratio in the mixture and the initially formed homologous phases. In the powder mixtures containing the addition of the pre-reacted powder with much coarser, plate-like grains of the $(\text{ZnO})_k \text{In}_2\text{O}_3$ homologous phases fast growth of the low- k phases ($\text{Zn}_5\text{In}_2\text{O}_8$ and $\text{Zn}_7\text{In}_2\text{O}_{10}$) at the expense of the much finer grains of ZnO and In_2O_3 , and also the high- k $(\text{ZnO})_k \text{In}_2\text{O}_3$ homologous phases was promoted, which eventually resulted in the formation of the equilibrium $(\text{ZnO})_k \text{In}_2\text{O}_3$ homologous phase. Nevertheless, the final microstructures of all the samples, regardless of the starting powder mixture, were similar. No texturing was observed in the samples prepared from the mixtures with the pre-reacted plate-like grains of the $(\text{ZnO})_k \text{In}_2\text{O}_3$ homologous phases, likely due to the presence of solid clusters of the pre-reacted plate-like grains, which prevented any alignment of plate-like seeds that might occur in pressing of the pellets. However, the presence of such solid clusters resulted in higher porosity of the samples in comparison to the samples prepared from a pristine mixture of ZnO and In_2O_3 .

Abstract

Oxide thermoelectric ceramics are needed for high-temperature applications that involve harvesting the waste heat by direct transformation into electricity. In the case of n-type materials, the homologous $(\text{ZnO})_k\text{In}_2\text{O}_3$ -type phases are very promising for tailoring the TE properties. In this investigation the thermoelectric $(\text{ZnO})_k\text{In}_2\text{O}_3$ -based ceramics for $k=5$ and 11 were prepared using a classic ceramics procedure and sintering at 1500°C . During their preparation, either a fresh powder mixture of ZnO and In_2O_3 or a mixture of ZnO and In_2O_3 also containing plate-like grains of the pre-reacted $(\text{ZnO})_k\text{In}_2\text{O}_3$ phases was used to induce possible microstructure texturing. It was demonstrated that the starting composition in terms of k value and the type of starting powder mixture affect the processes, leading to the formation of the equilibrium $(\text{ZnO})_k\text{In}_2\text{O}_3$ homologous phase and, consequently, also the microstructure development. Nevertheless, all the samples had similar final microstructures and no texturing was observed. Regardless of the use of different starting-powder mixtures, the samples with the same composition had a similar ZT: at 627°C it was 0.11 for the samples with $k=5$ and 0.08 for $k=11$, which is not so inferior if we take account of the significantly lower content of In_2O_3 in these samples.

Keywords: ZnO ceramics, In_2O_3 doping, microstructure, thermoelectric characteristics.

5.1 Introduction

Thermoelectric (TE) materials are characterized by the thermoelectric effect, which actually includes three separate effects: the Seebeck effect, the Peltier effect, and the Thomson effect. Cooling devices based on the Peltier effect, made from classic TE alloys, are already well established in various high technologies. The exploitation of another characteristic of TE materials, the Seebeck effect, nowadays represents one of the key technological challenges, as modules made from n- and p-type TE materials give the only viable possibility for harvesting waste heat by its direct conversion into electricity. The effective utilization of the waste heat, which represents almost 70% of all primary produced energy, could be an important pillar of energy sustainability. [3, 7, 166-168]

The thermoelectric (TE) characteristics of materials are usually expressed by the dimensionless figure of merit ZT , in accordance with the equation $ZT = S^2 T / \kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity. For good TE characteristics a reasonably good electrical conductivity, a high Seebeck coefficient and a low thermal conductivity of the material are required, which demands an intricate optimization of juxtaposed parameters. The best TE materials, i.e., metallic alloys, already have the required thermoelectric characteristics, with ZT values of approximately 2. However, they are thermally unstable in air at temperatures above 300°C and are made from expensive and toxic elements.[2,6,7][7] [8, 169] Their limitations suggest the potential advantages of oxide TE materials at higher temperatures: they are thermally and chemically stable in oxygen to at least 800°C , non-toxic and made from abundantly available and low-cost elements. However, these advantages can only be realized after a significant improvement of their TE characteristics, which are for polycrystalline ceramics much too low, with ZT values mostly well below 1. [78, 79, 96]

Oxide thermoelectric materials came into focus in 1997 with the report of Terasaki et al. [76] that the transition-metal oxide NaCo_2O_4 exhibits a large thermos-power and a low electrical resistivity. While NaCo_2O_4 is known to be highly unstable, due to its poor resistance to humidity and its volatility at elevated temperatures, other p-type Co-based oxides with a misfit layered structure, such as $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$, are much better in this regard and at the same time also very promising for further enhancements of the

TE properties. [78, 79] The properties of all these materials are closely related to their complex structure. In the case of $\text{Ca}_3\text{Co}_4\text{O}_9$ the structure consists of a CoO_2 layer of the CdI_2 type, ensuring an electrically conductive and an insulating Ca_2CoO_3 layer of the rock-salt type. The mismatch and the weak connection between these two substructure types contribute to the phonon scattering for a reduced thermal conductivity. Hence, the $\text{Ca}_3\text{Co}_4\text{O}_9$ has a noticeably higher electrical conductivity in the a-b (in-plane) direction along the CoO_2 layers than in the c (out-of-plane) direction with a lower thermal conductivity. The $\text{Ca}_3\text{Co}_4\text{O}_9$ phase also has a distinct plate-like morphology of the grains. Generally, a high density and texturing are considered as the main microstructural features for an improvement in the thermoelectric characteristics of materials with anisotropic properties, such as $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramics. Our research showed the limitations of such an approach; for a completely random orientation of plate-like grains and densities below 60% the $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramics had a ZT of 0.09 at 627 °C, while in perfectly textured and fully dense (99%) samples the ZT was 0.17. The highest ZT of 31 was obtained in modestly textured, but still highly porous, ceramics having a similar electrical conductivity and Seebeck coefficient in comparison to the perfectly textured ceramics, although with a much lower thermal conductivity. [85] To the best of our knowledge this is the highest ZT value reported so far for un-doped $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramics.

The n-type TE materials in the focus of our research are SrTiO_3 , CaMnO_3 and ZnO . They have a large Seebeck coefficient; however, for a higher ZT the low electrical and the high thermal conductivity should be significantly improved by proper doping and microstructure optimisation [79] The un-doped polycrystalline ZnO ceramics have a too low electrical conductivity of about 10 S/cm and a too high thermal conductivity of about 40 W/mK for good thermoelectric characteristics, despite the very high Seebeck coefficient of about -400 $\mu\text{V/K}$. [96] However, proper doping of the ZnO ceramics with either Al [170] or a combination of Al and Ga [112] resulted in the best ZT values for the n-type polycrystalline ceramics up to about 0.65 at 700 °C. A very interesting basis for the tailoring of the TE properties is offered by doping with In_2O_3 , introducing multiple complex planar defects into the relatively simple ZnO wurtzite-type structure and consequently the formation of homologous $(\text{ZnO})_k\text{In}_2\text{O}_3$ -type phases at temperatures above 1100 °C. [123] Basically, two types of defects are formed that primarily affect the TE characteristics: planar InO_2 defects along the (0001)-basal planes as highly electron-conductive pathways and “zig-zag”-type ZnO/In defects in between the planar ones, causing phonon scattering for a reduced thermal conductivity. The homologous $(\text{ZnO})_k\text{In}_2\text{O}_3$ phases are defined by the distance between the planar InO_2 defects in accordance with the expression $d = k+1$, where d is the number of the ZnO layers. The TE characteristics of $(\text{ZnO})_k\text{In}_2\text{O}_3$ -based ceramics were studied for compositions with $k = 3, 5, 7$ and 9, and so far the highest ZT of about 0.1 at 700 °C was based on $(\text{ZnO})_5\text{In}_2\text{O}_3$. [129, 130, 159] The planar defects and hence the homologous $(\text{ZnO})_k\text{In}_2\text{O}_3$ phases form through the mechanism of internal diffusion; this is driven by a local charge deficiency, initiated by the Zn vacancies as preferential sites for the incorporation of the In^{3+} ions into the wurtzite structure of ZnO [128]. The formation of the planar defects also strongly influences the grain growth and the grains of the $(\text{ZnO})_k\text{In}_2\text{O}_3$ homologous phases develop a plate-like morphology, which gives the possibility of tailoring a textured microstructure. In highly textured $(\text{ZnO})_5\text{In}_2\text{O}_3$ ceramics the ZT value was increased to 0.18 at 800 °C. [135] This again confirmed the importance of a microstructure optimisation for the improvement of the TE characteristics of ceramics in the $\text{ZnO-In}_2\text{O}_3$ system.

In this work the $(\text{ZnO})_k\text{In}_2\text{O}_3$ -based ceramics for $k = 5$ and 11 were prepared using a classic ceramics procedure and sintering at 1500 °C. The samples were prepared either from a fresh powder mixture of ZnO and In_2O_3 or from a mixture of ZnO and In_2O_3 with the addition of a pre-reacted powder with well-defined plate-like grains of the $(\text{ZnO})_k\text{In}_2\text{O}_3$

homologous phases for possible microstructure texturing. The influence of the composition in terms of k value and the starting powder mixture on the phase formation, the grain growth and the microstructure development, and consequently the TE characteristics of the $(\text{ZnO})_k\text{In}_2\text{O}_3$ -based ceramics, was studied.

5.2 Experimental

Powder mixtures with compositions $(\text{ZnO})_k\text{In}_2\text{O}_3$ for k values of 5 and 11 were prepared from powders of ZnO (Grillo Zinkoxide, GmbH, Pharma 4, > 99.9%) and In_2O_3 (Alfa Aesar, 99.9 % metals basis, 325-mesh powder), mixed with ethanol and homogenized in a polyethylene vial in a planetary ball mill for 1 h, and afterwards dried at 80 °C (fresh powder mixtures labeled ZkI). Part of each powder mixture ZkI was in a loose state pre-reacted at 1150 °C for 2 hours and subsequently grinded in an agate mortar. The pre-reacted powder of each composition k was mixed with a corresponding fresh powder mixture ZkI of ZnO and In_2O_3 in the weight ratio 1:1 and homogenized in an agate mortar (powder mixtures labeled ZkI 50-50). The powder mixtures, fresh (ZkI) and those containing pre-reacted powder (ZkI 50-50) were uniaxially pressed into pellets with a diameter of 12 mm and height of approximately 2 mm, followed by cold isostatic pressing under a pressure of 280 MPa with a 30 s holding time. The pellets were sintered at 1500 °C for 2 h in air. The density of the samples was measured using Archimedes' principle (DENSITEC). The phase composition of the sintered samples was analyzed using powder X-ray diffraction analysis (diffractometer PANalytical X'Pert PRO MPD, Almelo, The Netherlands). The microstructures in the cross-section direction across the disc samples, un-etched and thermally etched, were examined using a scanning electron microscope (SEM, JSM-5800, JEOL, Tokyo, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS; Link ISIS 300, Oxford Instruments Ltd., Oxfordshire, U.K.). Rods with lengths from 8 to 10 mm and a cross-section of about 2 x 2 mm² were cut from the sintered pellets for measurements of the Seebeck coefficient and the electrical conductivity using a commercial ZEM 3 device (ULVAC Technologies, Inc, Methuen, MA, USA) in a partial helium atmosphere. For the thermal diffusivity measurements, squares of 6 x 6 mm² and 1 mm thick were cut from the pellet and measured in air with a laser flash (NETZSCH, LFA 457 MicroFlash, Netzsch, GmbH, Germany) without any additional carbon coating. The thermal conductivity was calculated from the heat capacity (C_p), density (ρ) and thermal diffusivity (α), according to the formula: $\kappa = C_p * \rho * \alpha$.

5.3 Results and Discussion

The XRD patterns of the loose powder mixtures pre-reacted at 1150 °C are presented in Figure 5.1. Only in the powder mixture for $k=5$ with the highest amount of In_2O_3 added to the ZnO was the homologous phase of the starting composition $\text{Zn}_5\text{In}_2\text{O}_8$ (JC PDF 00-020-1440) formed. In the powder mixtures Z11I the $\text{Zn}_5\text{In}_2\text{O}_8$ and $\text{Zn}_7\text{In}_2\text{O}_{10}$ (JC PDF 00-020-1441) homologous phases were clearly detected, while the XRD pattern also indicates the possible formation of the phases for $k \geq 11$ towards the pure ZnO phase, which could be identified in accordance with the report of Moriga et al. [123] They also reported that only $(\text{ZnO})_5\text{In}_2\text{O}_3$ and $(\text{ZnO})_7\text{In}_2\text{O}_3$ are stable at 1100 °C.

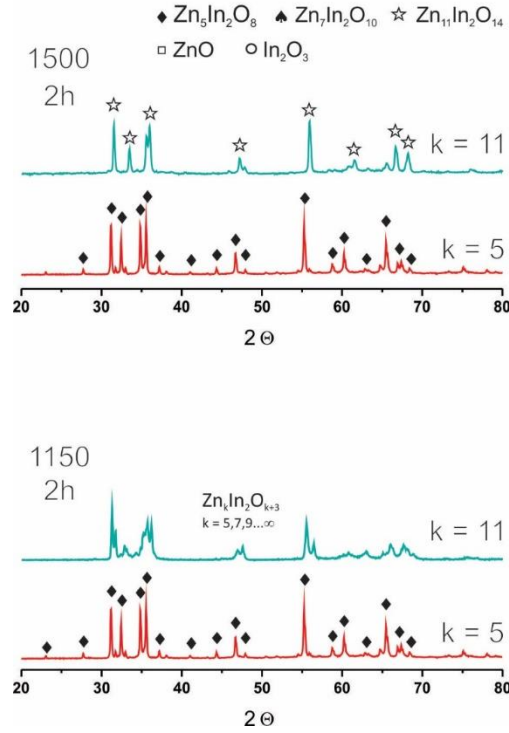


Figure 5.1: The XRD patterns of powder mixtures pre-reacted at 1150 °C and the samples sintered at 1500 °C.

Nevertheless, such a complete formation of the $(\text{ZnO})_5\text{In}_2\text{O}_3$ phase at 1150 °C was in a way surprising, having in mind the likely relatively weak contact between the reacting ZnO and In_2O_3 in the pre-reacted loose powder mixture Z5I. It was also demonstrated in the well-defined, plate-like morphology of the several-micrometer-sized grains Figure 5.2, with the largest having a length up to 5 μm and a thickness of approximately 0.8 μm . Poor homogeneity in the distribution of the In_2O_3 in the ZnO should also be taken into consideration, especially for the compositions with a higher k and small additions of In_2O_3 , even more so because the ZnO powder is much finer than the In_2O_3 (Figure 5.2). In the case of Z5I the addition of In_2O_3 to ZnO was obviously sufficient to ensure its presence everywhere in the pre-reacted mixture in an amount needed for the relatively uniform formation of the $(\text{ZnO})_5\text{In}_2\text{O}_3$ phase. However, in the Z11I a much smaller amount of In_2O_3 is likely to be un-homogeneously distributed; locally it could be, with respect to the nominal starting composition, either in excess or deficit with respect to the ZnO, which allowed, on the one hand, the formation of the $(\text{ZnO})_5\text{In}_2\text{O}_3$ and $(\text{ZnO})_7\text{In}_2\text{O}_3$ phases, and on the other hand, the formation of higher k homologous phases towards the pure ZnO, respectively.

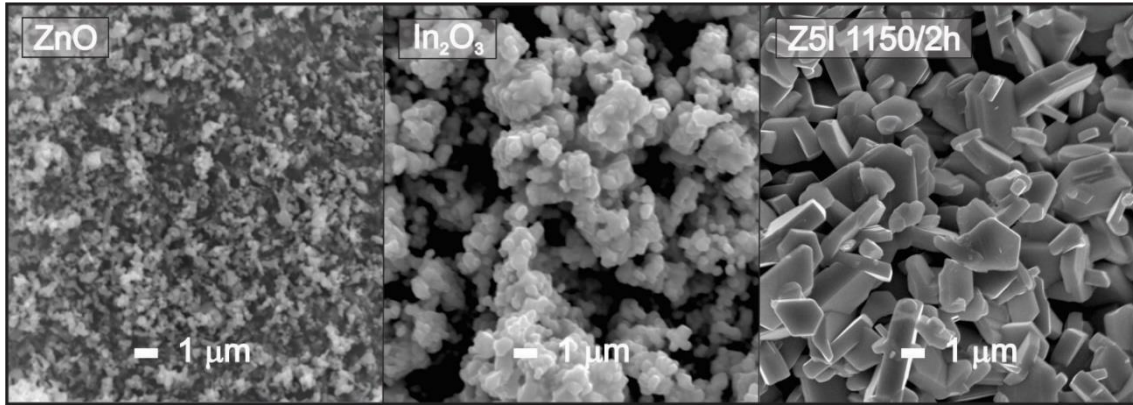


Figure 5.2: SEM images of the starting ZnO and In_2O_3 powders, and the powder with composition $(\text{ZnO})_5\text{In}_2\text{O}_3$ pre-reacted in loose form at 1150°C .

In comparison to the pre-reacted powder Z5I from essentially only the $(\text{ZnO})_5\text{In}_2\text{O}_3$ phase, the pre-reacted powder of Z11I has a much more complex phase composition containing some $(\text{ZnO})_5\text{In}_2\text{O}_3$ and $(\text{ZnO})_7\text{In}_2\text{O}_3$, and a significant share of phases for $k \geq 11$, towards the practically pure ZnO phase. Nevertheless, it also has a similar well-expressed, plate-like morphology of the grains. The addition of such pre-reacted powders of Z5I and Z11I with much larger grains and a well-defined, plate-like morphology to the corresponding fresh mixtures of ZnO and In_2O_3 with a much finer grain size (Figure 5.2) could strongly affect the microstructure development of the ZkI 50-50 samples. In accordance with Ostwald ripening, the preferential growth of the larger grains of the pre-reacted powders could be expected with the possible development of at least a certain degree of microstructure texturing due to the plate-like morphology.

The pellets prepared from the powder mixtures ZkI and ZkI 50-50 ($k = 5, 11$) were sintered at 1500°C . At such a high sintering temperature the rapid development of the homologous phases corresponding to the starting compositions, the $(\text{ZnO})_5\text{In}_2\text{O}_3$ in the Z5I and Z5I 50-50 samples, and the $(\text{ZnO})_{11}\text{In}_2\text{O}_3$ in the Z11I and Z11I 50-50 samples, could be expected. At temperatures above 1300°C a significant sublimation of the ZnO takes place, as reported by Anthrop and Searcy [171], which results in the increased formation of Zn vacancies. An abundance of Zn vacancies enhances the self-diffusion of the Zn . They are also preferential sites for the incorporation of In^{3+} and its diffusion into the ZnO , which leads to the formation of multiple planar defects and hence homologous phases in accordance with the mechanism of internal diffusion [128]. Accordingly, the XRD analysis clearly showed that all the samples sintered at 1500°C for 2 h have the composition of an equilibrium homologous phase for the starting k value, the $\text{Zn}_5\text{In}_2\text{O}_8$ or the $\text{Zn}_{11}\text{In}_2\text{O}_{14}$.

The microstructures of the samples sintered at 1500°C are presented in Figure 5.3. All the samples have a relatively homogeneous microstructure with randomly oriented, plate-like grains. The sample Z5I prepared from a fresh powder mixture of ZnO and In_2O_3 has a smaller grain size than the other samples, especially in comparison to the sample Z11I, also prepared from a fresh powder mixture. Such a microstructure development can be explained in terms of the distribution of the In_2O_3 in the powder mixture with ZnO and its local concentrations regarding the In_2O_3 -to- ZnO ratio; it controls the phase formation, as was already shown in the case of powders pre-reacted at 1150°C , and via phase formation consequently also the grain growth. In the Z5I sample the amount of In_2O_3 is sufficient to ensure that everywhere in the powder mixture at short range the In_2O_3 -to- ZnO ratio is

close to 5, which enables the formation of the $(\text{ZnO})_5\text{In}_2\text{O}_3$ homologous phase uniformly through the sample and hence uniform grain growth with a finer grain size.

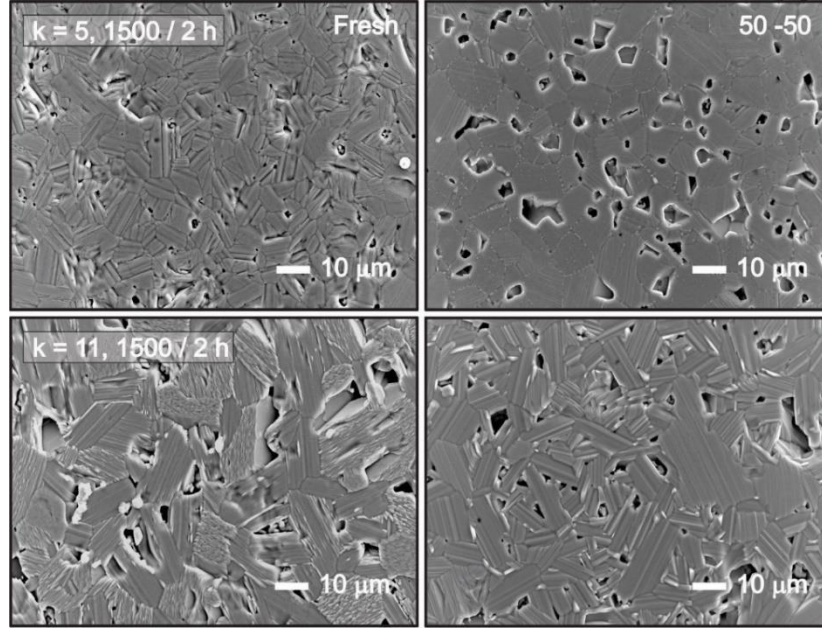


Figure 5.3: Thermally etched microstructures of the $(\text{ZnO})_k\text{In}_2\text{O}_3$ ($k=5,11$) ceramics., prepared from the fresh powder mixtures of ZnO and In_2O_3 (fresh) or starting mixture containing also pre-reacted powder (50-50), sintered at 1500 °C for 2 h.

For a much smaller amount than in the sample Z11I the coarse-grained In_2O_3 is distributed inhomogeneously in much finer ZnO, locally being either in excess (i.e., In_2O_3 -to-ZnO ratio < 11) or in deficit (i.e., In_2O_3 -to-ZnO > 11). As in the powder Z11I pre-reacted at 1150 °C, also in the sample sintered at 1500 °C (however at a much faster rate) grains of the $(\text{ZnO})_5\text{In}_2\text{O}_3$ and $(\text{ZnO})_7\text{In}_2\text{O}_3$ phases are initially formed at the In_2O_3 -rich locations. They are separated by grains of phases $(\text{ZnO})_k\text{In}_2\text{O}_3$ with $k > 11$ going towards the pure ZnO, which are formed in areas with a deficit of In_2O_3 . As the growth of the grains is dictated by the formation of planar defects with the diffusion of In_2O_3 into the ZnO, the grains of $(\text{ZnO})_5\text{In}_2\text{O}_3$ and $(\text{ZnO})_7\text{In}_2\text{O}_3$ with a larger concentration of defects are likely to be larger from the very beginning than the grains of the high- k phases. Also, the system tends to a thermodynamically stable state with a uniform chemical composition, so the equilibration of a chemical potential across the sample is an additional driving force to dilute the phases with a higher In_2O_3 content towards the formation of the equilibrium homologous phase $(\text{ZnO})_k\text{In}_2\text{O}_3$ for the starting value of k . Hence, in the Z11I sample the grains of the $(\text{ZnO})_5\text{In}_2\text{O}_3$ and $(\text{ZnO})_7\text{In}_2\text{O}_3$ phases preferentially grow at the expense of the phases with $k > 11$ until they consume them completely and all the grains have the composition of the equilibrium homologous phase $\text{Zn}_{11}\text{In}_2\text{O}_{14}$. Consequently, such grain growth results in the microstructure of the Z11I sample with large and thick plate-like grains. The samples Z5I 50-50 and Z11I 50-50 prepared from fresh and pre-reacted powders, respectively, have larger grains than the Z5I and slightly smaller than the Z11I from a fresh powder mixture. In these samples, much larger pre-reacted plate-like grains with the composition $(\text{ZnO})_k\text{In}_2\text{O}_3$ ($k=5,7,>11$) grow preferentially in accordance with Ostwald ripening at the expense of the much finer ZnO and In_2O_3 . However, the share of pre-reacted powder equal to 50% in the starting mixture of the samples Z5I 50-50 and Z11I 50-50 is

likely to be too high for the development of their microstructures with even larger grains. Also, no texturing was observed in these samples, which could be expected from a spontaneous alignment of the plate-like grains in the starting mixtures during uniaxial pressing in a direction perpendicular to the pressing direction, and their preferential growth during sintering in accordance with the templated grain-growth mechanism (TGG)[172]. In the case that the plate-like grains are separated from each other, some alignment could take place for such a large addition of plate-like grains during the pressing and this would result in at least some limited amount of texturing. However, in our pre-reacted powders the plate-like grains grew together into clusters with the grains oriented in all directions (Figure 5.2) and such clusters were not broken apart into separate plate-like grains during grinding in the agate mortar, which prevented any alignment during the pressing of the pellets and in the process of sintering promoted the random growth of the gains in all directions. The random growth of plate-like grains in all directions inevitably leads to empty spaces between the grains and reduces the density of the ceramics. The densities of the samples are given in Table 5.1. The more expressed plate-like morphology of the grains in the sample Z5I results in it having a lower density in comparison to the sample Z11I, both prepared from the fresh powder mixtures of ZnO and In₂O₃. The lower density of the samples prepared from powder mixtures containing pre-reacted powder (ZkI 50-50) is likely the result of the already lower density of the green pellets caused by the presence of rough clusters of plate-like grains in the powder mixture and also their preferential growth during sintering.

Table 5.1: Densities of the samples sintered at 1500 °C for 2 h.

Sample	Density (g/cm ³)	Theoretical TD (g/cm ³)	density- TD (%)
Z5I-fresh	5.58	6.12	91.2
Z5I 50:50	5.30	6.12	86.6
Z11I-fresh	5.78	5.97	96.8
Z11I 50:50	5.19	5.97	86.9

The thermoelectric characteristics of the samples sintered at 1500 °C are graphically presented in Figure 5.4. The sample Z5I prepared from the fresh powder mixture showed the highest electrical conductivity and a slightly metallic behavior; its conductivity decreased from about 310 S/cm at 100 °C to about 240 S/cm at 700 °C. The sample Z5I 50-50 prepared with the addition of the pre-reacted powder had, across the whole temperature range, an approximately 40 S/cm lower conductivity. The samples Z11I and Z11I 50-50 already had a significantly lower electrical conductivity, in the range from 133 S/cm to 110 S/cm, and from about 100 S/cm to 75 S/cm, respectively. The much higher electrical conductivity of the samples with the composition k = 5 in comparison to the samples with k = 11 could be attributed to the noticeably higher density of the InO₂⁻ planar defects, representing highly conductive paths in the homologous phase Zn₅In₂O₈ in the Zn₁₁In₂O₁₄ phase. The samples ZkI 50-50 had a similarly lower electrical conductivity in comparison to the samples ZkI with the same composition, which could be a consequence of their lower density and hence the likely weaker contacts between the grains.

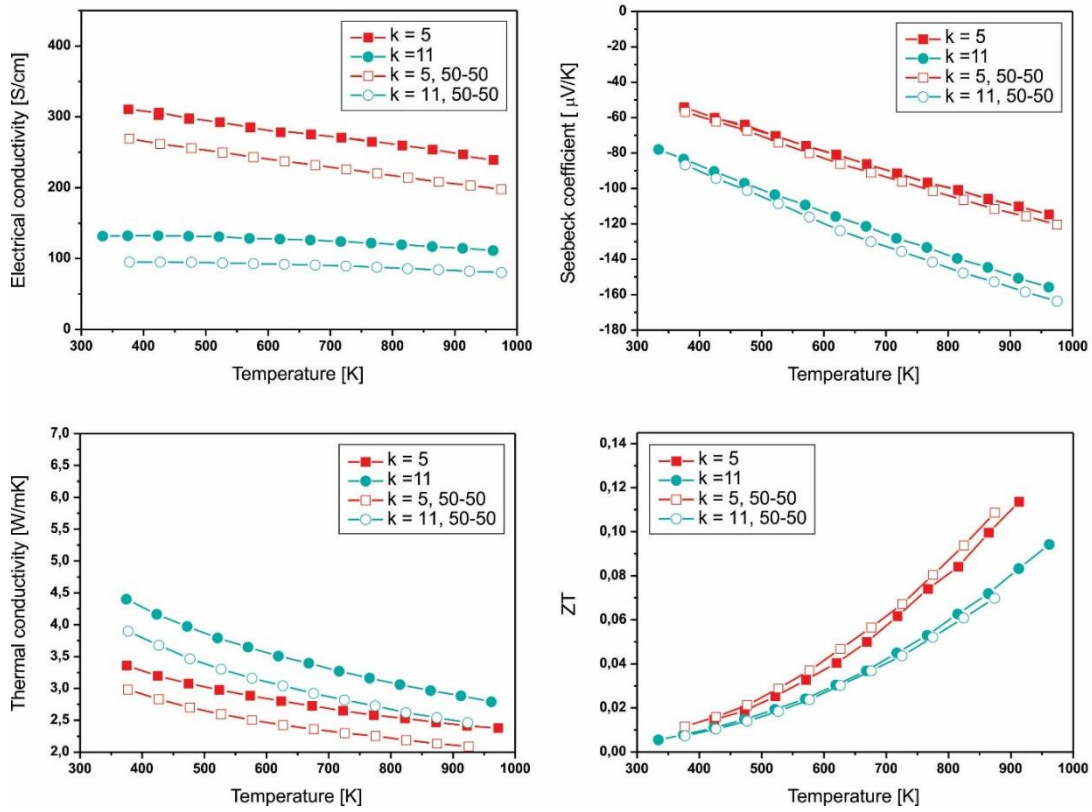


Figure 5.4: Thermoelectric characteristics of the samples sintered at 1500 °C for 2 h.

Unfortunately, the higher electrical conductivity in the case of the $(\text{ZnO})_k\text{In}_2\text{O}_3$ -based ceramics usually results in a lower Seebeck voltage (S): the samples with the composition $(\text{ZnO})_5\text{In}_2\text{O}_3$ had S in the range $-55 \mu\text{V/K}$ to $-110 \mu\text{V/K}$ and the samples with the composition $(\text{ZnO})_{11}\text{In}_2\text{O}_3$ were $-80 \mu\text{V/K}$ to $-155 \mu\text{V/K}$. The larger content of multiple planar defects caused by the In_2O_3 confirmed the benefit of a lower thermal conductivity also in this study: the samples composed of the $\text{Zn}_5\text{In}_2\text{O}_8$ homologous phase had a lower thermal conductivity than the samples of the $\text{Zn}_{11}\text{In}_2\text{O}_{11}$ phase. However, the influence of the density also clearly showed: the samples with a lower density had an approximately 0.5 W/mK lower thermal conductivity than the samples with the same composition and a higher density. The ZT value for the samples with composition for $k=5$ was about 0.11 at 627°C , and this is in agreement with other reports in the literature for the $(\text{ZnO})_5\text{In}_2\text{O}_3$ homologous phase. The samples with the composition $k=11$ had a ZT of approximately 0.08 , which is quite a promising result considering the much lower amount of In_2O_3 in these samples.

5.4 Conclusions

The thermoelectric $(\text{ZnO})_k\text{In}_2\text{O}_3$ -based ceramics for $k=5$ and $k=11$ were prepared using a classic ceramics procedure and sintering at 1500°C . For their preparation a fresh powder mixture of ZnO and In_2O_3 was used, or a mixture of ZnO and In_2O_3 to which pre-reacted powder with well-defined plate-like grains of the $(\text{ZnO})_k\text{In}_2\text{O}_3$ homologous phase was added to induce possible microstructure texturing in accordance with the templated grain-growth mechanism. In the case of a fresh mixture of ZnO and In_2O_3 the process of phase formation is controlled by the uniformity of the distribution of the In_2O_3 powder in the matrix of ZnO powder, which determines the local concentration of In_2O_3 and hence the local ZnO -

to- In_2O_3 ratio in the mixture. In compositions with larger additions of In_2O_3 than $k = 5$ it is present in sufficient amounts everywhere in the mixture for basically the direct formation of the $\text{Zn}_5\text{In}_2\text{O}_8$ homologous phase. In compositions with a much smaller addition of In_2O_3 than for $k = 11$ it is locally either in excess, which results in the formation of the $\text{Zn}_5\text{In}_2\text{O}_8$ and $\text{Zn}_7\text{In}_2\text{O}_{10}$ phases, or in deficit, so that the $(\text{ZnO})_k\text{In}_2\text{O}_3$ phases for $k > 11$ towards the pure ZnO are formed. With further processing the grains of the $\text{Zn}_5\text{In}_2\text{O}_8$ and $\text{Zn}_7\text{In}_2\text{O}_{10}$ phases grow at the expense of the high- k $(\text{ZnO})_k\text{In}_2\text{O}_3$ phases, which leads to the formation of the equilibrium $\text{Zn}_{11}\text{In}_2\text{O}_{14}$ phase. When the starting-powder mixture contains pre-reacted powder with much coarser, plate-like grains of the $(\text{ZnO})_k\text{In}_2\text{O}_3$ homologous phases, the low- k phases ($\text{Zn}_5\text{In}_2\text{O}_8$ and $\text{Zn}_7\text{In}_2\text{O}_{10}$) grow at the expense of the much finer grains of ZnO and In_2O_3 , and also the high- k $(\text{ZnO})_k\text{In}_2\text{O}_3$ homologous phases, which finally results in the formation of the equilibrium $(\text{ZnO})_k\text{In}_2\text{O}_3$ homologous phase for the starting k value in the whole sample. Nevertheless, the final microstructures of all the samples, regardless of the starting mixture, were similar. No texturing was observed in the samples prepared from the starting mixtures containing pre-reacted plate-like grains of the $(\text{ZnO})_k\text{In}_2\text{O}_3$ homologous phases. However, these samples had a lower density, likely the result of a lower density of green pellets caused by the presence of solid clusters of plate-like grains together with fine powders of ZnO and In_2O_3 in the starting mixture.

The TE characteristics of the samples $(\text{ZnO})_k\text{In}_2\text{O}_3$ are in general influenced by the starting composition for the k value. The results showed no significant influence of the starting-powder mixture on the ZT values and were similar for the samples with the same composition of k . The samples with $k = 5$, as expected, showed a higher ZT of 0.11 at 627 °C in comparison to the 0.08 for the compositions with $k = 11$. However, considering the much smaller amount of In_2O_3 in the sample with $k = 11$ the obtained result seems promising.

Acknowledgements: This work was supported by the Slovenian Research Agency (Young Researcher Program PR-04363, Project Grant L2-4192 and Program Contact Number P2-0084) and the Slovene Human Resources Development and Scholarship Fund (Contract No. 11012-12/2013).

Chapter 6

Structural Features and Thermoelectric Properties of Al-Doped $(\text{ZnO})_5\text{In}_2\text{O}_3$ Homologous Phases

In this chapter the paper [173] entitled “*Structural features and thermoelectric properties of Al-doped $(\text{ZnO})_5\text{In}_2\text{O}_3$ homologous phases*” by Mateja Košir, Cleve W. Ow-Yang, Emmanuel Guilmeau and Slavko Bernik is presented. For this article the author of this thesis performed sample preparation, solid-state sintering, XRD sample preparation, polishing and thermal etching of samples, SEM observations, sample preparation for TEM, thermoelectric measurements, analysis, processing and interpretation of the obtained data together with the listed co-authors.

The purpose of this article was to investigate the influence of Al-doping on the structure of the $(\text{ZnO})_5\text{In}_2\text{O}_3$ homologous phase and the thermoelectric characteristics of $(\text{ZnO})_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_3$ ceramics.

Samples with the composition $(\text{ZnO})_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_3$ $x = 0, 0.01, 0.03, 0.05, 0.1$ and 0.2 were prepared by the classical ceramic procedure and sintering at 1500°C for 2 h. Afterwards, the DSC, XRD, TEM were performed to monitor the phase formation and composition progress, and the thermoelectric properties were analyzed in regard to the increasing additions of Al-dopant. Slight enhancement of the solid state reaction and its initiation at lower temperatures was observed on DSC with the increasing additions of Al, due to the incorporation of the smaller Al ion with the formation of the $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$ homologous phase. The Rietveld analysis of the XRD patterns indicated the linear decrease in the lattice parameters for the $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$ homologous phase with the increasing Al-doping. This implied that the Al ions likely substitute on both primary sites of the In ions in the $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$ homologous phase, the octahedral sites in the basal-plane IBs and the trigonal bi-pyramidal sites in the zig-zag IBs, which was additionally confirmed by HRTEM. The thermoelectric characteristics were improved only for the small additions of Al for $x = 0.01\text{--}0.05$, which was explained by the increased carrier mobility at a lower number of charge carriers. However, with a further increase in the Al additions, the charge-carrier concentration and their mobility dropped due to the disturbance of their main conduction paths of the InO_2 layers inflicted with the strain accompanying structural shrinkage. These resulted in poor electrical conductivity and decreased ZT values of the $(\text{ZnO})_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_3$ ceramics in comparison to the un-doped composition.

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6.1 Abstract

In this work we investigated the influence of Al-doping on the structure of the (ZnO)₅In₂O₃ homologous phase and the thermoelectric characteristics of (ZnO)₅(In_{1-x}Al_x)₂O₃ ceramics for $x = 0, 0.01, 0.03, 0.05, 0.1$ and 0.2 , prepared by the classical ceramic procedure and sintering at $1500\text{ }^{\circ}\text{C}$ for 2 h. The Al substituted for In on both the primary sites in the Zn₅(In_{1-x}Al_x)₂O₈ homologous phase, the octahedral sites in the basal-plane inversion boundaries and the trigonal bi-pyramidal sites in the zig-zag inversion boundaries, which resulted in a uniformly increased shrinkage of the unit cell with the additions of Al. The a and c parameters were reduced for $x = 0.2$ by a maximum 0.8 %. All the samples had similar microstructures, so the differences in the TE characteristics mainly resulted from the effects of the substitution of Al for In, decreasing the charge carrier concentration and affecting their mobility. Slightly improved TE characteristics were observed only for Al additions with $x = 0.01\text{--}0.05$, while larger additions of Al only resulted in a reduced electrical conductivity and decreased ZT values in comparison to the un-doped composition.

Keywords: Zinc oxide; Indium oxide; (ZnO)₅In₂O₃; Al-doping; Thermoelectric properties.

6.2 Introduction

With their ability to directly convert waste heat to the electricity, the goal of minimizing the dependence on the fossil fuel energetics can be achieved by using environmentally friendly, thermoelectric (TE) materials. Their performance is evaluated using the dimensionless figure of merit ZT ($ZT = S^2 T / \kappa$), where S , and κ are the Seebeck coefficient, electrical conductivity and thermal conductivity, respectively. Over the past few years, it was realized that most of the highest ZT values are obtained from materials with a ‘special’ superlattice, cage-like (with rattling ions) or nano-inclusion structures. Such materials have a unique ability to selectively minimize the thermal conductivity, while at the same time retain a reasonable electrical conductivity. However, some well-known thermoelectric alloys and chalcogenides contain toxic elements (Pb, Te) and usually have problems with stability in the air above $250\text{ }^{\circ}\text{C}$ [8]. Compared to these materials, oxides are very suitable for high-temperature applications due to their high chemical and temperature stabilities in air [77–79, 97, 112, 150, 174, 175]. For the p-type TE materials, layered cobaltates are considered to be the best, with a maximum ZT up to 0.5 in polycrystalline specimens [76, 83, 176]. Among the n-type compounds, the In₂O₃-doped ceramics [81, 154], SrTiO₃ [86], CaMnO₃ [177, 178] and doped ZnO-based ceramics [97, 112] are showing great promise. In particular, the (ZnO)_kIn₂O₃ system of homologous phases based on the superlattice structure [118, 121, 123, 129, 135, 159, 164, 179, 180], is offering fertile ground for further ZT enhancements. They are formed via so-called internal diffusion of the In³⁺ along the close-packed {0002}-Zn planes [128]. This creates a series of {0002} basal plane defects with In³⁺ in the octahedral cavity positions (InO₂⁻ layers) [126, 128]. In order to obtain a structural stability and to compensate for the created charge surplus, the adjacent ZnO domains are inverted, creating a “head-to-head” type of inversion boundaries (IBs). Consequently, this results in a need for “tail-to-tail” IBs in between, which are manifested as the pyramidal (zig-zag) IB type {121 $\bar{l}$ } with In³⁺ in a trigonal bi-pyramidal configuration [127]. The In-ion in the structure is acting as a shallow donor and enables a high electrical conductivity along both the IB directions [181]. On the other hand, basal plane and zig zag IBs also induce a strong interfacial scattering of phonons, with virtually all possible wavelengths, resulting in a greatly decreased thermal conductivity [157, 181].

The best overall ZT values of around 0.1 were obtained from the $\text{Zn}_5\text{In}_2\text{O}_8$ (Z5I) phase. To improve it, co-doping was employed and it was shown that isovalent and/or heterovalent dopant ions can be introduced into the $(\text{ZnO})_k\text{In}_2\text{O}_3$ superlattice structure to obtain a series of $(\text{ZnO})_k(\text{In}_{1-x}\text{M}_x)\text{O}_3$ compounds (M = metal ion) [136, 137]. Substituting Zn and/or In with ions of Mg, Co, Y and Fe [138, 139] in general resulted in a decrease of the electrical and thermal conductivities, which was attributed to the lattice distortion due to the incorporation of dopants on the IBs in the basal-plane InO_2^- layers. Even more, with their increasing amount, the charge-carrier concentration decreases, which resulted in an increase of the carrier mobility, especially in the case of Co and Y. However, only doping with Y in amounts up to $x = 0.01$ was reported to result in a slightly increased electrical conductivity and hence improved ZT values to 0.13. The studies of Liang [182] showed that the Al doping of $(\text{ZnO})_9\text{InMO}_3$ in amounts up to 1.2 wt. % results in an immediate and drastic decrease in the electrical conductivity to about 0.1 S/cm, a significant improvement of the Seebeck coefficient to about 800 V/K and a two-fold reduction in the thermal conductivity. He attributed this to an increase in the electron potential barrier height of the InO_2^- layers due to the partial substitution of In^{3+} with Al^{3+} . According to other literature reports, Al ions with much smaller ionic radii should predominantly occupy only the trigonal bi-pyramidal sites in the Zn/In zig-zag defect, having less influence on the charge-carrier concentration and the electrical conductivity mechanisms [136, 137, 183-185]. However, preferential incorporation of Al into the bi-pyramidal sites has not been confirmed by DFT calculations [120, 136, 183] and was not observed experimentally so far [185]. This creates doubts about the actual incorporation sites of the Al ions inside the $(\text{ZnO})_k\text{InMO}_3$ system and their influence on the TE properties. Therefore, in this work we studied the influence of Al-doping on the structural parameters of the $(\text{ZnO})_5\text{In}_2\text{O}_3$ homologous phase with a perfectly periodic superlattice structure, and the thermoelectric characteristics of the $(\text{ZnO})_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_3$ ceramics for $x = 0, 0.01, 0.03, 0.05, 0.1$, and 0.2 .

6.3 Materials and Methods

Samples with the nominal formula $(\text{ZnO})_k(\text{In}_{1-x}\text{Al}_x)_2\text{O}_3$ for $x = 0, 0.01, 0.03, 0.05, 0.1$ and 0.2 were prepared by a conventional solid-state synthesis from powders of ZnO (Grillo, Zink oxide - Pharma 4, > 99.9 %) and In_2O_3 (Alfa Aesar, 99.9 % metals basis, 325-mesh powder). The Al-nitrate hydrate (Alfa Aesar, puratronic®, 99.999 %) was dissolved in distilled water and mixed together with the oxide powders in a planetary ball mill for 1 h, utilizing a polyethylene vial and YZT grinding balls. The obtained mixture was dried at 80 °C. The obtained powders were then reground and additionally sieved (mesh-size 35). The differential scanning calorimetry (DSC) measurements of the powder mixtures were performed with an STA 449F3 NETZSCH (NETZSCH, Germany) from room temperature to 1300 °C in air. Powder mixtures were uniaxially pressed at 50 MPa and additionally isostatically pressed at 750 MPa to obtain pellets with a diameter of 20 mm and a height of 3 mm, having a final relative green density of approximately 60 %. They were sintered in a packing powder (ZnO) at 1500 °C for 2 h in air with a 5 °C/min rate for heating and cooling. The densities of the samples were determined before and after the sintering with the Archimedes method.

For the X-ray diffraction measurements, sintered samples were pulverized in an agate mortar and analyzed with a PANalytical X'Pert diffractometer (PRO MPD, Almelo, The Netherlands), utilizing Cu-K α radiation. The measurement angle (2θ) was from 10° to 90° with a step of 0.017°, 1 s per step. For the Rietveld refinement [186] we used the Topas (Bruker AXS, version 2.1) software environment. The basic structural data for the undoped $(\text{ZnO})_5\text{In}_2\text{O}_3$ compound were taken from the article by Yoshinari et al. [187]. To

resolve the particular structural site occupancies, we changed the site occupations of In³⁺ in all four possible metal-ion sites with Al³⁺ in the proportional ratio. Due to the plate-like crystallite shape, the powder diffraction pattern exhibited slightly enhanced (00l) peaks due to a small preferred orientation, which was corrected with the Spherical Harmonics function. The background was eliminated by the Chebychev polynomial function.

Polished cross-sections of the samples were thermally etched at 1250 °C for approximately 10 min and afterwards coated with carbon for microstructural observations, which were performed on a scanning electron microscope (SEM; Zeiss Supra 55, Jena, Germany). The grain size analysis was performed using ImageJ software on digitalized images. The average grain size, grain size distribution and the aspect ratio were determined from measurements of approximately 300 grains.

Transmission electron microscopy (TEM) studies were carried out in a JEM-2010F and a JEM-ARM200F with a CFEG and Cs probe corrector (Jeol, Tokyo, Japan). HAADF STEM imaging was used rather than the HRTEM since the intensity of atom columns in the HAADF STEM experimental images depends on the average atomic number (Z) of each of the atom columns. The HAADF imaging was performed at angles from 70 to 175 mrad (ADF from 42 to 168 mrad). EDXS spectra were acquired using a JEOL Centurio Dry SD100GV SDD Detector. Thin foils for the TEM observations were prepared from the bulk materials using ion-milling techniques (Gatan, PIPS).

The samples were cut into rods with lengths from 8 to 10 mm and a cross-section of approximately 2 x 2 mm² for the Seebeck coefficient and electrical conductivity measurements using a commercial ZEM 3 device (Advance Riko, Japan) in a partial pressure of helium. For the thermal diffusivity (α) measurements, squares of 6 x 6 mm² and 1 mm thick were cut from the same pellet and measured in air with a laser flash (LFA 457, NETZSCH, Germany). The thermal conductivity was calculated from the heat capacity (C_p), density (ρ) and thermal diffusivity (α), according to the expression $\kappa = C_p \rho \alpha$. Hall measurements were performed on samples with approximate dimensions of 3 x 3 mm² and 0.2 mm thickness on a PPMS[®] device (Quantum design, San Diego, USA) using the Van der Pauw configuration in the room-temperature range. The contacts were made with metallic indium on the sample corners. The carrier concentration was calculated from the first derivative of the curve (B – I) with a polynomial fit [91]. The second derivative, the carrier mobility, was expressed using the data obtained in accordance with the expression $\sigma = ne\mu_e$.

6.4 Results and Discussion

6.4.1 Phase analysis

The obtained results from the DSC analysis of the (ZnO)₅(In_{1-x}Al_x)₂O₃ powders are presented in Figure 6.1. The solid-state reaction for the un-doped sample starts at temperatures above 900 °C, it proceeds intensively above 1000 °C, as indicated by the sharp endothermic peak with a maximum at 1153 °C, and is completed at 1230 °C. On the other hand, in the Al-doped samples with x = 0.05 the endothermic peak indicates a more intensive reaction already at temperatures above 900°C, while the maximum of the endothermic peak is also shifted to a lower temperature of 1129 °C. Nevertheless, the reaction finishes at the same temperature as in the case of the un-doped compound. In the sample with x = 0.1 a deflection from the trend line indicates the beginning of an endothermic process already at temperatures above 750 °C, the reaction intensifies above 900 °C resulting in distinct endothermic peak above 1000 °C, with the maximum further shifted to a lower temperature of 1116 °C, with the end of the endothermic peak indicating

the reaction's completion again at similar temperatures as with the other two compositions. The observed shift in the solid-state reaction to lower temperatures can be correlated with the incorporation of the smaller Al ion (ionic radii 0.535 Å) with a likely higher diffusion rate in comparison to the In^{3+} (0.8 Å) following the same mechanism of diffusion into the ZnO wurtzite-type structure [188]. Consequently, the formation of the $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$ homologous phase starts at a lower temperature with the increasing Al addition; however, it somehow proceeds at a slower rate compared to the un-doped composition. The formation of the ZnAl_2O_4 spinel phase, which typically forms in the temperature range from 600 °C to 800 °C [189], was not observed in our DSC pattern. However, at such small levels of Al-doping the amount of formed spinel phase would be very small and hence difficult to detect.

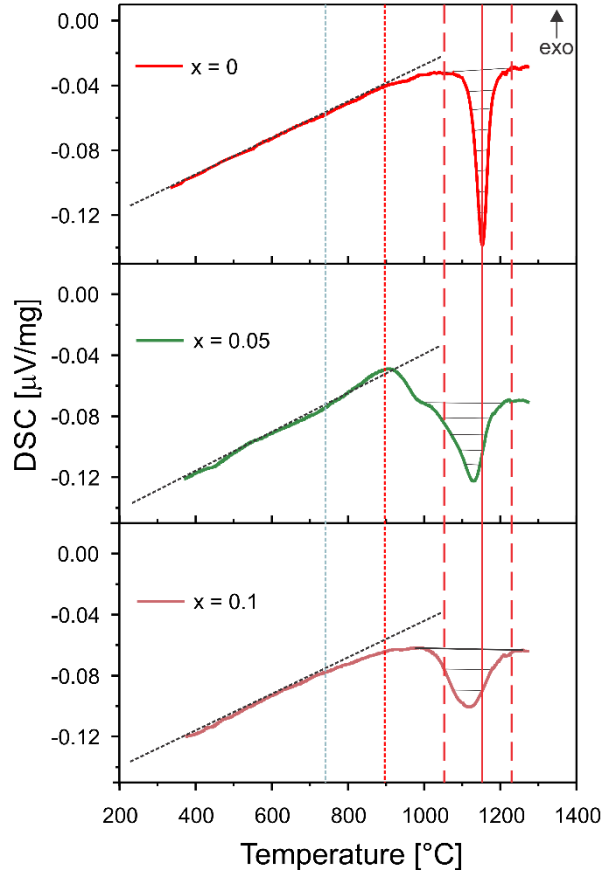


Figure 6.1: DSC analysis of the compositions $(\text{ZnO})_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_3$ for $x = 0, 0.05$ and 0.1 .

The X-ray diffraction patterns of the samples $(\text{ZnO})_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_3$ are presented in Figure 6.2. All the peaks could be indexed as the $R\bar{3}m$ structure of the $\text{Zn}_5\text{In}_2\text{O}_8$ homologous phase. No peaks corresponding to the ZnAl_2O_4 spinel phase were observed, even for the highest Al content. The peaks in the XRD patterns of the Al-doped samples are in between the peaks of the $\text{Zn}_5\text{In}_2\text{O}_8$ (JCPDF: 00-020-1440) and $\text{Zn}_5\text{InAlO}_8$ (JCPDF: 00-040-0262) phases, as seen in Figure 6.2. Since Al has a smaller ionic radius, its successful incorporation into the homologous phase as a substitute for In-ions would cause a unit-cell shrinkage, which was actually observed as a shift of the peaks to higher 2θ values. This is the most evident for the highest additions of $x = 0.2$, as can be seen in the magnification of the (110) peak in the inset of Figure 6.2.

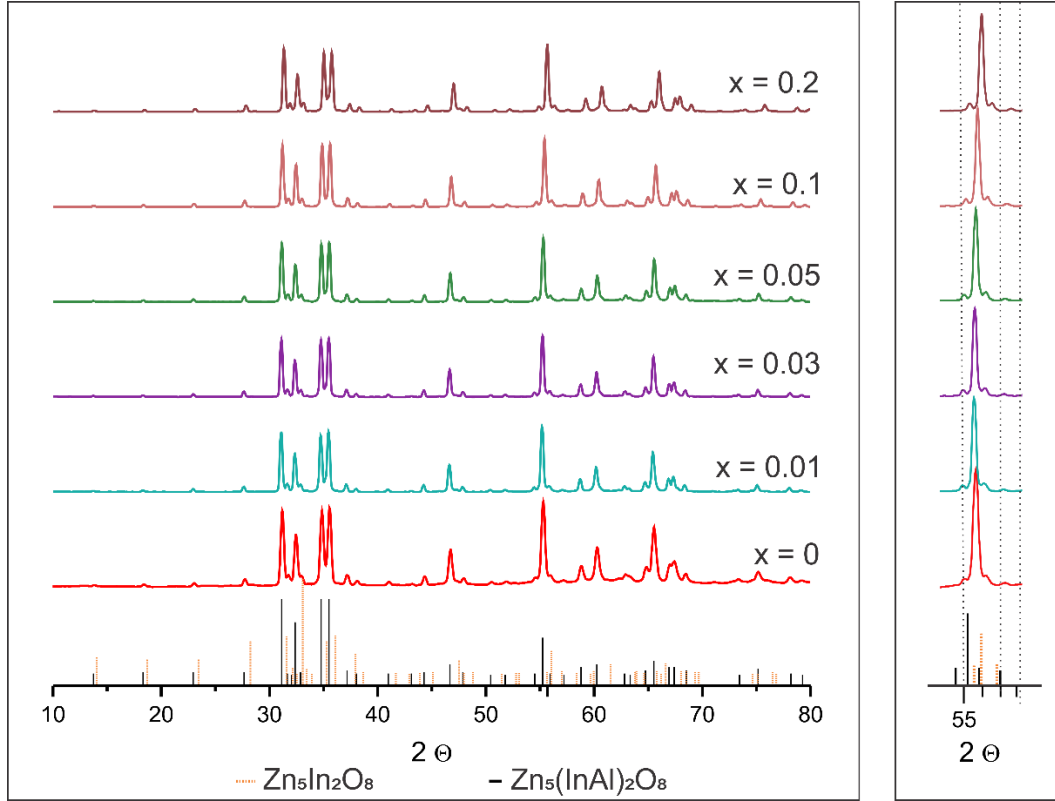


Figure 6.2: : XRD patterns of the samples $(\text{ZnO})_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_3$ with various additions of Al.

In order to evaluate the particular influence of Al doping on the lattice parameters of the $\text{Zn}_5\text{In}_2\text{O}_8$ homologous phase and to confirm which positions Al occupies inside the In-based superlattice structure, we performed a Rietveld refinement of all the XRD patterns. The main results are presented in Figure 6.3, Table 6.1 and in the Supplementary information (Rietveld refinement graphical outputs).

For the $\text{Zn}_5\text{In}_2\text{O}_8$ phase (Table 6.1) we obtained lattice parameters of $a = 3.3277 \text{ \AA}$ and $c = 58.1219 \text{ \AA}$, which are similar to the values reported by Yoshinari et al. [187] and Masuda et al. [138]. With increasing x values, the lattice parameters start to decrease linearly regarding the amount of added dopant, as seen in Figure 6.3. The smallest unit-cell dimensions were observed for $x = 0.2$, with $a = 3.3006 \text{ \AA}$ and $c = 57.6709 \text{ \AA}$. Therefore, the absolute shrinkages from the pure composition to the largest addition of Al are $0.0271 \text{ \AA}$ and $0.4510 \text{ \AA}$ for the a and c parameters, respectively, which is an approximately 0.8 % shrinkage in both directions in comparison to the initial un-doped $\text{Zn}_5\text{In}_2\text{O}_8$ and indicates a uniform decrease of the lattice parameters.

Table 6.1: Rietveld refinement output data.

Dim.	$x = 0$	$x = 0.01$	$x = 0.03$	$x = 0.05$	$x = 0.1$	$x = 0.2$
$a \text{ (\AA)}$	3.3277	3.3263	3.3228	3.3206	3.3141	3.3006
$c \text{ (\AA)}$	58.1219	58.1126	58.0683	58.0215	57.9227	57.6709
$V(\text{\AA})^3$	557.375	556.829	555.2566	554.0503	550.964	544.106
Rb	3.518	4.944	3.177	3.318	4.973	4.872
Rwp	14.85	15.20	12.40	12.80	14.07	16.16

The Al-ion occupation with the formation of the $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$ homologous phase has two possible sites, i.e., the octahedral in the basal-plane IBs and the trigonal bi-pyramidal in the zig-zag IBs, which corresponds to the primary sites of the In ion. In the Rietveld refinement, the particular occupation sites are strongly correlated, which makes their independent refinement practically impossible. According to some literature reports, Al should not preferentially occupy the octahedral sites of the $\{0002\}$ basal-plane IBs [184], because it is considered to be too small to obtain the structural stability and should primarily occupy only the trigonal bi-pyramidal sites. On the other hand, it was shown that the Fe^{3+} ion with a similar radius ($0.5 \text{ \AA}$) can occupy the octahedral sites [138]. Accordingly, the Al-ions could enter on both In-sites, which could lead to the observed uniform shrinkage of the lattice parameters with the increasing Al content. To elucidate the actual positions of the Al inside the superlattice structure, we performed TEM analyses with a particular focus on the octahedral cavities.

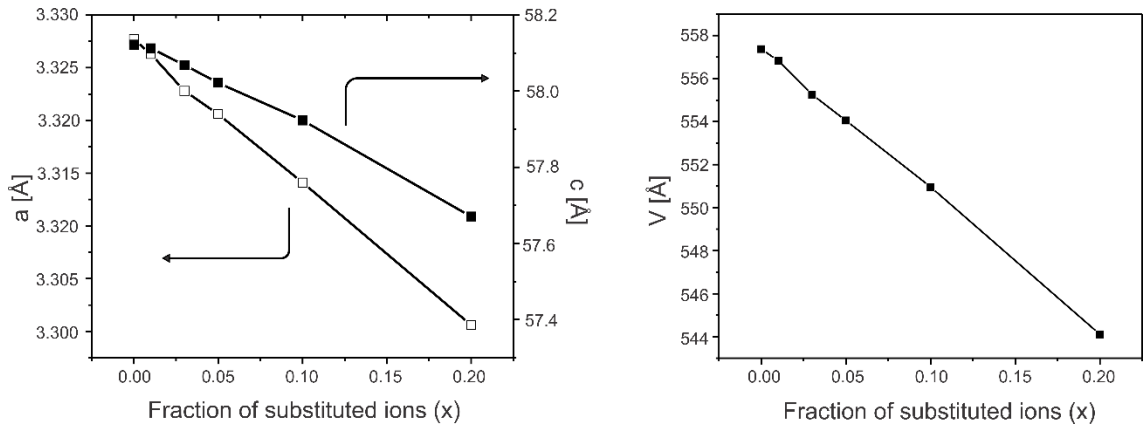


Figure 6.3: Rietveld refined lattice parameters with unit-cell dimensions (left) and unit-cell volume (right) of the $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$ homologous phase with the increasing additions of Al.

An atomic-resolution HAADF STEM image of the $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$ for $x = 0.1$ is shown in Figure 6.4a. Due to the high atomic number of In, as compared to Zn, the In-rich basal-plane IBs in the HAADF STEM micrograph are clearly resolved as the bright single-atom layers. The spacing between the In-rich basal plane IBs corresponds to the expected ideal ordering in the $\text{Zn}_5\text{In}_2\text{O}_8$ homologous phase where one In-rich basal-plane IB is followed by six ZnO lattice planes, as shown in the top-right inset of Figure 6.4a. No variations in the HAADF intensities can be observed in between in the Zn/In-O slabs, probably due to the possible lower ordering range of the pyramidal IBs, which for higher k phases manifest in a zig-zag pattern. The EDXS spectra from the In-rich basal plane IBs and the Zn/In-O slabs were acquired from the frame scans, as shown in Figure 6.4b, and exactly 17 atom columns were included in both window frames. The comparison of the EDXS spectra taken from the In-rich basal-plane IBs and the Zn/In-O slabs (Figure 6.4c) shows that the intensities of the Zn-K and In-L characteristic lines are inversely correlated, while the intensity of the Al-K line is comparable in both spectra. Since the EDXS analysis clearly shows the difference in In content between the basal-plane IBs and the Zn/In-O slabs, we can argue, also taking into consideration that both slices are in such close proximity equally thick, that the concentration of Al in the basal-plane IBs, as well as in the Zn/In-O slabs (zig-zag defects), is practically the same.

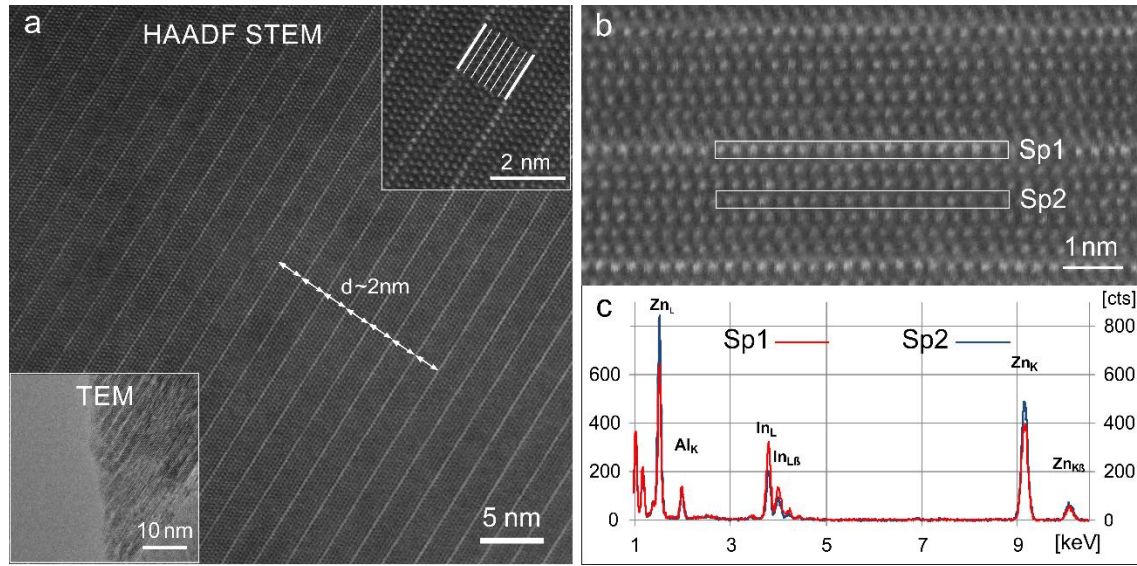


Figure 6.4: (a) HR HAADF STEM of $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$ as viewed in the $[2-1-10]$ zone axis. Top-right inset shows the ordering sequence. (b) Scan frames for EDXS acquisition. (c) Comparison between EDXS spectra acquired from the In-rich basal plane defect and the ZnO matrix.

To correctly evaluate the effect of the increasing additions of Al on the thermoelectric properties, we also performed a microstructural analysis in order to exclude any possible variations in the grain size and density among the observed samples. The results of the grain size analysis are shown in Figure 6.5. The three samples have a similar grain size distribution, with the majority of grains in the range from 2 to 8 μm and an average size of approximately 6 μm . The grains are slightly elongated in the direction of the basal-plane IBs, which is clearly visible after thermal etching on all three micrographs. The aspect ratios are around 1.6 (± 0.1) for all three samples and represent a moderate anisotropy in the grain shape. Variations in the densities between the samples are presented in Table 6.2

Table 6.2: Densities of the observed samples, calculated from the sample's geometry and mass.

Density	x = 0	x = 0.01	x = 0.03	x = 0.05	x = 0.1	x = 0.2
Absolute [g/cm^3]	5.80	5.89	6.09	5.91	5.89	5.62
Relative * [%]	95 %	96 %	99 %	96 %	96 %	92 %

*6, 12 g/cm^3 theoretical for $\text{Zn}_5\text{In}_2\text{O}_8$

The pure $\text{Zn}_5\text{In}_2\text{O}_8$ phase has a 95 % relative density and it increased to 99 % for $x = 0.03$. However, with a higher x the density starts to decrease and reaches the lowest value of 92 % for $x = 0.2$, which is even lower than in the pure $\text{Zn}_5\text{In}_2\text{O}_8$ phase. The increasing of density with additions of Al up to $x=0.03$ could result from the enhanced diffusivity due to incorporation of the smaller Al ions and formation of the $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$ homologous phase. However, at higher levels of Al-doping a decomposition of the $\text{Al}(\text{NO}_3)_3$ as doping agent could cause formation of pores and hence decreased density of the samples. Such porosity fluctuations from the un-doped to the heavily Al-doped samples could have an influence on the thermoelectric properties.

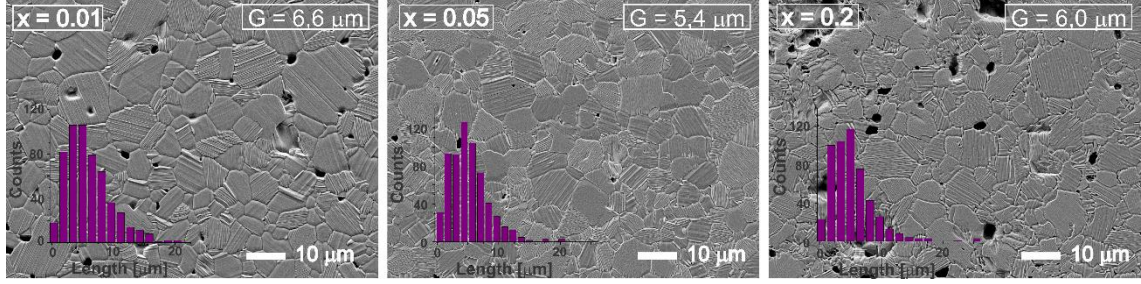


Figure 6.5: Microstructures of the samples $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$ with different additions of Al, their grain sizes (G) and histograms of the grain size distribution.

6.5 Thermoelectric Measurements

The temperature-dependent thermoelectric properties are presented in Figure 6.6 and Figure 6.7. The increasing concentrations of Al at the In-positions inside the superlattice structure and consequently the shrinkage of the lattice parameters greatly influenced the TE properties. In general, the electrical conductivity is becoming lower at room temperature with the increasing x values. The decreasing of the electrical conductivity with the increasing temperature (presented in Figure 6.6a) is showing a typical degenerate semiconductor behavior for all x values and has the highest rate of decrease for $x = 0.2$. The highest electrical conductivity is exhibited for the $x = 0.01$ sample, which is even higher than in the pure $\text{Zn}_5\text{In}_2\text{O}_8$ sample by almost 50 S/cm at around 100 °C. However, with the increasing x values and the larger amount of incorporated Al, the electrical conductivity drops significantly. The lowest value is observed for the $x = 0.2$ sample, confirming the negative effect of the high Al additions on the electrical conductivity. The results show comparable behavior with the reports of Park et al. [190], who stated that Al ions occupy the Zn sites and act as shallow donors. They attributed the drop in the electrical conductivity at higher concentrations to spinel phase formation [190]. However, with the techniques used in this study, we have not detected the spinel phase, although we cannot totally exclude its local presence, especially for the sample with $x = 0.2$. Nevertheless, such small amounts of segregated fine spinel grains would not affect the electrical conductivity significantly. In a recent study Liang [182] also observed the negative influence of Al-doping on the electrical conductivity of the Z9I samples.

To further investigate the cause of the electrical-conductivity decrease with Al additions, we also measured the carrier concentration and determined the electron mobility, which are presented in Figure 6.6b. The carrier concentration exhibits a drop over quite a large range, even with the smallest additions of Al. Therefore, we believe that Al occupation of the possible In-positions did not result in additional donor states, but it actually decreased the amount of In-based donor defects as the main charge-carrier sources, consequently reducing their concentration. On the other hand, the charge-carrier mobility values increased, but only for a doping level of x up to 0.05, and afterwards it slightly decreased. The increasing amount of Al on the In-sites increased the lattice strain and shrinkage, inevitably enhancing the charge-carrier scattering and decreasing their mobility. Hence, a slight increase of the electrical conductivity in comparison to the un-doped composition was only observed for $x = 0.01$. At such doping level the lattice shrinkage is negligible to cause any strain affecting the electron transport properties, while the electrical conductivity is even slightly increased due to the enhanced mobility at decreased carrier concentration.

The Seebeck coefficient (Figure 6.6c) of the degenerate semiconductors is typically inversely proportional to the electrical conductivity. It is the lowest for $x = 0$ and increases

with the amount of added Al. If we combine both electronic parameters in the power factor P (Figure 6.6d), we can see that those samples with x values in the range 0–0.05 present an increase or have a very similar P to the un-doped. When the number of Al-based defects is further increased for $x > 0.05$ the power factor also decreases at lower temperatures.

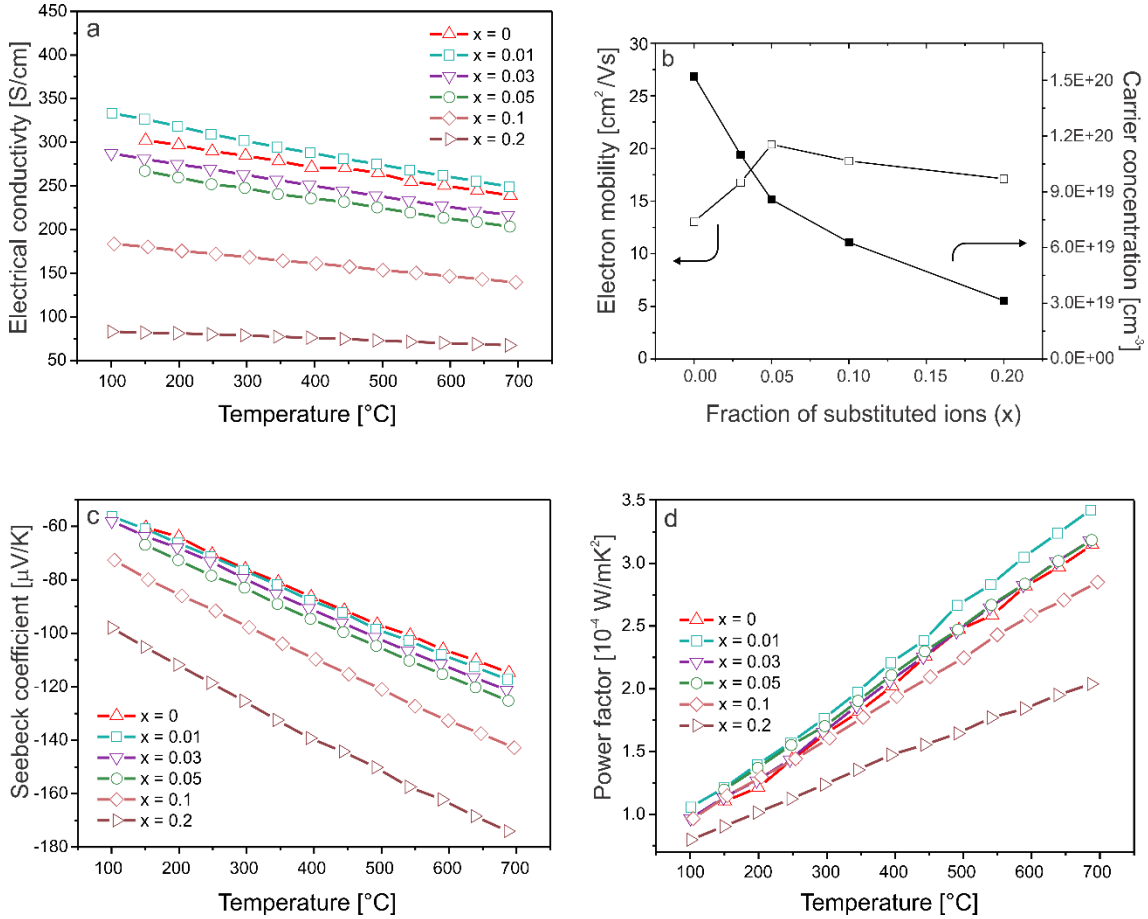


Figure 6.6: (a) Electrical conductivity, (b) electron mobility and concentration, (c) Seebeck coefficient and (d) power factor of the samples $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$ sintered at 1500 °C for 2h.

The thermal conductivity (Figure 6.7a) is initially increased for $x = 0.01$ and then shows a drop with x values, which is in agreement with our previous results. We evaluate the effect of the decreasing lattice parameters and increased strain inside the superlattice with higher Al concentrations by decoupling the lattice and electron thermal conductivities $\kappa = \kappa_l + \kappa_e$, where κ is the total thermal conductivity, κ_l is the lattice contribution and κ_e is the electronic thermal conductivity. The κ_e was calculated according to the Wiedemann-Franz law, $\kappa_e = \sigma L T$, and the corresponding Lorenz number (L) through expression[191] $L = \left(1.5 + \exp\left[-\frac{|S|}{116}\right]\right) \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$. The lattice contribution κ_l is shown in Figure 6.7b and reveals generally minor differences among the samples, mainly following the lattice shrinkage with the decrease in the lattice thermal conductivity, except for $x = 0.01$, where the lattice thermal conductivity is slightly increased. In this sample, the lattice shrinkage is minimal and the present isolated defects are obviously even slightly enhancing the thermal transport. Nevertheless, we can conclude that all the samples act similarly, which suggests that the superlattice structure based on the $(\text{ZnO})_5\text{InO}_3$ system mainly controls the thermal conductivity.

The figure of merit, ZT (Figure 6.7c), which combines all the presented properties and evaluates the performance of the material, shows slightly higher values for $x \leq 0.05$ in comparison to the un-doped composition, while the samples for $x = 0.1$ and 0.2 have lower values. Nevertheless, all the samples have ZT values close to the usual values for the $\text{Zn}_5\text{In}_2\text{O}_8$ homologous phase of 0.1 [129].

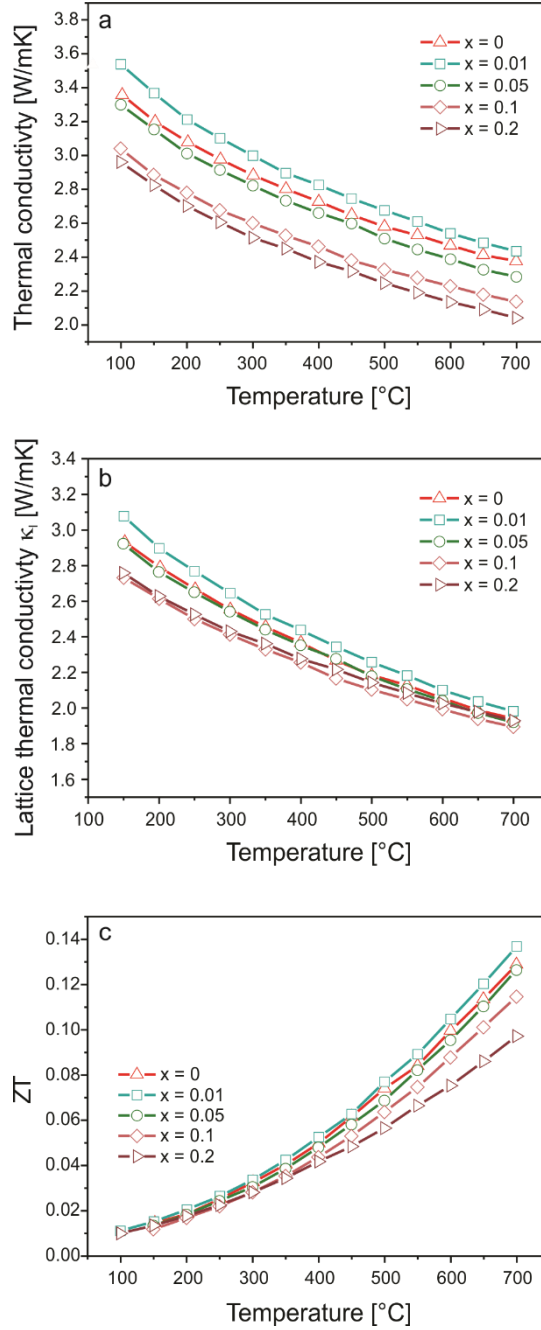


Figure 6.7: (a) thermal conductivity (b) and the final ZT values of the samples $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$, sintered at 1500 °C for 2h.

6.6 Conclusions

The influence of Al-doping on the structural parameters of the $(\text{ZnO})_5\text{In}_2\text{O}_3$ homologous phase and the thermoelectric characteristics of $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$ ceramics for $x = 0, 0.01,$

0.03, 0.05, 0.1, and 0.2, prepared by the classical ceramics procedure and sintering at 1500 °C for 2 h was studied. The shift of the onset of the solid-state reaction to lower temperatures shown by the DSC analysis in Al-doped compositions, in comparison to the un-doped, indicated slight enhancement of the solid-state reaction due to the incorporation of the smaller Al ion with formation of the Zn₅(In_{1-x}Al_x)₂O₈ homologous phase. The Rietveld analysis of the XRD patterns confirmed the lattice parameters of the un-doped Zn₅In₂O₈ homologous phase reported in the literature and showed that they linearly decrease in the Zn₅(In_{1-x}Al_x)₂O₈ homologous phase with increasing Al-doping. Accordingly, the sample with the highest addition of Al for x = 0.2 had the smallest unit-cell parameters of a=0.0271 Å and c=0.4510 Å, which means an approximately 0.8 % shrinkage in both directions in comparison to the un-doped Zn₅In₂O₈ phase. Such a uniform shrinkage of the lattice parameters with the increasing Al content implied that the Al ions likely substitute on both primary sites of the In ions in the Zn₅(In_{1-x}Al_x)₂O₈ homologous phase, the octahedral sites in the basal-plane IBs and the trigonal bi-pyramidal sites in the zig-zag IBs. This was further confirmed with the HRTEM (HAADF STEM) and EDXS analysis using the TEM. All the samples had similar microstructures, hence, the differences in the TE characteristics could only result from the effects caused by the substitution of Al for In on the charge-carrier concentration and also their mobility. In comparison to the un-doped sample we observed improved TE characteristics only for the small additions of Al for x = 0.01–0.05, which can be explained by the increased carrier mobility for a lower number of charge carries and decreased the thermal conductivity. However, with a further increase in the Al additions, the charge-carrier concentration and their mobility dropped due to the disturbance of their main conduction paths of the InO₂⁻ layers inflicted with the strain accompanying structural shrinkage; these resulted in poor electrical conductivity and decreased ZT values of the (ZnO)₅(In_{1-x}Al_x)₂O₃ ceramics in comparison to the un-doped composition. In general, all the samples have ZT values at 700 °C close to the usual values for the Zn₅In₂O₈ homologous phase of 0.10.

Acknowledgements

This work was supported by the Slovenian Research Agency (Young researcher program PR-04363, Program contract P2-0084 and Project grant L2-4192). Part of the work was conducted in the CRISMAT Laboratoire, with funding from the Slovene Human Resources Development and Scholarship Fund (Contract No. 11012-12/2013). The authors also acknowledge support from the Scientific and Technological Research Council of Turkey (TÜBİTAK) under the Fellows Program and from the EU under Seventh Framework Programme under grant agreement n°312483 (ESTEEM2). Special gratitude to Matejka Podlogar, Damjan Vengust, Jerome Lecourt and Pablo Diaz Chao for all fruitful discussions, help with the experimental parts and the thermoelectric measureme

Chapter 7

Microwave Sintering of the $(\text{ZnO})_k\text{In}_2\text{O}_3$ Homologous Phase System

7.1 Introduction

The unique ability of converting waste heat directly into the electricity by the thermoelectric (TE) materials gained intensive research in the recent decade [8]. The triggering factor was the Slack's introduction of the "phonon-glass electron crystal" concept [13], which led to the enormous improvement in the thermoelectric efficiency [143]. It was achieved through enhancing phonon scattering with specific structural disorders, while maintaining a sufficient electron mobility. The research has spread from conventional TE materials, based on tellurides [34, 192] to silicides [145, 193], selenides [40], skutterudites [149], clathrates [148, 194] and even semiconducting oxides, which proved to be stable in air and hence suitable for applications at high temperatures, above 700 °C [78, 79]. It is also important that they are made from cheaper elements with abundant resources and also environmentally benign. The most studied oxide thermoelectric materials are the Na-based and Ca-based cobaltates [76, 77, 83, 175, 177], SrTiO_3 [86, 195] and ZnO [97, 102, 196]. Among the ZnO based materials, the $(\text{ZnO})_k\text{In}_2\text{O}_3$ homologous phases have a superlattice structure, following the Slack's principle, which makes them promising for further development and hence, reported in many papers [118, 123, 129, 139, 157, 159]. Their structure is formed through the In-ion incorporation into the ZnO wurtzite structure [126, 127, 136], creating two types of defects, a planar InO_2^- along the basal planes (0001), and pyramidal $(\text{In}/\text{Zn})\text{O}$ in between them [127, 183]. With their ordering, the $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ -type homologous phases are formed for the starting k values, defined with the number of ZnO lattice planes (d) in between the InO_2^- planar defects according to an expression $d = k+1$. Therefore, with a higher k value, a lower amount of In-based planar defects will be present. The defect formation is based on the internal diffusion mechanism; it is influenced by the Zn vacancies as the starting point for incorporation of In^{3+} into the wurtzite structure, the higher concentration of which increases the diffusion higher sintering temperatures [128]. The most studied homologous phase $\text{Zn}_5\text{In}_2\text{O}_8$ (Z5I) starts to form already at temperatures above 1000 °C; it is formed at first also in compositions for higher k value and only with increasing sintering temperature and after longer time, higher k phases are gradually formed [142]. Therefore, the conventional heat treatment for preparing $(\text{ZnO})_k\text{In}_2\text{O}_3$ homologous phases inevitably requires high sintering temperatures in the range from 1300 °C to 1500 °C with dwell times from 2 h to even several days in order to reach the equilibrium homologous phase for the starting k value [123].

Processing these Zn_kIn₂O_{k+3}-type homologous phases is time and energy consuming; hence, different approaches are needed in order to accelerate the phase formation. The microwave (MW) sintering has emerged in recent years as a method, which showed significant advantages over conventional sintering procedures [197-201]. Microwave energy is delivered directly to materials through the molecular interaction with the electromagnetic field and provides volumetric heating, resulting in high heating rates and shortening of the overall processing time [197, 202-205]. The effects of the MW field on the material are divided in the “non-thermal effects” of the oscillating MW field and “thermal effects” dependent on the material’s dielectric properties. The “non-thermal” effects are manifested as the ponderomotive force [206, 207], known for the enhancement of the grain boundary diffusion, contributing to the faster pore closure and improved density of the sintered samples [208]. The “thermal effects” are dependent on the MW interaction with the material according to its particular dielectric properties and are given by the relation of the proportionality $P \propto \varepsilon E^2$, where P is the absorbed power per unit volume, ε is the material’s dielectric permittivity and E is the internal electrical field. In a heterogeneous material, one compound can more effectively couple with the MW field and reach a higher temperature in comparison to the less responsive compound. This leads to the selective heating and results in the acceleration or inhibition of the diffusion process, which consequently influences the sintering procedure and solid state reaction [209-213].

The ZnO response to the MW field has been reported in many papers [205, 214-217]. They studied ZnO behavior under several frequencies in regard to the temperature difference between inner and outer part of the sample (pellet) [214]. The most used MW frequency (2.45 GHz) in ZnO above 800 °C induces high temperature differences between the sample surface and the core due to a drastic decrease in the MW penetration depth. Consequently, the surface temperature increases and at such high temperatures equilibrates the negative effect of heat losses from the surface, which results in a more homogeneous heat distribution through the sample. The advantages of ZnO MW sintering were compared with the conventional sintering and they proved that the densification rate is enhanced under the MW field [205, 216]. The In₂O₃ response on the MW field was reported to be very high, with an extremely fast temperature increase from room temperature to the target temperature [210]. The use of MW field in the synthesis and sintering of homologous phases, such as (ZnO)_kFe₂O₃, (ZnO)₃In₂O_{k+3} and (ZnO)₅(InAl)₂O_{k+3}, has been reported so far. The desired family of homologous phases was formed, however, in these reports the peculiarities of the phase formation under the MW field were not examined [218].

The main goal of this investigation was to track the MW field response of the ZnO, the In₂O₃ and the (ZnO)_kIn₂O₃ system for $k = 5, 11$ and 18 to elucidate the effect of MW on sintering and formation of the homologous phases with the increasing temperature. We evaluate the influencing of processing parameters on the final microstructural characteristics and consequently, the thermoelectric properties.

7.2 Experimental

The compositions (ZnO)_kIn₂O₃ with k values 5, 11 and 18 were prepared from powders of ZnO (Grillo Zinkoxide, GmbH, Pharma 4, > 99.9%) and In₂O₃ (Alfa Aesar, 99,9 % metals basis, 325-mesh powder). The processing included a 1 h homogenization of powders in a planetary ball mill with ethanol as a milling media, polyethylene milling vial and YZT grinding balls. The obtained mixture was afterwards dried at 80 °C and sieved through the 500 µm mesh sieve. The acquired powder mixtures were uniaxially pressed into pellets with the diameter of 13 mm and 2 g weight which were additionally isostatically pressed at 750 MPa to achieve uniform green density of around 60 %.

The samples were sintered under the MW field in the MW furnace system based on a 2.45 GHz microwave generator (SAIREM GMP 20 KSM, France) delivering a variable power up to 2 kW along a standard WR340 rectangular twist and a waveguide (86.36 x 43.18 mm) that conducts microwaves to the TE10p single mode cavity. Cavity modes can be tuned by adjusting the length of the coupling iris and the short-circuit piston to maximize the electric (E-) or magnetic (H-) microwave field in the central cavity position. The system is also equipped with a water-cooled applicator for the absorption of reflected microwaves, which are adjusted with a short-circuit piston to maximize the absorption in the sample during MW sintering. The sample was positioned in an alumina-silicate box (Fiberfrax® - Duraboard®), which is transparent for microwaves and provides a good thermal insulation for the sample by reducing the thermal radiation from its surface. It was placed on a sintered alumina pellet, which decreased the thermal gradients in the contact and did not screen the incoming MW field energy. The insulating box with the sample was put in the center of the microwave cavity, aligned with the pyrometer (Ircon, Modline® 5, 350–2000 °C) axis to ensure the precise temperature monitoring and connected to the computer through ModView Software®. Experimental conditions were at the beginning set on the 200 W power output in the E-field maximization. This was chosen on the basis of a previous report, claiming the better response of ZnO to the E-field of the microwave range EM spectrum [217]. The resonance was manually tuned with the three stubs and the temperature was monitored by adjusting the incident power. Through the experiment, the power was increased approximately every 100 °C after reaching a plateau of around 800 °C for 20 W to ensure the consistent temperature rise. Three target temperatures were chosen, 1300 °C, 1400 °C and 1500 °C for 10 min, 20 min and 1 h duration time at each sintering temperature. After the dwell time elapsed, the microwave power was shut down immediately and the sample was cooled down naturally. For comparison, samples were conventionally sintered (marked CS -F) in a PID-controlled tubular furnace in the range from 1300 – 1500 °C in air atmosphere. They were put in an already preheated furnace at the target temperature, let until the dwell time (10, 20 or 60 min) expiry and afterwards immediately taken out (“quenched”) to cool down naturally. In order to compare with a normally used conventional procedure, a series of pellets (marked CS) were sintered with a heating and cooling rate of 10 °C /min and a 2 h dwell time on the target temperature.

Density of the samples was determined through geometrical calculations. Phase composition of the samples was identified by the powder X-ray diffraction at room temperature, utilizing Cu - K α radiation, with diffractometer PANalytical X'Pert (PRO MPD, Almelo, The Netherlands). The measurement angle (2θ) was from 10° – 80° with the step size of 0.033° per 1 s. The samples were cut and polished on Struers Labo Pol- 5 (Struers A/S, Denmark) device utilizing their MD-system® for polishing. Perfectly plane samples were thermally etched at 1250 °C for approximately 10 min and coated with carbon for microstructure analysis. This was performed on scanning electron microscope (SEM) JSM-5800 (JEOL, Tokyo, Japan). Samples were additionally cut in rods with a length from 8 till 10 mm and a cross section of 2 x 2 mm² for Seebeck coefficient and electrical conductivity measurements using a commercial ZEM 3 device (ULVAC Technologies, Inc, Methuen, MA, USA) in a partial helium pressure. For thermal diffusivity measurements, squares of 6 x 6 mm and 1 mm thick were cut from the same pellet and measured in air with laser flash (NETZSCH, LFA 457 MicroFlash, Netzsch, GmbH, Germany) without any additional carbon coating. The thermal conductivity was calculated from the heat capacity (C_p) density (ρ) and thermal diffusivity (α), according to the formula $\kappa = C_p * \rho * \alpha$.

7.3 Results and Discussion

7.3.1 MW induced temperature profiles

The temperature profile in Figure 7.1a presents the temperature increase for ZnO , In_2O_3 and a mixture of $(\text{ZnO})_5\text{In}_2\text{O}_3$, when they were exposed to the power output of 200 W in the E-MW field configuration. The profile of ZnO shows a late onset of the effective coupling with MW after 480 s, followed by a multi-step absorption behavior with two different rates of the temperature increase. The first step, from 480 s upwards, proceeds at around 48 °C/min until 530 °C. Afterwards, the rate is around 695 °C/min until 850 °C, where it reaches a plateau and triggers a need for the power input increase. On the other hand, the slope of In_2O_3 is having the onset of temperature rise after 80 s and it is increasing in the first part with the 450 °C/min until ~700 °C and afterwards with the 40 °C/min rate. The mixture of both $(\text{ZnO})_5\text{In}_2\text{O}_3$ has an extremely fast rate of temperature increase after 300 s (5 min). For the increase from 350 °C to 740 °C, the consumed time is around 40 s with an approximate heating rate of 600 °C/min.

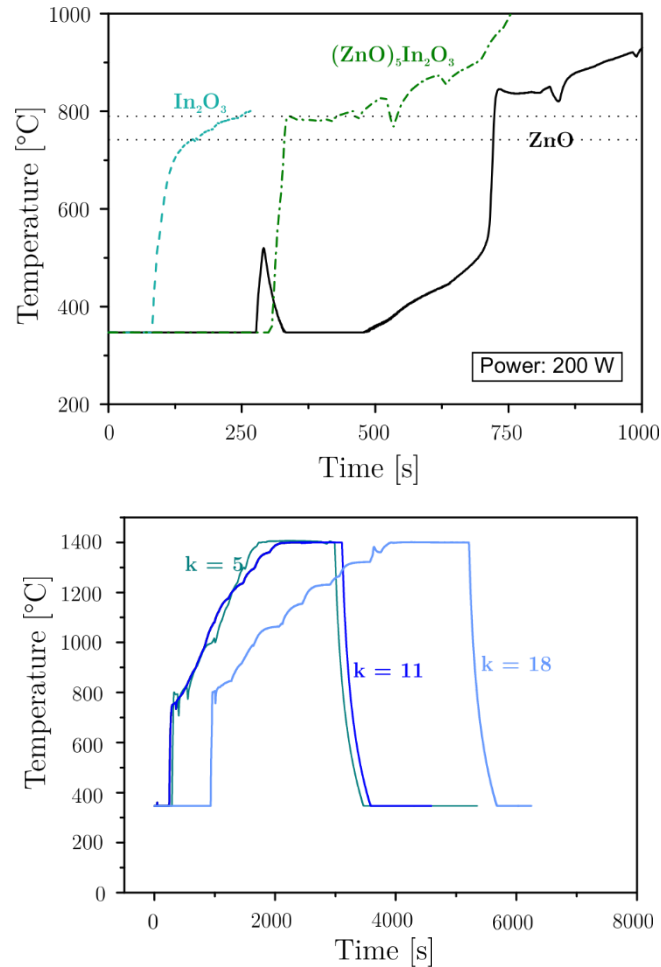


Figure 7.1: (a-top graph) Thermal profile of ZnO , In_2O_3 and $(\text{ZnO})_5\text{In}_2\text{O}_3$ powders during exposure to the E-MW field with the initial power input 200 W. (b-bottom-graph) The thermal profiles of compositions with $k = 5, 11$ and 18 , MW sintered at 1400 °C for 20 min.

The observed temperature profile for $(\text{ZnO})_5\text{In}_2\text{O}_3$ is behaving at the beginning as In_2O_3 , however, it reaches a plateau at temperatures of around 790 °C, similar as in the case of the ZnO MW sintering. The highly effective coupling with MW of In_2O_3 at the initial stage transfers some heat to the ZnO grains and enables the onset of sintering and a fast temperature increase. Nevertheless, after reaching a certain temperature above 600 °C, the dielectric losses of ZnO increase [219] and it further leads the fast temperature increase to 790 °C, when the temperature increase reaches a plateau.

The influence of various In_2O_3 quantities on the temperature profile in the system $(\text{ZnO})_k\text{In}_2\text{O}_3$ for $k = 5, 11$ and 18 is presented in Figure 7.1b. The compositions with $k = 5$ and 11 have the fast temperature increase after 250 s, however, $k = 18$ composition couples with MW later, after 930 s. All three compositions have similar temperature increase rates from 350 °C to 750 – 800 °C. Afterwards, with the similar power input increase for all compositions, the temperature rate is for $k = 5$ and 11 is following 22 °C/min, however for $k = 18$, it is slightly slower, with 13 °C/min and reaches the final temperature approximately 20 min later than the other two compositions since the initial heating up.

The observed differences confirm the dominant role of In_2O_3 in the MW sintering of the $(\text{ZnO})_k\text{In}_2\text{O}_3$ system. Since its concentration is the highest for $k = 5$ composition, it is heated faster than the composition with $k = 18$, with the lowest amount of In_2O_3 in this study. We also need to stress that the lower amount of In_2O_3 cannot be distributed as evenly as it is in the case for $k = 5$, therefore, not every ZnO grain has In_2O_3 in its surroundings to initiate the fast heat-up. Consequently, the heating rate for $k = 18$ is much slower than for $k = 5$ and 11 , which has the distribution of In_2O_3 sufficient enough for the effective and fast heating up.

7.3.2 XRD characterization

The detailed XRD analyses of the formed phases for $k = 5, 11$ and 18 in the $(\text{ZnO})_k\text{In}_2\text{O}_3$ system exposed to MW field and comparison with the CS-F and CS samples are presented in Figure 7.2, Figure 7.3 and Figure 7.4. In the case for $k = 5$, presented in Figure 7.2, the phase composition is for all observed temperatures presenting its equilibrium homologous phase $\text{Zn}_5\text{In}_2\text{O}_8$. However, at the lowest temperature of 1300 °C, the peaks are widened and they indicate the induced strain in the lattice due to the ongoing structural compensation caused by the extremely fast $\text{Zn}_5\text{In}_2\text{O}_8$ homologous phase formation. Furthermore, if we compare the CS-F and MW sintered samples at 1 h sintering time, we can still observe that MW sintered samples have slightly wider peaks, indicating the non-complete phase formation even at that prolonged time. With increasing the MW sintering temperature to 1400 °C, peaks are narrowed and present the equilibrium $\text{Zn}_5\text{In}_2\text{O}_8$ phase. The compositions with $k = 11$ (Figure 7.3) and 18 (Figure 7.4) exhibit similar behavior at 1300 °C, where peaks of MW sintered samples are much wider than CS-F sintered samples at the same dwell times. In the case of $k = 11$, MW sintered sample at temperatures above 1400 °C has the phase composition close to its equilibrium phase $\text{Zn}_{11}\text{In}_2\text{O}_{14}$, however, for $k = 18$, temperatures above 1500 °C are needed (Figure 7.4). This is in direct correlation to the phase formation procedure [142] where homologous phases start to form above 1000 °C with the first stable phase $\text{Zn}_5\text{In}_2\text{O}_8$ and proceed through several intermediate phases until they reach its equilibrium phase corresponding to their initial k values. The In_2O_3 is effectively coupling with MW, on the other hand, ZnO is a poor MW absorber in the E-field above 800 °C and could retard the solid state reaction. Since it is hard to monitor the exact mechanism, we can only speculate that the required defects (Zn-vacancies) for the initiation of the In-ion incorporation into ZnO under the MW field are either not mobile enough through the structure nor created in the quantities sufficient for the homologous

phase formation. This results in the delay of the phase formation in comparison to the conventional sintering process at the same temperature.

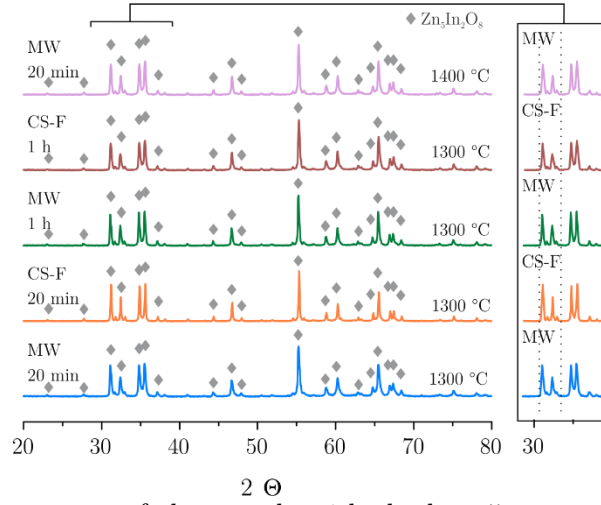


Figure 7.2: The XRD patterns of the sample with the $k = 5$ composition sintered under MW and compared with CS-F samples.

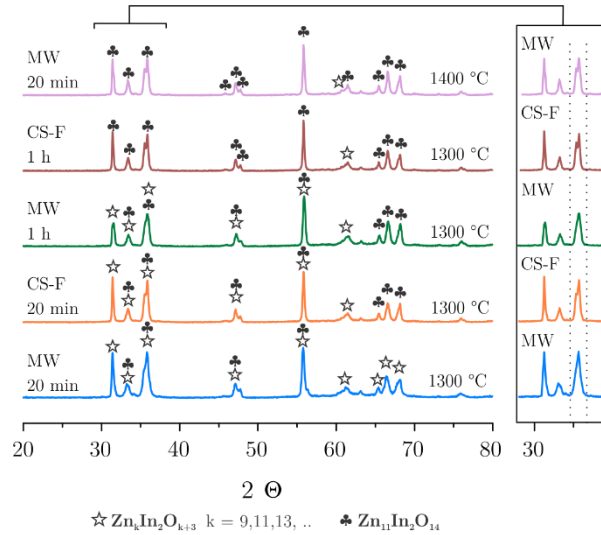


Figure 7.3: The XRD patterns for the $k = 11$ composition sintered under MW and compared with CS-F and CS samples.

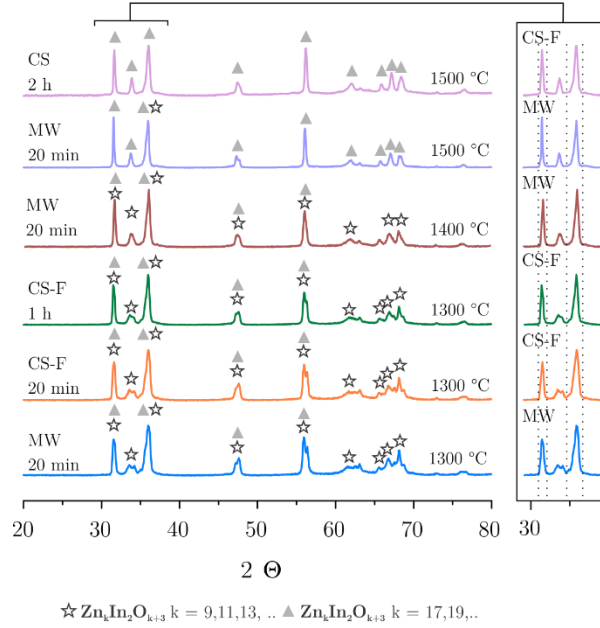


Figure 7.4: The XRD patterns for $k = 18$ composition of samples sintered under MW and compared with CS-F and CS samples.

7.3.3 Microstructural characteristics

The micrographs of all three compositions are presented in Figure 7.5, Figure 7.6 and Figure 7.7 for various temperature regimes, MW, CS-F and CS sintered. There are almost no observed differences in the grain size among MW and conventionally sintered samples at certain sintering temperature, regardless the sintering rate. The microstructures of MW sintered compositions with $k = 5$ are presented in Figure 7.5 and are compared with the CS-F sintered samples at the same dwell times. The MW sintered samples are exhibiting higher density at 1300 °C than CS-F sintered for 6 %, regardless of the sintering time, however in comparison with CS samples (not presented here), density is comparable. For the $k = 11$ composition presented in Figure 7.6, differences among densities were at 20 min dwell time negligible, but at 1 h they were at around 5 %. This behavior shifts at 1400 °C, where the MW sintered samples are less dense for $k = 5$, however for $k = 11$ and 18 the density is similar as in the comparable CS samples (Figure 7.6 and Figure 7.7).

The reason for the observed differences in densities is in the heating rates of MW, CS-F and CS samples. The CS-F samples were put directly on the target temperature, therefore, there was not enough time for the densification prior to the solid-state reaction and this resulted in poorly densified samples. In contrast, MW sintered samples had much slower heating rates above 800 °C, from 13 – 22 °C. This coincides with the beginning of the effective densification in the $(\text{ZnO})_k\text{In}_2\text{O}_{k+3}$ system [142] and samples consequently possess densities similar to the CS sintered samples.

Density variations between compositions are related to the complex homologous phase formation (Figure 7.2, Figure 7.3, Figure 7.4) [142], when at temperatures of around 1100 °C a series of intermediate homologous phases and non-reacted ZnO grains are present at $k = 11$ and 18. The anisotropic growth nature of the formed homologous phases leads to large triangular shaped pores and retard the densification rate [128, 142]. On the other hand, samples with the non-reacted ZnO parts are having higher sintering rates due to the ZnO isotropic growth direction during sintering. Therefore, the lowest density possesses

samples from $k = 5$ composition, whereas $k = 18$ has the highest density among the studied compositions.

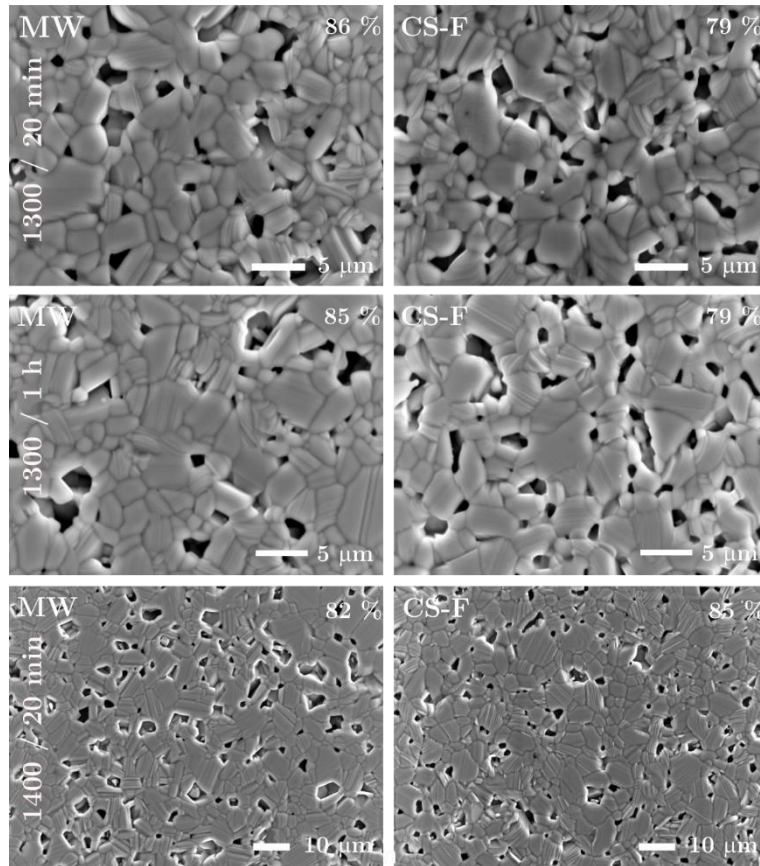


Figure 7.5: Thermally etched microstructures of the $k = 5$, composition sintered at 1300 °C for 20 min under MW field (left column) and samples sintered conventionally at the same temperatures and dwell times (right column).

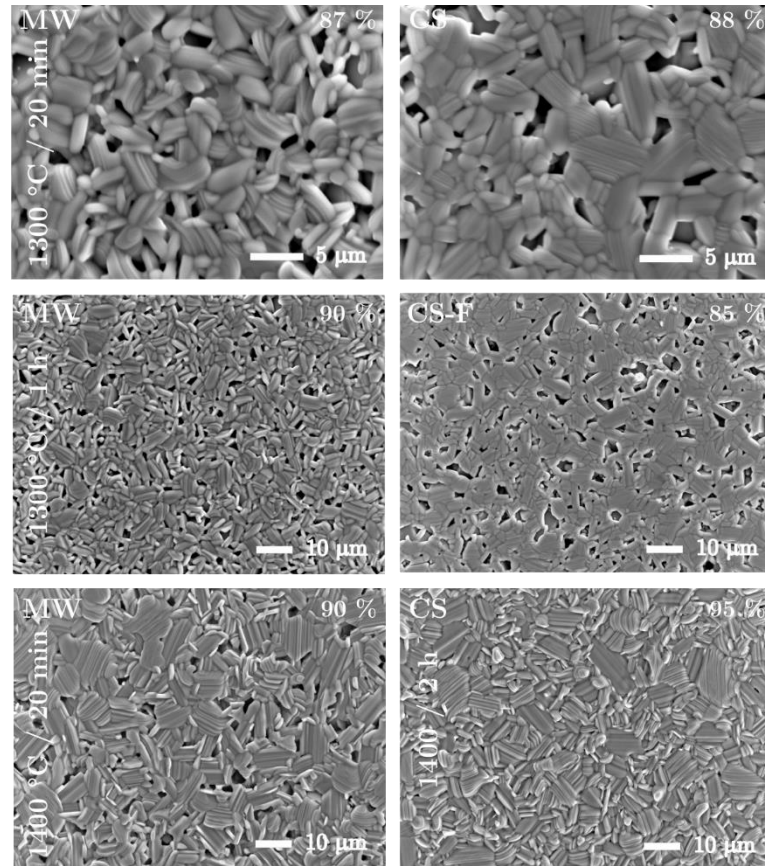


Figure 7.6: Thermally etched micrographs of samples from compositions with $k = 11$ sintered under MW field (left column) and by conventional synthesis (right column).

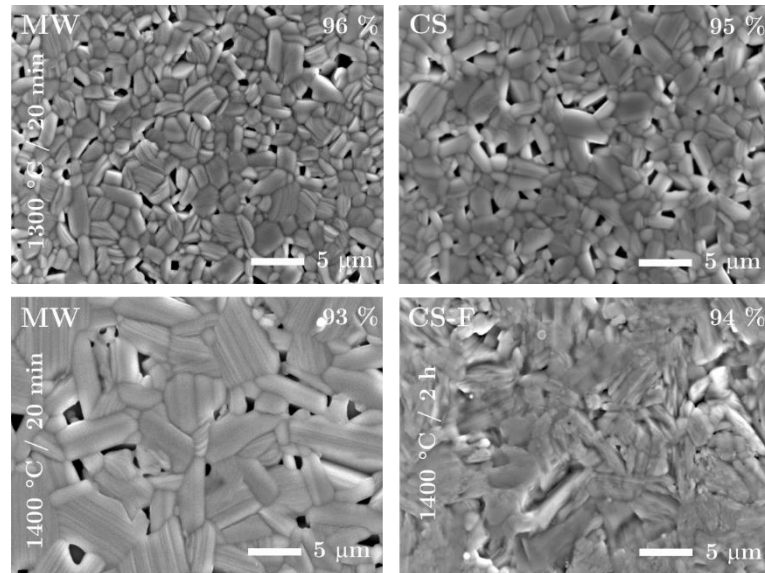


Figure 7.7: The thermally etched micrographs of samples from compositions with $k = 18$ sintered under MW field (left column) or by conventional synthesis (right column).

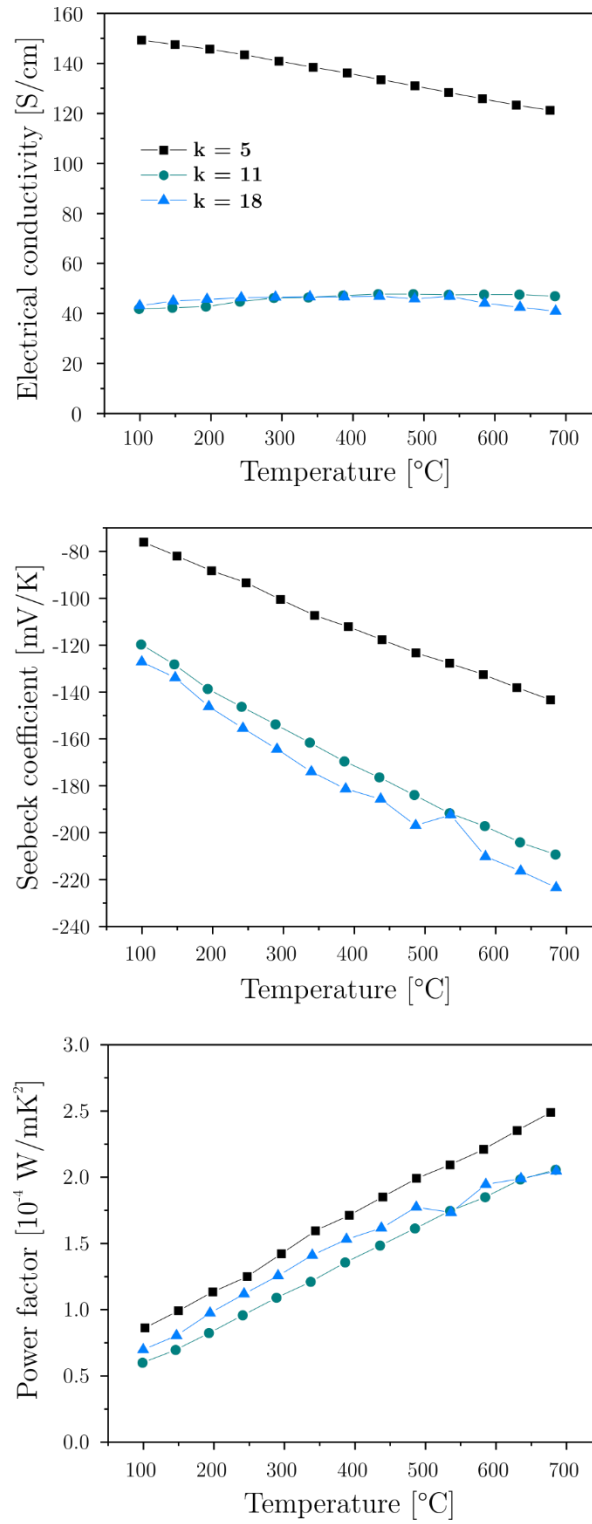


Figure 7.8: The temperature dependent electrical conductivity, Seebeck coefficient and power factor of MW sintered samples.

7.4 Thermoelectric Properties

The temperature dependent thermoelectric properties are for all three studied compositions presented in Figure 7.8. The electrical conductivity at 100 °C is the highest for $k = 5$ of 150 S/cm and is followed with $k = 11$ and 18 with values for both at around 40 S/cm. These values are generally lower than in the case of conventionally sintered samples presented in previous reports [118, 123, 129, 142], nevertheless, the observed samples in this study had much lower densities, which largely influence the electrical conductivity. The Seebeck coefficient is negative for all observed samples, indicating the n-type thermoelectric material behavior. Absolutely the highest among observed compositions at 100 °C is for $k = 18$ with 125 $\mu\text{V/K}$, followed by $k = 11$ with 120 $\mu\text{V/K}$ and lowest for $k = 5$ with 75 $\mu\text{V/K}$. For all three compositions it is increasing with temperature, and reaches the highest absolute value for $k = 18$ with 220 $\mu\text{V/K}$. Since it is in inverse relation with the electrical conductivity, this is the expected behavior and was already previously observed by other authors [123]. The calculated power factor is showing the best performance for $k = 5$ sample, however, $k = 11$ and 18 are still quite comparable. The obtained results are in the range of previously reported [129, 159] and endorse the MW one-step sintering in the $(\text{ZnO})_k\text{In}_2\text{O}_{k+3}$ system as a good alternative and cost-effective approach for the thermoelectric ceramics preparation.

7.5 Conclusions

This study presents the microwave sintering of the $(\text{ZnO})_k\text{In}_2\text{O}_{k+3}$ system of the homologous phases for the three compositions with $k = 5, 11$ and 18. We report on the role of constituent oxides and their solid-state reaction during the MW heating. The effective response of ZnO and In_2O_3 on the MW induced heating was different, with faster initial heating-up of In_2O_3 , transferring heat to the less-responsive ZnO. However, at temperatures above 600 °C, ZnO more effectively couples with MW field and brings the fast heating up with a rate of 600 °C/min to temperatures at around 790 °C. Afterwards, the temperature rate stalled, because of the large change in the ZnO MW absorption. It resulted in the delayed phase formation under the MW field for all three compositions, observed by the widened XRD peaks. The microstructural characteristics of samples generally did not show any differences in grain sizes among MW sintered samples and samples with partially analogous heating rates CS-F (conventionally sintered – fast) and CS (conventionally sintered). Good and comparable density with CS samples was attributed to the slower temperature increase above 800 °C and is not connected to the “non-thermal” effect of the ponderomotive force.

The observed thermoelectric properties were comparable to the previous reports, and with proper co-doping, tailoring grain size and density, we can expect further improvements. Nevertheless, the optimized and well controlled temperature profile under the MW sintering with the fast heating up until 750 °C and slower increase to initiate sintering and solid state reaction, results in a cost-effective approach for the $(\text{ZnO})_k\text{In}_2\text{O}_k$ thermoelectric ceramics preparation.

Chapter 8

FAST Sintering of the $(\text{ZnO})_k\text{In}_2\text{O}_3$ Homologous Phase System

8.1 Introduction

The pulsed field-assisted sintering (FAST) is a current and pressure assisted sintering method, which has been widely applied for thermoelectric materials processing in the recent years [141, 219-222]. Its main benefits are in a combination of current induced heating and pressure application, which result in well sintered samples [223]. It also offers shortened processing time and synthesis of new phases, which are with the conventional methods harder to synthesize. The FAST is causing “Joule heating” inside the sample due to the numerous discharges on particles and results in the acceleration of neck formation and thermal diffusion among sintered particles [224, 225]. Therefore, the diffusion based phase formation is enhanced and requires lower temperature and much less time than in the conventional sintering. Furthermore, the applied pressure plays a major role in the effective densification and sintering, resulting in the additional shortening of the processing time.

In the case of ZnO-based oxide thermoelectric materials, most of FAST research was done on the nanocrystalline ZnO [226, 227] and on the ZnO doped with Al [105, 108, 141, 222, 228]. They mainly obtained well dense ceramics at lower temperatures than in the conventional sintering and reported improved ZT values in comparison to the conventional sintering. The usage of the plate-like particles of ZnO and their consolidation under FAST [106] resulted in the partially textured microstructures and doubled electrical conductivity in the direction perpendicular to the applied pressure.

None of the reports dealt with the ZnO-In₂O₃ system, which has above 1000 °C the internal diffusion based solid-state reaction of In₂O₃ into the ZnO wurtzite lattice, with formation of plate-like grains. This initiated the study of the effects of FAST on the phase formation, microstructure development and following of the possible texturation development.

8.2 Materials and Methods

The samples were prepared from powder mixtures of ZnO (Grillo Zinkoxide GmbH, Pharma 4, > 99.9 %) and In₂O₃ (Alfa Aesar, 99.9 % metals basis, 325-mesh powder) in proper molar ratio, according to the phase formulation $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ for $k = 5, 11$ and 18 . These powder mixtures were further homogenized in a planetary ball mill with ethanol as a milling media for 1 h at 200 rpm in a polyethylene vial with YSZ milling balls (3 mm). The obtained slurry was dried (80 °C) and sieved through 500-mesh sieve. For few

experiments, powder mixture was put in an alumina crucible and heated up (5 °C/min) to 1150 °C for 2 h for the initiation of the solid state reaction.

For FAST experiments, graphite mold with diameter of 10 or 20 mm was used and additionally covered inside with graphite foil for easier disassembling of the sample. The powder was put inside the graphite mold, gently pressed and inserted in the FAST furnace chamber. During experiments, two types of FAST systems were used, the first was DR SINTER, SPS-615 model (SPS SYNTEX, Japan) and the second with the possibility of higher pressure application was FAST HPD 25 (FCT Systeme, GmbH, Germany). In both systems, the pulse on/off ratio was set on 12/2. Samples were sintered in a temperature range from 900 °C to 1100 °C, with a heating rate of 100 °C until 100 °C below the target temperature and then with 50 °C/min, 30 °C/min and 20 °C/min until the final temperature. The dwell time varied from 0 min up to 30 min. The temperature was monitored with the side thermocouple put in a small perforation inside the graphite mold. Selected samples were afterwards additionally annealed in air atmosphere in the temperature range from 1300 °C until 1500 °C for 2 h.

Phase composition of the sintered samples was analyzed using powder X-ray diffraction analysis (diffractometer PANalytical X'Pert PRO MPD, Almelo, The Netherlands). Microstructures in the cross-section direction across the disc samples, un-etched and thermally etched, were examined using the scanning electron microscope (SEM, JSM-5800, JEOL, Tokyo, Japan). Samples for TE measurements were cut in rods with 8 mm in length and a cross section of 2x2 mm². Seebeck coefficient and electrical conductivity were investigated with ZEM 3 (ULVAC-RIKO, Yokohama, Japan) in a partial helium pressure.

8.3 Results and Discussion

To evaluate the overall behavior of the ZnO-In₂O₃ system under FAST, samples of the pure ZnO, $k = 5$, 11 and 18 were studied and compared to CS sintered samples.

Since the homologous phase formation goes progressively from the starting $k = 5$ to the higher k phases [142], the $k = 5$ samples will be presented in detail. The XRD patterns of $k = 5$ in Figure 8.1 confirm that at 900 °C in both cases, in CS and FAST, regardless the sintering time, only initial powder peaks of ZnO and In₂O₃ are present. Nevertheless, the FAST sintered sample has slightly widened peaks, indicating an initiation of the solid state reaction. At the temperature of 1000 °C, the CS sample sintered for 2 h has remarkably widened peaks of primary ZnO and In₂O₃ phases, while in the FAST sintered sample at dwell time 0 the Zn₅In₂O₈ homologous phase is already present with some In₂O₃. After dwell time of 5 min the presence of starting reagents is minimal; however still widened peaks in comparison to the XRD pattern of the CS sample at 1200 °C for 2 h indicate that compositional homogeneity (i.e. equilibrium composition) of the equilibrium Zn₅In₂O₈ homologous phase for the $k = 5$ was not reached yet.

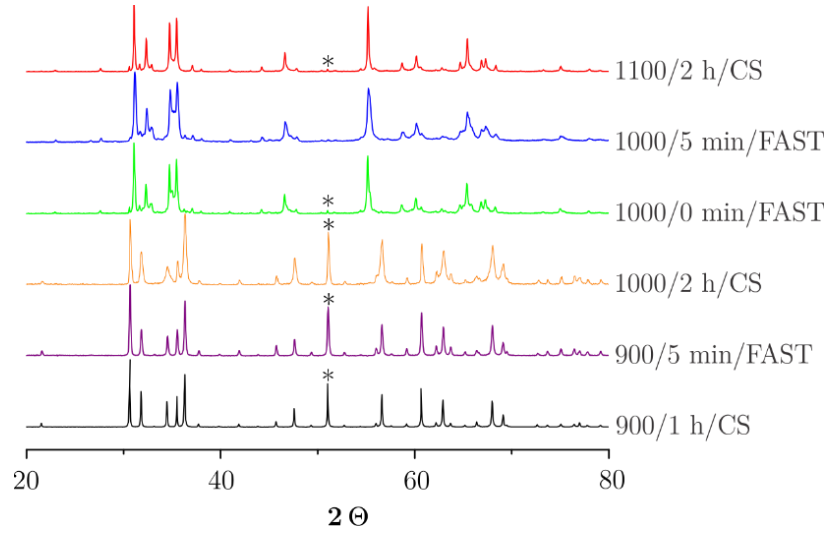


Figure 8.1: XRD patterns of samples with composition $k = 5$ sintered under different regimes in CS and FAST (* marks the selected In_2O_3 peaks).

At 1000 °C, the XRD patterns of CS samples $k = 11$ and $k = 18$ in Figure 8.2 still indicate the presence of In_2O_3 phase, however, in FAST samples, they are not present anymore. In comparison to the CS sintered samples at 1300 °C, which has almost the equilibrium homologous phase [142], the FAST samples have peak positions which indicate that the homologous phase formation is faster and closer to the equilibrium than in CS samples sintered at the same temperature.

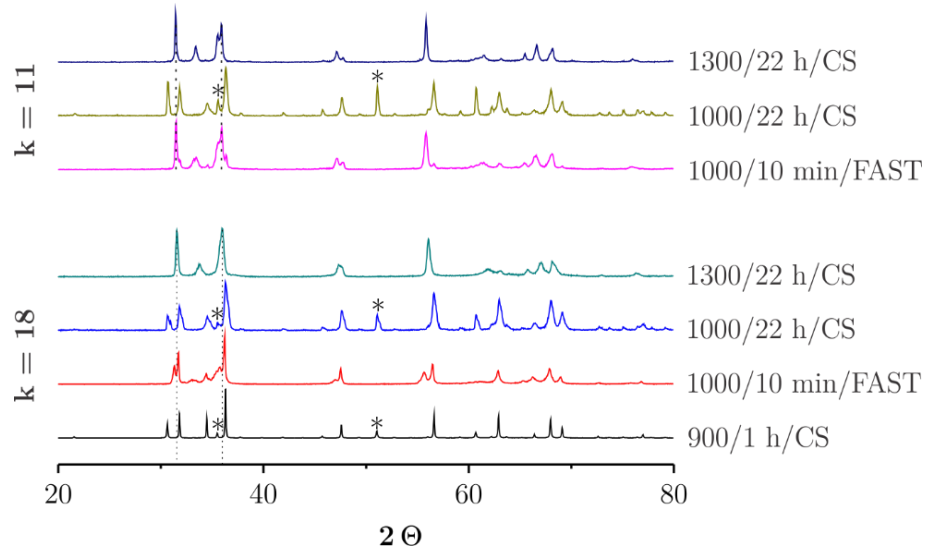


Figure 8.2: The XRD patterns of samples $k = 11$ and $k = 18$ sintered under different conditions under FAST and CS (* marks the selected In_2O_3 peaks).

The microstructures of ZnO and all three $(\text{ZnO})_k\text{In}_2\text{O}_3$ samples reveal the complex homologous phase formation under the current assisted sintering as well (see Chapter 4 for phase and microstructural evolution in CS samples) (Figure 8.3). In pure ZnO samples, the grain sizes are from 5-10 μm and generally have isotropic shapes with small cavities on their surfaces. This is due to the high ZnO vapour pressure in vacuum conditions, observed also in previous reports [107, 141]. On the other hand, the samples with $k = 5, 11$ and 18

have a much smaller grain size (around $2\text{ }\mu\text{m}$). From the BSE micrographs in Figure 8.3 it is clearly visible that $k = 5$ and 11 samples are compositionally homogeneous and hence close to their equilibrium homologous phase. However multiphase composition of sample for $k = 18$ sample with the presence of darker In_2O_3 -poor and brighter In_2O_3 -rich areas indicates that the system is still far from the homogeneous equilibrium composition of $\text{Zn}_{18}\text{In}_2\text{O}_{21}$ homologous phase for $k = 18$.

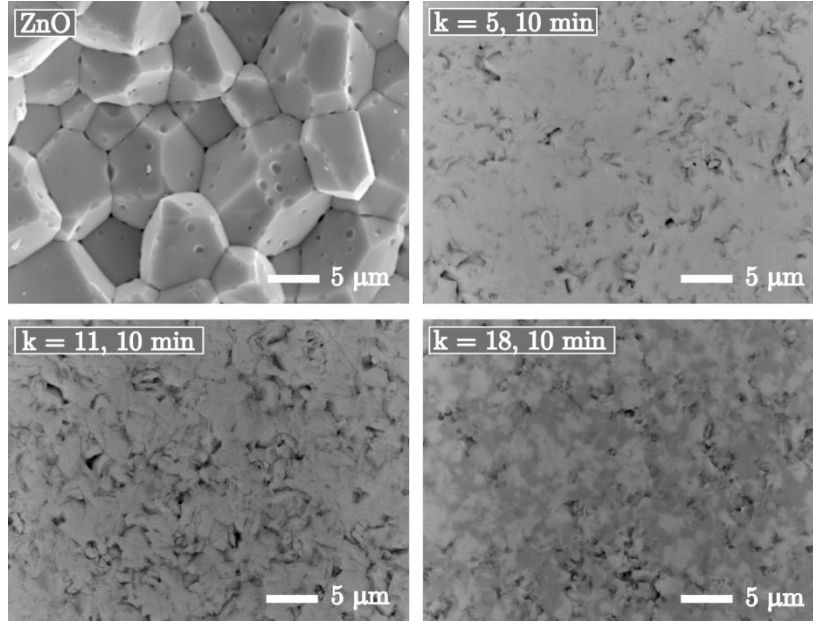


Figure 8.3: Micrographs of FAST sintered samples at $1000\text{ }^{\circ}\text{C}$ of ZnO and $k = 5$, $k = 11$ and $k = 18$.

The detailed microstructural development (Figure 8.4) for the composition $k = 5$ shows that at $900\text{ }^{\circ}\text{C}$ essentially two primary phases, the ZnO and the In_2O_3 are present; it does not indicate formation of the homologous $k=5$ phase yet. However, in only 3 minutes of rising time to $1000\text{ }^{\circ}\text{C}$ (dwell time at $1000\text{ }^{\circ}\text{C}$ 0 minutes) the phase formation already started with diffusion of In-ions into the ZnO lattice as observed in the vicinity of white In_2O_3 -rich areas. After dwell time of 5 min at $1000\text{ }^{\circ}\text{C}$, the equilibrium homologous phase is almost completely formed with elongated grains in the range from 2 to $5\text{ }\mu\text{m}$ and some isolated brighter parts, representing the In_2O_3 -rich phase.

The presented phase and microstructural evolution confirms that the electric field accelerates diffusion processes, leading to at least a $100\text{ }^{\circ}\text{C}$ lower temperature of the homologous phase formation in FAST in comparison to CS. Even more, due to different heat generation mechanisms (discharges on grain boundaries), it is more effective and faster than convective sintering (CS), where dwell time of a few minutes at sintering temperatures above $1100\text{ }^{\circ}\text{C}$ is not enough for the complete phase formation (see Chapter 4 and Chapter 8 for details). Actually with the CS the single $\text{Zn}_5\text{In}_2\text{O}_8$ homologous phase is obtained at $1200\text{ }^{\circ}\text{C}$ only after 22 h of sintering and at $1300\text{ }^{\circ}\text{C}$ after 2 h.

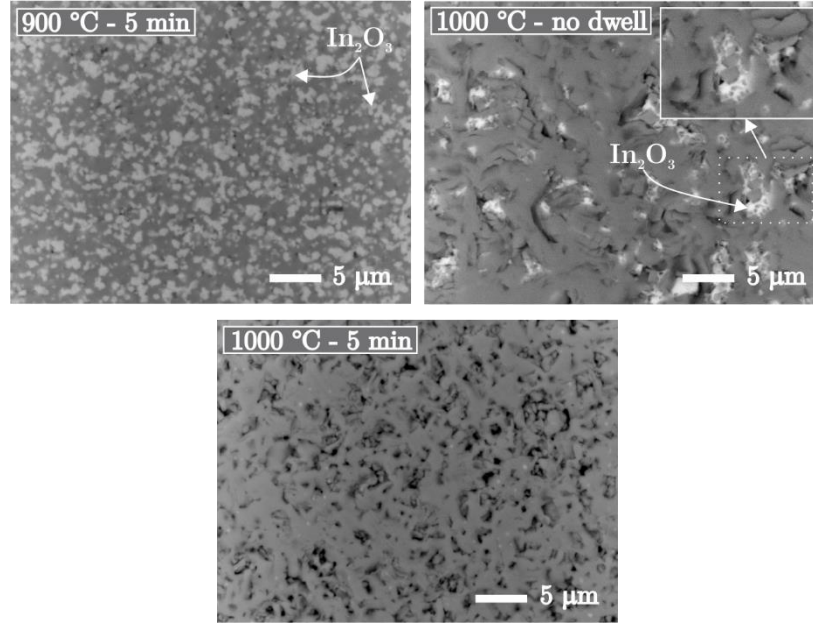


Figure 8.4: The microstructural development triggered by the homologous phase formation at $k = 5$ sample sintered under FAST.

Due to the evaporation and hence losses of the ZnO under vacuum conditions the equilibrium homologous phases for $k = 11$ and 18 would be hard to achieve in usual operation times of FAST. Therefore, we decided to focus our further research on the thermoelectric properties of composition with $k = 5$.

In order to evaluate the thermoelectric properties of FAST sintered samples, three samples with the composition $k = 5$ were prepared at different FAST conditions, using powders already pre-reacted at 1150 °C for 2 h by conventional sintering. The usage of the pre-reacted powder ensured the defined homologous phase composition and even more, the plate-like shaped grains could be aligned perpendicular to the pressing direction. This alignment would result in the increased electrical conductivity in the direction along their long axis and improved final ZT values in comparison to the non-textured samples.

The pre-reacted samples were processed by FAST at different dwell times and pressures and their corresponding microstructures are presented in Figure 8.5: A – 50 MPa , 5 min ; B – 75 MPa , 5 min ; and C – 75 MPa , 30 min . All the samples have a distinct plate-like morphology of fine grains having plane dimensions of about $5\text{ }\mu\text{m}$ and thickness up to a few micrometers. All the samples have high, about 98% theoretical density; however, in the samples sintered for 5 minutes grains are weakly connected to each other and hence pulled out during polishing, so their microstructures look much more porous.

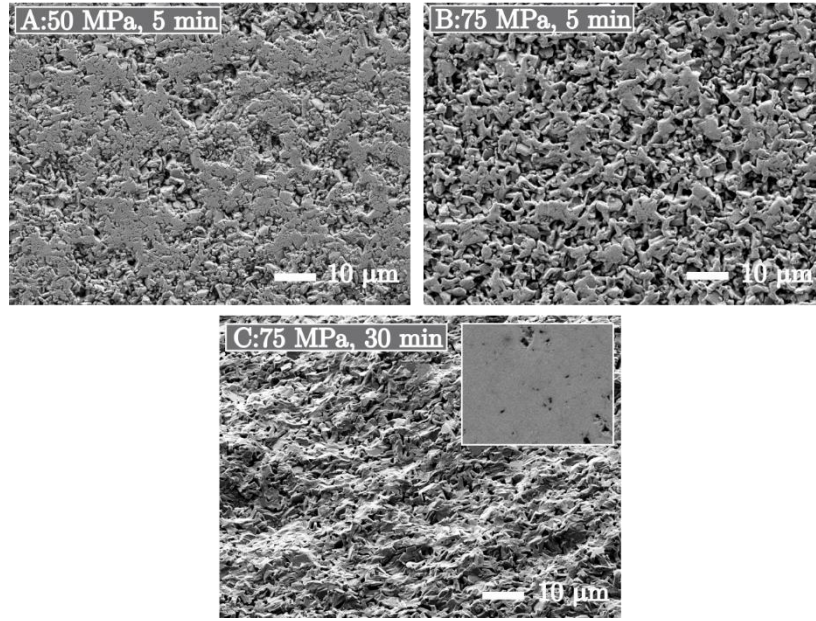


Figure 8.5: FAST samples of $k = 5$ composition sintered at 1000 °C at different dwell times and pressures.

The measured electrical conductivity of the samples showed that it is strongly influenced by the FAST processing parameters, i.e. pressure and dwell time. The comparison between the samples A and B reveals that the electrical conductivity at 100 °C is doubled from 200 S/cm to 400 S/cm for the pressure increase of 15 MPa, regardless of their similar density and grain size. With the further prolongation of the dwell time to 30 min (sample C) the electrical conductivity increased to 1000 S/cm. The Seebeck coefficient behavior is usually reversely proportional to the measured electrical conductivity, which was confirmed also with analyzed samples so the highest value has the sample A.

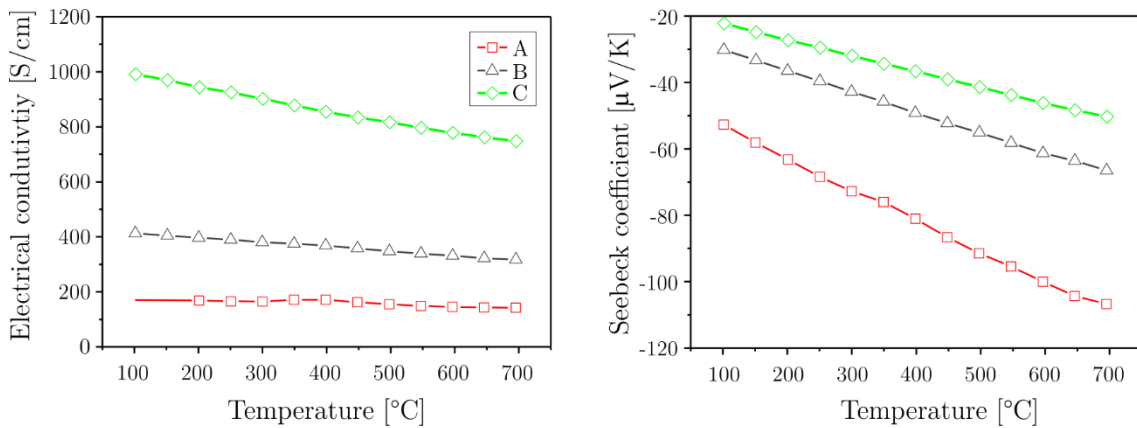


Figure 8.6: The electrical conductivity and the Seebeck coefficient of the samples A (FAST, 50 MPa, 5 min), B (FAST, 75 MPa, 5 min) and C (FAST, 75 MPa, 30 min).

The results also indicated the possible influence of partial texturing of the plate-like grain observed in the sample C. Also, the FAST is performed in high vacuum conditions and hence the samples are reduced to some degree due to the lower oxygen partial pressure.

Consequently, additional defects, i. e. oxygen vacancies (V_o) are likely formed in the ZnO wurtzite-type matrix, contributing additional (deep) donor states which could also increase the electrical conductivity. In order to shed a light on the possible effect of texturing, we prepared a sample using FAST at temperature 400 °C and even higher uniaxial pressure of 400 MPa, which was afterwards conventionally sintered (CS) in air at 1500 °C for 2 h. Its thermoelectric characteristics (electrical conductivity, Seebeck coefficient) were compared with the sample made directly from the fresh (unreacted) powder mixture of ZnO and In_2O_3 using CS at the same temperature regime. The microstructures of these two samples are presented in Figure 8.7; in general the FAST sample has larger grains than the CS sample. Also slight texturing of the grains could be observed in the microstructure of the FAST sample, which is not present in the CS sample.

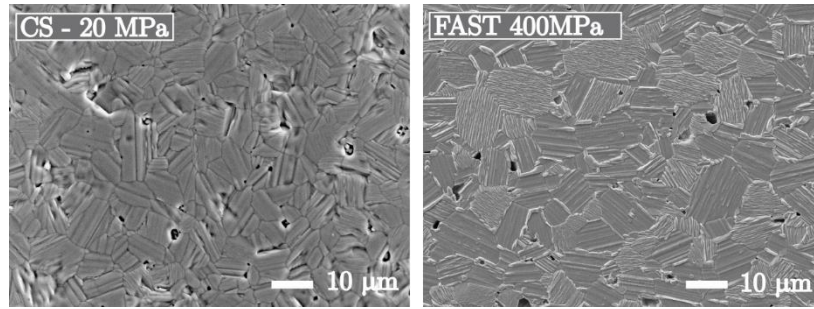


Figure 8.7: The microstructural development in CS and FAST samples prepared under different uniaxial pressures and both in the final step sintered conventionally at 1500 °C for 2 h.

The electronic part of the thermoelectric properties (electrical conductivity and Seebeck coefficient) is presented in Figure 8.8. The FAST sample has the electrical conductivity for almost 100 S/cm higher than the CS sintered sample, which could be attributed to texturing and also larger grain size. Accordingly, as could be expected the FAST sample has a lower Seebeck coefficient in comparison to the CS sample.

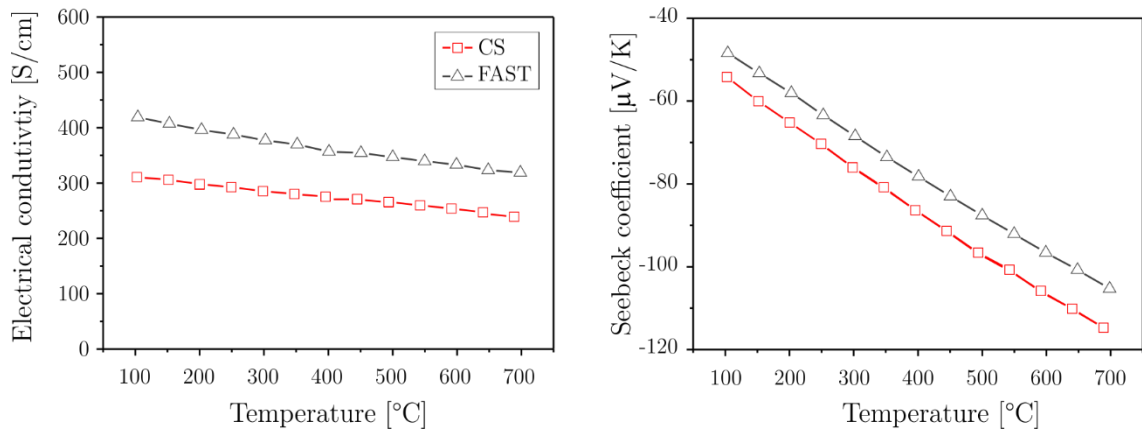


Figure 8.8: The electrical conductivity and the Seebeck coefficient of the samples prepared by FAST processing at 400 °C and pressure of 400 MPa for CS and prepared under different uniaxial pressures and both in the final step sintered conventionally at 1500 °C for 2 h.

8.4 Conclusions

Field assisted sintering technique (FAST) is a current activated and pressure assisted sintering and synthesis technique, which has been successfully applied in many materials during recent years. The simultaneous application of pulsed electric current and pressure usually results in well densified ceramics at lower temperatures and sintering/synthesis times. In the case of the $(\text{ZnO})_k\text{In}_2\text{O}_3$ system, we investigated the phase formation under FAST process for k values of 5, 11 and 18. The formation of the equilibrium $\text{Zn}_5\text{In}_2\text{O}_8$ phase from the $k = 5$ composition started already at 900 °C, which is about 100 °C lower in comparison to the conventional sintering. The formation of the equilibrium $\text{Zn}_5\text{In}_2\text{O}_8$ homologous phase is almost completed already after 5 minutes at 1000 °C. For comparison, in the CS process the reaction of the $\text{Zn}_5\text{In}_2\text{O}_8$ phase formation is completed at 1200 °C after 22 h and at 1300 °C after 2 h. In the case of compositions for $k = 11$ and 18, as expected, the $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ homologous phase formation has not been completed yet in the FAST processing at 1000 °C for 5 min; however, the pure In_2O_3 was not present anymore in the samples as in the samples conventionally sintered even for 22 h at 1000 °C. The results clearly confirmed that FAST is effectively lowering temperature and time for the formation of the $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ homologous phase.

The FAST processing proceeds in vacuum and results in creation of oxygen vacancies (V_o) acting as shallow donors, which contributes to higher electrical conductivity of the samples in comparison to the classically sintered in air. In the case of composition for $k=5$ it also showed that when a pre-reacted powder of ZnO and In_2O_3 with plate-like morphology of grains is used, the FAST processing results in slight texturing of the grains in dependence to the applied pressure and dwell time. Accordingly, the conductivity of the samples increased with higher pressure, which could be attributed to better connectivity among the slightly textured grains and with longer dwell temperature, which could result from increased concentration of V_o . Comparison of the untextured sample prepared by classical sintering at 1500 °C in air and slightly textured FAST sample, which was post-annealed in air at the same conditions that confirmed the positive effect of texturing on the electrical conductivity.

Chapter 9

Conclusions

In the present thesis, the focus was put on the n-type ZnO-based thermoelectric ceramics, specifically on the system of the $(\text{ZnO})_k\text{In}_2\text{O}_3$ homologous phases, possessing the superlattice structure with the high potential for the effective tailoring of the thermoelectric properties.

In this work I studied the consequences of the $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ homologous phase formation process on the sintering, composition, structure and microstructure, and consequently the thermoelectric properties of the ZnO-In₂O₃-based ceramics. The samples with the compositions $(\text{ZnO})_k\text{In}_2\text{O}_3$ ($k = 5, 11$ and 18) were prepared by the classic ceramic procedure from powder mixtures of ZnO and In₂O₃ and sintered at temperatures from 900 °C to 1500 °C. Results revealed that sintering is hindered by the presence of In₂O₃ at the grain boundaries, more in the compositions with a larger amount of In₂O₃; it proceeds in the shadow of the diffusion of In³⁺ into the wurtzite-type ZnO, which leads to the formation of the multiple planar defects and the homologous phases, as long as the In₂O₃ is not sufficiently removed from the grain boundaries to allow the intergranular diffusion of the Zn-ions. The formation of the homologous phases starts at temperatures above 1000 °C and is substantially determined by the initial distribution of In₂O₃ in the starting mixture with ZnO and consequently the local ZnO-to-In₂O₃ ratio. In the composition with $k = 5$, the amount of added In₂O₃ is sufficiently high to ensure ZnO-to-In₂O₃ ratio close to 5 at short-range distances in the starting powder mixture, which enables direct and uniform formation of the equilibrium homologous phase $\text{Zn}_5\text{In}_2\text{O}_8$. As a consequence of this soon-reached compositional homogeneity, the grain growth in these samples with $k = 5$ is quite uniform, regardless of the sintering temperature. In the compositions with a much lower content of In₂O₃ (i.e., high $k = 11$ and 18 values), the local ZnO-to-In₂O₃ ratio facilitated an initial formation of the lower k $\text{Zn}_5\text{In}_2\text{O}_8$ and $\text{Zn}_7\text{In}_2\text{O}_{10}$ phases in In-rich areas and the higher k $\text{Zn}_k\text{In}_2\text{O}_{3+k}$ phases for $k > 9$ towards pure ZnO ($k \rightarrow \infty$) in the In-depleted regions. Consequently, the equilibrium homologous phase for the starting high- k composition is formed only after the extensive diffusion of Zn-ions from grains of higher- k phases to the grains of lower- k phases, which required higher sintering temperatures and longer sintering times. Therefore, the exaggerated growth of grains with a higher content of In₂O₃ is manifested in these samples as long as the compositional homogeneity of the equilibrium homologous phase for the starting k -value is not established in the whole sample. In general, the TE characteristics decreased with an increasing k value in relation to the density of the In-planar defects. The ceramics with $k = 5$ had similar ZT values after sintering at 1300 °C and 1500 °C (i.e., 0.12 at 700 °C). However, the ZT of the samples with $k = 11$ and $k = 18$ after sintering at 1500 °C significantly increased, reaching values surprisingly close to the sample with $k = 5$, which can be attributed to the improved compositional homogeneity and a much larger grain size.

The $(\text{ZnO})_k\text{In}_2\text{O}_3$ polycrystalline ceramics have a plate-like morphology of grains; hence plate-like grains of pre-reacted phases were used as seed grains to induce possible microstructure texturing in order to improve the thermoelectric properties as was reported in the literature. The $(\text{ZnO})_k\text{In}_2\text{O}_3$ -based ceramic for $k = 5$ and $k = 11$ was prepared by a classic ceramic procedure and sintering at 1500°C . Either a fresh powder mixture of ZnO and In_2O_3 was used, or a mixture of ZnO and In_2O_3 to which pre-reacted powder with a well-defined plate-like grains of the $(\text{ZnO})_k\text{In}_2\text{O}_3$ homologous phase was added. In the powder mixtures containing the addition of the pre-reacted powder, these much coarser plate-like grains of the low- k phases ($\text{Zn}_5\text{In}_2\text{O}_8$ and $\text{Zn}_7\text{In}_2\text{O}_{10}$) preferentially grow at the expense of the much finer grains of ZnO and In_2O_3 , and also the high- k $(\text{ZnO})_k\text{In}_2\text{O}_3$ homologous phases, which eventually resulted in the formation of the equilibrium $(\text{ZnO})_k\text{In}_2\text{O}_3$ homologous phase for the starting k -value. Nevertheless, the final microstructures of all the samples, regardless of the starting mixture, were similar and no texturing was observed in the samples prepared from the mixtures with the addition of pre-reacted phases. This could be explained by the presence of solid clusters of the plate-like grains in the pre-reacted powder added to a fresh mixture of ZnO and In_2O_3 , which prevented any alignment of plate-like seeds that might occur in pressing of the pellets. The results showed no significant influence of the starting-powder mixture on the ZT values and were similar for the samples with the same composition (k values).

In order to additionally improve the final ZT values, the Al-doping of the most promising $(\text{ZnO})_5\text{In}_2\text{O}_3$ homologous phase and its influence on the structure and the thermoelectric characteristics were studied. Samples with compositions $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$ for $x = 0, 0.01, 0.03, 0.05, 0.1$ and 0.2 were prepared by the classical ceramic procedure and sintering at 1500°C . Slight enhancement of the solid state reaction and its initiation at lower temperatures was observed on DSC with the increasing additions of Al, due to the incorporation of the smaller Al ion with the formation of the $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$ homologous phase. The Rietveld analysis of the XRD patterns indicated the linear decrease in the lattice parameters for the $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$ homologous phase with increasing Al-doping. This implied that the Al ions likely substitute on both primary sites of the In ions in the $\text{Zn}_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_8$ homologous phase, the octahedral sites in the basal-plane IBs and the trigonal bi-pyramidal sites in the zig-zag IBs, which was additionally confirmed by the HRTEM. The thermoelectric characteristics were improved only for the small additions of Al for $x = 0.01\text{--}0.05$, which was explained by the increased carrier mobility at a lower number of charge carries. However, with a further increase in the Al-additions, the charge-carrier concentration and their mobility dropped due to the disturbance of their main conduction paths of the InO_2^- layers inflicted with the strain accompanying structural shrinkage, which resulted in poor electrical conductivity and decreased ZT values of the $(\text{ZnO})_5(\text{In}_{1-x}\text{Al}_x)_2\text{O}_3$ ceramics in comparison to the un-doped composition.

In order to optimize and shorten the time and energy consuming the formation of the ZnO- In_2O_3 -based thermoelectric ceramics under the conventional synthesis, the microwave (MW) and field assisted sintering (FAST) were used and their effects on the formation and characteristics of the $(\text{ZnO})_k\text{In}_2\text{O}_{k+3}$ homologous phases were evaluated.

First, the microwave sintering of the $(\text{ZnO})_k\text{In}_2\text{O}_{k+3}$ homologous phase system for $k = 5, 11$ and 18 was employed. The effective response of ZnO and In_2O_3 on the MW induced heating was different; faster initial heating of In_2O_3 transferring heat to the less-responsive ZnO. However, at temperatures above 600°C ZnO more effectively couples with MW field and brings the fast heating up with a rate of $600^\circ\text{C}/\text{min}$ to temperatures at around 790°C . Afterwards, the temperature rate stalled, because of the large change in the ZnO MW absorption. It resulted in the delayed phase formation under the MW field for all three compositions, observed by the widened XRD peaks. The microstructural characteristics of samples generally did not show any differences in grain sizes among MW sintered samples

and samples with partially analogous heating rates CS-F (conventionally sintered – fast) and CS (conventionally sintered). Good and comparable density with CS samples was attributed to the slower temperature increase above 800 °C. The observed thermoelectric properties were comparable to results obtained from conventional synthesis in Chapter 1. The optimized and well controlled temperature profile under the MW sintering with the fast heating up until 750 °C and further slower increase to initiate the sintering and solid state reaction results in a cost-effective approach for the $(\text{ZnO})_k\text{In}_2\text{O}_k$ thermoelectric ceramics preparation.

Second, the influence of the FAST processing on the phase formation, microstructure development with possible development of texturing and electrical conductivity was studied. To evaluate the overall behavior of the ZnO-In₂O₃ system under FAST, samples of the pure ZnO and $(\text{ZnO})_k\text{In}_2\text{O}_{k+3}$ for $k = 5, 11$ and 18 were studied and compared to the CS sintered samples. The formation of the equilibrium $\text{Zn}_5\text{In}_2\text{O}_8$ phase from the $k = 5$ composition started about 100 °C lower in comparison to the CS and was almost completed already after 5 minutes at 1000 °C. For comparison, in the CS process the reaction of the $\text{Zn}_5\text{In}_2\text{O}_8$ phase formation is completed at 1200 °C after 22 hours and at 1300 °C after 2 hours. In the case of compositions for $k = 11$ and 18 , as expected, the $\text{Zn}_k\text{In}_2\text{O}_{k+3}$ homologous phase formation has not been completed yet in the FAST processing at 1000 °C for 5 minutes; however, the pure In₂O₃ was not present anymore in the samples as in the samples conventionally sintered even for 22 h at 1000 °C. The FAST processing proceeds in high vacuum and results in the creation of oxygen vacancies (V_o) acting as shallow donors, which largely contributes to higher electrical conductivity of the samples in comparison to classically sintered in air. Furthermore, when a pre-reacted powder with plate-like grain morphology is used, the FAST processing results in slight texturing of the grains in dependence to the applied pressure and dwell time. Comparison of the un-textured sample prepared by classical sintering at 1500 °C in air and slightly textured FAST sample, which was post-annealed in air at the same conditions, confirmed the positive effect of texturing on the electrical conductivity.

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Publications Related to the Thesis

Journal Articles

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Biography

The author of this thesis, Mateja Košir, was born on September 21th, 1985 in Kranj, Slovenia. After graduating from Gymnasium Škofja Loka in 2004, she enrolled in the bachelor study at the Department of Geology, Faculty of Natural Sciences and Engineering in University of Ljubljana. During her study, she was working part-time in the field of natural heritage protection (Conservation center, Institute for the Protection of Cultural Heritage of Slovenia) and in the field of solid-state chemistry (Advanced Materials Department, Jožef Stefan Institute). She defended her bachelor thesis in 2011 entitled “*Provenance of pyroclastic rocks from archaeological site Mošnje*” under the supervision of Prof. Nina Zupančič and Asst. Prof. Sabina Kramar. Afterwards, she worked part-time in the Geological Survey of Slovenia as a project assistant on a European project addressing the problematics of “sustainable approach to aggregates” and in the evaluation of critical raw materials. In October 2011, she enrolled in the postgraduate study of Nanosciences and Nanotechnologies at the Jožef Stefan International Postgraduate School under the “Young Researcher Programme” financed by the Slovenian Research Agency and started working at the Department for Nanostructured Materials. Her field of research was thermoelectric materials based on ZnO. In 2013, she was a research visitor for 4 months in the CRISMAT laboratory in Caen, France, under the supervision of Dr. Emmanuel Guilmeau. She presented her work in several international conferences and is the first author of two papers and co-author in three papers published in recognized international journals with SCI index.