

University of Crete Department of Physics

Doctoral Thesis

Study of Spinel Oxide alloys Mn₃O₄ based for Printed Temperature Sensors

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Abstract

Temperature is an important parameter in our daily life, monitoring and controlling of which can be achieved with corresponding sensors. Among the various types existing, negative temperature coefficient (NTC) thermistors, made by spinel oxides, hold a prominent position, due to the wide range they cover. The need for surfaces that can accurately monitor spatial and temporal changes in temperature are critical for many applications. Realizing such surfaces requires the deposition of hundreds of sensors over large areas, a task ideally accomplished by printing technologies. However, significant bottleneck obstructing their use are their complex and high temperature fabrication process and high stiffness, prohibiting their integration in large area or flexible applications combined with understanding of their conduction mechanism.

In this study we investigate the transport mechanism of the ternary $Zn_{0.5}Ni_xMn_{2.5-x}O_4$ and $Zn_xNi_{0.5}Mn_{2.5-x}O_4$ spinel oxide alloys, with Ni and Zn content ranging between $0 \le x \le 1.25$. Conductivity studies resulted to an unusual exponential dependence with the temperature associated with structural and vibrational analysis. In particular, for the system with Ni addition, theoretical calculations using density functional theory (DFT) oriented on structural and electronic properties were made. For intermediate Ni content, both experiment and theory revealed the co-existence of cubic and tetragonal phases, along with the presence of various metastable magnetic conformations at room temperature. Considering nearest-neighbor polaron transfer in such energetically inhomogeneous landscape, a new hopping mechanism model is proposed, which consistently describes the temperature dependence of conductivity in these ternary alloy spinel oxide systems.

In addition, a printable NTC composite is demonstrated. It consists of a manganese-based spinel oxide powder dispersed in a benzocyclobutene resin. This printed sensor shown an excellent stability at different environmental temperature profiles and the choice of the binder led to a composite exhibiting less than 1°C change in resistance to humidity changes. Finally, sensors' scalability was validated by demonstration of a hand placed on a mat consisting of over 400 sensors where the outline and temperature changes were clearly resolved.

Περίληψη

Η θερμοκρασία αποτελεί σημαντικό παράγοντα στην καθημερινότητα του ανθρώπου και με τη χρήση αντίστοιχων αισθητήρων μπορεί να επιτευχθεί η καταγραφή και ο έλεγχος της. Υπάρχουν διάφορα είδη αισθητήρων θερμοκρασίας, μεταξύ των οποίων οι αισθητήρες τύπου θερμίστορ με αρνητικό συντελεστή αντίστασης (NTC). Συνήθως είναι κατασκευασμένοι από οξείδια σπινελίων και λόγω του μεγάλου εύρους θερμοκρασιών που καλύπτουν κατέχουν εξέχουσα θέση. Η ανάγκη για επιφάνειες που να μπορούν να καταγράφουν τη χωρική και χρονική μεταβολή της θερμοκρασίας κρίνεται σημαντική για πολλές εφαρμογές. Η υλοποίηση τέτοιων επιφανειών απαιτεί την εναπόθεση εκατοντάδων αισθητήρων σε μεγάλες περιοχές, και αυτό επιτυγχάνεται ιδανικά με τεχνολογίες εκτύπωσης. Ωστόσο, σημαντικό εμπόδιο στην χρήση τέτοιων τεχνολογιών είναι η πολυπλοκότητα και οι υψηλές θερμοκρασίες που απαιτούνται κατά την κατασκευή τους σε συνδυασμό με τα άκαμπτα υποστρώματα. Συνεπώς, κρίνεται δύσκολη η ενσωμάτωση τους σε μεγάλες ή/και εύκαμπτες επιφάνειες, σε συνδυασμό με την κατανόηση του μηχανισμού αγωγιμότητας τους.

Σε αυτή τη διδακτορική διατριβή, μελετάμε το μηχανισμό αγωγιμότητας κραμάτων τριμερών οξειδίων των σπινελίων Zn_{0.5}Ni_xMn_{2.5-x}O₄ και Zn_xNi_{0.5}Mn_{2.5-x}O₄, με την περιεκτικότητα των νικελίου (Ni) και ψευδαργύρου (Zn) να κυμαίνεται μεταξύ $0 \le x \le 1.25$ αντίστοιχα. Η μελέτη ως προς την αγωγιμότητα των κραμάτων, κατέληξε σε μια ασυνήθιστη εκθετική εξάρτηση με τη θερμοκρασία, η οποία σχετίζεται κυρίως με τα δομικά χαρακτηριστικά τους. Ειδικότερα, για το σύστημα με την προσθήκη νικελίου, πραγματοποιήθηκαν και θεωρητικοί υπολογισμοί (DFT) εστιασμένοι στις δομικές και ηλεκτρονικές ιδιότητες. Συγκεκριμένα για τις ενδιάμεσες περιεκτικότητες Ni, παρατηρήθηκε τόσο μέσω των πειραματικών αποτελεσμάτων όσο και μέσω των θεωρητικών υπολογισμών η συνύπαρξη κυβικών και τετραγωνικών φάσεων μαζί με την παρουσία μετασταθών μαγνητικών διαμορφώσεων σε θερμοκρασία δωματίου. Λαμβάνοντας υπόψη τη μεταφορά πολαρονίου σε πλησιέστερο ιοντικό γείτονα (nearestneighbor polaron) σε ένα ανομιοιογενές ενεργειακό τοπίο, προτείνεται ένα νέο μοντέλο μηχανισμού αγωγιμότητας (τύπου hopping), το οποίο περιγράφει ακριβώς την εξάρτηση της αγωγιμότητας με τη θερμοκρασία σε αυτά τα υλικά.

Επιπλέον, παρουσιάζεται ένας εκτυπώσιμος αισθητήρας θερμίστρ τύπου NTC ο οποίος κατασκευάστηκε με τη χρήση ενός μικτού υλικού. Αυτό αποτελείται από ένα σύνθετο οξείδιο σπινελίου με βάση το μαγγάνιο σε μορφή σκόνης, διασκορπισμένο σε πολυμερές υλικό, ρητίνη βενζοκυκλοβουτενίου (BCB). Ο εκτυπώσιμος αισθητήρας έδειξε εξαιρετική σταθερότητα σε διαφορετικές θερμοκρασίες περιβάλλοντος και η επιλογή του συγκεκριμένου πολυμερούς ανέδειξε την αντοχή του σε διαφορετικά επίπεδα υγρασίας, με μεταβολή στην αντίσταση λιγότερο από 1°C. Τέλος, η επιτυχής εναπόθεση των αισθητήρων πάνω σε μεγάλες επιφάνειες επιβεβαιώθηκε με την επίδειξη ενός χεριού τοποθετημένου πόλυω το περίγραμμα του χεριού και οι αλλαγές της θερμοκρασίας αναδείχθηκαν εμφανώς.

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Acronyms

NTC	Negative temperature coefficient
РТС	Positive temperature coefficient
J-T	Jahn – Teller
XRD	X-ray diffraction
SEM	Scanning electron microscopy
EDX	Energy-dispersive X-ray
RT	Room Temperature
ATR	Attenuated total reflectance
PET	Polyethylene terephthalate
PEN	Polyethylene naphtholate
PI	Polyimide
OPVs	Organic photovoltaics
RTDs	Resistance temperature detectors
ICs	Integrated circuit sensors
Eg	Bandgap
PEEK	Polyetheretherketone
AC	Alternating current
SAM	Self-assembled monolayer
XPS	X-ray Photoelectron spectroscopy
VFT	Vogel-Fulcher-Tammann
NNH	Nearest neighbor hopping
VRH	Variable range hopping
VE-NNH	Variable energy – nearest neighbor hopping

List of Publications

Peer reviewed Journal Publications

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Katerinopoulou D, Moschovis K, Gagaoudakis E, Aperathitis E, Binas V, Kiriakidis G. A Comparable Study on ZnO based Room Temperature Ozone Sensing Characteristics utilizing Conductometric and Surface Acoustic Waves Techniques. Madridge J Nanotechnol Nanosci. 2017; 2(1): 44-51. doi: 10.18689/mjnn-1000109

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Chapter I

Introduction

The energy demands of human activity in the modern world, are increasing with serious consequences for the ecological footprint of humanity. For this reason, the use of alternative energy sources as well as energy efficient devices are of fundamental importance. Sensors have a decisive role to this direction and can provide the necessary information for more efficient control. An example of the energy management approach is the "smart buildings" in which installed sensors monitor the environment and support the use of devices to meet different needs. This category mostly covers the detection of physical quantities, such as light, temperature, position and mechanical stimuli.

Temperature is one of the most important factors in our daily lives. Regulation and control of temperature is a necessity in an abundant number of applications not only in domestic and industrial fields but also in medical processes. A variety of temperature sensors are available to serve such purposes. Depending on the application used, they should be characterized by high sensitivity, durability and reproducibility.

Thermistors, is one of the main types of temperature sensors that are used in a variety of applications. They are normally used to protect a circuit against inrush over-voltage or

against over-current conditions and to a lesser extent as temperature sensors. Consequently, accurate determination of temperature is of critical importance.

In the last decades, technology has been focused to the development of flexible electronics. An emerging topic in tomorrow's electronics industry is that of printed flexible and stretchable devices. It promises a paradigm shift in production process as well as the way future electronics are perceived and implemented. The prospect of developing flexible printed sensors over large areas opens up new applications such as low-cost sensing devices. On this direction, the lack of a stable and accurate printed temperature sensor is a major obstacle to realizing these kinds of applications. Currently all reported printed temperature sensors suffer from undesirable instabilities, hampering their wide practical commercial use.

1.1 Research questions

In this PhD thesis, synthesis and characterization of spinel oxides are presented. Subsequently, the vibrational and electrical properties of two co-ternary alloys are studied, followed by theoretical calculations in order to realize whether experiment data meets the predicted theory and vice versa. In addition, a more complex spinel oxide is investigated as a printed temperature sensor. The main research questions that have been addressed during this work are:

- i. Can co-ternary spinels enhance the performance of thermistor type temperature sensors?
- ii. Can the manganese-based materials system give accurate temperature measurements with high sensitivity?
- iii. Which is the exact transport mechanism in manganese-based spinel oxide alloys which results their excellent response?
- iv. Are the structural properties related to their transport?
- v. Is the printing technique suitable in order to realize a temperature sensor with competitive characteristics?
- vi. Can a composite maintain the properties of a bulk ceramic material?

1.2 Goals and Scope

This thesis aims to investigate new ceramic materials as components in innovative thermistor type temperature sensors. This is achieved initially by studying the structural, vibrational of the ceramic spinel oxide alloys with different compositions and by differentiating by cooling procedures. It also aims to understand the charge transport mechanism by applying different models, like the Arrhenius type and Mott's theory for transport and concluding to a **new variable energy model**. Moreover, this study complements the structural and electrical characteristics through density functional theory calculations. Finally, the goal is concluded by integrating, with the screen-printing technique, a temperature sensor on a large area and flexible substrate by defining a composite. The aim was that, the performance of these new generation sensors can be characterized by high strength and durability. Based on the ceramic materials used, these new structures are characterized by high accuracy, with the mean of large changes in their electrical characteristics to very small changes in temperature and high reliability in measurement, that is a high degree of conformity of the measurements and actual value. Moreover, this study aimed to prepare thermistors that will be distinguished by stability over time and good thermistor performance (B-value > 3000 K and low resistivity). In conclusion, this work contributes to understanding the cause of the environmental stabilities of the printed composites and evaluate the mechanical properties of the printed sensors.

1.3 Thesis structure

This PhD thesis consists of 7 chapters. In this first chapter, a brief introduction and some basic information in regards to the thesis are presented. Specifically, research questions, goals and the scope of the work, as well the thesis structure are submitted.

In the second chapter, a theoretical background is given. In this chapter, an intro on printed and flexible electronics is introduced. After that, a section on temperature sensors and the common types that are widely used, with orientation on thermistors properties and their applications is considered. The chapter continues with the definition of spinels and the spinel structure and concludes with the theory behind the charge transport mechanism with a brief intro in polarons.

Consequently, the experimental part is presented. Specifically, in chapter III the experimental procedures are elaborated. The samples that have been fabricated and methods used together with the techniques, instrumentations and the design of a home-made set up which used for the electrical characterization are conferred in details.

In the following chapter IV, the as prepared spinel oxide alloys are presented along with their structural and morphological characterization, as well as their vibrational properties are analyzed. In this chapter, part of the experimental data is compared with theoretical calculations in view of the expected structures.

Chapter V, elucidates the electrical characteristics of the ceramic materials. This chapter begins with the general approximation of the Arrhenius relationship. Moves forward with the examination of the most common model used describing the transport mechanism in spinels and concludes with a proposed model for resistance functional dependence on temperature. Also, with the density functional theory calculations of polytypes bandgaps distributions the proposed transport model is clarified.

In the sixth chapter, the fabrication procedure where the performance of the ceramic is combined with the flexibility of a polymer binder is presented, realizing an environmentally stable screen-printable composite temperature sensor. Concluding, we are demonstrating a mat with hundreds printed sensors on top, showcasing the accurate measurement in regards of temperature of a hand placed on it. Finally, discussion follows highlighting conclusion remarks are given in Chapter VII.

Chapter II

Theoretical Background

2.1 Printed and Flexible Electronics

Historically, the term printed electronics was first phrased by the German engineer Albert Hanson back in 1903 when he described flat foil conductors laminated to an insulating board in multiple layers^[1]. Nowadays, printed electronics is often considered to be part of flexible electronics. It refers to the method used to create electronic devices by printing them on various (often flexible) substrates. Even though printed and flexible electronics are not new technologies, they have succeeded an increasing development over the years. According to IDTechEx, the market in 2020 worthed \$41.2 billion and it is expected to grow up to \$74 billion in 2030^[2]. Their growth, is based on the advantages they present and therefore the benefits provided to users. Compared with silicon technologies, flexible electronics are lightweight, portable, low-cost in regards to manufacture, since the substrates that are used are cheaper compared to rigid substrates, they are innovative and can be more easily recycled compared to conventional electronics^[3]. Another significant advantage is the possibility of fabrication/printed over a large area^[4]. Printed flexible and stretchable electronics are perceived and implemented.^[5] In applications where thin,

flexible, and stretchable properties are required, printed sensors detecting a multitude of parameters represent an elegant solution.^{[6][7][8][9]} Printing techniques that are commonly used include: screen printing, inkjet,^[10] offset lithography and gravure.^{[4][11]} Typical imprint rigid and robust substrates used are glass and silicon. The new technological era for flexible electronics turned the attention to the use of Poly(ethylene terephthalate)-(PET),^[12] Poly(ethylene naphthalate)-(PEN)^[13] for moderate temperatures (max 150°C) and poly(imide)-foil (PI) for higher temperatures up to 300 °C^[14] as well as paper (cellulose)^[15] even though the wettability and roughness are still the main bottlenecks.

Printed and flexible electronics cover a wide range of applications, including both consumer and industrial segments. In the energy sector, organic photovoltaics (OPVs)^[16] opened up applications in solar energy. Flexible electronics are also used for other energy application such as batteries^[17] and capacitors,^[18] although these are still very much under development. In electronic devices and appliances, for instance, the new trend is foldable smartphones and displays. The future for wearable electronic devices is brighter. Already many studies have been performed in this direction with the use not only of plastic substrates but also textiles,^[19] so that clothes could interact with touch gestures, measure body values and activate digital services. Moreover, they are used in medical procedures, electronic skin,^{[20][21]} UV radiation tracking patch^[22] and many more. The highlight in this area is that the products have the potential to be used on and in the human body, since when organic materials are used, better compatibility with the human bio-system is possible as compared to silicon-based alternatives.^[23]

2.2 Temperature sensors

Temperature sensors are devices that provide accurate temperature measurements through an electrical signal. As already mentioned in Chapter I, temperature sensors occupy a wide range in many areas in our daily life. Depending on the application, the selection is based on some of their characteristics. These are, the required temperature range, accuracy, cost, linearity, sensitivity and response time. Temperature sensors can be categorized based upon the connection mode into contact and non-contact.^[24] Within these categories there are four main types in use. The most common commercially available (Figure 2.1), in various types, shapes and sizes^{[25][26]} are listed below:

- Resistance Temperature detectors (RTDs)
- Thermocouples
- Integrated circuit sensors (ICs)
- Thermistors



Figure 2.1 Various types of temperature sensors (a) RTD, (b) Thermocouple, (c) Thermistor and (d) IC Obtained by <u>https://realpars.com/tag/ptc-thermistors/</u>

2.2.1 Resistance Temperature detectors (RTDs)

A resistance temperature detector is a sensor that measures temperature using the basic principle of the metal resistance change upon temperature changes.^[27] RTDs are mostly made by platinum wires wrapped around a ceramic or glass core, making them more expensive compared to other types. Besides, other conducting metals can be used like copper and nickel,^[28] which have the merit of low price in contrast to platinum but are less accurate when operating at high temperatures^[29]. Based on the resistance that is measured in a given type of metal, we can determine what the temperature is. Their main advantages are the high level of accuracy, making them the best choice in situations where temperature measurement is critical, as well their response, where direct (linear) and repeatable relationship between resistance and temperature occurs.

2.2.2 Thermocouples

Thermocouples consist of two dissimilar metals, joined at one end forming a junction. This junction is called the sensing junction and is connected with extension wires.^[30] When the temperature changes a voltage is produced based on the Peltier effect. Thermocouples, are used in many applications due to the robustness and size; they are low in cost; the response time can be characterized medium to fast and most importantly they cover a large temperature range (-210 °C up to 2300 °C). It should be noted that the wide range of temperature can be achieved by using different types (such as J, K, N, T and more). Their main disadvantages are the low sensitivity and accuracy as well as their non-linear response.^[31]

2.2.3 Integrated circuits (ICs)

An integrated circuit (IC) is an electronic circuit on a piece of a semiconductor material (usually silicon). An IC is a two terminal temperature transducer that produces an output current proportional to the absolute temperature. In the weaknesses are accounted the narrow temperature range and the need for a power supply. On the contrary, the highly linear output over the operated temperature window and the low cost make them suitable for specific applications. An example of an IC sensor is shown in Fig.1.1d.

2.2.4 Thermistors

Thermistors are thermally sensitive resistors (**Therm**al + Res**istors**). Most like RTDs, thermistors rely on the change of electrical resistance to measure temperature^[32]. Although these two types have a few similarities, there are several differences that make them a good alternative in some situations. The materials they are made-off, can vary depending on the thermistor to be used. With that said, they are all operate in a similar way. What makes thermistors special is that they exhibit large change in resistance proportional to small change in temperature.^[24] Usually, they are made of metallic oxides, pressed into a bead, disc or cylindrical shape and then encapsulated with an impermeable material, like epoxy

or glass depending on the temperature range that is being measured (**Figure .1(c**)). Thermistors are categorized into two types:

- Negative Temperature Coefficient (NTC)
- Positive Temperature Coefficient (PTC)

The NTC are commonly used to measure temperature. The resistance in NTC thermistors drop with temperature, while in PTC increases with the temperature. In both types the correlation of resistance change to temperature is not linear. Occasionally, self-heating effects could take place causing inaccurate temperature readings, because of the current flow passing through them. On the advantages of thermistors are, the low cost due to their small size and the ability to, can measure changes in temperature faster than RTDs.^[33] Tin general, they can provide better accuracy within the range they measure^[34].

2.3 Electrical properties of thermistors

2.3.1 Conductivity and Temperature dependance

The electrical characteristics of ceramics are more complex than in semiconductors. The conductivity might be electronic or ionic due to electron or ion movement respectively. The resistivity depends on temperature according to the following Arrhenius equation:

$$\rho(T) = \rho_{\infty} exp\left(\frac{E_a}{k_B T}\right) = R_{\infty} exp\left(\frac{B}{T}\right)$$
(2.1)

where, ρ_{∞} is the resistivity at infinite temperature, E_a is the activation energy for conductivity and k_B is the Boltzmann's constant^{[35][36]}. The second part of Eq. 2.1 is a rewriting of the initial terms of resistance with the precondition that the device has fixed dimensions, where, R_{∞} is the resistivity at infinite temperature and B is a material constant (B-value, in Kelvin), directly related with the activation energy for conduction. Note that in this thesis, we will elaborate and present all the data and the analysis in terms of resistance (R). As it is apparent from this formula the resistance exponentially decreases as temperature increases, which is a typical characteristic of NTC thermistors, as already mentioned in section 2.2.4. Typical NTC thermistor B-values given anywhere range between 3000 and 5000K^{[37][38]} and can be calculated by using the following Equation 2.2 with R_1 , R_2 the resistances at measured temperatures T_1 , T_2 respectively.

$$B = \frac{T_1 \cdot T_2}{T_2 - T_1} \ln \left(\frac{R_1}{R_2}\right) \tag{2.2}$$

Differentiation of equation 2.1 results to the sensitivity coefficient α (% / °C). It is also called temperature coefficient of resistance since is the rate of resistance change with temperature to the resistance at specific temperature.

$$\alpha = \frac{1}{R} \cdot \frac{dR}{dT} = -\frac{B}{T^2} \tag{2.3}$$

As it can be concluded from Eq. 2.3, by increasing temperature the sensitivity decreases. This automatically imposes the need for materials/devices with high B-values. In practice, the linear approximation of the Arrhenius Eq. 2.1 is accurate over a limited temperature range.

2.4 Spinels

Spinels in mineralogy are referred to, as a class of minerals represented by the general formula AB₂X₄, and owe their name to the mineral MgAl₂O₄ where A is a divalent cation (A²⁺), B is a trivalent cation (B³⁺) and X can be an anion from the family of chalcogenides, such as oxygen (O), sulfur (S) or selenium (Se) etc.^[39]. Alternatively, there could be another cation combination with A⁴⁺ and B²⁺, maintaining in any case the valence equilibrium. It is noteworthy that some elements, especially transition metals, like Mn and Co have multiple valences and can occupy both A and B sites. Spinels are classified into tree types, namely normal, inverse and complex. The difference between them is the cation distribution and consequently the general formula changes. Hence, for the normal t is the reported AB₂X₄ and for the inverse could be denoted as B[AB]X4^[40]. In order to understand also the complex type, a more accurate format of A_{1-λ}B_λ(A_λB_{2-λ})X4 is introduced, where λ is the degree of inversion and defines the fraction of A ions on the octahedra. Therefore, when $0 < \lambda < 1$ reflects the complex Spinel and for the extremes 0 and 1 the normal and

inverse respectively^[41]. The λ factor can be influenced by temperature, the size of ions, covalent bonding effects and the crystal field stabilization energy (CFSE)^[42].

Spinels containing transition metal ions are a class of materials with a broad range of industrial interest, including sensors, such as gas sensors serving the demand for monitoring of harmful and toxic gases, in electrochemical storage and conversion^[43], like Li-ion batteries^[44] and (photo)catalytic applications^[45]. Regarding temperature sensing implementations, they are used in thermistors, devices whose resistance is strongly temperature dependent^[6].

2.4.1 Crystal structure of spinel oxides

The crystallography of spinels has been determined by Bragg^[46] and Nishikawa^[47] back in1915. The crystal structure is described to be the closed-packed cubic, in the space group $Fd\overline{3}m$ in Wyckoff notation, (No. 227 in the International Table of X-ray Crystallography)^[48]. The unit cell consists of 8 FCC cells. The anions, usually oxides (O²⁻), occupy the FCC lattice points. Since the effective number of ions per unit cell of FCC is four, the number of oxides anions in the unit cell is $(8 \times 4) = 32$. In the case of the normal spinel, the A cations occupy the 1/8th of the centers of tetrahedrally coordinating positions. Given that, the number of the tetrahedral voids per unit cell of FCC is 8, so the corresponding A cations number is $8 \times (1/8 \times 8) = 8$. The trivalent B cations occupy half of the centers of octahedrally coordinating positions. Considering that the number of octahedral voids in FCC is 4, the number of B cations is equal to $8 \times (1/2 \times 4) = 16$. From these calculations the ratio of A^{2+} : B^{3+} : $O^{2-} = 8:16:32 = 1:2:4$. Thus, confirming the general formula $(A)[B_2]O_4$, with the parenthesis representing the tetrahedral site and the brackets the octahedral^[42]. In the inverse spinel, all the A^{2+} ions occupy the octahedral voids, one half of the B^{3+} ions occupy the tetrahedral voids and the other half the octahedral sites; hence, the empirical formula becomes (B)[AB]O₄.

In the FCC there are two types of sub unit cells as shown in Figure 2.2. With the yellow circles are represented the oxide ions, the blue circles represent the A^{2+} cation and with the orange the B^{3+} cations. In each sub unit cell, the oxide ions are occupying FCC lattice points, as already mentioned (Fig**Figure** . 2.2a). In the one type (Fig. 2.2b) there are two

divalent cations occupying tetrahedral voids, whereas the trivalent cations partially occupy the edges centers as well as the centers of the cube which represent the octahedral voids. For the sake of clarity only one octahedral void is shown in the sub unit cell-2 in Fig.**Figure** 2.2c. Visualizing the sub unit cell-1 it is clear that the AO₄ tetrahedra are unconnected to each other, where the BO₆ octahedra are edge sharing. In the sub unit cell-2, six edge centers and the center of the unit cell are occupied by B³⁺ cations. The complete unit cell, with the 8 FCC cells can be constructed by arranging sub unit cell-1 and -2 alternately (Appendix I).



Figure 2.2 (a) Anions occupying FCC lattice points, (b) Sub unit cell-1, with two tetrahedral voids, (c) Sub unit cell-2 with one octahedral void.

2.4.2 Jahn – Teller distortion

Even though it is well known that spinels crystallize in a cubic (Spinel) structure, it is often reported in the literature that they may formulate in the tetragonal (Hausmannite, space group I4₁/amd, No 141) structure, or in a transition from Spinel to Hausmannite and vice versa. This transition accompanied with the reduction of crystal symmetry, is known as Jahn-Teller (J-T) distortion. The Jahn – Teller effect describes the geometrical distortion of a non-linear molecule that reduce its symmetry and energy. This distortion typically observed in octahedral complexes. Also, it can be found in tetrahedral complexes but it is not pronounced. The J-T distortion depends upon the electronic state of the system. If a molecule with a specific symmetry occupies degenerate states, there is at least one nonsymmetric perturbation that splits the degenerate states and results to the lowering of

the energy system. In simpler words, the one cubic axis become elongated or compressed with respect of the other (Fig. 2.3). Without any other symmetry breaking, a parameter to refer to the tetragonal distortion is the ratio of the unit cell parameters, c/a.^{[49][50]}



Figure 2.3 Jahn-Teller distortion, elongation of the c-axis (cubic to tetragonal).

Among to various studies, phase transition is a result of temperature and composition dependences. According to Heiba et al. ^[51], ZnMn_{2-x}V_xO₄ ($0 \le x \le 0.4$) samples prepared by sol-gel method, shown a tetragonal phase for x < 0.4 where beyond that point other minor phases are present. On the other hand, Zn-substituted manganese ferrites exhibit cubic spinel structure with single phase^[52]. Guo et al.^[53] prepared by a wet chemical method, Mo modified MnFe₂O₄, where the undoped samples fitted well with the spinel structure, while introducing Mo impurities were observed. Regarding different reduction temperatures, MgFe₂O₄ pellets produced and the XRD peaks were indexed by Fd3m space group^[54]. For the complex system of Mn_{1.95-x}Co_{0.21}Ni_{0.84}Na_xO₄ the analysis with reference to calcination temperature shown a cubic phase for temperatures up to 900°C. For temperatures higher than 1100°C impurities of Na_{0.7}Mn_{2.05} observed. In parallel, the study of Na-doping shown the maintenance of cubic structure after x=0.03^[55]. The study on cobalt manganates spinels revealed that the structure strongly depends on the composition

and temperature. More specifically, $Mn_{1+x}Co_{2-x}O_4$ for x=0, 0.25, 0.5, 0.75, 1.0 & 1.5 were fabricated by the EDTA gel process. For x=0 and 0.25 the cubic structure observed over the whole range of temperatures ($373 \le T \le 1073K$), while the other compositions exhibited both tetragonal and cubic structures; with the cubic phase being dominant for the higher temperatures^[56]. In respect to different processing routes, (Ni,Co,Mn)O₄ samples were prepared. XRD data verified that conventional sintering and spark plasma sintering (SPS) with micro-size powder have a mixture of tetragonal and cubic phase while SSP with nanopowders crystallized in a pure cubic phase according to Han et al.^[57]. For the quaternary system of Ni_{1-x}Zn_xMn₂O₄ ($0 \le x \le 1.0$) the structural analysis shown a single cubic phase for x=0, 0.1, 0.2, 0.25 and 0.4. With increasing Zn content a mixed phase (cubic & tetragonal) detected while for x=1 the single tetragonal phase was formed.^[58]

2.4.3 The Nickel Manganese spinel oxide system

For decades, the attention to study nickel manganite spinel (NiMn₂O₄) arises from the unusual electrical properties which are important in the commercial manufacture of NTC thermistors and not only. The first studies focused their interest on the cation distribution in order to explain their electrical conductivity. Back in 1986, Macklen E. D.^[59] realized that valence distribution and an extent conductivity could be controlled by the degree of inversion factor. Thus, confirmed Braber and Terhell^[60] who suggested the following distribution in the stoichiometric NiMn₂O₄ system:

$$Ni_{1-y}^{2+}Mn_{y}^{2+}(Ni_{y}^{2+}Mn_{2(1-y)}^{3+}Mn_{y}^{4+})O_{4}^{2-}$$

in which, parameter y is a variable determined by the temperature history of the sample, showing a remarkable change in conductivity above 450°C. Other groups proposed that only Mn^{3+} is present on both tetrahedra and octahedra imposing an insulating character^[61] and claim that Mn^{2+} are thermally generated in order to explain their semiconducting nature^[62]. Fritsch et al. ^[63] reported the distribution of cations in the spinel structure via neutron diffraction. It was found that the manner in which samples are cooled after sintering affects the Ni site occupancy. A Ni_{0.8}Mn_{2.2}O₄ sample was sintered with two different ways a) at 1160°C and cooled at a rate of 5°C/min and b) at 1160°C and then

quenched at 900°C. The resulted distribution shown that after slow cooling only few Ni cations occupy A-sites, since Ni²⁺ favored to inhabit the B-sites. The opposite behavior was exhibited by the quenched samples, suggesting that the degree of inversion decreases at elevated temperatures^[63].

Schmidt et al.^[64] screen print ceramic NiMn₂O_{4+ δ} films on alumina substrates with the powder synthesized via co-precipitation method and temperature dependent measurements over the range of 122–345 K were performed. After fitting their experimental data to various models, they conclude that the conduction is attributed to variable range hopping between Mn of different valence in the octahedra sites. Two years later the same group enhanced their results through AC impedance spectroscopy, while RC (resistancecapacitance) element shown resistance vs temperature characteristics similar to the DC variable range hopping model^[65] with parabolic density of states (DOS) also confirmed via scanning tunneling microscopy.^[66] Additionally, NTCR thermistors produced by the spray pyrolysis technique has shown the cubic phase as the main structure of the deposited thin films. Likewise, AC and DC conductivity measurements revealed that the charge transport process agrees with the VRH model.^[67] The sintering method is an important factor for the single-phase formation, Ma et al.^[67] resulted that the two-step sintering method gives high crystallinity with uniform microstructure, low resistivity and adjusted properties of thermistors. Further thermistor films deposition via electron beam evaporation technique using ceramic oxides materials resulted in a cubic phase for annealing temperatures higher than 750°C. The conductive behavior of MNO spinel films was less at low temperatures (650 °C) due to the interdiffusion of Ni/Mn cations.^[68]

In 1989 Tang demonstrated a metastable single-phase region of cubic spinel below 400°C between the compositions 0.6 < x < 1.2 as shown in Fig. 2.4. The large region immediately to its left is a dual phase region of spinel and NiO, a rock salt structure. The spinel phase was larger when higher oxygen partial pressure was used. The far right of the diagram shows the Mn₂O₃ forming for intermediate temperatures while for higher temperatures the tetragonal Mn₃O₄ formed.^[69]



Figure 2.4 Phase diagram for the thermal decomposition of $Mn_{3-x}Ni_x(C_2O_4)_3*6H_2O$. *Produced by Tang et al.*^[69].

2.4.4 The Zinc Manganese spinel oxide system

Among the various spinel oxides could be found in the literature, there are only few studies up to date addressing zinc manganese. $ZnMn_2O_4$ is a functional material with potential applications as NTC thermistors^[70] due to the unique electrical properties and lately are commonly used as a cathode for Zn-ion batteries because of their excellent electrochemical properties.^{[71][72]}

In 1963 M. Rosenberg et al.^[73] studied the crystal symmetry and the electrical conductivity as a function of the composition and temperature for the $Zn_{1+x}Mn_{2-x}O_4$ ($0 \le x \le 0.2$). They claimed a tetragonal distortion at room temperature for the reported composition and proposed the following cation distribution:

$$Zn^{2+}(Zn_x^{2+}Mn_x^{4+}Mn_{2-2x}^{3+})O_4^{2-}$$

According to their , the electrical conductivity involves hopping mechanism of electrons between Mn^{3+} and Mn^{4+} at the octahedra sites.^[73] Contrary to previous spinel systems, zinc manganese have not been studied in details regarding their transport mechanism since most reports deled with their structural and magnetic properties.^[74] R. Cherbi et al.^[75] explained that Mg-doped ZnMn₂O₄ exhibit conduction which is associated with the small polaron hopping and it is attributed to the bands nature of cationic character.
A study for the phase diagram performed by Blasco and Carcia^[76] for Zn-Mn-O system was made at low temperatures between 450°C and 750°C and analysis indicated the existence of cubic spinels in the system, appeared to be stable at low temperature ~600°C in a narrow composition range (x~1.6–1.7). Upon heating, a structural phase transition was observed giving rise to a tetragonal spinel. This single phase was reduced for T=700°C and shifted to lower composition values (x~1.55) as it can be seen in Fig. 2.5. A couple of years later, Peiteado et al. presented results on nitrogen quenched samples Zn_xMn_{3-x}O₄ for higher temperatures. The spinels, according to the XRD data, exhibited cubic symmetry for temperatures below 650°C and a tetragonal symmetry with increasing temperature for x=1, 1.26, 1.41, 1.67 and 2.^[77]



Figure 2.5 Proposed phase diagram for part of the Zn–Mn–O system in air up to 700°C. H, Z, C and T stands for hetaerolite, zincite, cubic spinel and tetragonal spinel phases, respectively. T* indicates that secondary C-phase is also present and the exact amount depends on the cooling process.^[76] Reprint from J. Solid State Chem., 179, J. Blasco, J. García, Stable cubic spinels in the Zn-Mn-O system in air, 2199-2205, © 2006, with permission from Elsevier Inc.

2.5 Transport mechanism

For understanding the conduction mechanism in transition metal oxides where the interaction between charged carriers and phonons is strong, many theoretical and experimental studies have been performed.^[78] The ongoing research manifest polarons as the predominant particles impacting on the materials properties and functionalities.^[79] Polaron models are used in a variety of groups of materials for realization of the charge transport, such as ceramics^[80] and polymers. Consequently, in the following subsections a brief introduction in the hopping transport, polarons and the small polaron hopping will be elaborated.

2.5.1 Hopping transport

The hopping transport theory was first introduced as an idea in semiconductors. In low doped or heavily compensative semiconductors the usual transport radically difference than the transport due to freely moving carriers in a conduction or valance band. In those case transport in mainly dictated by hopping of carrier between sites. Hence, considering the situation below the mobility edge in the bandgap (E_g) there are states randomly distributed due to impurities or dopants and carriers can hope from an occupied to an unoccupied site strongly localized in the bandgap.^[81] To quantitively understand the connection between transport properties and hopping from site to site, the Abraham and Miller model is a description where the overall transport of hopping between cations with

different valances and can be deemed as a percolation of carriers in a random resistor network. So, between two sites a resistor can be imagined that corelates with the probability of hopping of a carrier of site i to site j (Fig. 2.6). ^[82]. It is based on the separation of localized donors and acceptors in real and energy space. In this theory, the resistance is dominated by resistors close to the percolation threshold, ξ_c . In this random network the resistances



Figure 2.6 Representation of a random resistor network.

 (R_{ij}) between any other site can vary largely due to the exponential function dependence on the percolation parameter. Additionally, as mentioned the resistance depends on the spatial and the energy picture of the sites, and in Fig. 2.7 is represented the main idea of hopping probability. In details, considering a carrier at an occupied state at the localized site, this carrier can hope to an unoccupied state to the nearest neighbor largely independently of the energy difference but the probability is strongly dependent of the spatial distance between those sites (r_{ij}) where this spatial distance arises from the overlapping wavefunction. The probability of such jumps, depend on the spatial distance parametrized by the parameter a that reflex the expand of the wavefunction at each site. On the other point of view, Mott introduced the idea that hopping can happen between more distant sites. In this case, the probability depends on the energy difference between those sites (ε_{ii}) and is normalized by $k_B T$ since it is related with phonon assisted jumping. Through this description it can be summarized that the contribution on the percolation between the sites *i* and *j* is coming from two parameters, the spatial overlap of the wavefunctions and the possibility of hopping to closely energy sites. By combining these two pictures, the resistance is given by the following general expression:

$$R_{ij} = R' \cdot exp\left(\xi_{ij}\right) = R' \cdot exp\left(\frac{2r_{ij}}{a} + \frac{\varepsilon_{ij}}{k_BT}\right)$$
(2.4)

where α is a localization length, k_B is the Boltzmann's constant and R' is a material related property. The percolation threshold is equivalent parameter to the ξ_{ij} that takes into account the whole statistics of the system and relates to the least resistance roots for transport between remote sites.

Depending on the dominant term in Eq. 2.4 the hopping conduction referred as nearest neighbor hopping (NNH) either variable range hopping (VRH). In the VRH model, the value ξ_{ij} is lower compared to NNH process since the pairs (acceptors, donors) are separated in an energy space^[83]. A formula that includes both cases can be expressed subsequently as:

$$R(T) = R_0 T^{\alpha} exp\left(\frac{T_0}{T}\right)^p \tag{2.5}$$

Therefore, the resistance as a function of T can be approximated, where R mainly depends on the exponential with reversed T and an exponent p. The values of exponents a, p and the parameter T_0 depend on the particular aspects of the hopping process. These values are different in different condition mechanism. In the low temperature regime, given a uniform density of states (DOS), Mott VRH model predicts a $p = \frac{1}{4}$, ^[84] while in the case of vanishing DOS at the Fermi level, due to Coulomb gap, Efros and Shklovskii^[85] calculated the exponents a = 2p and $p = \frac{n+1}{n+4}$ for a DOS functional dependence $g(\varepsilon) \sim |\varepsilon - E_F|^n$, where $g(\varepsilon)$ is a parametrized density of state and ε is the energy of charge with zero energy to the Fermi level. In the case of the non-adiabatic limit at higher temperatures, where the importance of spatial separation of hopping sites dominates, the NNH model is mostly applicable^[86] and the temperature dependence of resistance tends to an inverse Arrhenius one with the corresponding exponent values p = a = 1:

$$R_{NN}(T) = R_{NN,0} \cdot k_B T \cdot exp\left(\frac{T_0}{T}\right)$$
(2.6)

In order to elucidate the hopping motion of a certain system whether is VRH or NNH, all needed is to determine the p value. Also, it should be noted that in ceramic materials, the hopping conduction could be from the grain but also from the grain boundary.



Figure 2.7 Spatial and energy parameters of the percolation threshold ξ_{ij} .

2.5.2 Polaron

Apart from the hopping transport, an important aspect to understand transport in Spinel oxides is the idea of polarons. The roots of polaron theory, with the main idea being the electron self-trapping by a crystal lattice, are attributed to Lev Landau in 1933^[87], where explained the optical properties of alkali halides. Later in 1946 the term 'polaron' was defined by Solomon Pekar^[88]. According to their description in polarizable dielectric oxide crystals, there is always the possibility that the large effective mass of free charged carrier (electron or hole) interacts strongly with neighboring ionic species. This electrostatic interaction between the charged carrier and the lattice causes local lattice distortions.^[87] As a result, there is a change in the local potential (deeper potentials) around this point and self-localization is induced (Fig. 2.8). When the self-localized carriers interact with the lattice vibration (phonons) results in the formation of a quasiparticle called polaron.^{[89][90][82][91]} Thus, this quasiparticle is nothing else than the charged carrier dressed with a cloud of phonons, and regarding the range of interaction between electron (or hole) and phonons, a classification of small and large polarons can be addressed. The theories developed for small and large polarons are ascribed to T. Holstein^{[92][93]} and H. Fröhlich^[94] respectively, who formalized the dichotomy between small-radius and large-radius polaronic states by establishing quantum-field Hamiltonians.^{[95][96]} Small distortion with respect to the unit cell is called small polaron, while when the distortion extends beyond the unit cell is defined as large polaron. Their discrepancy can also be realized in terms of electron phonon coupling. When the coupling is strong, the electrons are localized around a single atom with their effect confined to nearest neighbors. Conversely, when the coupling is weak, long-range interactions are pronounced.^[89] Another distinguish between small and large polarons is their electrical transport. Large polarons have a band-like transport, while small polarons undergo hopping transport. In general, the most of the studies are focused in small polarons.



Figure 2.8 Schematic representation of small polaron in crystal. a) undistorted lattice, the gray circles are the O sites b) Self-trapped configuration, the charge (e^{-}/h^{+}) is localized on the orange O atom. Graph inspired by Geneste et. Al.^[97]

2.5.3 Small Polaron Hopping

In spinels the underline transport mechanism is attributed to the small polaron hopping. Hereby will be described how the notion of small polaron is connected with the hopping transport. In Fig. 2.9 is a schematic given by Mott and Davis^[86] that explains the trapping of small polaron and how it is connected to the hopping mechanism. In the upper part (a) is depicted a periodic potential created by ions, which is periodically arranged. In the normal picture the electrons can be either localized or non-localized depending on the conduction band edge. If there is a strong interaction between these carries and the surrounding lattice which creates polarons, then the carriers have a localized wavefunction that extents to very few lattice periods as shown in Fig. 2.9b. Thus, instead of having a free electron there is a polaron potential (Fig. 2.9c) that is a result of the short-range extent of the wavefunction and the distortion of the lattice. This potential reflects the self-trapping of the polarons at the lattice sites. In the case of spinels, this potential reflects the localization of charged carriers close to ionic sites. As in consequence, there are polarons that they can hope from site to site through the phonon interaction.^[91]



Figure 2.9 (a) The potential energy of the electron in the undistorted lattice; (b) the wavefunction, (c) The polarization well.^[86]

Chapter III

Experimental Procedure

3.1 Introduction

In this chapter we will briefly describe the fabrication procedure of the ceramic materials employed to realize thermistors with high sensitivity and stability for the purpose of this thesis, as well as the experimental methods used for the materials and the device characterization. In the beginning, we will refer to the basic flow steps of the solid-state reaction method followed by the structural and optical characterization methods. Then the techniques and instrumentation used for the electrical characterization of the Mn-based NTC ceramics will be presented. Also, the home-made oil bath set up that we designed in order to take more accurate measurements on the electrical properties of the bulk materials will be demonstrated.

3.2 Materials synthesis

3.2.1 Solid state reaction

For the preparation of ceramic powders there are several methods. Solid-state reactions are widely used. The solid-state reaction is a method to obtain polycrystalline material from solid reagents. Usually, this method employs high-temperatures since the solids do not react together at room temperature. In solid state reaction at least one reagent should diffuse into the other so that the reaction may be initiated and propagated. Solid state reactions are mainly classified as reactions involving a change in physical composition (e.g., from solid to vapor) or not such as sintering and phase transition, therefore are used to synthesize raw particles and to sinter advanced ceramics^[98]. The advantages of this synthesis procedure are: the cost efficient, mass production and easily controlling operating conditions. On the other hand, it is a time-consuming technique, especially when is used for the production of ceramic powders since high temperatures are needed which means that is not easy to deposit the material directly on a substrate.

It should be noticed that, in this thesis the detailed materials processing conditions will not be revealed, since they were used by the industry and thus are kept as trade secrets. Hence, only the basic steps for the fabrication of the NTC ceramic materials will just be mentioned. Also, in the literature there are no available processing conditions because a thermistor with commercially desirable properties is of high market value.

Fabrication steps

The reported materials were synthesized via solid-state reaction method also known as "shake and bake". Initially the metal oxides used, weighed in appropriate ratios and mixed on a roller bench for several hours. Further mixing with a dispermat bead mill with Zr marbles for the homogenization took place. Then the material was placed in an oven to dry. Later, pestle and mortar to break up agglomerates and obtain finer powders was used. The resulted powder was then sieved through a mesh followed by calcination of the powders at high temperature in an air oven for few hours. Note, that this step (calcination) serves the solid-state reaction between the metal oxides which result in a homogenous phase reaction and it's the reason controlling the desirable electrical properties of the materials. Following

calcination, the powders were cooled and placed again on the roller bench for further mixing. Then the materials were mechanically pressed into pellets with dimensions of 5mm in diameter and 1mm thickness. This is called the forming process, through which the material is formed into a shape (green body). The final step was sintering in an air furnace at temperature of 1250°C for several hours, resulting the ceramic nature of the pellets. Sintering consists of neck formation, where the particles are increasing their size and bonding, followed by shrinking the pores from large porosity to actually pore free bodies. Consequently, sintering was performed for densification purposes. Regarding the cooling of the materials, two different ways were employed. In the first one, the samples cooled in air with a constant rate and in the second they were quenched, meaning rapid cooled. Furthermore, Au contacts were deposited via evaporation on both sides of the pellets for the performance of electrical characterization (Fig. 3.1).



Figure 3.1 Top view of the ceramic pellets with (right) and without (left) Au contacts.

Samples

The synthesized materials consisted of two different ternary systems. In details, the first series with the composition of Mn2.5-xZn0.5NixO4 ($0 \le x \le 1.25$) is a Mn-based system substituted by Ni content while Zn element was kept constant. The second one was again a Mn-based system but this time Mn was substituted by the Zn element and the Ni kept constant with the corresponding formula being Mn2.5-xZnxNi0.5O4 ($0 \le x \le 1.25$). The resulting ceramic materials were investigated in terms of structural, vibrational and electrical properties in the pellet form.

For the printing of the temperature sensors, a complex system was used with the composition of Mn1.71Ni0.45Co0.15Cu0.45Zn0.24O4. This material was studied in a powder form for its structural characteristics and as a composite after been printed.

3.2 Structural properties

3.2.1 X-Ray diffraction

X-Ray diffraction (XRD) relies on the use of X-rays to obtain information about the structure of crystalline materials. A primary use of the technique is the identification and characterization of compounds based on their diffraction pattern. Specifically, with this technique one may measure the average spacing between layers of atoms; determine the orientation of a single crystal or grain; find the crystal structure of an unknown material; and obtain the size and internal stress of small crystalline regions^[99]. The ex-situ XRD is preferred because it is a non-destructive technique. However, there is the option of the insitu XRD in kinetic studies to follow the reaction progress. Here, for the ceramic pellets examined, a Bruker AXS D8 Advance copper anode diffractometer (CuKa radiation, $\lambda = 0.15406$ nm) equipped with a Nickel foil monochromator was used.

The X-ray analysis requires monochromatic radiation which cause a constructive and destructive interference of the scattered X-ray beam, generating a diffraction pattern which is the fingerprint of periodic atomic arrangements in a given material^[100]. The detector reads a signal only at the angles where constructive interference occurs. The incident X-ray beam is scattered at different planes of the materials. The signal is translated as XRD peaks, known as Bragg diffraction peaks. The constructive interference, comes out of with the precondition that the optical path difference, of two or more X-rays in the material, should be a multiple (n=1, 2,...) of the monochromatic wavelength λ . Hence, as Fig. 3.2 shows, for a set of crystalline planes with interplanar distance d and for a monochromatic wavelength λ , the Bragg diffraction occurs only when the incident X-ray beam forms angle θ with the crystal planes following the formulation:

$$n\lambda = 2d\sin\theta \tag{3.1}$$

where n: denotes the order of the reflection and is an integer number, λ : is the wavelength of the beam, *d*: is the perpendicular distance between pairs of adjacent planes and θ : is the angle of incidence (Bragg's angle). Eq. 3.1 is known as the Bragg's law.



Figure 3.2 Schematic representation of Bragg's equation.

The obtained diffraction pattern typically has many distinct peaks, which correspond to different interplanar spacings d. Specifically, for crystals with cubic structure the lattice parameter α , can be calculated by Eq. 3.2 and for crystals with tetragonal, the lattice parameters α and c by Eq. 3.3.

Cubic
$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{\alpha^2}$$
 (3.2)

Tetragonal

$$\frac{1}{d^2} = \frac{h^2 + k^2}{\alpha^2} + \frac{l^2}{c^2}$$
(3.3)

where *hkl* are the Miller indices and are used to index the atomic plane of the crystal.

3.2.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a technique that is used for surface imaging, where information about topography, morphology, and the chemistry of the material can be extracted. The surface of the specimen is scanned with a focused electron beam and an image with high quality and spatial resolution is created. The electrons of the incident beam interact with the sample, producing various signals. The interactions cause the X-rays emission of backscattered electrons (BSE), secondary inelastic electrons (SE) and Auger

electrons that can be used to acquire details about the surface topography and materials composition^[101]. Regarding the information that is needed, different electrons are collected. More specifically, for the sample's morphology with high resolution the secondary electrons are the most valuable, while X-rays are used for elemental identification based on the use of X-Ray dispersive (EDX) analysis technique. In this study, for the surface morphology an SEM JEOL JSM-6390LV operating at 20 kV was used, while the elemental analysis of the as prepared samples was obtained by an EDS, INCA PentaFET-x3.

Typically, an SEM instrument consists of an electron gun, which produces and accelerates the electrons. The gun is places at the top of the column in which the electrons travel through electromagnetic lenses and apertures that are used to focused the beam and define a small spot on the examined sample. The sample is mounted on a stage in the chamber area and both the column and the chamber are evacuated by a combination of pumps, in order to ensure the high energy electron beam. A signal detector and a computer are also used in order to display and view the image recording form the surface of the material^[102].

In the majority of SEM systems, the detection of SE emitted by atoms, is the most common mode used. The number of secondary electrons that can be detected depends, among other things, on the angle at which beam meets the surface of the sample. By collecting the SE that are emitted and by employing a special detector, an image of the surface is created (Fig. 3.3). Furthermore, the surface of the specimen should be conductive and grounded with the aim to avoid charge accumulation at the surface. So that, often the surface of the samples are covered with electrically conducting materials (Au, Pt or alloys of Au/Pd)^[103].



Figure 3.3 Schematic representation of a typical SEM.

Normally, modern full-sized SEMs provide resolution between 1-20 nm whereas smaller desktop system can provide a resolution of 20 nm or more. The maximum resolution depends on multiple factors, such as the electron spot size and interaction volume of the electron beam with the sample. While scanning electron microscopy cannot provide atomic resolution, few systems can achieve resolution below 1 nm.

3.4 Optical properties

3.4.1 Raman Spectroscopy

Raman spectroscopy measures molecular vibration to determine the chemical structure and identity of a sample thus identify the compounds present. It is a non-destructive technique and it is based to the interaction of light with the chemical bonds within a material^[104].

When a sample is exposed to monochromatic light in the visible region, the sample absorbs light and a big part of the light gets transmitted through the sample. However, a minor part of the light is scattered by the sample in all directions. The incident light has a particular frequency (v_i). If the scattered light has a frequency (v_s) same as the incident light ($v_s = v_i$), then the scattering is called Rayleigh scattering (or elastic scattering). Nevertheless, it has been observed that a small amount of the total scattered intensity occurs at frequencies different from the incident frequency ($v_s \neq v_i$) and this is known as Raman effect (or inelastic scattering). Raman scattering is a two-photon process. The electrons have different vibrational levels and they are defined by specific energy differences. When an incident monochromatic light interacts with an electron in the specimen, the electron absorbs energy from the incident photon and rises to a virtual state of energy (E=hv), where v is the frequency and h is Plank's constant. Then the electron returns back to the energy level by losing energy. As it can be understood, if the energy lost equals the energy of the incident photon, then the electron gets back to its initial vibrational level and emits another photon and consequently since they have same energy that implies same frequency as the incident photon resulting to the Rayleigh scattering. However, sometimes electrons, when losing energy from the virtual state, can return back to a different vibrational level. In this case the energy lost is different than the energy absorbed from the incident photon. As a result, the emitted photon has different frequency than the incident and this gives rise to the Raman scattering. Depending on the final vibrational level of electron, Raman scattering can be divided into Stokes and anti-Stokes energy bands. Raman shift is associated with these two different energy bands. Specifically, when the shift is at higher frequencies than that of the incident light defines the Stokes scattering and this happens when the electron absorbs energy. Similarly, a shift to lower frequencies defines the anti-Stokes scattering, meaning that the energy is released by the electron (Fig. 3.4b)^[105].

In this project we used a micro-Raman with a laser at wavelength $\lambda = 473$ nm, high resolution and spot size of 0.6µm and magnification ×50. In the resulting spectrum from a Raman spectroscopy, the vertical axis is the intensity of the scattered light and the horizontal axis is the wavenumber of the Raman shift in units of cm⁻¹.



Figure 3.4 a) Energy band for Raman effect and Rayleigh scattering b) Raman shift (Stokes and anti-Stokes).

3.5 Electrical characterization

3.5.1 Current – Voltage measurements

The electrical resistivity is the most common gauge, in order to quantify the material's opposition to current flow. There are two main methods that can measure the electrical resistivity of bulk materials, namely the two-point and the four-point. The choice of the technique is made according to certain characteristics, like the shape and type of the material and the thickness and the magnitude of the resistance. In this research the two-point uniaxial technique was used. With this method, the electrical resistance is defined as the resistivity against the current flow (charge movement) when a DC voltage is applied between the probes (Fig. 3.5). Through this technique, the bulk resistance is measured^[106]. The resistivity (ρ) is proportional to the resistance (R) obtained at the unit area/length of the specimen and is given by:

$$\rho = R \frac{A}{l} = \frac{VA}{l}$$
(3.4)

with *A* and *l* representing the cross sectional and length of the sample respectively on the SI unit of ohm meter. The resistance is calculating by applying the current measured by the multimeter into Ohm's law, as shown in the right part of Eq. 3.4, when homogeneous and isotropic materials are assumed. The resistivity of a material depends upon several factors such as environmental conditions, material doping and the geometry. Moreover, the examined materials resistivity can affect the characteristics of a device such as the, series resistance, capacitance, threshold voltage and other parameters. The inverse of resistivity $(1/\rho)$ is the electrical conductivity with units of Siemens per meter (S/m).



Figure 3.5 Two-probe method, to measure the electrical resistivity of a pellet.

3.5.2 Oil bath set up

An oil bath is a type of heated bath. It is used for many laboratory purposes such as to heat reaction mixtures or to filter particulates out of air. Since in this project we are working on temperature sensors, it is considered necessary to perform the temperature dependence measurements in an environment where the heating will be uniform and constant in the heating vessel and any loss from the system will be avoided. The use of an oil bath lurks and some disadvantages, such as the user exposure to physical hazards including spilling of the heating element (glycerol, silicon oil, mineral oil or medical paraffin) and obnoxious smells. Hence, it is clear that performing the measurements of the ceramic pellets in air and on a hotplate is not preferable. For this reason, we designed a homemade oil bath set up in order to serve these specifications.

The main parts of our set up are the vessel, the head of the vessel through which the electrical signal is transferred and the temperature controller as shown in Fig. 3.6. The set up chosen was fabricated by stainless steel to withstand breakage, since the measurements should withstand temperatures up to 300°C. In more detail, the vessel has a cylindrical shape with double walls. The thickness of each wall is 2 mm, the outer diameter is 16cm while the inner 13 cm. the height of the vessel is 22 cm with the inner height being approximately 14 cm and 2 cm left as an extension of the top. Glass wool was placed in the middle of the double wall for insulating purposes, to prevent the user from skin burns. Choosing the bath fluid is one of the most crucial points during the designing of an oil bath. The selected fluid was from Fragol, (FRAGOLTHERM® Q-HTF). This is a heat transfer fluid based on hydrogenated mineral oils used in a range of -18°C to 325°C. This fluid has been selected because offers high thermal stability compared with other mineral-based media and therefore has longer service life, even if it's working to the upper temperature limits. Furthermore, it's boiling point is at 380°C and in the case of thermal decomposition no toxic products arise since it has low tendency to oxidation. Here we should notice that we didn't overfill the vessel with the oil because it expands in volume when heated. Transparent marbles were placed in the vessel due to their high heat capacity. Regarding the head of the vessel, many factors had to be counted for the successful fabrication. Again, the outer part was made of stainless steel, while the part enclosed was the vessel is made

by a PEEK (polyetheretherketone) rod (25 mm diameter) by RS Pro with two cupper parts attached at the edges. Again, the main reason for choosing the PEEK rod as a material was the temperature range it can be used (up to 260°C), it's light-weight and its strength to survive longer operational periods under harsh conditions compared to other materials. The cupper parts served the electrical conduction of the pellets. That was achieved with the use of pogo pins on each side. Exactly on the top of the pellet and through the PEEK rod, a thermocouple was placed. The type K thermocouple was selected due to its wide ambient temperature specification and measurement range (-100°C to 450°C) with a response time of 0.1 sec. This sensor is made by a Fibre Glass wire constructed as a twisted pair and the wire is alloys of NiCr / NiAl. The thermocouple coupled with the temperature controller (Shimaden), from which the desired temperature was set each time. Before the measurements the PIDs (proportional Band, Integaral time constant and derivative time constant) of the controller were adjusted accordingly. At the bottom of the tank, two cartridge heaters were placed, as the heating elements. The wires needed for the conduction had to address high temperatures, so an Alpha wire (procured by ThermoThin) applied on the set up with operating temperature range -150°C to 300°C. This type is suitable also for the exceptional small size and lightweight and the excellent dielectric properties as well as its outstanding chemical resistance. The wires were hooked up on the cupper parts/pogo pins to the outer side of the head on BNC connectors. The BNCs were connected with the Keithley 4200A-SCS semiconductor analyzer through which the dc current-voltage measurements performed. In the following Fig. 3.6 are presenting the designs of the homemade oil bath set up (Note, the listed dimensions and distances has been changed).





Figure 3.6 Design of the oil-bath set up. a) The vessel and b) The head of the vessel.

3.5.3 Climate chamber

A climate chamber, also known as environmental test chamber, is mostly defined as a temperature and humidity chamber, for the conditioning of samples prior to testing. It is an enclosed space used to test the effects of specified environmental conditions on materials, industrial products, electronic devices and components. A variety of climate chambers exists, depending on the application they are needed for. They can simulate diversity of temperature and humidity conditions simultaneously for environmental testing. Additionally, ageing and storage of the samples can also be checked. When a device, like thermistors in our case, comes to the point of implementation in every day's needs, then the environmental test chamber is employed in order to replicate conditions which the device might be exposed. In addition, it is used to accelerate the effects of exposure to the environment, even at conditions that sometimes are not expected. Here we used a climate chamber from Philips Innovation Services (espec SH-242) in order to test the printed matrix array made by the complex spinel oxide system in varying temperature and humidity levels.

3.6 Printing technique

3.6.1 Screen printing

Screen printing is maybe the oldest printing technique with its origins being estimating in ancient Egypt around 3000 BC. Sometimes it is called silk screen printing or serigraphy. The method that is used in this technique is quite simple. The ink is forced to pass through a mesh over a stencil and onto the surface being printed with the use of a blade/squeegee. The amount of the ink deposited on the screen is largely determined by the mesh size of the screen. The screen printing technique is used in many fields, from clothing, medical devices, printing electronics, thick film technology and more^[107]. Its main advantage is the reproducibly that offers, since the same stencil can be used for several depositions. Compared to the simple stencil printing technique, which is a printing made by human, it gives uniformity over the printed layers. In this project all layers (electrodes, dielectric bridges and ceramic composite) were screen printed using a Dek Horizon 03i screen printer.

Chapter IV

Characterization of the spinel oxide alloys

4.1 Introduction

Even though spinel oxides have been studied for many decades up today for uses in many different fields, there is a rare literature dedicated to the ternary system of Mn-Ni-Zn oxides and even fewer theoretical studies are performed based on this class of materials. The identification of the crystal structure is of crucial importance since can be directly related with the charge transport mechanism, although the systematic characterization across a wide range of compositions consisting by manganese zinc and nickel is lacking.^[108] Additionally, micro-Raman technique has proven to be a suitable technique to detect small inversion degrees in tetragonally distorted systems.^[109] Nonetheless, although Raman studies oriented in pure spinel oxides appeared in the literature, a systematic study is unsatisfactory. The correlation between vibrational modes and cation substitution in systems with more than one metal is complex due to the fact that the bonding forces, the mass of each cation and the ionic radii should be taken into account.^[110]

In this chapter, the structural analysis via XRD and SEM techniques along with vibrational analysis as the fingerprint to identify the different modes of the as prepared ternary spinel oxide alloys will be presented.

4.2 Experimental details

Zn_{0.5}Ni_xMn_{2.5-x}O₄ and Zn_xNi_{0.5}Mn_{2.5-x}O₄ spinel oxide alloys were fabricated via the solidstate reaction method as described in Chapter III with different Ni and Zn contents as shown in Table 1 and Table 2 respectively. With the ticks in the Tables are representing the existing pellets and with the dash the non-available ceramic pills. Their sintering history was as follows: ramp up 5 K/min up to 400°C and hold at this temperature for 1 h, followed by ramp up of 5K/min up to 1250°C for 6 h. The structural properties of the spinel oxides alloys were investigated with the XRD and SEM techniques. About the XRD patterns, the measurements' parameters were: scan of θ - 2 θ varying from 10° to 70°, with a scan rate of 0.01°/s and collection time 10 sec with fixed X-ray tube voltage and current at 40 kV and 40 mA respectively. The SEM images obtained from the surfaces of the spinel oxide alloys for 3000 × magnification and accelerating voltage at 20 kV. For the vibrational analysis, in terms of the various phonon modes of molecular species in the samples, the Raman spectroscopy was employed. It was performed at RT, over a wavenumber range of 100-1700 cm⁻¹, since for oxides the characteristics frequency regions for various anionic groups are < 1200 cm⁻¹.^[111]

Table 1 Mn2.5-xZn0.5NixO4 samples.

Composition	Air-cooled	Quenched
Zn0.5Mn2.5O4	\checkmark	-
Zn0.5Ni0.25Mn2.25O4	\checkmark	\checkmark
Zn0.5Ni0.5Mn2.0O4	\checkmark	✓
Zn0.5Ni0.75Mn1.75O4	\checkmark	✓
Zn0.5Ni1.0Mn1.5O4	✓	✓
Zn0.5Ni1.25Mn1.25O4	✓	✓

Table 2 Mn2.5-xZnxNi0.504 samples.

Composition	Air-cooled	Quenched
Ni0.5Mn2.5O4	\checkmark	-
Zn0.25Ni0.5Mn2.25O4	\checkmark	-
Zn0.5Ni0.5Mn2.0O4	\checkmark	-
Zn0.75Ni0.5Mn1.75O4	\checkmark	\checkmark
Zn1.0Ni0.5Mn1.5O4	\checkmark	\checkmark
Zn1.25Ni0.5Mn1.25O4	\checkmark	\checkmark

4.3 Structural properties

4.3.1 X-ray diffraction study

A. Zn_{0.5}Ni_xMn_{2.5-x}O₄ alloys

In Fig. 4.1 the obtained XRD patterns are presented, for the air-cooled and quenched samples. Beginning with the air-cooled specimens and specifically for the pellet without Ni content (x=0), the diffraction pattern was in a good agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) with card No. 77-0471 and is indexed as Hausmannite, tetragonal structure (space group I41/amd) without any impurities. Further on, the (103) reflection emerges with the highest intensity. With the addition of Ni content in the composition, an intermixing of tetragonal and cubic phase is detected. Explicitly, for Ni contents x=0.25 and x=0.5 a mix of the two phases is observed with the tetragonal phase being more pronounced. Reversely for x=0.75 the cubic phase is unambiguous, showcasing that this phase is promoted. Finally, further Ni addition for x=1.0 and x=1.25 pure cubic phases are observed and are identified with the card No. 71-0852 (JCPDS). In relation to the intensity of the peaks for Ni content x=1.0 the (311) reflection is the highest, whereas for x=1.25 the (400) plane is dominant, which might be attributed to the Ni excess and the possible formation of nickel oxide phase. The extracted experimental data are in line with the group of Cheng et al.^[58] which shown a phase transition from cubic to tetragonal for ceramic pellets prepared with the same method and having the stoichiometry of Ni₁₋ $_{\rm x}$ Zn_xMn₂O₄ (0 \leq x \leq 1.0). Looking into the XRD patterns for the quenched pellets in Figure 4.1b a mixed phases in all concentrations is noticed, even at the extremes of x=0 and x=1.25. In this case, high probability of intermixing is expected, due to trapping of the less energetically favorable phase existing in higher temperatures by fast cooling.



Figure 4.1 XRD patterns of Zn0.5NixMn2.5-xO4 a) Air-cooled pellets. The red stars represent the cubic phase and the blue hashtags the tetragonal phase. b) Quenched pellets.

Complementary to the experimental procedures, theoretical calculations with respect to the coordination site preference (octahedra and/or tetrahedra) employing the DFT+U method were performed by *E. Pervolarakis*. In brief, through these calculations the following output emerged. Mn atoms can occupy both tetrahedral and octahedral sites, while Zn atoms exhibit strong preference to the tetrahedral site. The site preference of Ni seems to be more complicated and indicates to be structure dependent, preferring tetrahedral sites in the Hausmannite (by about 50 meV/f.u./Ni, where f.u. stands for formula unit) and octahedral sites in the Spinel (by about 100 meV/f.u./Ni). Positioning Ni to the octahedra, since it does not yield the J-T distortion the Spinel structure is favored. Contrarily when placing Ni to the tetrahedral sites, the J-T effect from the octahedra Mn dominates making the cubic structure less energetically favored. The concentration with Ni content x=1.25 was an exception to the above, in which after the half octahedra where filled, the extra Ni atoms preferred to replace tetrahedra entailing that replacing more than half of the

octahedral Mn is unfavorable. The calculated energy difference between the most stable Hausmannite and Spinel structures for the whole range of Ni content x that was studied can be plainly seen in Fig. 4.2, where the values for Ni content x=0.25, x=0.5 and x=0.75 are closer to zero meaning that both phases are possible to these concentrations. Certainly, by combining the XRD patterns with the formation energies difference, turns out that theory impressively agrees with the experiment.



Figure 4.2 Difference in formation energy of the most stable Hausmannite and Spinel structures as calculated from DFT+U.

The lattice parameters for the air-cooled ceramic pellets were determined by applying to Equations 8 and 9 the reflections from several planes. The calculated lattice constants along with the theoretical computations through DFT+U method are presented in **Table 3**. Apparently, the experimental data agrees with the theoretical predictions, deviating by the most by 5 %. Besides for direct compare of Spinel and Hausmannite lattice parameters is needed to multiply the a of Hausmannite with $\sqrt{2}$, $a'_H = a_H * \sqrt{2}$.^[108] For the Hausmannite phase, the ratio c/a of the lattice parameters is greater than one, as anticipated due to the reduced crystal symmetry caused by the J-T effect^[41].

	Experimental		Theoretical	
$7n_0 \in Ni_1 Mn_2 \in O_1$	Hausmannite	Spinel	Hausmannite	Spinel
Z110.51 (1x101112.5-x04	a=b, c (Å)	a=b=c (Å)	a=b, c (Å)	a=b=c (Å)
x = 0.00	5.723, 9.317	-	5.799, 9.597	8.614
x = 0.25	5.722, 9.389	8.346	5.774, 9.555	8.565
x = 0.50	5.733, 9.284	8.386	5.764, 9.539	8.511
x = 0.75	-	8.356	5.741, 9.502	8.468
x = 1.00	-	8.334	5.721, 9.469	8.427
x = 1.25	-	8.331	5.699, 9.432	8.394

Table 3 Lattice parameters of $Zn_{0.5}Ni_xMn_{2.5-x}O_4$ ($0 \le x \le 1.25$) as calculated from the XRD patterns (Experimental) and DFT+U calculations (Theoretical).

B. Zn_xNi_{0.5}Mn_{2.5-x}O₄ alloys

In the following Fig. 4.3 are listed the XRD patterns as collected for the case of $Zn_xNi_{0.5}Mn_{2.5-x}O_4$ alloys. Although the reversed behavior was expected in these compositions, videlicet from cubic structure to the tetragonal distortion, this is not the case. All patterns possed almost the same diffraction peaks exhibiting shift to higher 2 θ values. Concerning the previous results with the theoretical study, this characteristic can be attributed to the favored positioning of the metallic species in the unit cell.^[112] Therefore, for the case of Zn content x=0 the cubic structure as the dominant phase was anticipated. However, three peaks appeared in the pattern revealing the coexistence of a second phase. This phenomenon is consistent up to Zn content x=0.5. Further Zn addition (x \geq 0.75) ascribe these extra peaks to the NiO phase with the characteristic peaks located at 37.1°, 43.1° and 62.5°, also observed in the pattern located at 31.7° and 57.2°. These investigations are in agreement with Chanel et al.,^[113] where they detect the existence of cubic phase with additional ZnO and NiO, for pellets sintered at temperatures higher than 1150°C. Regarding the quenched pellets, in this case study, the extracted patterns are quite similar

with the air-cooled exhibiting a subtle shift to lower 2θ , also a couple of extra peaks appear for all reported quenched cases.

	Experimental		
Zn _{0.5} Ni _x Mn _{2.5-x} O ₄	Spinel a=b=c (Å)	Additional structures	
x = 0.00	8.366	-	
x = 0.25	8.377	-	
x = 0.50	8.352	-	
x = 0.75	8.387	NiO	
x = 1.00	8.353	NiO + ZnO	
x = 1.25	8.409	NiO + ZnO	

Table 4 Lattice parameters of air-cooled ZnxNi0.5Mn2.5-xO4 ($0 \le x \le 1.25$) as calculated from the XRD patterns (Experimental).



Figure 4.3 XRD patterns of Zn0.5NixMn2.5-xO4 a) Air-cooled pellets. b) Quenched pellets. with the dots are the NiO peaks, the triangles ZnO, the yellow stars are the Mn3O4 and the red are the spinel cubic structure.

4.3.2 Scanning Electron Microscopy

The SEM images for both spinel oxides alloys are shown in Figure 4.4. and Figure 4.5. From these images the micron-sized particles were confirmed. The density of the ceramic pellets deduced via the standard Archimedes principle with distillated water in line with Equation 4.1 and the theoretical density by Equation 4.2.

$$\rho = \rho_w \left(\frac{W_a}{W_a - W_w}\right) \tag{4.1}$$

$$\rho_{th} = \frac{ZM_w}{N_A V_c} \tag{4.2}$$

where the indices w and a correspond to water and air respectively, ρ is the density and W the weight of the pellets, Z is the number of atoms, M_w the molecular weight of elements,

 N_A the Avogadro's number and V_c the unit cell volume. It should be pointed that in each measurement the temperature of the water was recorded since the density slightly changes, also ensuring that there were no bubbles in the bicker as well as more than one pellet measured for each Zn/Ni content in order to obtain an average value. For all specimens the degree of densification was higher than 92 % (Table 5). Furthermore, the obtained images reveal good uniformity without any notable signs of porosity supporting the calculated densities and revealing the Archimedes method as a reliable method. Additionally, as stated in the literature, high sintering temperature (>1100°C) results to lower porosity.^[113]

Content	Ν	li	Z	in
	Air-cooled	Quenched	Air-cooled	Quenched
x = 0.00	93.5	_	97 7	_
x = 0.00	-	95.8	96.6	_
x = 0.23 x = 0.50	96.3	95.0	96.0	_
x = 0.30	90.5	93.9	90.0	-
x = 0.73	93.4	94.3	74.7	94.2
x = 1.00	94.3	94.0	-	93.9
X = 1.25	92.9	93.4	94.1	93.1

Table 5 Degree of densification of the air-cooled Mn/Zn/Ni ceramics at different content x.

Examining the images of the alloys with Ni addition and specifically for the Ni-free case (x=0 in Fig. 4.4a), bigger grains compared with the rest samples were discerned. With increasing nickel; grains exhibited an erratic shape without consistency. Also, the grains in the quenched series were rounder and smoother while increasing Ni content ($x \ge 0.75$ lead) featured more irregular shapes.

Degree of densification (%)



Figure 4.4 SEM images of $Zn_{0.5}Ni_xMn_{2.5-x}O_4$ ceramics obtained from the surface of the pellets. a) Air-cooled and b) Quenched samples.

Regarding the spinel oxide alloys with the introduction of Zn to the composition, the obtained images are presented below both for air-cooled and quenched materials (Fig. 4.5). It is evident, that there is a difference compared with the other ceramics series (with Ni addition). Initially, there is not any content x depicting big grains as in the case of Ni-free

content. For Zn-free and low Zn content the images exhibit grains with polygonal irregular shape with many folds while increasing Zn element in the composition, smoother and rounder grains pop up with distinguished grain boundaries. These structural observations were in a good agreement with the literature.^[114] The images of the quenched pellets exhibited similar characteristics, that is that the grains were rounder and smoother while for extreme Zn incorporation few porous appears in the structure while the white spots enhance the structural observation for NiO formation in the system.



Figure 4.5 SEM images of ZnxNi0.5Mn2.5-xO4 ceramics obtained from the surface of the pellets. a) Aircooled and b) Quenched samples.

Additionally, EDX and elemental mapping in order to ensure the introduced elements in the composition were performed. In Appendix II (Fig. A.II.) two examples of these analysis method are depicted where the uniform distributions of the elements are displayed.

It should be noted that the image with Ni content x=0.25 and Zn content x=1.00 both from the air-cooled series as shown in Fig. 4.4a and Fig. 4.5a, were produced by another laboratory (JSI, Slovenia) by applying the same experimental process conditions. For that reason, they exhibit noticeable surface morphology compared with the rest samples, but as will be shown in the next chapter, their electrical characteristics are consistent following the trend with the Ni and Zn contents each time.

4.4 Vibrational properties

4.4.1 Raman Spectroscopy

In the existing literature, characterization for the Mn-Zn-Ni oxide spinels in terms of vibrational spectroscopy is limited, especially for the tetragonally distorted structures.^[115] For spinels belonging to the $I4_1/adm$ space group, factor group analysis performed via correlation method indicated 10 allowed Raman modes with $\Gamma = 2A_{1g} + 3B_{1g} + B_{2g} +$ $4E_{g}$,^{[116][117]} while for these belonging to the *Fd3m* space group, gave 5 active modes $\Gamma =$ $A_{1q} + E_q + 3F_{2q}$.^[118] The letters A, B, E and F refer to the degeneracy, so the A and B mean that the vibration is singly degenerate, while the letters E and F corresponds to doubly and triply degenerate respectively.^[111] Regarding the bands for the spinel oxides and particularly in manganese oxides, wavenumbers higher than 600 cm⁻¹ are assigned to the A_a symmetry and are characteristic energies of stretching vibrations involving oxygens motion inside the octahedral unit MnO₆. The $F_{2g}(3)$ bands are assigned between 500-600 cm⁻¹ and are antisymmetric bending modes of oxygen concerning the A-site cation. The bands in the range of 400-500 cm⁻¹ are assigned to the E_a symmetry and refers to the symmetric bending motion of the oxygen anions within the AO₄ unit. The modes located between 200-400 cm⁻¹ are assigned to the first and second F_{2g} symmetry species. Additional bands might appear in the spectra and it is reported to be related with the distortion of the lattice, whereas may not be detected through XRD. Nevertheless, vibrational spectra is sensitive to these defects.^[110]

A. $Zn_{0.5}Ni_{x}Mn_{2.5-x}O_{4}$ alloys

Fig. 4.6 shows the Raman spectra of the $Zn_{0.5}Ni_xMn_{2.5-x}O_4$ system for both air-cooled and quenched pellets. For the pure Hausmannite phase, that is for Ni content x=0, only five peaks out of ten predicted Raman modes were observed with three major peaks located at 667, 373 and 321 cm⁻¹ and two lower at 579 and 297 cm⁻¹. In detail, the stronger peak located at 667cm⁻¹ was consider as a vibrational mode between Mn-O atoms (A_g symmetry) which is consistent with the literature.^[109] While adding Ni content, this particular mode is located approximately at the same position progressively with lower intensity and a characteristic broadening. Initially, for Ni content x=0 this broadening appears as a shoulder at the side of lower wavenumbers while increasing Ni to the system convolutes with the main peak. This observation can be an indication of the existence of Mn cations with different valences in the B-sites.

Further on, the less intense peak located at 579 cm⁻¹ was ascribed to antisymmetric Zn-O bending mode (F_{2g} symmetry). This band was detected also for Ni content x=0.25, where for Ni ≥ 0.50 (where transition from mixed phase to pure Spinel structure occurs) a new peak appears with increasing intensity and steeper characteristics. Regarding the group of modes in the range of 250-400 cm⁻¹, they were clearly detected for x=0.00, x=1.00 and with lower intensity for x=0.25, assigned to the F_{2g} symmetry as stated to the literature.

Furthermore, for the air-cooled pellets with Ni content x=1.00 the appearance of five peaks reconfirmed the formation of spinel phase, while for the observed mixed phases, all peaks appeared to be broader. Complementary to that, for the cases of x=0.00 and x=1.00 the fact that the values of FWHM are lower than the rest x Ni content, points out towards a better crystallinity of these pellets. The changes of the intensity and the shift of the Raman peaks can be attributed to the redistribution of cations in the unit cell, consequently these changes arise from the reduce mass change and bond length.

On the other hand, in the quenched ceramic pellets all spectra shown common features with two major peaks around 525 and 660 cm⁻¹ (Fig. 4.6b). Likewise in the air-cooled samples, a group of modes between 250-400 cm⁻¹ for Ni content x=0.25 and x=1.00 was observed but clearly with lower intensity compared to the air-cooled. The stronger peaks at 660 cm⁻¹ were assigned to the A_{1g} vibration mode of the Mn-O in the B-sites. It is notable that with
the increase of Ni content in the composition, the intensity of this major peak decreased while the intensity of the peak located at 525 cm^{-1} increased. That was expected since from the DFT calculations Ni substituted more than half of Mn on the octahedral sites for x =1.25. Similarly with the air-cooled specimens both dominant peaks were broad enough revealing the contribution of different cations in the same symmetry. Supposing that the exact positioning of the cations and their valances are known, by deconvoluting the broad peaks the integrated intensity under each peak can give a quantitative value for the corresponding cations in the unit cell.^[119] The exact location of the peaks was obtained by fitting the data to a superposition of Gauss curves.



Figure 4.6 Raman spectra of Mn2.5-xZn0.5NixO4 a) Air-cooled pellets. b) Quenched pellets.

B. Zn_xNi_{0.5}Mn_{2.5-x}O₄ alloys

Investigation for the identification of the vibrational modes for the alloys with constant the nickel element in the composition have been performed and is depicted in Fig. 4.7. Concerning the air-cooled samples, with respect of the composition without Zn, two bands were observed. Both shown broad characteristics with the main mode located at 644 cm⁻¹ and 517 cm⁻¹, which are assigned as described to the introduction of this chapter to the stretching vibration modes of Mn-O at the octahedra and Ni-O at the tetrahedra with A_{Ig} and F_{2g} symmetry respectively. Similarly with the previous system, this broadening can be attributed to overlapping signal of more than one cation in the corresponding sub-unit cells. Moreover, with increasing Zn content to the system, the peak at 644 cm⁻¹ decreased and another one at 680 cm⁻¹ for x=0.75 appeared. This observation can be correlated with the NiO phase, while for x=1.00 and x=1.25 decreases. This seems to arise from the existence of the detected ZnO phase for the extremes Zn contents.



Figure 4.7 Raman spectra of ZnxNi0.5Mn2.5-xO4 a) Air-cooled pellets. b) Quenched pellets.

In regards to the quenched pellets, the obtained spectra (Fig. 4.7b) revealed resemble modes for all reported Zn contents ($x \ge 0.75$). Explicitly for Zn content x=1.25 and x=1.00 the spectra were identical exhibiting bands at 680, 642, 522 and a broad band at 342 cm⁻¹. In the case of x=0.75 the different signals overlapping was more intense but within the same range of wavenumbers. In similar manner with the previous analysis, the broadening of these modes was again a consequence of ZnO and NiO existence in the structure.

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Chapter V

The electrical properties of the ceramic materials

5.1 Introduction

The functional behavior of conductivity on temperature is directly related to the underlying transport mechanism. Understanding the mechanisms of transport charges in ternary and higher order spinel oxides would shed light into their electronic properties.^[120] As stated above, in manganese based spinels, the conduction is commonly reported to occur due to electron hopping between Mn³⁺ and Mn⁴⁺ ions,^{[121][63]} which is associated with the small polaron hopping^{[122][123]} mechanism between localized polaron states^[91]. Among the many hopping models construing the conduction mechanism, the variable range hopping model plays a vital role in understanding the electrical properties of both bulk and thin-film specimens.^[124] Additionally, this model is used to explain the conduction mechanism not only of compounds but also of composites.^[125] However, the polaron hopping model describes accurately the binary spinels. In general, a stoichiometric spinel oxide is experimentally difficult to be obtained and consequently, intrinsic electronic and ionic defects appear to occur at multiple lattice sites.^[126] Higher order spinels, exhibit

configurational variations that are not included in the small polaron hopping model. Moreover, the cation site occupancy can change with varying degrees of configurational disorder in the system.^[120]. Therefore, it is clear that a deeper understanding of the transport mechanism in higher order than binary spinels is needed.

In this chapter a closer insight on the charge transport mechanism is investigated. Initially, the classical Arrhenius equation was used to verify or not the presence of a linear relationship and to obtain a first approximation of the activation energy. Based on various other models applied in reference to published studies, this study concludes to a new model for the resistance functional dependence on temperature.

5.2 Experimental details

The electrical conductivity of the ceramic pellets was characterized by temperature dependent current-voltage (I-V) measurements, performed in the home-made oil bath set up as described in Chapter III. The temperature was ranging from 300 to 515 K and the applied voltage was 1.2 V with a step of 10 K and 0.05 V respectively. Typically, the *I-V* characteristics gave a linear response without hysteresis when cycled upon heating and cooling, in all cases except for the Ni-free (Zn_{0.5}Mn_{2.5}O₄) air-cooled pellets where a minimal hysteresis was observed at temperatures lower than 320 K.

5.3 Electrical properties

A. $Zn_{0.5}Ni_{x}Mn_{2.5-x}O_{4}$ alloys

An example of temperature dependent I-V measurements that corresponds to an air-cooled pellet with Ni content x=1.0, is given in Fig. 5.1a. It was found that the I-V characteristics were fully reproducible, without hysteresis upon voltage sweep. To a first approximation, the resistance dependance on temperature follows an Arrhenius relation according to Eq. 2.1, from which arises the exponentially decrease of resistance with increasing temperature. Further, it is apparent from Fig. 5.1b a drop of resistance of about 3 orders of

magnitude in the studied temperature window, revealing the NTC behavior of the thermistors. The corresponding Arrhenius plot is depicted in Fig. 5.1c, through which the activation energy E_a is derived from the slope of the natural logarithm of resistance as a function of the reciprocal temperature in absolute values.



Figure 5.1 Thermoelectric behavior of the ceramic materials. (a) Current – Voltage characteristics from RT to 240 °C. Note, only 5 temperatures are depicted for clarity purposes. (b) The exponential drop of resistance with increasing temperature and (c) Arrhenius plot of resistance vs temperature for the case air-cooled pellet with Ni content x=1.0.

A summary of the temperature dependent electrical characteristics for both air-cooled and quenched samples of $Zn_{0.5}Ni_xMn_{2.5-x}O_4$ alloys is presented in Fig. 5.2, where the corresponding values of the exponential pre-factor R_0 and the activation energy E_a are plotted. The latter is accompanied with the thermal constant *B* which is directly related to E_a as already mentioned in Chapter II. Both series follow the same trend with regard to the

different Ni content, with E_a exhibiting swift drop at lower values of x (x \leq 0.5), while at higher Ni content it was gradually increasing. Note that the Ni-free case displayed a significantly higher resistance performance, as observed by the much higher R_0 value and an increased drop rate upon heating.



Figure 5.2 (a) The pre-exponential factor R0 and (b) the determined activation energies for all cases of Ni context x. Note the y-axis breaks in both plots.

B. $Zn_xNi_{0.5}Mn_{2.5-x}O_4$ alloys

Similarly, for the case of Zn addition to the manganese-based alloys ($Zn_xNi_{0.5}Mn_{2.5-x}O_4$), an example of the corresponding plots is depicted in Fig. 5.3. The thermoelectric behavior of the as-prepared pellets of this series was alike the previous (Ni content, x). The main difference between the two series was the extremely high resistance at Ni content x=0.

In the following Fig. 5.3a, the sum up of the pre-exponential factor R_0 and the activation energy E_a as well the corresponding *B*-values are depicted. As in the previous case, the quenched samples have shown the same tendency with the air-cooled. Moreover, there was a slight increase of the activation energy after the Zn content x=0.50, as observed and in the case of substituting Mn with Ni content.



Figure 5.3. (a) The pre-exponential factor R_0 and (b) the determined activation energies for all cases of Zn context x.

5.4 Conductivity mechanism

From the engineering point of view, the mono-exponential Arrhenius behavior of the dependence of resistivity on temperature is a useful approximation to acquire a figure-ofmerit parameter on the performance of relative materials in NTC applications. In reality this approximation does not strictly reflect all examined cases, since a small deviation from linearity was observed in the Arrhenius plots. According to preliminary studies on this family of compounds, the expected transport mechanism is the polaron hopping. The conductivity is dictated by charged carrier jumps due to polaron-phonon interactions^[127] and is approximated as a percolation process in a random resistor network^[128] which is well described for low temperatures regimes alike the case of the low impurity semiconductors. As mentioned in Chapter II, the resistance dependence on temperature has the form:

$$R(T) = R_0 \cdot T^{\alpha} exp\left(\frac{T_0}{T}\right)^p \tag{2.5}$$

To determine the values for the p exponent in Eq. 2.7 the methodology of Efros and Shklovskii^[129] was applied, by calculating the dimensionless activation energy W:

$$W(T) = T^{-1} \cdot \frac{d(\ln R)}{d(T^{-1})}$$
(5.1)

through the plot of resistance as a function of temperature R(T) and retrieving the p values by linear regression to the -lnW versus lnT plots, in each dataset case of both series. Two examples of this analysis method are depicted in the data of Fig. 5.4 for the case of aircooled sample with Ni content x=0.50 and quenched sample with Zn content x=1.25. Scatter in the data was observed, as expected due the fact that stabilization of temperature during the measurement plays crucial role in the data accuracy. Note that this scatter observation was evident in all cases. Note that in Fig. 5.4a the measurement was performed with a step of 5 K in order to have more data points aiming to preserve, to the major extent, the accuracy of the fitted curves.



Figure 5.4 Example of lnW vs lnT for the case of a) air-cooled sample with Ni content x = 0.5 *and b) quenched sample with Zn content x*=1.25.

The resulting exponent p values for all cases are summarized in Fig. 5.5. In detail, the observed data in Fig. 5.5a for low (x \leq 0.25) and high (x > 1.00) Ni content, are consistent with the non-adiabatic limit of the NNH model according to which $p \approx 1$ (as described in the theoretical background chapter). Similar behavior was also observed for high (x \geq 1.00) Zn content in Fig. 5.5b. Such a NNH type conduction is consistent with the elevated temperature measurement range investigated. However, in the intermediate nickel and the lower zinc composition cases, the temperature scaling exponent p exceeds unity, thus excluding simple VRH or NNH mechanisms association with the underlying physical

processes. Instead, a super-Arrhenius behavior was observed, with a function of the form $exp\left[-\left(\frac{c}{T}\right)^p\right]$ with p > 1. In extreme cases, it approached a quadratic dependence of the logarithm of conductance on inverse temperature, a fact that was also confirmed by direct fitting of the R(T) data. Interestingly, similar temperature dependences have also been observed for the electrical conductivity in a number of ionic glass systems.^{[130][131][132]}



Figure 5.5 Collective plot of p values versus with a) Ni content x and b) Zn content x.

The physical processes involved in the electrical conductivity of this spinel ternary alloy oxide system, can be elucidated by considering correlations between two parameters. The first one is the experimentally derived values of the conductivity activation energies E_a (Fig. 5.2b & 5.3b) and the extracted scaling exponent p (Fig. 5.5). The second is the calculated ranges of possible energy bandgap values E_g , for the most stable lattice and spin configurations of the Zn_{0.5}Ni_xMn_{2.5-x} system, represented in Figure 5.6. The pre-exponential factor R_0 values (Fig. 5.2a) followed the trend of the calculated Spinel bandgaps, pointing to the fact that the Spinel phase component is the dominant one, concerning the conductivity properties, as expected due to the lower corresponding bandgap values. This is particularly highlighted in the case of Ni-free specimen where a pure Hausmannite phase is theoretically predicted and confirmed by XRD pattern and whose resistivity is much higher compared to the nickel containing cases.



Figure 5.6 The calculated band-gaps of the most stable structures of $Zn_{0.5}Ni_xMn_{2.5-x}O_4$ and their magnetic polytypes that are apart in energy at most by 1 k_BT at room temperature (25meV/f.u.). The band-gaps were obtained from Density of States (DOS) calculations in which the k-point sampling was increased to 12x12x8 and 8x8x8 for Hausmannite and Spinel, respectively.

Furthermore, an important relationship between the XRD patterns and the exponent values for the system with nickel addition is apparent. In the case of compositions where stable configurations lead to narrow distribution of E_g (closely spaced Spinel energy gaps), the electrical conductivity tends to follow an Arrhenius type temperature dependence, conformity with the NNH mechanism. On the other hand, in cases with broader distribution values E_g , the exponent value increases and the conductivity behavior deviates to a super-Arrhenius relationship. In the latter case, the conductivity process relates to percolation by hopping in a complex, largely inhomogeneous energy landscape, where the distribution of nearest neighbors' energy differences is broad. In the following Fig. 5.7 is given a graphical description of the inhomogeneous energy landscape. In depth, supposing the simpler case with a single bandgap and by imagining the NNH from polaron to adjacent free polaron state, it is expected it that these sites have the same localization depth as depicted in Fig. 5.7a. As the adjacent sites may belong to different spin configurations, the related bandgaps changes and that creates a different landscape, where the adjacent polaron sites do not have the same localizing potential, but are distributed randomly (Fig. 5.7b).



Figure 5.7 Graphical description of energy landscape. (a) Single bandgap case and (b) Inhomogeneous energy landscape.

To examine conduction by small polarons transfers between neighboring sites in such case, called here-in "variable-energy nearest-neighbor-hopping" (VE-NNH), a gaussian distribution of sites' energy with mean value ε_0 (referenced to the system quasi-constant Fermi level) and with standard deviation σ was assumed:

$$g(\varepsilon) = \frac{1}{\sigma\sqrt{2\pi}} \cdot exp\left(\frac{-(\varepsilon - \varepsilon_0)^2}{2\sigma^2}\right)$$
(5.2)

Then, the mean time needed for a polaron with energy ε_i to move to an unoccupied site with energy $\varepsilon_i + \Delta \varepsilon$, due to interaction with phonons, is given by:

$$\tau(\varepsilon_i) \propto \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{+\infty} d\Delta\varepsilon \, e^{\beta\Delta\varepsilon} \, e^{-\frac{(\varepsilon_i - \varepsilon_0 + \Delta\varepsilon)^2}{2\sigma^2}} \cdot \left(1 - e^{-\beta(\varepsilon_i - \varepsilon_0 + \Delta\varepsilon)}\right) \tag{5.3}$$

Where, the approximation of polaron sites' occupation by Boltzmann's distribution is justified, assuming $\beta \varepsilon_0 \gg 1$, by the presence of the gaussian term in the integrand. Then the resistivity $\rho(T)$, using again Boltzmann approximation for sites; occupation probability, can be evaluated as:

$$\rho^{-1}(T) = \rho_0^{-1} \cdot \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{+\infty} d\varepsilon \ e^{-\frac{(\varepsilon-\varepsilon_0)^2}{2\sigma^2}} e^{-\beta\varepsilon} \frac{1}{\tau(\varepsilon)}$$
(5.4)

which leads to the functional dependence of the resistance on temperature:

$$R_{VE-NN}(T) = R_0 \cdot e^{\frac{T_0}{T}} \cdot \left(e^{\frac{\delta^2}{T^2}} - 1\right)$$
(5.5)

where the scaled parameters $T_0 = \frac{\varepsilon_0}{k_B}$ and $\delta = \frac{\sigma}{\sqrt{2}k_B}$ relate to the mean position and the broadening of the energy gaussian distribution of polarons states. In the case that very narrow distribution is considered, $g(\varepsilon) \rightarrow \delta(\varepsilon - \varepsilon_0)$, the usual NNH relation of Eq. 2.7 is retrieved. It should also be pointed out that Eq. 5.5 should rather be considered as a phenomenological model, given the approximate nature of the hopping transport analysis and the assumptions used. In a more rigorous treatment, more complex dependencies of the parameters T_0 and δ on the parameters of sites' energy distribution, as well as, for the overall temperature functional form are expected.

Based on the above, the temperature dependence of resistance R(T) of both examined ternary oxide alloys, as a function of x (Ni or Zn) context, was examined in the context of the small polaron VE-NNH transport mechanism. In Fig. 5.7 and 5.8 are shown the plots of resistance vs the reciprocal absolute temperature for both air-cooled and quenched samples each time. Note, that some data series and the corresponding curves were translated vertically by a multiplication factor as indicated in the plots for reasons of clarity. The data are fitted using NNH (blue dashed lines) and VE-NNH (red solid lines) transport models. While applying the NNH model, fittings were performed in the upper part of the temperature data, for consistency with the non-adiabatic limit. Notable differences between the two models were observed, with the proposed VE-NNH model accurately describing all experimental data in the entire range. Especially for the Zn_{0.5}Ni_xMn_{2.5-x}O₄ spinel oxides alloys, this is emphasized in the case of intermediate compositions where DFT calculations predicted a broader distribution of possible bandgaps between different magnetic configurations and lower overall bandgap values, for the dominating spinel phase.



Figure 5.7 Plots of resistance vs reciprocal temperature of $Zn_{0.5}Ni_xMn_{2.5-x}O_4$ for the case of (a) air-cooled and (b) quenched samples and the corresponding fitted curves for the case of VE-NNH (red solid lines) and NNH (blue dashed lines) transport mechanisms.

The obtained values of the parameters for the VE-NNH model fits are presented in the following Table 6 for the $Zn_{0.5}Ni_xMn_{2.5-x}O_4$ system. The values and their dependence on Ni composition were in agreement with the DFT calculations, thus emphasizing the underlying physical mechanism leading to the variable energy nearest neighbor hopping type of transport mechanism, namely the reduction of and the coexistence of a wide distribution of bandgaps due to the presence of metastable spinel magnetic polytypes.

	Air-cooled		Quenched	
Mn _{2.5-x} Zn _{0.5} Ni _x O ₄	T_0 (K)	δ (K)	<i>T</i> ₀ (K)	δ(K)
	2122 222	10.5	2 6 4 2 2 2 2	
x=0.25	3120 ± 220	425 ± 73	2640 ± 88	476 ± 24
x=0.50	1330 ± 200	684 ± 31	1040 ± 210	718 ± 30
x=0.75	1470 ± 180	664 ± 30	1700 ± 150	618 ± 27
x=1.00	2390 ± 170	532 ± 38	2350 ± 150	495 ± 38
x=1.25	3310 ± 220	290 ± 120	3150 ± 150	372 ± 57

Table 6 Fitted values of the parameters T_0 and δ for the VE-NNH model for the $Zn_{0.5}Ni_xMn_{2.5-x}O_4$.

Applying the same procedure in the $Zn_xNi_{0.5}Mn_{2.5-x}O_4$ spinel oxide alloys the corresponding temperature dependence of resistance plot and the extracted values from the proposed VE-NNH model for the two parameters obtained are depicted in Fig. 5.8 and Table 7, respectively. Similarly with the previous results, the VE-NNH model is in line with the calculated exponent *p* values with the deviation of the NNH model for the close to quadratic Zn contents, been x=0.75 for the quenched samples and x \leq 0.50 for the aircooled.



Figure 5.8 Plots of resistance vs reciprocal temperature of $Zn_xNi_{0.5}Mn_{2.5-x}O_4$ for the case of (a) air-cooled and (b) quenched samples and the corresponding fitted curves for the case of VE-NNH (red solid lines) and NNH (blue dashed lines) transport mechanisms.

	Air-cooled		Quenched	
Mn _{2.5-x} Zn _{0.5} Ni _x O ₄	<i>T</i> ₀ (K)	δ(K)	<i>T</i> ₀ (K)	δ(K)
x=0.00	579 ± 246	766 ± 32	-	-
x=0.25	1277 ± 250	688 ± 39	-	-
x=0.50	1072 ± 212	706 ± 32	-	-
x=0.75	2220 ± 194	510 ± 46	1432 ± 201	655 ± 34
x=1.00	2443 ± 86	477 ± 23	2490 ± 247	443 ± 74
x=1.25	2461 ± 185	467 ± 52	1904 ± 125	595 ± 24

Table 7. Fitted values of the parameters T_0 and δ for the VE-NNH model for the $Zn_xNi_{0.5}Mn_{2.5-x}O_4$.

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Chapter VI

Printed temperature sensor

6.1 Introduction

Accurate distinguishing of spatial and temporal temperature gradients are critical not only for microbolometers, process control and flow sensors but also for applications like soft robotics and electronic skin (E-skin)^{[133][134][135]}. Surfaces with these needs require the deposition of hundreds of sensors over large areas^[136]. Towards this challenging direction, a scalable process for integrating many sensors over large areas with mechanical flexibility is necessary. Printing technologies are ideally suited since both provide this possibility and is a cost-efficient manufacturing route.

In this last experimental part, the development of a printed temperature sensor will be illustrated, whereby the stability and reliable performance of a complex micrometer-sized manganese based NTC ceramic are combined with the flexibility and adaptability to manufacture of a polymer binder^[137]. It will be shown that the printable ink can be processed on flexible plastic foils while retaining the properties of the bulk ceramic

material. Hence, applications demanding quite few sensors on a flexible surface may be enabled.

6.2 Synthesis of the ceramic material and composite

6.2.1 Powder fabrication

A Manganese based doped spinel oxide has been produced in order to fabricate and study the properties of a fully printable temperature sensor. The composition of the spinel oxide was $Mn_{1.71}Ni_{0.45}Co_{0.15}Cu_{0.45}Zn_{0.24}O_4$. The selection of this composite was done based to the reported superior stability and resistivity according to Park et al. ^{[138][139]}. The recipe for the synthesis of the composition was taken from published procedures^[138] and was as follows:

- Powders of Mn₂O₃, NiO, Co₃O₄, CuO and ZnO mixed for 24 h on a roller bench.
- For homogenization a dispermat bead milled with Zr marbles for 6 h.
- Dried overnight in an oven at 80°C.
- To avoid agglomerates, passed from mortar and pestle and later from a 325-mesh sieve.
- Calcined at 950°C in air oven for 2 h.
- Mixed again on the roller bench overnight.
- Pressed into pellets mechanically ($\approx 40 \text{ mm wide}$).
- Sintering at 1100°C for 24 h in a furnace and left to cool down.
- Grinded with a ball miller and sieved with different size meshes with the smallest 45 μm.
- Passivation of the particles.

In details, the particles passivated overnight in a 1 mM solution of dodecylphoshonic acid, hexylphosponic acid and octadecylphosphonic acid in isopropanol to form a self-assembled monolayer (SAM). Then the particles were vacuum filtered over a filter paper (MN 85/220 Macherey- Nagel ø100) and rinsed with isopropanol followed by drying at 110°C in an oven overnight.

To ensure that the particle size distribution of the obtained powder is between 100 nm to 10 μ m, dynamic light scattering analysis was employed (Malverin Instruments, Hydro 2000), using water as the dispersant media with obscuration $\approx 14\%$. In Figure 6.1 is depicted the analysis result, where the majority of the particles size was estimated to be $(1 - 40) \mu$ m.



Figure 6.1. The particle size distribution after sieving the ceramic powder.

Moreover, in the interest of the composition's verification, X-ray fluorescence (XRF) was performed by grinding the sample for 5 min in a Fritch Pulverisette 6 ball mill. The mixture was pressed into a pellet at a pressure of 300 kN. Measurements were performed using an AxiosmAX-Advanced spectrometer. Quantification was done using the software package "Omnian". Through this study some extra elements (except the imported) emerged in unimportant quantities as expected, since the "bake and shake" technique can be characterized as a dirty synthesis method.

Element	w/w (%)	Element	w/w (%)
Mg	0.02	Fe	0.02
Al	0.06	Со	5.2
Si	0.11	Ni	16
S	0.02	Cu	16
Ca	0.05	Zn	8.5
Mn	54	Cl	0.01

Table 8 X-ray fluorescence data on the chemical composition of the ceramic powder.

6.2.2 Substrate and ink formulation

Regarding the printing of the sensors, it is necessary a composite to be formed. Consequently, for the ink formulation, the as prepared ceramic powder was blended with a commercial binder precursor, cyclotene resin (3022-35, DOW Chemicals), in a weight ratio of 85:15 and mixed for 2 min at 2000 rpm in a planetary mixer and cured for 10 min at 100°C. The choice of the binder was made based on the characteristics exhibiting the benzocyclobutene (BCB) based resins binders, such as the excellent chemical, thermal and dielectric stability as well the low water absorption^{[140][141]}. In addition, other binders were used and evaluated in the climate chamber in terms of stability to the environmental conditions. These were the Electrodag PM404 (Henkel), PDMS and CYTOP binders with the same ratio. Since the performance of the devices with these binders suffered in terms of stability to humidity variations or shown extremely high resistivity (Appendix III), no further tests took place in the context of this study.

The electrical characteristics were performed using a planar integrated arrangement. For the electrical contact Ag electrodes (DuPont 5025) were printed on the top of polyimide (DuPont Kapton CR) of 75 µm thickness and cured at 120°C for 10 min in an oven. The channel width of the electrodes were 30 mm and the length 250 μ m, W/L=120. Also, dielectric bridges were printed using DuPont 8153 and cured at 120°C for 10 min in an oven, which served as the passive matrix structures (Figure 6.2). The ceramic ink layers were printed atop of the electrodes and cured in three steps as follows:

95°C for 45 min → 150°C for 1 h → 200°C for 2 h.

To avoid any condamination of the sensors from the environment or from condensation, a polyethylene naphthalate (PEN) foil was laminated atop the sensor using a thermoplastic polyurethane film as an adhesive.



Figure 6.2. (*left*) Picture of a 12×6 passive matrix arrays, screen printed on polyimide. (right) The backside of the passive sensor array, showing clearly the interdigitated electrode structure (scale bar = 1 cm).

6.3 Structural and morphological characterization

The as-prepared NTC powder was studied in terms of crystal structure. From the powder XRD pattern, shown in Figure 6.3 the cubic spinel (space group Fd3m) as the main phase was identified whereas traces of the tetragonal phases appeared. The lattice parameter for the main phase was 0.8364(2) nm as calculated by using Eq. 3.2.

Regarding the morphological characterization, SEM images were obtained from the surface of the as prepared composite. In Fig. 6.4 images for accelerating voltages at 1 and 10 kV with $2500 \times$ magnification are presented. As it can be seen, the surface of the composite is quite smooth with few voids and no large or isolated agglomerates formed. From Fig. 6.4 the good adhesion of the BCB precursor to the particles was evident, since

the particles seemed to be well dispersed and surrounded by the polymer binder. Besides, when the surface was bombarded with higher energy (Fig. 6.4b) the polymer phase became transparent and the heavy ion–based ceramic elements of the film were probed, showing mainly the distribution of ceramic particles. In Appendix II (Fig. AIII.a) more images with other magnifications are shown.



Figure 6.3 X-ray powder diffraction pattern of the asprepared NTC powder. Red star represents the cubic phase.



Figure 6.4. SEM images of the screen-printed temperature sensor. a) at 1kV. b) at 10 kV.

6.4 Electrical properties

Regarding the charge transport characteristics, the temperature dependent I - V behavior was investigated. The measurements took place in a cryostat under vacuum of about 10^{-7} mbar, the voltage sweep was ±10 V and the temperature was ranging from 340 down to 180 K. The realized curves (Figure 6.5a) indicated that there is no hysteresis during the sweeps but a deviation from linearity while temperature decreases was observed, which implies an electric field dependent charge transport mechanism^[142]. The calculated resistance obtained by fitting the data to Ohm's law (red dotted lines in Figure 6.5a). As it was expected, the resistance dropped about 4 orders of magnitude in the mentioned temperature range, confirming an NTC behavior. Additionally, the calculated resistances exhibited a linearity in regards to the Arrhenius plot of resistance as a function of the reciprocal temperature, shown in Figure 6.5b, confirming theoretical predictions for the polaron hopping as the domain transport mechanism in the low temperatures regimes^[86]. After applying Equation 2.1 to the Arrhenius plot, the activation energy was estimated at 302 meV and the thermal constant of the sensor (B-value) was 3512 K.



Figure 6.5 Temperature dependent of the printed sensors. a) I-V characteristics. b) Arrhenius plot of the determined resistance.

Moreover, the dependance of the printed temperature sensors resistance was assessed considering the electrodes dimensions. In detail, the width was kept fixed at 10000 µm while six different lengths were checked (200, 100, 50, 20, 10 & 5 µm). The scaling follows the reciprocal of the electrode's width over length, indicative of a scalable device with a low contact resistance even for short channel lengths as depicted in Fig. 6.6a. While the channel length reduces a nonlinear behavior at higher voltages is noticeable. Also, after normalizing the *I* - *V* characteristics according to the electrode geometries [$I_{normalized} = I * (L/W)$], the electrical characteristics closely crumbled to a single curve, validating the scalability of the sensor (see Fig. 6.6b).



Figure 6.6 a) Th I-V characteristics of the printed sensors with changing electrodes length. b) The normalized I-V characteristics. c) The pattern and the image of the printed sensor with varying W/L.

6.5 Validation of sensors at environmental conditions

6.5.1 Thermal cyclical stability

Another important aim regarding the applicability of the printed temperature sensor is to ensure the stability under different environmental conditions. The majority of the reported printed sensors are lucking in this direction, in terms of the resistance changes, originating from swelling of the films due to humidity variations or/and morphological changes upon heating and cooling loops^{[143][144]}. For this purpose, a climate chamber was employed so that the thermal cycling and stability to humidity of the sensor could be investigated. In Fig. 6.7, are presented the experimental data regarding thermal cycling. The temperature was initially set at 40°C and held for 1 h followed by a ramp up to 140°C kept as well for 1 h and returned back to 40°C in 1 h, with the humidity not being administered. The climate chamber programmed to perform 26 cycles with 90 h total duration. Furthermore, a commercially available NTC thermistor was subjected to the temperature profile in comparison with the printed sensor. The resistance of the printed sensor was 31.5 k Ω at 40°C and dropped to 2.6 k Ω at 140°C. It should be noted that the output for both commercial and printed sensor is incredibly alike during all cycles.



Figure 6.7 Cyclical heating and cooling of a commercial NTC thermistor (solid black line), our printed temperature sensor (solid red line). The climate chamber's temperature and relative humidity are represented by the dotted green and blue lines, respectively.

6.5.2 Humidity stability

As mentioned above, the temperature sensor was evaluated supplementary with respect to the humidity stability at varying conditions. In this case the temperature was kept constant at 30°C and the humidity levels were changing stepwise from 25 % up to 85 %, with a step of 15 %. Each step lasted for 1 day. Similarly with the thermal cycling test, in the climate chamber, a commercial NTC thermistor was placed for the sensor's evaluation. It is obvious (Figure 6.8) that the printed temperature sensor showed a drift regarding temperature of about $\approx 1^{\circ}$ C under the reported profile, while the commercial NTC thermistor abide by chamber's temperature. Even so, the resistance of the printed sensor recovers while reinstates to lower humidity levels. This stability characteristic is attributed to the binder selection, as discussed. It should be noted that for both evaluations an integrated Si sensor was placed in the climate chamber accompanied with the printed temperature sensor and the commercial NTC thermistor.



Figure 6.8 The stability of a commercial NTC thermistor (solid black line) and the printed temperature sensor (solid red line) at a fixed temperature of ≈ 30 °C (dotted green line) and at various humidity conditions (dotted blue line).

6.5.3 Flexibility of the sensor

Studying with printed sensors on plastic substrates, the flexibility of the sensors was verified by bending them on aluminum rods with known radii. At first, the choice of the applied strain levels was made following testing the sensor at RT conditions at different strains as depicted in Fig. 6.9 with the resistance, without applying any strain, was measured at $R_{RT} = 14.28 \text{ k}\Omega$. From the extracted data it was clear that the subjected strains should be lower than 1.5%, so that the resistance read-outs would not change much. Thus, a known radii of 0.8 and 1.0 cm was applied to the sensor, while measuring their temperature response in the climate chamber, with the relative humidity level being constant at 50%. Indeed, as a function of strain, the initial resistance of the sensors was changed, namely to 51 k Ω (0.0 % strain), 124.2 k Ω (0.97 % strain), and 239.6 k Ω (1.21 % strain) while the temperature scaling remained unaffected. Strains were calculated by the following formula for a given radii (*r*): $\varepsilon = \frac{d}{2r}$ with *d* being the total thickness of the sensor.



Figure 6.9 a) Resistance changes as a function of the applied strain to the sensor. b) Temperature response of the sensor while applied strain in the climate chamber.

6.6 Application

Having managed to obtain a fully printable temperature sensor which may have a significant impact in the technology sector, a flexible temperature sensor was fabricated on a thick (50 μ m) polyimide substrate (A4-sized sheet). In total the sheet contained 414

sensors and had a total thickness of just 285 µm. In the passive matrix sensor sheet, the measured sensor was biased to 1 V while the others were grounded^[145]. The measured current, as mentioned multiple times in the previous chapters, was used to extrapolate the sensor's resistance. Obviously, leakage currents expected from dielectric bridges along with wiring resistances should be kept in mind, but in this case accounting the resistance of the sensor they are negligible (e.g., the maximum parasitic resistance in series has $\approx 0.2\%$ error in the measured current). Initially, the average sensor resistance was (12 ± 3) k Ω at 23°C. Fig. 6.10, shows a human hand placed on the A4-sized sensor sheet and the configuration of the temperature variation caused by the placement of the hand was clearly shaped. Unquestionably, printed temperature sensors like these can give an accurate output.



Figure 6.10 a) Calibrated readout of the temperature of a hand placed on a passively addressed A4-sized sensor sheet. b) Photo of the hand placed on the mat.

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Chapter VII

Discussion and Conclusions

Discussion

Ceramic spinel oxides are widely used in many areas of technology, including sensors, electrochemical and catalytic applications. However, their electrical properties, especially for the higher order spinel oxides remain unclear and poorly controlled, since the repartition of the cations among the crystallographic sites greatly affect the electrical characteristics.

In this study, dense spinel oxide pellets have been fabricated. XRD analysis on the system of Ni substituting Mn revealed a phase transition from the tetragonal (Hausmannite) for x=0, to cubic for $x \ge 1.00$, with an intermixing of the two phases in the intermediate Ni contents $0.25 \le x \le 0.75$. For the system with Zn incorporation, all compositions shown cubic structure as the dominant phase but with traces of NiO for Zn content $x \ge 0.75$.

The contribution of various heat treatments on the structural and electrical characteristics of the ceramics have been investigated. In the case of the air-cooled pellets, low oxidation during cooling was anticipated compared with the quenched ones. Thus, oxidation starting from the grain boundaries, resulting to a cationic vacancy concentration was expected in the samples. As mentioned already, the calculated E_a of the quenched pellets were slightly lower compared with the air cooled while their phase structure couldn't be clearly identified. These outcomes were an indication of disordering of the cation in the lattice as well and the diffusion of cation vacancies in the grains with increasing temperature in the quenched ceramic pellets causing gently poor electrical characteristics.

Regarding the electronic transport properties of both spinel oxide alloys, the drop of resistance with increasing temperature observed, revealed the NTC behavior of thermistors. The resistances at RT were in the order of few k Ω while at 240°C these were only few Ω . All samples gave an E_a value in the range of 330-380 meV, with the analogous B-values been in the range 3500-4000 K, indicating all the examined compositions as good candidates for temperature sensors applications, with high sensitivity. An exception was monitored only for the Ni-free case, where the initial resistance was too high leading to higher activation energy.

Two different laboratories were engaged on the preparation of the ceramic pellets. Nevertheless, the performance of the bulk materials, regarding the electrical characteristics was identical and consistent, although the microstructure of their surface shown differences. This output implied that the key factor ware not the morphology of the material but the phase of the structure which is a consequence of the fabrication procedure. Moreover, a common composition from the two series was found to be $Zn_{0.5}Ni_{0.5}Mn_{2.0}O_4$. All the results (SEM, XRD & electrical characteristics) for this composition in both series were similar entailing that materials can give reproducible results from batch to batch.

In realizing the transport mechanism, a non-trivial super-Arrhenius conductivity relation with the temperature was revealed and various analysis methods performed. Small polaron hopping schemes considered, in spinel oxides, to be the transport mechanism, did not describe these deviations (from classical Arrhenius). This kind of deviations normally are found on the rate of chemical kinetics and biophysical processes as well as on transport phenomena. A tool that can yield to a first order linearization is Tsallis classical statistical mechanics. After applying, in our study, this approach, the data were not well defined for all cases. Besides, when dealing with super-Arrhenius behavior, the most popular equation for modeling is the Vogel-Fulcher-Tammann (VFT) where they describe this behavior as an Arrhenius-like, but involving one additional parameter called VFT-temperature $(R(T) = R_0 exp\left(\frac{B}{T-T_{cr}}\right))$. Neither this modeling could explain the phenomenological deviations accurately. First principle DFT+U calculations for the system with Ni addition, shown a variety of atomic spin configurations with small formation energy differences, in the range of 25 meV, but different bandgaps ware predicted, leading to an inhomogeneous energy landscape. Considering small polaron transport by nearest-neighbor hopping in such an environment, approximated by a gaussian distribution of sites' energetic positions, led to a new "variable energy nearest neighbor hopping" (VE-NNH) model for the resistance functional dependence on temperature, which elucidated the origin of super-Arrhenius conductivity activation and consistently described the experimental data.

Putting in a nutshell the structural characteristics with the transport results for the aircooled series, concluded to a direct relation between them. In detail, looking into the alloys with Ni addition, for the cases where a mixed phase was observed, the transport mechanism was associated with the VE-NNH, while for the pure structures, the simple NNH approximation was also well fitted. On the other hand, for the system with Zn addition, for contents at which the second phase of NiO is clearly resolved ($x \ge 0.75$), the transport mechanism was clarified by the NNH model, while for the rest contents $x \le 0.50$ where the cubic phase is dominant the transport was assigned to the proposed model of VE-NNH. Summarizing, the two systems act in a reversed manner with respect to the conduction which alerts that the favored positioning of the cations in the coordination sites are responsible for the structure and therefore for the type of conduction.

Finally, an environmentally stable screen-printable composite temperature sensor has been demonstrated. It was found that careful selection of the polymer binders is crucial for obtaining stable sensor characteristics in changing environmental conditions. Hence, the choice of the BCB resulted in the performance of the sensor with low overall resistance, good environmental stability in regards to different temperature and humidity profiles, low thickness of about 285 µm, and excellent uniformity over large area, as enabled by screen printing.

The development of printable sensors allows for the rapid fabrication of thousands of sensors per square meter, enabling the realization of accurate and reliable electronic skins for a range of applications. The total thickness and flexibility of the sensing surface permits the placement of a large number of sensors in areas and on shapes previously impossible. We anticipate that in the future, the use of other binder materials could also be used to realize stretchable and more conformable temperature sensors, especially on exciting for growing fields expected to revolutionize the field of flexible electronics such as soft robotics and electronic skins.

Conclusions & Recommendations

During this PhD Thesis, the structural and electrical properties of ceramic spinel oxide alloys have been studied and the development of a printable temperature sensor has been performed. Two different manganese-based spinel oxide alloys were analyzed and studied under different compositions and cooling procedures and the performance of the printed temperature sensors have been evaluated.

The synthesis of the ternary $Zn_{0.5}Ni_xMn_{2.5-x}O4$ and $Zn_xNi_{0.5}Mn_{2.5-x}O_4$ ($0 \le x \le 1.25$) and of the complex $Mn_{1.71}Ni_{0.45}Co_{0.15}Cu_{0.45}Zn_{0.24}O_4$ spinel oxides alloys was achieved with the solid-state reaction. The most outstanding results of this study are listed below:

- Resistances' drop revealed that all spinel compositions exhibited high sensitivity.
- The experimental data are impressively in line with theoretical calculations.
- A new *VE-NNH model was proposed* which described accurately the transport mechanism.
- A printed temperature sensor was realized by a composite, consisted of the ceramic powder and the BCB as the polymer binder.
- The electrical properties of the composite were comparable to the bulk ceramics.

- The printed sensor presented good stability to environmental conditions, in respect of humidity and temperature.
- Mechanical tests revealed that the printed sensors maintained their electrical response for applied strains < 1.5%.
- Successful demonstration of a hand placed on a mat with printed temperature sensors, proved the accuracy of the readout in printed sensors like these.

Further study should be performed in view of getting deeper insight to understand the performance in detail higher order spinel oxides similar with this study. Specifically, X-ray photoelectron spectroscopy (XPS) should be applied in order to identify the oxidation state of the Mn ions and understand at which position they are introduced in the lattice (A-sites or B-sites). Besides, in-situ XRD can show the presence or not of a phase transformation during heating. Collecting the above knowledge, it will be easier to fully understand the structure of the materials and correlate them in a more accurate way with their electrical characteristics.

Additionally, through impedance spectroscopy (IS), which is a technique that often used to characterize ceramics, the contribution of grains and grain boundaries in the electrical conduction can be extracted. Preliminary measurements, with the appropriate modification of the oil-bath set up have already been performed. The bottlenecks were our instrumentation, which was limited in terms of the frequency range (1Hz -1Mz) and the type of circuit concerned (series or parallel and/other addition elements e.g., constant phase element, CEP). Experiments over a wide range of temperature, including lower regimes might also give useful results on the deviation of activation energy with temperature evolution.

Regarding possible application of this class of materials, they may be considered in the aerospace engineering sector, due to the fact that they are lighter compared to metals. This enables faster speed, have high temperature resistance which allows CO_2 and NO_x reduction, resistance to corrosion, ability to withstand vibration and more. An idea for example is to use them as air flow sensors.

References

- [1] Printed electronics, Wikipedia, accessed on 2021-08-12, https://en.wikipedia.org/wiki/Printed_electronics.
- [2] R. Das, X. He, Flexible, Printed and Organic Electronics 2020-2030: Forecasts, Technologies, Markets.
- [3] N. X. Williams, G. Bullard, N. Brooke, M. J. Therien, A. D. Franklin, *Nat. Electron.* 2021, 4, 261.
- [4] C. Bali, A. Brandlmaier, A. Ganster, O. Raab, J. Zapf, A. Hübler, *Mater. Today Proc.* 2016, *3*, 739.
- [5] M. L. Hammock, A. Chortos, B. C. Tee, J. B. Tok, Z. Bao, 2013, 5997.
- [6] O. S. Aleksic, M. V. Nikolic, M. D. Lukovic, N. Nikolic, B. M. Radojcic, M. Radovanovic, Z. Djuric, M. Mitric, P. M. Nikolic, *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* 2013, 178, 202.
- [7] T. Someya, Y. Kato, T. Sekitani, S. Iba, Y. Noguchi, Y. Murase, H. Kawaguchi, T. Sakurai, Proc. Natl. Acad. Sci. U. S. A. 2005, 102, 12321.
- [8] J. A. Rogers, R. Ghaffari, D.-H. Kim, Eds., *Stretchable Bioelectronics for medical Devices and Systems*, Vol. 2002-Janua, Springer International Publishing Switzerland 2016.
- [9] T. Yokota, Y. Inoue, Y. Terakawa, J. Reeder, M. Kaltenbrunner, T. Ware, Proc Natl Acad Sci U S A 2015, 112, 14533.
- [10] F. Mathies, H. Eggers, B. S. Richards, G. Hernandez-Sosa, U. Lemmer, U. W. Paetzold, *ACS Appl. Energy Mater.* **2018**, *1*, 1834.
- [11] M. D. Dankoco, G. Y. Tesfay, E. Benevent, M. Bendahan, *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* **2016**, 205, 1.
- [12] A. Rivadeneyra, M. Bobinger, A. Albrecht, M. Becherer, P. Lugli, A. Falco, J. F. Salmerón, *Polymers (Basel).* **2019**, *11*.
- [13] A. Aliane, V. Fischer, T. Card, R. Coppard, I. Chartier, Proc. 2013 5th IEEE Int. Work. Adv. Sensors Interfaces, IWASI 2013 2013, 188.
- [14] K. J. Baeg, J. Lee, Adv. Mater. Technol. 2020, 5, 1.
- [15] D. Zhao, Y. Zhu, W. Cheng, W. Chen, Y. Wu, H. Yu, Adv. Mater. 2021, 33.
- [16] J. Lee, J. Wu, M. Shi, J. Yoon, S. Il Park, M. Li, Z. Liu, Y. Huang, J. A. Rogers, Adv. Mater. 2011, 23, 986.
- [17] Z. Wang, W. Zhang, X. Li, L. Gao, J. Mater. Res. 2016, 31, 1648.
- [18] S. Palchoudhury, K. Ramasamy, R. K. Gupta, A. Gupta, Front. Mater. 2019, 5, 1.
- [19] L. M. Castano, A. B. Flatau, Smart Mater. Struct. 2014, 23.
- [20] K. Sanderson, *Nature* **2021**, *591*, 685.
- [21] J. C. Yang, J. Mun, S. Y. Kwon, S. Park, Z. Bao, S. Park, Adv. Mater. 2019, 31.
- [22] W. Kurz, A. K. Yetisen, M. V. Kaito, M. J. Fuchter, M. Jakobi, M. Elsner, A. W. Koch, Adv. Opt. Mater. 2020, 8.
- [23] N. R. Council, In *The Flexible Electronics Opportunity*, The National Academies Press, **2014**, p. 314.
- [24] J. Fontes, In Sensor Technology Handbook, 2005, pp. 531–561.
- [25] P. R. N. Childs, J. R. Greenwood, C. A. Long, *Rev. Sci. Instrum.* 2000, *71*, 2959.
- [26] S. Jagtap, S. Rane, U. Mulik, D. Amalnerkar, *Microelectron. Int.* 2007, 24, 7.
- [27] S. Basu, A. K. Debnath, In Power Plant Instrumentation and Control Handbook, 2019, pp. 251– 320.
- [28] S. Mokhatab, W. A. Poe, J. Y. Mak, In Handbook of Natural Gas Transmission and Processing, 2019, pp. 615–642.
- [29] T. D. McGee, Principles and Methods of Temperature Measurement, Wiley-IEEE, 1988.
- [30] K. Siren, G. Rosen, J. Vad, P. Y. Nielsen, In *Industrial Ventilation Design Guidebook*, Academic Press, 2001, pp. 1106–1195.
- [31] A. Morris, R. Langari, In *Measurement and Instrumentation Theory and Application*, Elsevier Inc., **2020**, pp. 413–468.
- [32] J. A. Becker, C. B. Green, G. L. Pearson, Trans. Am. Inst. Electr. Eng. 1946, 65, 711.
- [33] P. R. N. (University of S. Childs, In *Advances in Heat Transfer*, Elsevier, **2003**, pp. 111–181.
- [34] O. S. Aleksic, P. M. Nikolic, Facta Univ. Ser. Electron. Energ. 2017, 30, 267.
- [35] J. S. Steinhart, S. R. Hart, Deep. Res. Oceanogr. Abstr. 1968, 15, 497.
- [36] J. Fraden, Handbook of Modern Sensors, Physics, Designs and Applications Fourth Edition, Vol. 53, **2012**.
- [37] Q. Shi, W. Ren, W. Kong, B. Gao, L. Wang, C. Ma, A. Chang, L. Bian, J. Mater. Sci. Mater. Electron. 2017, 28, 9876.
- [38] A. Veres, J. G. Noudem, O. Perez, S. Fourrez, G. Bailleul, Solid State Ion. 2007, 178, 423.
- [39] K. E. Sickafus, J. M. Wills, N. W. Grimes, J. Am. Ceram. Soc. 1999, 82, 3279.
- [40] G. J. Redhammer, G. Tippelt, Acta Crystallogr. Sect. E Crystallogr. Commun. 2016, 72, 505.
- [41] Q. Zhao, Z. Yan, C. Chen, J. Chen, *Chem. Rev.* 2017, 117, 10121.
- [42] A. Feteira, J. Am. Ceram. Soc. 2009, 92, 967.
- [43] K. Zhang, X. Han, Z. Hu, X. Zhang, Z. Tao, J. Chen, Chem. Soc. Rev. 2015, 44, 699.

- [44] G. Hao, Q. Lai, H. Zhang, J. Energy Chem. 2021, 59, 547.
- [45] T. Tatarchuk, B. Al-Najar, M. Bououdina, M. A. Aal Ahmed, In *Handbook of Ecomaterials*, Springer, Cham, **2018**, pp. 1701–1750.
- [46] W. H. Bragg, London, Edinburgh, Dublin Philos. Mag. J. Sci. 1915, 30, 305.
- [47] S. Nishikawa, Proc. Tokyo Math. Soc. 2nd Ser. 1915, 8, 199.
- [48] N. F. . Henry, K. Lonsdale, Dame, *International Tables for X-ray Crystallography*. *Volume I. Symmetry Groups*, Kynoch Press, **1952**.
- [49] H. J. Noh, S. Yeo, J. S. Kang, C. L. Zhang, S. W. Cheong, S. J. Oh, P. D. Johnson, *Appl. Phys. Lett.* 2006, 88, 081911.
- [50] S. C. Tarantino, M. Giannini, M. A. Carpenter, M. Zema, *IUCrJ* 2016, *3*, 354.
- [51] Z. K. Heiba, M. M. Ghannam, M. M. S. Sanad, A. A. Albassam, M. B. Mohamed, J. Mater. Sci. Mater. Electron. 2020, 31, 8946.
- [52] D. R. Kumar, C. A. Lincoln, D. Ravinder, S. I. Ahmad, Appl. Phys. A Mater. Sci. Process. 2020, 126, 1.
- [53] J. Guo, H. Zhang, Z. He, S. Li, Z. Li, J. Mater. Sci. Mater. Electron. 2018, 29, 2491.
- [54] J. Guo, L. Shi, L. Wu, S. Pan, X. Yuan, J. Zhao, Mater. Res. Express 2018, 5.
- [55] H. Li, I. P. L. Thayil, X. Ma, X. Sang, H. Zhang, A. Chang, Ceram. Int. 2020, 46, 24365.
- [56] T. Brylewski, W. Kucza, A. Adamczyk, A. Kruk, M. Stygar, M. Bobruk, J. Dabrowa, *Ceram. Int.* 2014, 40, 13873.
- [57] H. S. Han, H. Lee, J. Lim, K. M. Kim, Y. R. Hong, J. Lee, J. Forrester, J. H. Ryu, S. Mhin, *Ceram. Int.* 2017, 43, 16070.
- [58] F. Cheng, J. Wang, H. Zhang, A. Chang, W. Kong, B. Zhang, L. Chen, J. Mater. Sci. Mater. Electron. 2015, 26, 1374.
- [59] E. D. Macklen, J. Phys. Chem. Solids 1986, 47, 1073.
- [60] V. A. M. Brabers, J. C. J. M. Terhell, *Phys. Status Solidi* **1962**, *69*, 325.
- [61] B. Boucher, R. Buhl, M. Perrin, Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem. 1969, 25, 2326.
- [62] M. S. Islam, C. R. A. Catlow, J. Phys. Chem. Solids 1988, 49, 119.
- [63] S. Fritsch, J. Sarrias, M. Brieu, J. Couderc, J. Baudour, E. Snoeck, A. Rousset, Solid State Ionics 1998, 109, 229.
- [64] R. Schmidt, A. Stiegelschmitt, A. Roosen, A. W. Brinkman, J. Eur. Ceram. Soc. 2003, 23, 1549.
- [65] R. Schmidt, A. W. Brinkman, J. Eur. Ceram. Soc. 2005, 25, 3027.
- [66] R. Schmidt, A. Basu, A. W. Brinkman, Z. Klusek, P. K. Datta, Appl. Phys. Lett. 2005, 86, 1.

- [67] T. Larbi, A. Amara, B. Ouni, A. Inoubli, M. Karyaoui, A. Yumak, F. Saadallah, K. Boubaker, M. Amlouk, J. Magn. Magn. Mater. 2015, 387, 139.
- [68] W. Ren, Y. C. Zhang, N. N. Zhu, A. L. Feng, S. G. Shang, *Ceram. Int.* 2020, 46, 11675.
- [69] X. X. Tang, A. Manthiram, J. B. Goodenough, J. Less Common Met. 1989, 156, 357.
- [70] S. Guillemet-Fritsch, C. Chanel, J. Sarrias, S. Bayonne, A. Rousset, X. Alcobe, M. L. M. Sarriòn, Solid State Ionics 2000, 128, 233.
- [71] N. Zhang, F. Cheng, Y. Liu, Q. Zhao, K. Lei, C. Chen, X. Liu, J. Chen, J. Am. Chem. Soc. 2016, 138, 12894.
- [72] J. C. Knight, S. Therese, A. Manthiram, J. Mater. Chem. A 2015, 3, 21077.
- [73] M. Rosenberg, P. Nicolau, R. Manaila, P. Pausescu, J. Phys. Chem. Solids 1963, 24, 1419.
- [74] P. Patra, I. Naik, H. Bhatt, S. D. Kaushik, Phys. B Condens. Matter 2019, 572, 199.
- [75] R. Gherbi, Y. Bessekhouad, M. Trari, J. Alloys Compd. 2016, 655, 188.
- [76] J. Blasco, J. García, J. Solid State Chem. 2006, 179, 2199.
- [77] M. Peiteado, S. Sturm, A. C. Caballero, D. Makovec, Acta Mater. 2008, 56, 4028.
- [78] I. G. Austin, N. F. Mott, Adv. Phys. 1969, 18, 41.
- [79] A. S. Alexandrov, J. T. Devreese, Advances in Polaron Physics (Eds.: Cardona, M.; Fulde, P.; Klitzing, K. von; Merlin, R.; Queisser, H.-J.; Stormer, H.), Vol. 159, Springer Series in Solid-State Sciences, 2010.
- [80] C. B. Carter, M. G. Norton, *Ceramic Materials Science and Engineering*, 2nd ed., Springer, 2013.
- [81] M. Pollak, B. Schklovskii, Eds., *Hopping Transport in Solids*, Elsevier B.V., **1991**.
- [82] R. Schmidt, A. Basu, A. W. Brinkman, *Phys. Rev. B* 2005, 72, 115101.
- [83] H. Han, J. S. Lee, J. H. Ryu, K. M. Kim, J. L. Jones, J. Lim, S. Guillemet-Fritsch, H. C. Lee, S. Mhin, J. Phys. Chem. C 2016, 120, 13667.
- [84] H. Han, K. Ryeol, Y. Hong, K. Shim, S. Mhin, J. Alloys Compd. 2018, 732, 486.
- [85] A. L. Efros, B. I. Shklovskii, J. Phys. C Solid State Phys. 1975, 8, L49.
- [86] N. F. Mott, E. A. Davis, *Electronic Processes In Non-Crystalline Materials* (Eds.: Marshall. W.; Wilkinson, D. H.), 2nd ed., Vol. 37, Oxford University Press, Oxford, 1993.
- [87] L. D. Landau, Phys. Z. Sowjetunion 1933, 3, 644.
- [88] S. I. Pekar, Zh. Eksp. Teor. Fiz 1946, 16, 341.
- [89] Y. Natanzon, A. Azulay, Y. Amouyal, Isr. J. Chem. 2020, 60, 768.
- [90] J. T. Devreese, *Polarons*, Wiley VCH Verlag GmbH & Co. KGaA, **1996**, pp. 383–409.

- [91] C. Franchini, M. Reticcioli, M. Setvin, U. Diebold, Nat. Rev. Mater. 2021, 6, 756.
- [92] T. Holstein, Ann. Phys. (N. Y). 1959, 8, 325.
- [93] T. Holstein, Ann. Phys. (N. Y). 1959, 8, 343.
- [94] H. Fröhlich, H. Pelzer, S. Zienau, London, Edinburgh, Dublin Philos. Mag. J. Sci. 1950, 41, 221.
- [95] R. P. Feynman, *Phys. Rev.* **1955**, *97*, 660.
- [96] W. H. Sio, C. Verdi, S. Poncé, F. Giustino, Phys. Rev. B 2019, 99, 1.
- [97] G. Geneste, B. Amadon, M. Torrent, G. Dezanneau, Phys. Rev. B 2017, 96.
- [98] J. Hojo, Materials Chemistry of Ceramics (Ed.: Hojo, J.), Springer, 2019.
- [99] C. Outline, In Developments in Surface Contamination and Cleaning, Volume 12, Elsevier Inc., 2019, pp. 23–105.
- [100] B. Fultz, J. Howe, In *Transmission Electron Microscopy and Diffractometry of Materials, Graduate Texts in Physics*, Springer Berlin Heidelberg, **2013**.
- [101] M. Kaliva, M. Vamvakaki, In *Materials Research Society Symposium Proceedings*, Elsevier Inc., **2010**, pp. 401–433.
- [102] W. Zhou, R. Apkarian, Z. L. Wang, D. Joy, In Scanning Microscopy for Nanotechnology: Techniques and Applications, Springer, New York, NY, 2006, pp. 1–40.
- [103] C. Krishnamoorthy, R. Chidambaram, In *Emerging Applications on Nanoparticles and Architecture Nanostructures* (Eds.: Makhlouf, A. S. H.; Barhoum, A.), Elsevier, 2018, pp. 279–304.
- [104] S. S. Leong, W. M. Ng, J. K. Lim, S. P. Yeap, Handbook of Materials Characterization (Ed.: Sharma, S. K.), Springer, 2018.
- [105] Y. C. Cho, S. Il Ahn, Sci. Rep. 2020, 10, 1.
- [106] H. Dehghanpour, K. Yilmaz, SN Appl. Sci. 2020, 2, 1.
- [107] J. J. Licari, In *Hybrid Microcircuit Technology Handbook* (Eds.: Licaru, J. J.; Enlow, L. R.), Elsevier Inc., **1998**, pp. 104–171.
- [108] K. R. Park, H. S. Han, D. Hou, J. L. Jones, N. Oh, C. Ahn, J. Lee, S. H. Lee, S. Mhin, *Mater. Today Commun.* 2020, 25, 101298.
- [109] L. Malavasi, P. Galinetto, M. C. Mozzati, C. B. Azzoni, G. Flor, *Phys. Chem. Chem. Phys.* 2002, 4, 3876.
- [110] B. D. Hosterman, Raman Spectroscopic Study of Solid Solution Spinel Oxides Raman Spectroscopic Study of Solid Solution Spinel Oxides Repository Citation Repository Citation, University of Nevada, Las Vegas, 2011.
- [111] V. D'Ippolito, Linking crystal chemistry and physical properties of natural and synthetic spinels: an UV-VIS-NIR and Raman study, Sapienza, University of Rome, **2013**.

- [112] C. Chanel, S. Fritsch, C. Drouet, A. Rousset, M. L. Martínez Sarrión, L. Mestres, M. Morales, *Mater. Res. Bull.* 2000, 35, 431.
- [113] C. Chanel, S. Guillemet-Fritsch, J. Sarrias, A. Rousset, Int. J. Inorg. Mater. 2000, 2, 241.
- [114] M. L. M. Sarrion, M. Morales, J. Am. Ceram. Soc. 1995, 78, 915.
- [115] H. Li, B. Song, W. J. Wang, X. L. Chen, Mater. Chem. Phys. 2011, 130, 39.
- [116] W. G. Fateley, N. T. McDevitt, F. F. Bentley, Appl. Spectrosc. 1971, 25, 155.
- [117] N. Guo, X. Q. Wei, X. L. Deng, X. J. Xu, Appl. Surf. Sci. 2015, 356, 1127.
- [118] C. M. Julien, M. Massot, *Ionics (Kiel)*. 2005, 11, 226.
- [119] B. Nandan, M. C. Bhatnagar, S. C. Kashyap, J. Phys. Chem. Solids 2019, 129, 298.
- [120] A. Bhargava, C. Y. Chen, K. Dhaka, Y. Yao, A. Nelson, D. Kenneth, C. J. Pollock, M. C. Toroker, R. D. Robinson, *Chem. Mater.* 2019.
- [121] E. Elbadraoui, J. L. Baudou, F. Boureeb, B. Gillot, S. Fritschd, A. Roussetd, Solid State Ionics 1997, 93, 219.
- [122] S. T. Kshirsagar, C. D. Sabane, Jpn. J. Appl. Phys. 1971, 10, 794.
- [123] B. Gillot, R. Legros, R. Metz, A. Rousset, Solid State Ionics 1992, 51, 7.
- [124] H. J. H. Ma, J. F. Scott, Phys. Rev. Lett. 2020, 124, 146601.
- [125] B. S. Kumar, Y. N. Kumar, V. Kamalarasan, C. Venkateswaran, J. Mater. Sci. Mater. Electron. 2020, 31, 22312.
- [126] K. Hoang, J. Mater. Chem. A 2014, 2, 18271.
- [127] J. Schnakenberg, Phys. Status Solidi 1968, 28, 623.
- [128] A. Miller, E. Abrahams, *Phys. Rev.* **1960**, *120*, 745.
- [129] B. I. Shklovskii, A. L. Efros, *Electronic Properties of Doped Semiconductors*, 1st ed., Springer, Berlin, Heidelberg, 1984.
- [130] J. Kincs, S. W. Martin, Phys. Rev. Lett. 1996, 76, 70.
- [131] S. Murugavel, Phys. Rev. B 2005, 72, 134204.
- [132] Y. Okada, M. Ikeda, M. Aniya, Solid State Ionics 2015, 281, 43.
- [133] T. Q. Trung, N. E. Lee, Adv. Mater. 2016, 28, 4338.
- [134] R. Di Giacomo, L. Bonanomi, V. Costanza, B. Maresca, C. Daraio, Sci. Robot. 2017, 2, 1.
- [135] S. Harada, K. Kanao, Y. Yamamoto, T. Arie, S. Akita, K. Takei, 2014, 21, 1213.
- [136] R. S. Dahiya, G. Metta, M. Valle, G. Sandini, *IEEE Trans. Robot.* 2010, 26, 1.

- [137] J. Jeon, H. B. R. Lee, Z. Bao, Adv. Mater. 2013, 25, 850.
- [138] K. Park, J. K. Lee, Scr. Mater. 2007, 57, 329.
- [139] K. Park, J. K. Lee, J. Alloys Compd. 2009, 475, 513.
- [140] A. K. Sadana, R. K. Saini, W. E. Billups, C. C. Approaches, B. D. A. Reactions, *Chem. Rev.* 2003, 103, 1539.
- [141] A. Modafe, N. Ghalichechian, B. Kleber, R. Ghodssi, *IEEE Trans. Device Mater. Reliab.* 2004, *4*, 495.
- [142] W. F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P. A. Bobbert, P. W. M. Blom, M. De Leeuw, M. A. J. Michels, *Phys. Rev. Lett.* 2005, 94, 1.
- [143] C. Wei, L. Dai, A. Roy, T. B. Tolle, J. Am. Chem. Soc. 2006, 128, 1412.
- [144] J. Huang, P. F. Miller, J. S. Wilson, A. J. De Mello, J. C. De Mello, D. D. C. Bradley, Adv. Funct. Mater. 2005, 15, 290.
- [145] T. D'Alessio, Sensors Actuators, A Phys. 1999, 72, 71.

Hosting Institutions

This thesis started in January 2017, with the collaboration between three Institutes; the **University of Crete (UoC)** and the **Foundation for Research and Technology Hellas, Institute of Electronic Structure and Lasers (FORTH/IESL)** and **TNO/HOLST Centre.** During the first 15 months, the PhD candidate worked at Holst Centre on the High-Tech Campus in Eindhoven, The Netherlands as a visiting student for the project Temperature sensor | Sensors printed on ultrathin film enable large area monitoring. During this period the theoretical background along with the material synthesis and the printed technique where involved. The following 3 years, the project was completed at FORTH in Crete, where the understanding of the materials used in terms of structural and the electrical properties performed.



Appendix I



Figure A1 Complete unit cell of spinel crystal structure. It is divided into 8 building blocks, half tetrahedra and half octahedra, which alternate. The octahedra are edge sharing while tetrahedra have corners sharing with octahedra.

Appendix II



Figure AII EDS color mapping of a) $Mn_{1.25}Zn_{0.5}Ni_{1.25}O_4$ from the air-cooled pellets, b) $Mn_{2.0}Zn_{0.5}Ni_{0.5}O_4$ from the quenched pellets. Elementary EDS analysis c) for x=1.25 (air-cooled) d) for x=0.5 (quenched).

Appendix III



Figure AIII.1 SEM images of the screen-printed composite film (measured at an acceleration voltage of 1 kV) at a, 250 x magnification b, 2500 x magnification c, 10,000 x magnification, and d, 50,000 x magnification.



Figure AIII.2 The stability of a commercial NTC thermistor (solid black line), the printed temperature sensor with BCB binder (solid red line), and a printed temperature sensor with Electrodag PM-404 (Henkel, solid purple line). Measured in a climate chamber at fixed temperature of 30C (dotted green line) and at varying relative humidity conditions (dotted blue line).



Figure AIII.3 Examination of the PDMS binder in a climate chamber. The sensor has a very high starting resistance and does not exhibit a stable change in resistance change with temperature in varying humidity conditions.



Figure AIII.4 Examination of the CYTOP binder in a climate chamber. The sensor has a very high starting resistance and while it does show a relatively good response to changes in temperature, the resistance of the sensor is very high.