

Development and Optimization of Bismuth Telluride Nanoplates for Thermoelectric Devices

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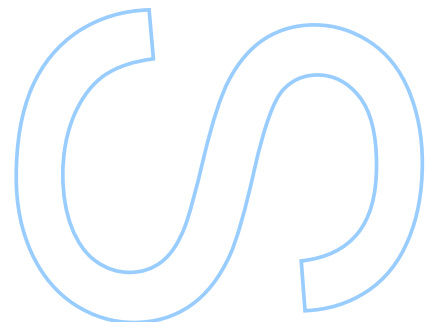
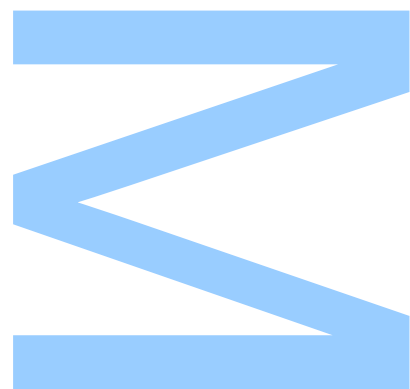
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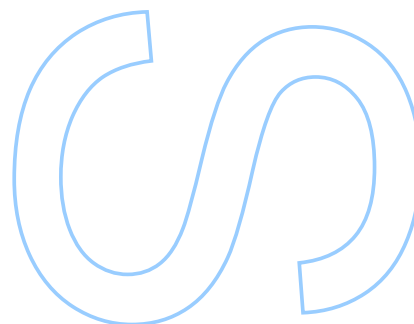
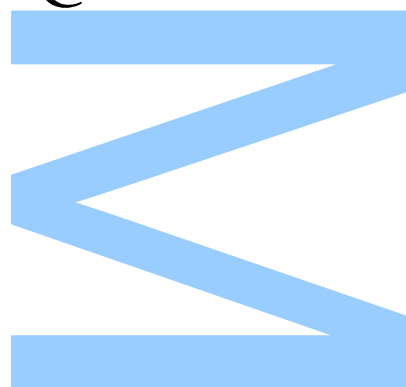
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“ When the day becomes the night and the sky becomes the sea, when the clock strikes heavy and there’s no time for tea; and in our darkest hour, before my final rhyme, she will come back home to Wonderland and turn back the hands of time. ”

Lewis Carroll in the book Alice’s Adventures in Wonderland

Acknowledgements

First and foremost, I'd would like to express my appreciation and gratitude to my supervisors, Dra. Mariana Rocha and Prof. Dr. André Pereira, for their patience, devotion, and guidance throughout. Dr. Mariana Rocha, whom I had the honor of being her first master's student, I want to thank for all of her patience and inspiration, as well as for introducing and motivating me to the world of chemistry. For all of the meticulous thesis corrections, also a special thanks to Tomás. Professor Dr. André Pereira, thank you for your motivation and guidance not only throughout my dissertation but also during my academic courses at FCUP and IFIMUP-IN.

I would like to show my appreciation to Dr. Rui Costa, for the help during the XRD measurements. I would like to show my gratitude to Professor Dr. Joaquim Moreira and Dr. Rui Vilarinho for providing the access to the Raman spectroscopy equipment.

Ana Pires deserves special recognition for her generosity and kindness, for always keeping me inspired and assisting in any way she could, and for all of the messages and motivational calls that were really important during the entire process.

I can't thank enough my mentor, the soon-to-be doctor Margarida Maia, for all of her companionship, inspiration, support, and motivation, not only throughout this last year but since the beginning of my academic path. She is without a doubt the closest friend I have made in this institution, and without a doubt one of the most important persons in my life. Thank you for everything.

Furthermore, I'd want to thank all of my colleagues at IFIMUP for their assistance and support throughout these long months of hard work. To my classmates, for whom I am grateful for their friendship and mutual support during our difficult moments together. A special thank you to Inês Ornelas for all of your friendship over meals and coffee breaks.

A particular thank you to my academic buddies (Hugo Lebre, Ricardo Brandão, Ana José, Sofia Gonçalves, Marco Ramos, David Almeida, Patrícia Vieira, Ana Rita Bugalhão, Carolina Silva, Luís Dias, Bruno Mota, and João Silva).

A very special thank you to my boyfriend for all of his love and support throughout this year, for always being there to raise me up and believe in me, and for all of his compassion during the difficult moments.

Last but not least, I want to thank my family and friends. I can't thank my mother enough for being the first person to ever believe in me, for whom I owe my life, for all

the support, for always lifting me up, when I'm down, for always being my safe haven, and for being my best friend no matter what. To my father, for always making me smile, for remembering me to relax, and encouraging me to face the world with my head held high. Thank you, to my lovely sister Beatriz, who gave me the most precious nephew and godson, for always believing in me and protecting me. Thank you to my sweet friend Délia, who has reared me since I was a baby, for all of your friendship and love, for all of your laughter, and most importantly, for always being my second mother. Thank you to my best friend Margarida Santos for always being there for me no matter what. To my late great-uncle, who constantly encouraged me throughout my educational life. Thank you to my grandparents, especially my grandfather Armindo Moreira da Silva, for always believing in me and for all the life lessons; my greatest desire is that you were still living to witness it. And finally, a very special thank you to my soon-to-be-born son Pedro Miguel, this is for you.

This thesis was embedded in the WiPTerm FET- Open Project, that has received funding from the European Union's Horizon 2020 FET Open programme under grant agreement No. 863307. The work was financially supported by Fundação para a Ciência e a Tecnologia (FCT)/MEC and FEDER under Program PT2020 through the projects UIDB/04968/2020, and NORTE- 01-0145-FEDER022096 from NECL. The authors thanks the funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement No. 863307 (Ref. H2020-FETOPEN-2018-2019-2020-01).

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Abstract

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The growing quest for new, improved and sustainable ways to harvest energy and the unprecedented expansion of the Internet of Things (IoT) market keeps pushing technology to the limit nowadays. In 2021 IoT counted with more than 10 billion active devices, however, this number is expected to surpass 25.4 billion by 2030. Despite that, their expansion has been slowed down by the lack of viable power supply methods capable of replacing the old wires or batteries. The latter has several drawbacks such as the requirement of manual maintenance, a finite lifespan, and possible safety risks and environmental harm. Thermoelectricity seems to be promising in solving this problem since it does not produce pollutants, uses waste heat, and has reliable conversion. Thermoelectric materials convert thermal energy into electrical energy through the temperature difference-induced separation of positive and negative charges generating a voltage inside it.

With the main objective of this study being to develop bismuth telluride nanomaterials, a chemical reduction approach was used to produce the nanomaterials, with 1-Amino-2-Propanol (MIPA) serving as the reducing base.

The results show that the variation in MIPA molar concentration affects the morphology of the nanoplates, particularly the crystallite size, which ranged between 41.30 and 52.30 nm, with the largest value obtained for the sample 2 M MIPA. For MIPA molar concentrations of less than 1, the results show that the reaction environment was not alkaline enough for the formation of Bi_2Te_3 , resulting in the formation of oxides. The molar concentration of MIPA applied to the process also affects the stoichiometry of the nanoplates; the finest value was obtained for the sample 2 M MIPA, whose stoichiometry is $Bi_{2.14}Te_3$. The samples' Seebeck coefficients proved that the material is n-type. The conductivity values ranged from 3.29×10^{-6} to $2.126 \times 10^{-5} \text{ } (\Omega^{-1}m^{-1})$, with the sample 2 M MIPA achieving the highest value that has a power factor of $0.0635 \text{ } \mu Wm^{-1}K^{-2}$.

The amount of Ethylene Glycol (EG) added to the reaction at the time of the procedure influences the crystallite size as well; reducing it also decreases crystallite size. The SEM images revealed that decreasing the substance amount of EG leads the samples to become more homogenous and morphologically defined. This substance amount decrease also benefits the stoichiometry, as a stoichiometry of $Bi_{2.02}Te_3$ was reached for a substance amount of 1.79 and a MIPA molar concentration of 2 M. The TEM technique confirmed the attainment of the nanoplates and their hexagonal shape, with diameters ranging from 400 to 650 nm, for the sample 2 M MIPA 1.79 EG. This sample's nanoplates also had the highest powerfactor of $0.789 \mu W m^{-1} K^{-2}$, being the most promising candidate.

It was also possible to produce by screen-printing a prototype of a planar geometry device using the nanoplates produced with a molar concentration of MIPA of 2 M and molar amount of EG of 1.79. With this a Seebeck coefficient of $361 \mu V K^{-1}$ was obtained.

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Resumo

Faculdade de Ciências da Universidade do Porto

Departamento de Física e Astronomia

Mestrado Integrado em Engenharia Física

Desenvolvimento e Otimização de Nanoplates de Bismuto de Telúrio para Dispositivos Termoelétricos

por [Isabel MOREIRA DA SILVA](#)

A procura crescente de formas novas, melhoradas e mais sustentáveis de conversão de energia e a expansão sem precedentes do mercado da Internet das Coisas (IoT) continua a levar a tecnologia ao limite hoje em dia. Em 2021 a IoT contava com mais de 10 mil milhões de dispositivos ativos, contudo, espera-se que este número ultrapasse os 25,4 mil milhões até 2030. Apesar disso, a sua expansão tem sido retardada pela falta de métodos viáveis de fornecimento de energia capazes de substituir os antigos fios ou baterias. Este último tem vários inconvenientes, tais como a exigência de manutenção manual, uma vida útil finita, e possíveis riscos de segurança e danos ambientais. A termoelectricidade parece ser promissora na resolução deste problema, uma vez que não produz poluentes, utiliza calor residual, e tem uma conversão fiável. Os materiais termoelétricos convertem energia térmica em energia eléctrica através da separação das cargas positivas e negativas que geram uma tensão no seu interior, induzida pela diferença de temperatura.

Tendo como principal objectivo deste estudo o desenvolvimento de nanomateriais de bismuto de telúrio, foi utilizada uma abordagem de redução química para produzir os nanomateriais, com 1-Amino-2-Propanol (MIPA) como base redutora.

Os resultados mostram que a variação na concentração molar de MIPA afeta a morfologia das nanoplacas, particularmente o tamanho da cristalite, que variava entre 41.30 e 52.30 nm, com o maior valor obtido para a amostra de 2 MIPA. Para concentrações molares de MIPA inferiores a 1, os resultados mostram que o ambiente de reação não era suficientemente alcalino para a formação de Bi_2Te_3 , resultando na formação de óxidos. A concentração molar de MIPA aplicada ao processo também afeta a estequiometria das

nanoplacas; o valor mais preciso foi obtido para a amostra de 2 MIPA, cuja estequiometria é $Bi_{2.14}Te_3$. Os coeficientes de Seebeck das amostras provaram que o material é do tipo n. Os valores de condutividade variaram entre 3.29×10^{-6} e $2.126 \times 10^{-5} (\Omega^{-1}m^{-1})$, com a amostra de 2 MIPA alcançar o valor mais alto que possui ainda um fator de potência de $0.0635 \mu W m^{-1} K^{-2}$.

A quantidade de etileno glicol (EG) adicionada à reação no momento do procedimento também influencia o tamanho da cristalite; a sua redução também diminui o tamanho da cristalite. As imagens SEM revelaram que a diminuição da quantidade de substância de EG leva a que as amostras se tornem mais homogêneas e morfologicamente definidas. Esta diminuição da quantidade da substância também beneficia a estequiometria, uma vez que uma estequiometria de $Bi_{2.02}Te_3$ foi alcançada para uma quantidade de substância de 1.79 e uma concentração molar MIPA de 2 M. A técnica TEM confirmou a obtenção das nanoplacas e a sua forma hexagonal, com diâmetros entre 400 e 650 nm, para a amostra de 2 MIPA 1.79 EG. As nanoplacas desta amostra tinham também o fator de potência mais elevado de $0.789 \mu W m^{-1} K^{-2}$, sendo o candidato mais promissor.

Foi também possível produzir por serigrafia um protótipo de um dispositivo de geometria planar usando as nanoplacas produzidas com uma concentração molar de MIPA de 2 M e uma quantidade molar de EG de 1.79. Com isto foi obtida um coeficiente Seebeck de $361 mVK^{-1}$.

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Symbols

Symbol	Name	SI Unit
ΔT	Temperature Gradient	K
S	Seebeck Coefficient	VK^{-1}
ΔV	Voltage Difference	V
ρ	Electrical Resistivity	Ωm
σ	Electrical Conductivity	$\Omega^{-1}m^{-1}$
ZT	Figure of Merit	Dimensionless
$S\sigma^2$	Power Factor (PF)	$W^{-1}m^{-1}K^{-2}$
κ	Thermal Conductivity	$W^{-1}m^{-1}K^{-1}$
T	Temperature	K
λ	Wavelength	m
θ	Angle	°
R	Resistance	Ω
I	Current	A
P	Power	W

Glossary

TE	Thermoelectric
TEG	Thermoelectric Generator
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
EDS	Electron Dispersion Microscopy
BSE	Backscattered Electrons
SE	Secondary Electrons
TC	Temperature Controller
NPs	Nanoparticles
RT	Room Temperature

*To my mother and grandfather, for their unconditional love and
support, and to my beloved son.*

Chapter 1

Introduction

1.1 Motivation

According to the 2019 revision of the World Population Prospects (WPP), the United Nations predicts that the world's population is expected to increase by 2 billion persons over the next 30 years, from the current 7.7 billion to 9.7 billion in 2050 [1]. The modern lifestyle led to the escalation of energy consumption, and predictions show that in the future, the rise of this consumption will continue. The endless demand for energy increased the dependence on fossil fuels, such as oil, coal, and natural gas, presenting a negative impact on the environment. Thus, there is a growing quest for new, improved and sustainable ways to produce and harvest energy.

The Internet of Things (IoT) has revolutionized the way of living into a high-tech lifestyle, from smart cities, pollution control, and smart homes. Although scientists aim for a fully connected planet through the IoT, this strategy may fail in 50-100 years due to a fossil resources shortage [2]. In 2021 IoT counted with more than 12.3 billion active devices, however, this number is expected to surpass 27.1 billion by 2030 (Figure 1.1) [3]. Despite this, the lack of viable power supply methods capable of replacing the old wires or batteries has slowed its further expansion. Batteries have some drawbacks, such as the need for manual maintenance, the need to transmit less data frequently in order to conserve battery life, a finite lifespan, and high toxicity after disposal [4, 5].

Thermoelectricity seems to be promising in solving this problem since it does not produce pollutants, uses waste heat, and has reliable conversion. Thermoelectric materials convert thermal energy into electrical energy through the temperature difference-induced separation of positive and negative charges generating a voltage inside it.

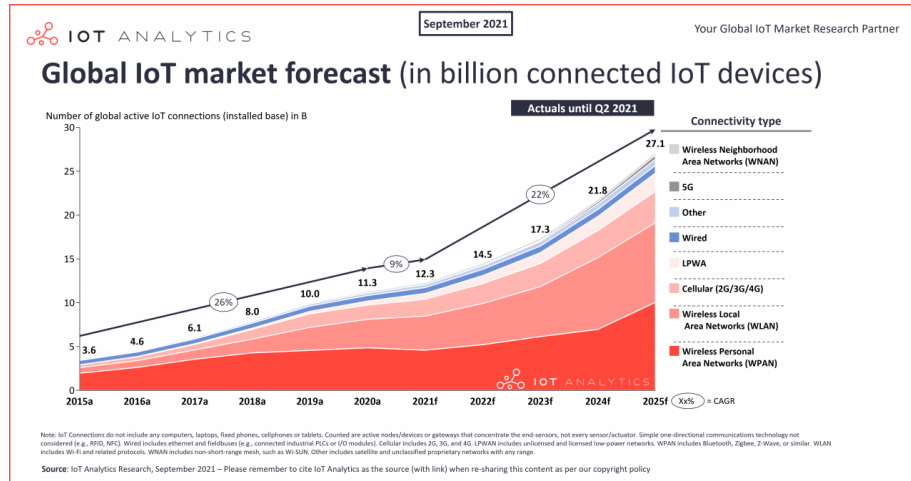


FIGURE 1.1: State of IoT 2021: Evolution of the number of connected IoT devices. Reproduced from [3]

1.2 History

The thermoelectric effect was discovered by the German physicist Thomas Johann Seebeck in 1821. Seebeck found out that a copper strip connected to a bismuth strip forming a closed circuit and heated at one junction induces current of electricity to flow around the circuit for as long as the temperature difference existed [6]. Thomas analyzed various materials and compared them in terms of the product Seebeck Coefficient (S) and electrical conductivity (σ) creating the "Seebeck Series", which is similar to the nowadays thermoelectric series, which uses the Figure of Merit zT as the order parameter, as discussed in section 1.3.1.

Thirteen years later, in 1834, Jean Charles Athanase Peltier observed a complementary effect, named the Peltier effect, which is considered the opposite of the Seebeck effect, that is the effect of applying a current and generating a temperature gradient[7].

A few years later Lord Kelvin considered these two effects to be dependent. With this consideration, Kelvin predicted the existence of a third thermoelectric effect, called the Thomson effect. This relates to the heating or cooling in a single homogeneous conductor whenever a current passes through it, in the presence of a temperature difference, this is a special case of the Seebeck effect, where the Seebeck coefficient depends on the temperature [8].

1.3 Basic Concepts on Thermoelectricity

The thermoelectric effect is the conversion of temperature gradients to electric voltage due to the diffusion of charge carriers across the material and vice versa. In a thermoelectric material, the charge carriers carry both charge and heat. When a temperature gradient is applied to a thermoelectric semiconductor, the energy conduction band also experiences a gradient, due to the flow of the mobile charges from the higher energy side (hot side) to the lower energy side (cold side), as represented in Figure 1.2.

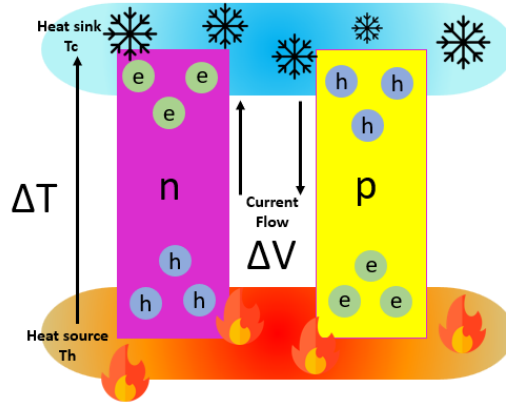


FIGURE 1.2: Scheme of the thermoelectric effect according to the type of the material (n-type or p-type).

Due to this flow of the majority carriers, the charges build up on the cold side, generating a voltage difference (ΔV) [9] between both sides of the thermoelectric material. This effect can be expressed by the Seebeck Coefficient (S) [8],

$$S = - \lim_{dT \rightarrow 0} \frac{dV}{dT} \quad (1.1)$$

and discretizing, one has

$$\Delta V = -S\Delta T \quad (1.2)$$

ΔV is measured in Volts (V), while ΔT is measured in Kelvins (K) S is expressed in Volts per Kelvin (VK^{-1}) in SI units, and is the indicator of the thermoelectric capability of a material.

Semiconductors can be classified according to the type of majority charge carriers i.e., in *p-type* material, holes are more abundant whereas in a *n-type* material, have more abundance of electrons. The S is either positive if the energy and temperature gradients have

the same direction, or negative otherwise (Figure 1.2), and it's larger if we are in the presence of only one kind of charge carrier. If a material contains both *n-type* and *p-type* conduction, the two kinds of charge carriers will move to the cold end, recombining themselves and canceling out the induced voltage.

1.3.1 Figure of Merit

To evaluate the thermal-to-electrical conversion a dimensionless quantity was defined, named figure of merit, ZT . This quantity evaluates the potential of a material for thermoelectric applications, and it is given by

$$ZT = \frac{S^2 \sigma}{\kappa} T \quad (1.3)$$

where σ is the electrical conductivity ($S m^{-1}$), κ is the total thermal conductivity ($W m^{-1} K^{-1}$), T is the temperature (K), and S is the Seebeck Coefficient ($V K^{-1}$) [8, 10]. Another method to evaluate the performance of a material is through the Power Factor (PF) $S^2 \sigma$, where the thermal conductivity of the material is not taken into account.

The enhancement of ZT remains a challenge because the transport characteristics depend on interrelated material properties. According to the previous equation, it is possible to see that in order to maximize the ZT of a material, it requires a large Seebeck, high electrical conductivity, and low thermal conductivity. The total thermal conductivity itself can be divided into two parts, the lattice contribution from phonon transport (κ_l) and the electronic contribution from the electron/hole transport (κ_e), given by the following equation,

$$\kappa = \kappa_l + \kappa_e \quad (1.4)$$

Metals have a high electrical conductivity because the partially filled conduction band allows the free movement of electrons along the crystal structure. The electronic contribution of thermal conductivity is dominant in metals, however, it is limited by the Wiedemann-Franz law (equation 1.5) [11],

$$\frac{\kappa_e}{\sigma} = LT \quad (1.5)$$

where L is the proportionality constant ($W^{-1} \Omega K^{-2}$), named Lorenz number, T is the temperature (K) and σ electrical conductivity ($S m^{-1}$).

On the other hand, the lattice contribution for the thermal conductivity can be written as

$$\kappa_l = \frac{1}{3} C_v v_s \lambda_{ph} \quad (1.6)$$

where C_v is the thermal capacity, v_s is the velocity of sound and, λ_{ph} is the mean free path of phonons. Therefore, the best strategy to decrease the thermal conductivity is to decrease the mean free path of the phonons. This strategy is called Phonon-Glass-Electron-Crystal [12] (Figure 1.3), which suggests that an ideal TE material should possess the combination of glass-like thermal conductivity and crystal-like electronic properties. Another strategy is the use of nanostructured/nanosized materials, which offers a solution by using a phenomenon on a small length scale to effectively decouple the relationships between σ , S , and k [13].

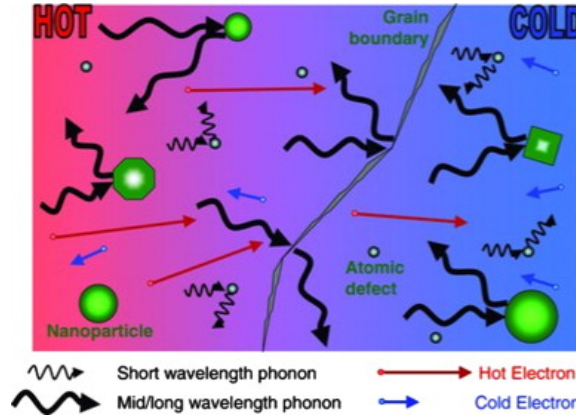


FIGURE 1.3: Phonon scattering phenomenon caused by the changes in the grain boundary of the material. Reproduced from [12].

To evaluate the potential of a thermoelectric material it is possible to define its efficiency, which can be expressed as a function of the Figure of Merit,

$$\eta = \frac{\Delta T}{T_h} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_c}{T_h}} \quad (1.7)$$

where T_h and T_c are the temperatures of the hot and cold sides, respectively [14]. The term $\frac{\Delta T}{T}$ is the Carnot efficiency, and it limits the maximum efficiency of a thermoelectric device. The remaining term is a reduction factor, which is a function of the material's figure of merit $Z = S^2 \rho^{-1} \kappa^{-1}$ [14].

However, the previous equation is often used to determine the efficiency of a thermoelectric device, which is not necessarily equal to the material's efficiency, which can be

seen as,

$$\eta = \frac{\text{provided energy}}{\text{heat energy absorbed at the hot junction}} \quad (1.8)$$

1.4 Thermoelectric Materials

The research for the ideal thermoelectric material has been going on since its discovery, and are classified as chalcogenides, clathrates, skutterudites, Half-Heusler (HH) compounds, silicides, oxides and Zintl phase materials [15], etc., based on the material's structure and composition. The ZT of the previous materials aren't enough for efficient conversion to electricity. Thermoelectric materials are divided into three groups based on the temperature range applications. For low-temperature range applications (< 451 K) materials such as bismuth-based alloys, middle range (451 – 851 K) materials such as lead-based alloys, and high-temperature range (> 1301 K) materials such as SiGe-based alloys, as shown in the Figure 1.4 [16].

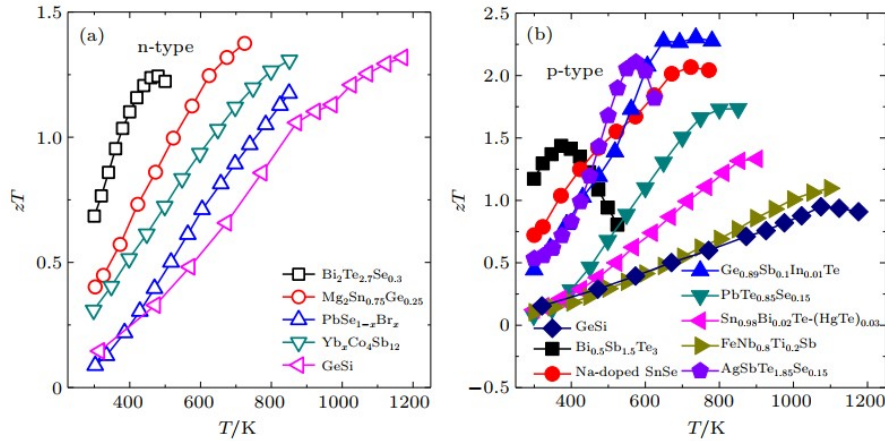


FIGURE 1.4: State-of-the-art figure of merit values for n-type (a) $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, $\text{Mn}_2\text{Sn}_{0.75}\text{Ge}_{0.25}$, $\text{PbSe}_{1-x}\text{Br}_x$, $\text{Yb}_x\text{Co}_4\text{Sb}_{12}$, and GeSi ; p-type (b) $\text{Ge}_{0.89}\text{Sb}_{0.1}\text{In}_{0.01}\text{Te}$, $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$, $\text{PbTe}_{0.85}\text{Se}_{0.15}$, $\text{Sn}_{0.98}\text{Bi}_{0.02}\text{Te}-(\text{HgTe})_{0.03}$, $\text{FeNb}_{0.8}\text{Ti}_{0.2}\text{Sb}$, $\text{AgSbTe}_{1.85}\text{Se}_{0.15}$, and GeSi . Adapted from [18].

Lead telluride (PbTe) was also found to have thermoelectric properties for temperatures between 300 and 700 K. From the chalcogenides system materials such as PbS and PbSe are similar to PbTe . Lead telluride forms isomorphous solid solutions with lead selenide and tin telluride, leading to lower thermal conductivity and improved ZT values. Another system that has similar properties are TAGS (TAGS thermoelectric materials are those that contain Ag, Ge, Sb, or Te.), like AgSbTe_2 and GeTe [19–21]. SiGe alloys are

outstanding for thermoelectric generation because silicon has a large band gap which reduces the problems with minority carrier dominance. Therefore, silicon-rich alloys, such as $Si_{0.7}Ge_{0.3}$, are suitable for high-temperature applications [21, 22]. As mentioned before Bi_2Te_3 is a good thermoelectric material with high performance at room temperature, which is the case of this study. For $T > RT$, the relatively narrow bang gap causes mixed conduction due to both electrons and holes. This causes the Seebeck coefficient to reduce.

One of the most difficult aspects of improving the Figure of Merit value is the difficulty in lowering κ because one of its components is directly related to electric conductivity. The solution comes from manipulating the lattice through κ , which reduces the phonon mean free path due to interface scattering. In the case of semiconductors, the phonon mean free path is typically around 100 nm, which can be reduced by using nanomaterials, thus reducing the lattice component of κ , κ_l . The benefits of working at this scale are obvious [23]. Over the last few decades, it has been discovered that increasing efficiency is inextricably linked to the size of the structures. Initially, the study of TE materials in bulk form resulted in the discovery of materials with ZT close to one, which seemed to be the limit for more than 30 years. Nonetheless, that value was only recently surpassed by the discovery of various nanostructures. It is now possible to achieve ZT values greater than three [24]. The strategies to improve the Figure of Merit value often begin by looking at the nanoscale, to increase the $S^2\sigma$ factor and decrease κ_l , Hicks and Dresselhaus suggested working at lower dimensions, such as thin films (2D) and quantum wire structures (1D) [25, 26].

The first research to test Hicks and Dresselhaus predictions was performed on Bismuth nanowires and showed a thermopower increase by a factor of 104 when compared with the bulk material [25, 26]. It is also possible to increase the power factor by doping semiconductors, which changes their density of states and approximates it to the ideal, guaranteeing the maximum Seebeck coefficient [25, 26].

1.4.1 Bi_2Te_3 as a Thermoelectric Material

Bismuth telluride is the working material in almost all Peltier cooling devices and thermoelectric generators. This is because Bi_2Te_3 has the highest thermoelectric figure of merit, ZT , of any material around room temperature [27].

Although the production technology of Bi_2Te_3 -based devices has remained almost the same since the 1960s, the knowledge about such materials suffered a huge advance [27].

Nowadays the thermal conductivity of Bi_2Te_3 can be also decreased, in particular by the production of nanomaterials/structures.

1.4.1.1 Crystalline Structure

Bismuth telluride, Bi_2Te_3 , crystallizes in a tetradymite crystal structure, as shown in Figure 1.4, and the coordination of Bi and Te is octahedral.

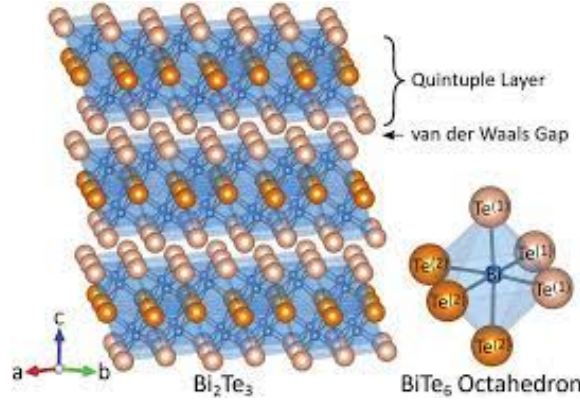


FIGURE 1.5: Layered structure of Bi_2Te_3 . Reproduced from [27].

The fact that Bi is slightly less electronegative when compared with Te justifies the association of valence as Bi^{+3} (s^2p^0) and Te^{-2} (s^2p^6). The large Te^{-2} anions of Bi_2Te_3 form a close-packed layer with cations Bi^{+3} in octahedral holes. Bi_2Te_3 has a hexagonal close packing (HCP) arrangement of Te layers, belonging to the space group R-3m (JCPDS 15-0863).

1.4.1.2 Electronic Structure

Besides the low lattice thermal conductivity, Bi_2Te_3 is also a great thermoelectric due to the complex electronic band structure which has been intensively studied experimentally and theoretically.

Although the semiconducting electronic structure of Bi_2Te_3 can be explained using simple valence rules, spin-orbit interactions complicate the band structure and confer exceptional electronic properties on Bi_2Te_3 [27]. To comprehend the band structure of Bi_2Te_3 , one must consider the interactions of both atoms' valence p-states within the quintuple layer [28]. The sp-hybridization is weak because the s and p valence levels in Bi and Te are sufficiently separated. The van der Waals interaction between neighboring quintuple layers is essentially nonbonding and contributes near the top of the valence band, whereas Te-bonding states are generally lower in energy [28, 29].

1.4.1.3 Nanomaterials/Nanostructures of Bi_2Te_3

The research in thermoelectric materials is continuously increasing, due to the growing demand for energy, and new ways of renewable energy production. Over the last decades, it was discovered that the improvement of efficiency is deeply connected to the size of the structures.

Nanostructures are classified according to their dimensionality, such as 0D, which includes molecules, clusters, fullerenes, rings, metcarbs, thoroids, domens, particles, powders, grains, schwartzons, nanoplates, and so on. Nanotubes, fibers, filaments, whiskers, spirals, belts, springs, horns, columns, needles, pillars, helicoids, wires, and ribbons are examples of 1D materials, as are 2D thin films [30, 31], Figure 1.6.

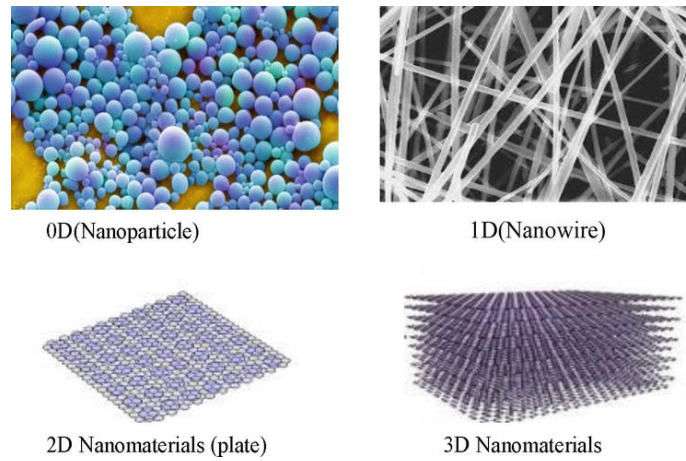


FIGURE 1.6: Types of nanomaterials (0D, 1D, 2D, and 3D). Reproduced from [32].

- 2D Bi_2Te_3 nanostructures synthesis methods

Cha et al. [33] used the vapor-liquid-solid and vapor-solid growth methods to create $Bi_2(Se_xTe_{1-x})_3$ nanoribbons and nanoplates. Following synthesis, the nanoribbons were grown using a metal catalyst (Au film). The nanoplates, on the other hand, were grown directly on SiO_x substrates. The electrical properties of nanoplates and nanoribbons were also found to be comparable. However, the nanoplates had higher carrier densities than the nanoribbons [30].

Using spin coating and drop casting techniques, Du et al. [34] created $Bi_{0.5}Sb_{1.5}Te_3$ (BST) nanosheet composite films. The experiment was divided into three steps: BST exfoliation, BST preparation, and BST characterization. The electrical conductivity of the drop cast composite film containing 4.10 wt% Bi_2Te_3 based alloy NSs was 1295.21 S/cm, which was higher than that (753.8 S/cm) of a dimethyl sulfoxide doped PEDOT:PSS film

prepared under the same conditions and that (850-1250 S/cm) of the Bi_2Te_3 based alloy bulk material.

Son et al. [35] created ultrathin Bi_2Te_3 nanoplates on a large scale. These chemically synthesized nanoplates were then used to create n-type nanostructured bulk thermoelectric materials using spark plasma. The nanoplates were created by reacting bismuth thiolate with tri-n-octylphosphine telluride in oleylamine. The nanoplates had a thickness of 1 nm.

Zhang et al. [36] also used a bottom-up approach to create a $Bi_2Te_3 - Te$ nano-micro heterostructure. In a powder matrix, the as-prepared heterophase nanoparticles were mixed. For the preparation of the heterophase $Bi_2Te_3 - Te$, a wet chemical surfactant-free synthesis approach was investigated. The nonstoichiometric $Bi_2Te_3 - Te$ nanoparticles were grown using galvanic replacement [30].

Punita and Kedar [37], on the other hand, conducted a combined study on the synthesis of Bi_2Te_3 nanoparticles, nanosheets, and nanotubes. At 50°C, 70°C, and 100°C, they used the surfactant-assisted wet chemical procedure. Sheets were observed forming on the surface of the nanoparticles at 50°C. At 70°C, wrinkled nanosheets were observed. Finally, as the temperature increased (to 100°C), the nanosheets formed the nanotubes. The methods for synthesis of 2D Bi_2Te_3 reported in the literature are summarized in Table 1.1.

TABLE 1.1: 2D Bi_2Te_3 structures synthesis methods reported in the literature.

Ref.	Structure	Preparation Technique
[38]	superlattice	nano alloying approach
[39]	thin films	flash-evaporation method followed by a hydrogen annealing process
[40, 41]	thin films	molecular-beam epitaxy (MBE)
[42]	thin films	ganic vapor phase deposition (MOCVD)

- 1D Bi_2Te_3 nanostructures synthesis methods

For the fabrication of 1D Bi_2Te_3 nanostructures, various synthesis methods were used. The method of fabrication can be both top-down and bottom-up [30].

Mi et al. [43] devised a straightforward biomolecule-assisted hydrothermal method for producing Bi_2Te_3 nanomaterials. The product has a hierarchical nanostring-cluster structure made up of ordered and aligned platelet-like crystals. The platelets produced

had a diameter of around 100 nm and a thickness of 10 nm. The self-assembly of the Bi_2Te_3 hierarchical structure appears to be the case. The nanorods are first formed using alginic acid as both a reductant and a template. As a result, Bi_2Te_3 grows in a specific direction on the surface of the Te rods, forming the nanostring structure. The nanostrings recombine side by side with one another to form the ordered nanostring clusters.

Xiao et al. [44] also synthesized Bi_2Te_3 nanotubes using a controlled composition electrochemical process of galvanic displacement reaction. In the galvanic displacement process, nickel nanowires were immersed in an acidic nitric electrolyte containing Bi^{3+} and HTeO^{2+} ions. They also created Bi_2Te_3 nanotubes by combining the magnetic assembly of a single nickel nanowire across microfabricated electrodes and the galvanic displacement reaction [30].

Lee et al. [45] were the first to report an annealing process for a high aspect ratio Bi-Te nanostructure. They proposed a method to prevent tellurium element evaporation in the temperature range of 300°C-623°C. The Bi-Te nanowires were created using a pulsed electrodeposition technique in an anodic aluminum oxide membrane. To avoid evaporation of the Te element, nanowires were enclosed in a completely sealed ceramic. Chen et al. [46] also used electrodeposition to create and characterize Bi_2Te_3 nanowires. Their research aimed to shed light on the low-dimensional effects of TE materials. As a result, they used potentiostatic electrodeposition. Picht et al. [47] then used electrodeposition to fine-tune the geometric and crystallographic properties of Bi_2Te_3 nanowires. Polymeric membranes were used in the study to grow the nanowires [30]. The Table 1.2 summarizes the 1D Bi_2Te_3 synthesis methods.

TABLE 1.2: 1D Bi_2Te_3 structures synthesis methods reported in the literature

Ref.	Structure	Preparation Technique
[48]	nanotube	low-temperature aqueous chemical method (hydrothermal synthesis)
[49]	nanotube	ultrasonic-assisted hydrothermal method
[50]	nanotube	solvothermal synthesis
[51]	nanobelt	vapor-liquid-solid (VLS) method
[52]	nanotube	microwave-assisted synthesis
[44]	nanotube	galvanic displacement reaction (electrochemical process)
[53]	nanotube	solution phase method
[54]	nanowire	electrodeposition
[55]	nanowire	physical vapor deposition method

- 0D Bi_2Te_3 nanostructures synthesis methods

A review of the various methods and techniques for fabricating 0D Bi_2Te_3 nanostructures will be presented here. Metal-organic CVD, molecular-beam epitaxy (MBE), sputtering, and electrodeposition methods have all been used to create Bi_2Te_3 (0D) nanostructures [30].

Chen et al. [12] used cryogenic grinding techniques to create nano-sized Bi_2Te_3 powders. The starting material was zone-melted n-type Bi_2Te_3 ingots. Steel mortar was used to crush these into coarse particles of about 5 mm. The 5 mm particles were then ground in liquid nitrogen using cryogenic grinding. The average particle size produced was around 70 nm.

Novaconi et al. [56] used an ultrasonically assisted hydrothermal method in alkaline aqueous solution with different concentrations of $NaBH_4$ as a reducing agent at 200°C for 3 hours to prepare nanocrystalline powders of doped Bi_2Te_3 with Ag, Sb, and Sn ions with different morphology and particle size 30-50 nm. Kaspar et al. [57] also developed a simple scalable wet-chemical synthesis of Bi_2Te_3 nanoparticles. These were made using a polyol method, which involved reacting Na_2Te in solution with a variety of bismuth(III) salts in boiling ethylene glycol. Depending on the reaction temperature and time, the particle size ranged from 20 nm to 400 nm.

Kim et al. [58] conducted three experiments to investigate the effect of starting powder morphology on the thermoelectric anisotropy of Bi-Te-based thermoelectric materials. A chemical reaction method (nano-sized particles with a spherical shape), a conventional pulverization method (flake-like shape), and a gas atomizing method are used to create starting powders with three different morphologies (spherical shape). Each sintered body's thermoelectric anisotropy is determined by measuring its electrical resistivity and thermal conductivity in both parallel and perpendicular directions to the spark plasma sintering pressing direction. The p-type $Bi_{0.5}Sb_{1.5}Te_3$ -sintered body made of spherically shaped powder exhibits isotropic thermoelectric properties, whereas the same material made of flake-like powder exhibits anisotropic behavior.

Synthesis procedures for near mono dispersed sub-nanometer bismuth telluride nanoparticles, which can be used as starting materials in the reduction route to form rhombohedral bismuth telluride, have also been reported [30, 59]. Scheele et al. [60] investigated a microwave-assisted polyol method. A simple synthesis of ultra-small [61] bismuth telluride nanoparticles with Raman spectroscopy-dependent nanostructure morphology has

been investigated. Pyrolysis of organometallic compounds was used to create high crystalline, impurity-free bismuth telluride nanoparticles (as small as 2 nm). Table 1.3 summarizes the synthesis methods employed so far in the fabrication of 0D Bi_2Te_3 nanostructures.

TABLE 1.3: 0D Bi_2Te_3 structures synthesis methods reported in the literature

Ref.	Structure	Preparation Technique
[62]	nanoparticle	one-pot two-step solution-based procedure
[63]	nanocrystalline	microwave-assisted polyol method
[64]	hollow nanosphere	microwave-assisted method
[12]	nanoparticle	pyrolysis of organo metallic compound
[36]	nanoparticle	galvanic replacement reaction
[65]	nanocrystalline	solvothermal method
[66]	nanoparticle	water-based chemical reaction
[67]	nanocrystalline	mechanical alloying (MA) method
[68]	nanoplate	van der Waals epitaxy
[61]	nanoplate	pyrolysis of organometallic compound method

Among the different shapes of nanosized Bi_2Te_3 materials, nanoplates are the most appropriate shape to take advantage of the inherent features of the Bi_2Te_3 crystal structure. Since Bi_2Te_3 nanoplates are single-crystalline and have a hexagonal shape similar to their unit cell [69]. The chemical reduction process was chosen for this work because it has some advantages over the other processes, such as the fact that the other processes require very specific equipment, extreme conditions, and are difficult to scale up.

1.5 Applications

There is an increasing search for new, improved, and sustainable energy generation methods. This is also due to the unprecedented growth of the Internet of Things market, which pushes technology to its limits on a daily basis. The most promising solution to this problem appears to be energy harvesting. As a result, thermoelectricity is important because it is silent, vibrationless, and non-pollutant. Furthermore, it makes use of waste heat and has a reliable conversion.

Thermoelectric energy can be used in a variety of applications including refrigeration, air conditioning, electricity generation, biomedical devices, industrial utilities, transportation tools, and space applications, to name a few [70]. Some relevant thermoelectric applications are discussed further below.

- Thermoelectric Refrigerator

A thermoelectric refrigerator operates on the Peltier effect, which converts electricity into heat for cooling and heating [71]. Domestic and portable refrigerators are the two main types of TE refrigeration devices. The availability of electrical power is the primary distinction between these two. Refrigerators, both domestic [72, 73] and portable [74, 75], have been extensively researched.

- Electronic Cooler

Many high-power electronic devices, such as microprocessors, power amplifiers, and computers used in servers, run continuously and provide service to customers; during this time, a large amount of heat is generated within the system and must be dissipated from the system to avoid hardware failure and malfunction. As a result, cooling is required to improve the performance and life of electronic devices. Because traditional cooling systems are difficult to use in these situations, thermoelectric devices were tested.

Manno et al. [76] recently provided an excellent review of various device configurations for hot spot cooling that have been tested by various groups. Chowdhury et al. [77], for example, modeled heat transfer in a thermoelectric Peltier cooler attached to a localized hot spot and measured the on-demand cooling achievable [78].

- Thermoelectric Generator (TEG)

Thermoelectric generators (TEG) convert heat energy directly into electric energy without the use of a rotating part or mechanism. The use of power plants for waste heat recovery in automobiles has been shown to increase fuel efficiency by 10% [70]. TEGs can be configured in a variety of ways, including planar, radial, vertical, and origami, depending on their purpose and application, as seen in Figure 1.7 [79]. TEG has been used in power plants for waste heat recovery, automobiles for fuel efficiency, and other applications, according to Angonda et al. [70]. TEG has been used in a variety of applications, including automotive, aerospace, industrial, domestic, and thin film, according to Zheng et al. [80].

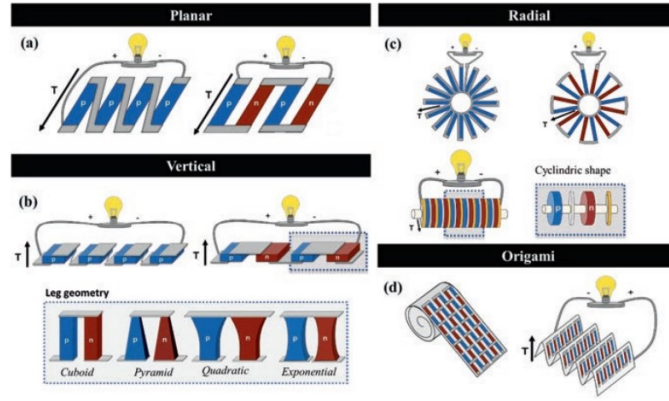


FIGURE 1.7: Schematic illustration of possible TEG configurations such as (a) planar, (b) vertical, (c) radial, and (d) origami configuration. Reproduced from [79].

There are many other applications of thermoelectric energy, such as in medicine, where thermoelectricity is present for example, in wearable sensors for electroencephalography (EEG), electrocardiography (ECG), electromyography (EMG) etc, in human implantable devices such as pacemakers, neurological stimulators, etc [70, 81].

1.6 Objectives

After detailed research of information regarding the state of the art and taking into account the huge advances that have been made in the thermoelectric field in the past years, it is natural that the main objective of this work is to develop bismuth telluride nanoplates and optimize them for thermoelectric applications at room temperature. Aside from improving the nanoplates, another objective is to incorporate a stable chemical reaction that enables scalability and mass production.

After the nanoplate's production and optimization, a planar thermoelectric generator was produced and tested, capable of producing energy, this being the main and final objective of this work.

Chapter 2

Experimental Methodology

In this chapter, a general overview of the synthesis method and characterization techniques used in this work will be presented. As a result, this chapter is divided into three major sections. To begin, the process used to fabricate the materials will be presented, specifically the chemical reduction process used to produce bismuth telluride nanoplates.

Second, the stencil printing technique will be explained, as it was the printing technique used to assemble the thermoelectric generator (TEG).

Finally, the characterization techniques used to study the produced nanoplates and/or the produced device will be presented, beginning with their structural and morphological characterization and progressing to their transport properties characterization. To characterize the nanoplates/device structure and morphology were used techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), electron dispersion microscopy (EDS), transmission electron microscopy (TEM), and Raman spectroscopy. Relatively to the characterization of the transport properties it was performed the materials/device measurement of the Seebeck coefficient and electrical conductivity.

2.1 Materials' Synthesis

Due to its high efficiency, Bi_2Te_3 is one of the most well-known thermoelectric materials. A chemical reduction process was used to produce the bismuth telluride nanoparticles.

The first step in the process is to measure the liquid solvents, which are the surfactant/solvent 1-amino-2-propanol (MIPA), 94% purchased from ThermoScientific and the solvent ethylene glycol (EG) 99%. The previous two are then poured to a round bottom

flask and placed in a silicon bath at 40°C for 10 minutes with magnetic stirring. Throughout this work, the molar concentrations of MIPA and EG will be varied to study their effect on the reaction (Table 2.1).

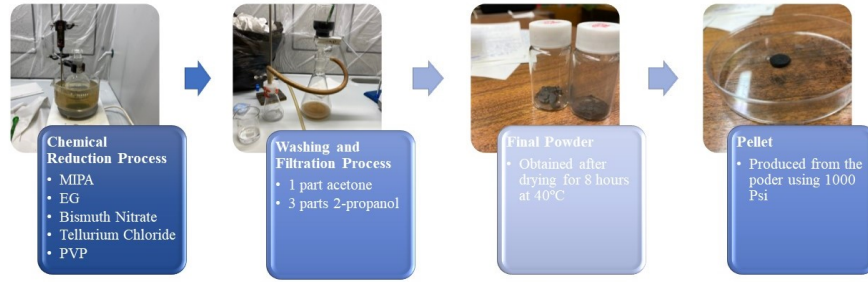
TABLE 2.1: Employed MIPA and EG molar concentrations

Samples	MIPA molar concentration	EG substance amount
1 M MIPA 7.17 EG	1	7.17
1 M MIPA 3.59 EG	1	3.59
1 M MIPA 1.79 EG	1	1.79
2 M MIPA 7.17 EG	2	7.17
2 M MIPA 3.59 EG	2	3.59
2 M MIPA 1.79 EG	2	1.79
3 M MIPA 7.17 EG	3	7.17
3 M MIPA 3.59 EG	3	3.59
3 M MIPA 1.79 EG	3	1.79

Following that, the last three reactants are weighed and mixed together: polyvinylpyrrolidone (PVP), M.W. 10000, a surfactant used to limit crystal growth, and the reagents 8.26 mmol of bismuth(III) nitrate pentahydrate 98% ($Bi(NO_3)_3 \cdot 5H_2O$) and 2.48 mmol of tellurium(IV) chloride 99% ($TeCl_4$), the first two were purchased from Alfa Aesar and the last at Thermo Scientific. This mixture is then added to the round bottom flask, and the temperature is raised to around 190°C, where it remains for 3 hours and under vigorous magnetic stirring.

After 3 hours, the flask is removed from the bath and allowed to cool down to room temperature before washing and filtering the nanoparticles with a mixture of one part acetone (100 ml) and three parts of 2-propanol (300 ml).

Following the washing and filtration processes, the product was dried in an oven for 8 hours at 40°C. The final powder, to allow the material characterization using some techniques, such as electrical conductivity and Seebeck coefficient, was then formed into a pellet using a press machine (1000 psi). The all process is schematized in Figure 2.1.

FIGURE 2.1: Method of fabrication of the Bi_2Te_3 nanoparticles.

2.2 Devices assembly using Screen-Printing

Screen printing is the process of transferring a stenciled design onto a substrate using a mesh screen, ink, and a squeegee (rubber blade). The basic process of screen printing involves creating a stencil on a mesh screen and then pushing the ink to create and imprint the design on the below surface. This technique involves closed nonimage areas, where the mesh is coated with UV-sensitive emulsion, and open image areas through which the pattern can be printed.

The screen is held at a distance of around 0.5 mm from the substrate. The ink is poured onto the top surface of the screen, and the squeegee moves across the screen, pressing the mesh down into contact with the substrate and forcing the paste through the open areas. Directly behind the squeegee the mesh peels away from the substrate and leaves a deposit of the ink, having the required pattern, on the substrate surface [82]. This process is schematized in Figure 2.2.

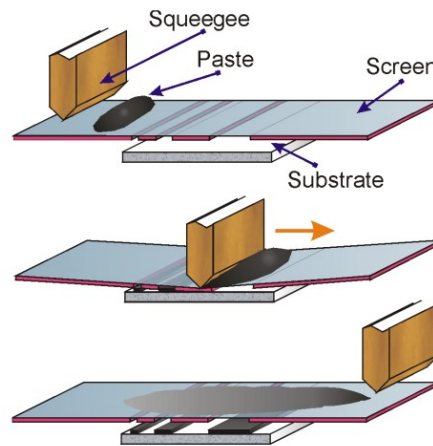


FIGURE 2.2: Process of screen-printing. Reproduced from [82].

The resolution of this technique depends on various factors, such as the viscosity and texture of the ink, print designs on the mesh, and also the adhesion of the ink to the substrate.

2.2.1 Bi_2Te_3 NPs Inks

Because the previously produced powder can agglomerate into larger pieces, it is ground with a mortar and pestle to facilitate the ink mixture. As shown in Figure 2.3, the ink must have two main components: an organic binder and inorganic functional particles. The organic binder used in this study was poly(vinyl alcohol) (PVA, 99%) doped with orthophosphoric acid (H_3PO_4 , 85% - analytical grade) purchased from Fisher Chemical. Deionized water was also added during the manufacturing process to improve the quality of the ink, facilitate the mixing of all the components and to obtain the ideal viscosity for screen-printing.

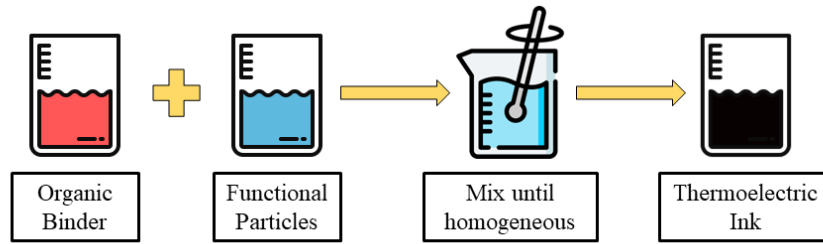


FIGURE 2.3: Inks formulation for screen-printing applications.

2.2.2 Substrate treatment

The device created was a planar thermoelectric device. The device was assembled using Kapton, a polyimide film commonly used in flexible printed circuits. Before using it, the Kapton underwent a treatment to improve its adhesion, as reported by [83]. At room temperature, the Kapton was treated with a 10% potassium hydroxide (KOH) aqueous solution for 60 minutes. The excess KOH was washed away with running water. The Kapton was then poured for 5 minutes at room temperature in a 10% wt. chloridric acid (HCl) aqueous solution. The films were then dried in an oven at 40°C.

The first solution of KOH breaks the bonds and introduces functional groups of carbon-oxygen, increasing adhesion, and the second solution removes the freed ions and introduces hydrogen, increasing the chemical interaction between the substrate and the printing.

2.2.3 Electrical contacts and thermoelectric printing

The device's contacts were then printed in the Kapton substrate using a commercial silver ink with a resistivity of less than $3.8 \times 10^{-5} \Omega m^{-3}$ acquired from VFP ink technologies. The contacts are then dried in an oven at 150°C for 10 minutes. After that, the device can be printed with the thermoelectric ink described in Section 2.2.1. The final device is presented in Figure 2.4.

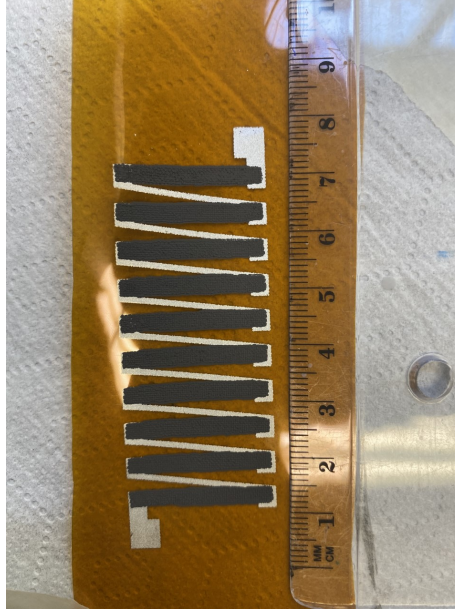


FIGURE 2.4: Final printed thermoelectric device.

2.3 Structural and morphological characterization techniques

2.3.1 X-Ray diffraction (XRD)

In 1912 Max von Laue discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths close to the spacing of planes in a crystal lattice [84]. A year later W. L. Bragg and his father W. H. Bragg disclosed its application to structure determination.

These discoveries were fundamental for the determination of the crystal structures of all kinds of crystalline materials. This technique can provide information about the crystallite size, lattice strain, grain size, chemical composition, epitaxy, and preferred orientation of the materials [84, 85].

The working principle of X-ray diffraction is based on constructive interference on monochromatic X-rays and a crystalline sample. A cathode ray tube generates the X-rays, that are collimated, filtered to produce only monochromatic radiation, and directed in the sample direction. When the conditions satisfy Bragg's law, the interaction between the incident rays and the sample generates a constructive interference, according to the configuration represented in Figure 2.5.

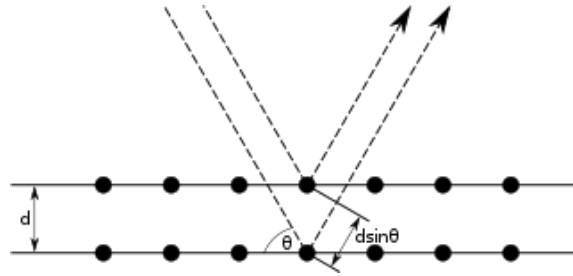


FIGURE 2.5: Schematic illustration of Bragg's Law. Reproduced from [86]

This phenomenon follows the equation

$$\lambda = 2d_{hkl} \sin \theta_B \quad (2.1)$$

known as the Bragg's Law. This equation relates the electromagnetic radiation's wavelength (λ) to the diffraction angle (θ_B) and the distance between two adjacent atomic planes (d) with indexes (hkl), known as the Miller Indexes. The diffracted X-rays are then detected, processed, and counted.

This technique allows the determination of all possible diffraction directions of the lattice by scanning the sample through a range of 2θ angles due to the random orientation of the powdered material. The identification of the mineral is performed through the conversion of the diffraction peaks to d-spacings because each mineral has a set of unique d-spacings. This is achieved by comparing the obtained d-spacings with the standard reference patterns.

2.3.1.1 Working principle of X-ray powder diffraction (XRD)

The three main elements of X-ray diffractometers are an X-ray tube, a sample holder, and an X-ray detector, as shown in Figure 2.6.

The X-rays are generated in a cathode ray tube by heating a filament to produce electrons, then a voltage is applied and the electrons are accelerated toward a target. When

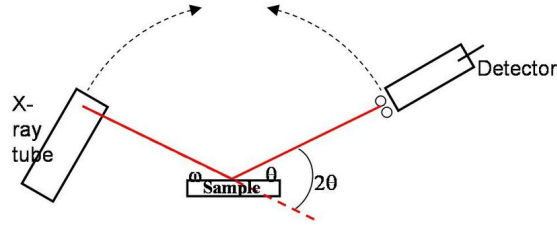


FIGURE 2.6: Schematic representation of the Bragg-Brentano geometry. Reproduced from [87]

the electrons have enough energy, they dislodge the inner shell electrons of the target material. The characteristic X-ray diffractogram are produced when electrons have enough energy to dislodge the inner shell electrons of the target. These spectra consist of several components, the most common are K_α and K_β . The wavelengths are characteristic of the target materials, such as Copper (Cu), Iron, (Fe), Molybdenum (Mo), and Chromium (Cr). In this work, it was used the most common target material, Copper, which has a wavelength of $\lambda_{Cu} = 1.5406\text{\AA}$. The X-rays are collimated and headed to the sample. As the detector rotates, the intensity of the reflected X-rays is recorded. Then the detector records and processes the X-ray signal converting it into a count rate. The collected diffraction patterns were represented as the intensity of diffracted particles versus 2θ and were compared to known ones from the JCPDS database published by the International Centre for Diffraction Data. The crystallite size was calculated from X-ray diffraction profiles of strong reflections with intensity % by measuring the full width at half maximum (FWHM). The Debye-Scherrer equation for calculating the crystallite size is

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (2.2)$$

where K is the Scherrer constant, λ is the wavelength of light used for the diffraction, β is the “full width at half maximum” of the sharp peaks, and θ is the angle measured.

2.3.2 Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS)

Scanning electron microscopy (SEM) is a type of electron microscope that produces images of a sample through the scanning of the surface with a focused beam of electrons. Its principle was demonstrated by Knoll in 1935, and the first SEM device was developed in 1938 by von Ardenne [88].

The signals obtained from electron-sample interactions give information about the sample regarding the shape, size, composition, crystallography, and other chemical and physical properties of the sample. The operating principle of the SEM starts with the creation of a focused beam of energetic electrons emitted from an electron source, with an energy of up to 40 keV. Following the emission, the electron beam is accelerated to high energy, and the diameter is reduced by passing the beam through apertures, magnetic or electrostatic lenses. The incident electron beam is scanned in a raster pattern across the surface of the sample. The focused beam is then used to scan the sample in the x and y directions at discrete locations, to create a pattern (Figure 2.7). At each point of interaction between the electron beam and the sample, two main types of electron signals are produced: backscattered electrons (BSE), which are beam electrons that emerge intact from the sample after being scattered and deflected by the electric fields of the atoms in the sample, emerge from the sample with most of their incident energy intact, and secondary electrons (SE), which are electrons that emerge from the sample surface after being ejected by the electron beam [89, 90].

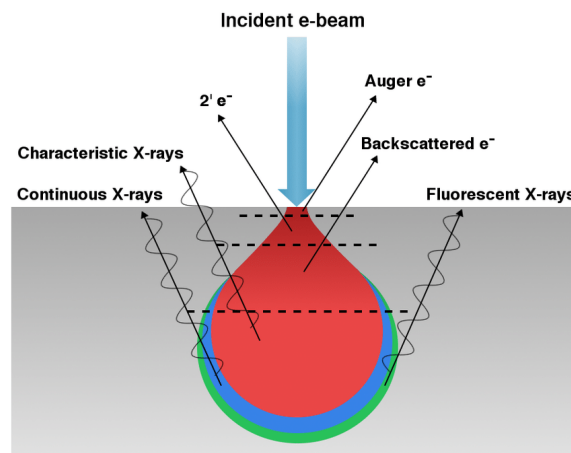


FIGURE 2.7: Interaction volume of an incident beam of electrons and the different electron signal responses. Reproduced from [90].

At each point of interaction between the beam and the sample, the electron signals generated are measured by one or more electron detectors. For each of these detectors, each measured signal is digitized and recorded and then used to determine the grey level at the corresponding x-y position of a computer screen that forms a single pixel. This technique has a lateral spatial resolution of about 10 to 100 nm, depending on the composition of the sample and the energy chosen for the beam [91].

The electron beam interaction with the sample produces two types of X-ray photon emissions, the characteristic X-rays, whose specific energies provide a fingerprint specific to each element, and continuum X-rays, which occur at all photon energies. This X-ray spectrum can be used to identify and quantify the present elements within the beam-excited interaction volume, which has dimensions ranging from approximately 100nm to $10\mu\text{m}$, depending on composition and beam energy, over a wide range of concentrations. This X-ray spectrum is measured with the semiconductor energy dispersive X-ray spectrometer, i.e, EDS [92].

SEM and EDS provide important information, not only about high-resolution spatial information and contrasts but also about the nature of the atoms excited by the electrons during the interaction, allowing analysis of the chemical composition of the sample [93]. The backscattered electrons provide information about the composition, topography, mass thickness, and crystallography of the investigated sample. On the other hand, secondary electrons influence SEM images of compositional structures and topographic structures in complex ways and guarantee high resolution [91]. The SEM/EDS data obtained during this work were acquired at FCUP installations by a FlexSEM 1000 Hitachi.

2.3.3 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is an excellent tool to obtain information on a morphological, structural, and nanoscale level. The first TEM was demonstrated by Max Knoll and Ernst Ruska in 1931, and Ruska was awarded the Nobel Prize in physics for its development. TEM is a microscope that uses a high-energy (80 keV or higher) electron beam to visualize specimens and generate highly magnified images. The schematic ray diagram of a typical TEM in image mode is shown in Figure 2.8.

In the diffraction mode, another intermediate lens needs to be inserted to image on the screen the diffraction pattern of the back focal plane. This type of electron microscope has three main systems, the first being the electron gun, which produces the electron beam, and the condenser lens system, which focuses the beam toward the sample. The second is the image-producing system, which includes the objective lens, the movable specimen stage, and the intermediate and projector lenses, which focus the electrons that pass through the sample to form a real, highly magnified image. Finally, the third is the image-recording system, which converts the monochromatic electron image into another form visible to the human eye, this is done either by allowing the electron the electrons to fall on

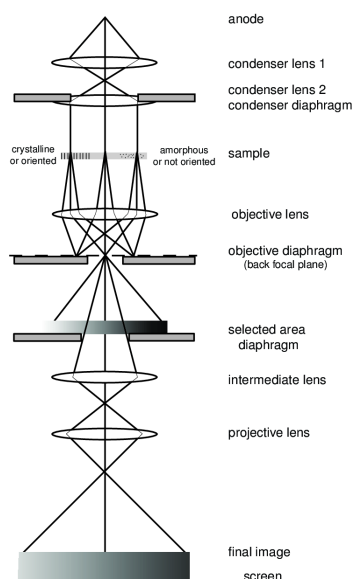


FIGURE 2.8: Schematic representation of a transmission electron microscopy (TEM). Reproduced from [94].

a fluorescent screen fitted at the base of the microscope or by capturing the image digitally on a computer monitor. The TEM analysis was performed at HEMS/i3S of the University of Porto on a JEOL JEM 1400 TEM at 120 kV. The images were digitally recorded using a CCD digital camera Orious 1100 W. The samples were prepared by dispersion in ethanol under sonication, followed by the immersion of formvar/carbon-coated 400 mesh copper grids in the resulting suspensions and subsequent air-drying.

2.3.4 Raman spectroscopy

Raman spectroscopy is named after the Indian scientist Sir Chandrasekhara Venkata Raman, who won the Nobel Prize in Physics in 1930 for his work on the scattering of light and the discovery of the effect named after him [95].

Raman spectroscopy is a non-destructive chemical analysis technique, that can provide chemical and structural information, such as the chemical structure, crystallinity, molecular interactions, and phase. This information is obtained due to the interaction between light and the material's chemical bonds. The scattered light measures the vibrational energy modes of the sample.

According to the Raman effect when incident light excites molecules in a material, the molecules will reflect light in a different wavelength. The most common wavelength used is 785 nm (near-infrared). However, visible light lasers, such as green (500-565 nm), and ultraviolet light (10-400 nm), are also used in Raman spectroscopy. To characterize the

material of this work was used, the laser used was a green laser, with a wavelength of 532 nm.

The incident light can undergo three types of scattering processes when interacts with a molecule, as shown in Figure 2.9. The Rayleigh Scatter is light that is the same wavelength (color) as the light source and does not provide useful information. On the other hand, the Raman Scatter is scattered at different colors depending on the structure that bonds the molecules of the material together. The anti-Stokes scattering results from an increase in photon energy, which leaves the molecule in a lower vibrational energy state.

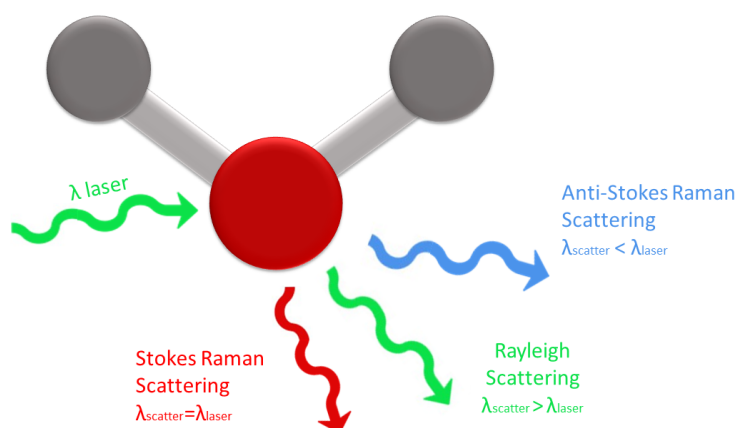


FIGURE 2.9: Three types of scattering processes that can occur when light interacts with a molecule.

2.4 Transport Properties

2.4.1 Seebeck coefficient

The Seebeck coefficient is an essential property to analyze the thermoelectric capabilities of the materials. One is directly related to the material's Figure of Merit (Equation 1.3). In this work, to measure the Seebeck coefficient it was used a home-build set-up represented in Figure 2.10.

The set-up consists of two electrically isolated copper support pillars, one of them is connected to the temperature controller (Lake Shore 331 TC) and works as the heat source while the other is kept at room temperature. The distance between the pillars is adjustable, allowing the system to adapt to samples of different sizes. The temperature of the pillars

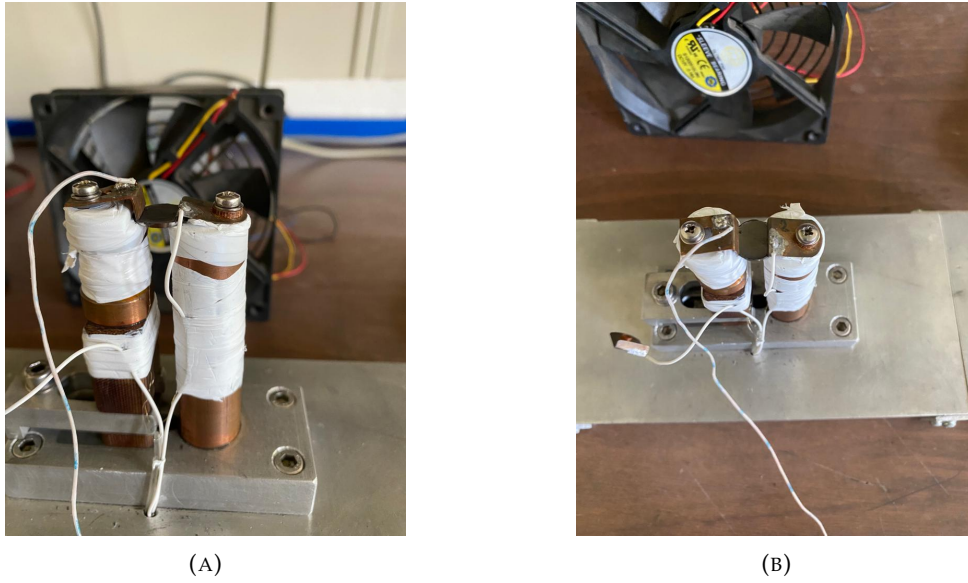


FIGURE 2.10: (A) Home-build set-up for the Seebeck coefficient. (B) Contacts and placement of the sample

is measured using a K-type thermocouple in each pillar and is connected to the thermocouple, so it automatically checks the gradient between them. The potential generated by the temperature gradient on the sample is measured using a nanovoltmeter (Keithley 2182). The voltmeter terminals are connected to two tabs, that are pressed on top of the sample, guaranteeing electrical contact. Once the temperature gradient reaches a stable level the potential difference values are acquired through a developed LabView software. The gradient used ranged from 10 to 26 Kelvins with a step of 2 and a stabilization time of 2 minutes.

2.4.2 Electrical resistivity

The resistance that a material offers to the flow of electrical current is an important property of a thermoelectric material. All the resistivity measures were made using the four-point collinear probe method, the scheme of the set-up presented in Figure 2.11.

The four-point collinear probe method requires a current being applied between the two outer probes, and the voltage is measured across the inner ones. The Ohm's Law given by,

$$V = R \times I \quad (2.3)$$

V is measured in Volts (V), R is measured in Ohms Ω , and I is expressed in amperes (A). It enables the determination of the sample's resistance. The usage of the four-probes method

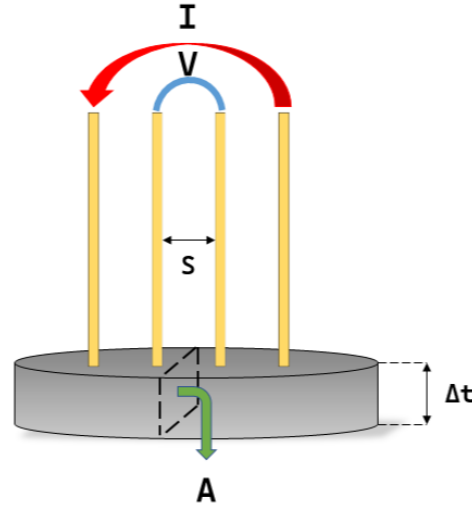


FIGURE 2.11: Scheme of the four-point collinear probe method.

greatly reduces the measurement errors, when compared with the two-probes method. Using four probes instead of two to apply and detect the signal creates a low impedance circuit that counteracts the current that passes in the measurement connections, clearing the contribution of this pair, only remaining the signal that comes from the sample. All four probes are equally spaced and centered in contact with the sample.

The derivation of the formula for the electrical conductivity of the material is not easy due to the special arrangement of the four-point collinear probe. The whole explanation is available in [96] and is summarized below.

The bulk conductivity is derived by calculating the voltage of one arbitrary point with one probe and extrapolating to the specific situation of four collinear probes that are evenly separated by s . An arbitrary sample's bulk conductivity is given by,

$$\sigma = \frac{1}{\rho} = 1 / \left(2\pi s F \frac{V}{I} \right) \quad (2.4)$$

with ρ (Ωm) being the electrical resistivity, I (A) the applied current, V (V) the measured voltage between the two inner probes, s is the distance between the two inner probes, and F is the correction factor related to the probe placement, sample thickness and the probe location to the edges.

F is defined as $F = F_1 F_2 F_3$, where F_1 refers to sample thickness, F_2 refers to lateral sample dimensions, and F_3 refers to probe placement in respect to the edges. Although just three correction variables were examined in this research, different correction factors can be used in other instances.

In terms of sample thickness, F_1 is given by,

$$F_1 = \frac{t/s}{2 \ln \left(\frac{\sinh(t/s)}{\sinh(t/2s)} \right)} \quad (2.5)$$

where t is the sample thickness. For thin samples, where $t/s \ll 1$, one can consider $\sinh t/s \approx t/s$, thus

$$F_1 = \frac{t/s}{2 \ln 2} \quad (2.6)$$

only valid for samples with $t \leq s/2$.

Given the sample's lateral dimensions, F_2 may be calculated by,

$$F_2 = \frac{\ln 2}{\ln 2 + \ln \left(\frac{(D/s)^2 + 3}{(D/s)^2 - 3} \right)} \quad (2.7)$$

where D is the diameter of the (circular) sample.

Finally, because only circular samples were used in this study, and the probes were put in the center and away from the edges, the adjustment for this aspect may be ignored, resulting in $F_3 = 1$.

In this project, the electrical conductivity values were calculated using Equation 2.4 with the F_1 and F_2 correction factors. The electrical conductivity is the calculated using the equation

$$\sigma = \frac{1}{\rho} \quad (2.8)$$

The equipment used to perform the measurements was a 2410-C SourceMeter© from Keithley Instruments, Inc.

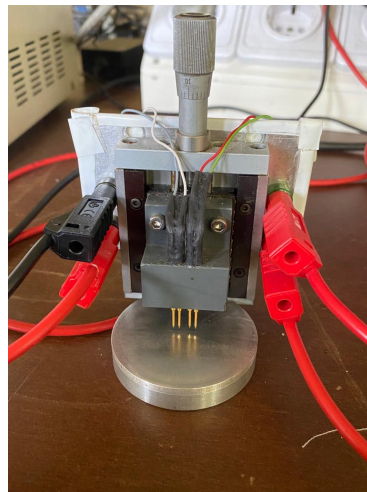


FIGURE 2.12: Set-up of the four-point collinear probe method.

2.4.3 Power Factor

After the determination of the Seebeck coefficient and electrical conductivity, one is now able to calculate the power factor, given by

$$PF = S\sigma^2 \quad (2.9)$$

where S is the Seebeck coefficient, and σ is the electrical conductivity.

Chapter 3

Experimental Results and Discussion

To study the properties of a material, it is necessary to first understand how the fabrication conditions affect these properties. In this regard, the bismuth telluride nanoplates preparation was optimized regarding the amount of MIPA and EG added during the chemical reduction process. Under the same synthesis conditions, five different molar concentrations of MIPA (0.25 M, 0.5 M, 1 M, 2 M, and 3 M) were evaluated to ensure that this was the only parameter responsible for possible changes in Bi_2Te_3 properties. EG variation was performed in the produced nanoplates for three distinct substance amounts of 7.17, 3.59, and 1.79. This variation was evaluated for three different MIPA molar concentrations (1, 2 and 3 M).

3.1 MIPA molar concentration dependence

To examine the variation of the MIPA molar concentration, all other quantities remained constant, such as the EG molar concentration, which remained constant at 1 M. The samples will be labeled as 0.25 M MIPA, 0.5 M MIPA, 1 M MIPA, 2 M MIPA, and 3 M MIPA.

3.1.1 Structural and Morphological Characterization

The XRD diffractogram for each sample with different MIPA concentrations is shown in Figure 3.1. the intensity of the peaks of all diffractograms was normalized by dividing the values by the maximum intensity. The results showed that Bi_2Te_3 has a rhombohedral tetradymite-type crystal structure with the space group R-3m (JCPDS 15-0863) [97].

The diffractograms for samples with MIPA molar concentrations of 1 M, 2 M, and 3 M are shown in Figure 3.1. The peaks with angle (2θ) 17.42, 27.65, 37.88, 40.58, 41.17, 44.56,

50.33, 53.84, 57.08, 62.26, 66.02, 66.96, 70.02, 72.78, and 75.04 are identified for all concentrations, and correspond to the miller indices (006), (015), (1010), (0111), (110), (116), (205), (1016), (0210), (1115), (0120), (125), (0216), (1022), and (1211). Additional reflections (highlighted in Figure 3.1) are visible in the diffractogram of the sample 2 M MIPA at angles 8.69 and 11.6. These peaks are caused by the formation of bismuth hydroxide ($Bi(OH)_3$) as reported by Poursalehi et al. [98]. This contamination is likely to occur since the synthesis was not carried out in a controlled environment, and so contact with the air promotes the formation of oxides. It should be mentioned that producing in a controlled environment would greatly raise production costs, which is not the primary goal of this thesis.

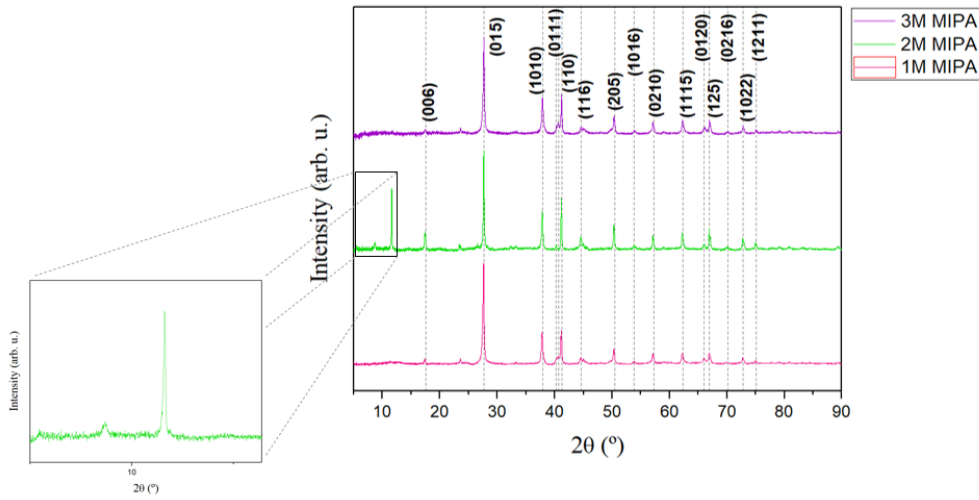


FIGURE 3.1: XRD spectrum of different Bi_2Te_3 samples based on the amount of MIPA added during the chemical reduction process. The highlighted peaks are the additional reflections caused by the formation of bismuth hydroxide ($Bi(OH)_3$).

The other two lower MIPA concentrations were investigated and depicted in 3.2. It is patent that they are different from Figure 3.1, and so do not match the Bi_2Te_3 spectrum. After examining and comparing both, it is feasible to determine that the diffractogram of the sample 0.5 M MIPA fits the spectrum of bismuth hydroxide ($Bi(OH)_3$) as reported by Poursalehi et al. [98]. The diffractogram of the sample 0.25 M MIPA, on the other hand, corresponds to a junction of the spectra of bismuth hydroxide ($Bi(OH)_3$) [98], tellurium oxide (TeO_2) [99], and bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$) [100], the latter being a reaction precursor, indicating that the reaction was not complete.

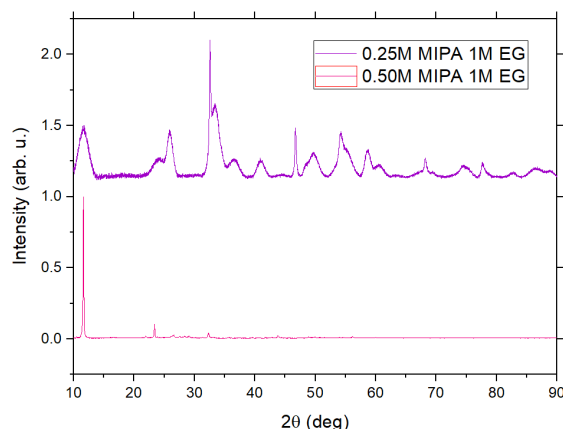


FIGURE 3.2: XRD spectrum of samples with MIPA molar concentrations of 0.25 and 0.5.

Because MIPA is a base, and a high pH environment promotes the formation of oxides, the formation of these oxides and the persistence of the precursors are extremely likely to occur as the molar concentration of MIPA decreases. As a result, raising the molar concentration of MIPA promotes the formation of the precursors bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \bullet 5\text{H}_2\text{O}$) and tellurium chloride (TeCl_4) over the oxides. The research article on which this materials synthesis is based employs sodium hydroxide (NaOH) instead of MIPA, which is likewise very alkaline, which is consistent with the results [101]. MIPA was employed instead of NaOH in our synthesis since it can impact and limit the rise in particle size, as proven by Pereira et al. [102].

Each sample's crystallite size was then calculated using the Debye-Scherrer technique, as described in section 2.3.1.1. The Origin software was used to extract the necessary data from the XRD diffractogram for the crystallite size calculation, such as the angle (2θ) and FWHM of each peak. The calculations were performed using the peak with the highest intensity and direction (015). Figure 3.3 depicts the results of the crystallite size.

The crystallite sizes range from 41.30 and 52.30 nm and are clearly at their maximum with a MIPA molar concentration of 2. The more narrower the peaks, the more crystalline the sample is; this can be confirmed by looking at the Debye-Scherrer equation 2.3, which indicates that whenever the FWHM value is lower, the crystallite size is larger. The XRD diffractograms match those previously reported by Hosokawa et al. [97] for the growth of Bi_2Te_3 hexagonal nanoplates.

Following the XRD analysis, a morphological analysis is required to examine the morphological differences between the samples (see Figure 3.4).

When the appearance of the particles is examined, it is possible to see that the particles

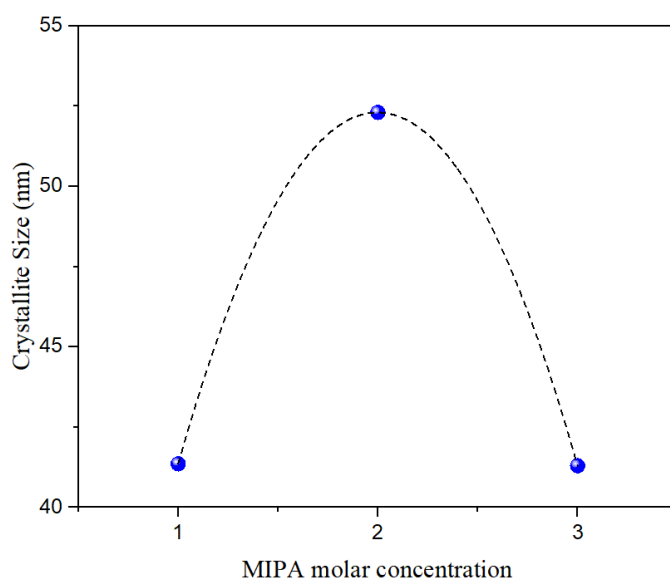


FIGURE 3.3: Crystallite Size of each sample.

appear to be more or less homogeneous in the sample 1 M MIPA, whereas some tubular structures are present in the sample 2 M MIPA, and finally, the images suggest that the particles are more homogeneous and less morphologically defined in the last sample with MIPA molar concentration of 3.

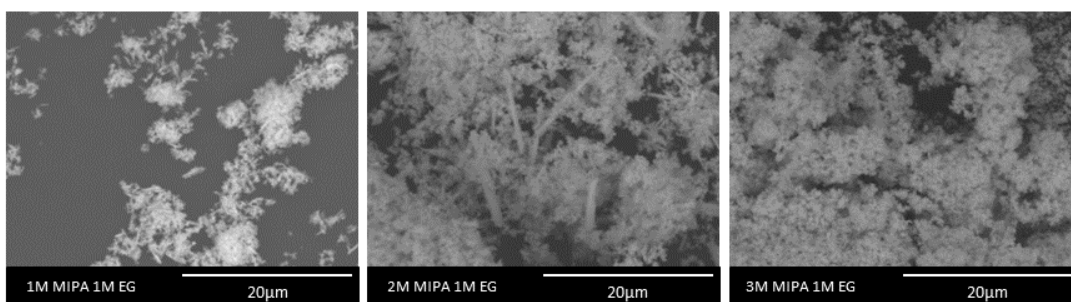


FIGURE 3.4: SEM images of Bi_2Te_3 nanoplates at 5000x, obtained with 15.0 kV.

The EDS analysis of each sample is described in Table 3.1, where the stoichiometry of each sample is determined.

As previously stated, the ideal stoichiometry is 2 parts bismuth and 3 parts tellurium (Bi_2Te_3). The sample that matches the most with the desired stoichiometry is 2 M MIPA (variation within the instrument error).

When it comes to the Bi_2Te_3 main phase, the results show that the structural properties of the Bi_2Te_3 nanoparticles change depending on the molar concentration of MIPA added

TABLE 3.1: Summary of the EDS analysis of each sample

Sample	Element	Atomic %	Stoichiometry
1 M MIPA	Bi	43.77	$Bi_{2.34}Te_3$
	Te	56.22	
2 M MIPA	Bi	41.63	$Bi_{2.14}Te_3$
	Te	58.37	
3 M MIPA	Bi	48.95	$Bi_{2.88}Te_3$
	Te	51.05	

to the reaction.

The nature of the chemical bond and the local atomic configurations of all the produced Bi_2Te_3 nanoplates samples were examined using Raman spectroscopy (see Figure 3.5).

Before digging into the Raman optical properties of Bi_2Te_3 nanoplates, we must first examine the crystal structure of Bi_2Te_3 . It has been stated that bulk Bi_2Te_3 crystals have five atoms in each primitive cell and correspond to the space group D_{3d}^5 [103]. As a result of inversion symmetry, bulk crystals have fifteen lattice vibration modes. There are three acoustic vibration modes and twelve optical phonons. According to group theory, twelve optical modes are represented by $2A_{1g} + 2E_g + 2A_{1u} + 2E_u$ [104]. Due to the crystal's inversion symmetry, these phonon modes are only Raman or infrared (IR) active [104]. In the A_{1g} and E_g phonon modes, atoms vibrate in-plane and out-of-plane. The atoms vibrate along the basal plane in E_g modes, while in A_{1g} modes, the atoms vibrate along. Due to crystal inversion symmetry, the IR-active modes (A_{1u}) must be odd parity, but the Raman-active modes (E_g, A_{1g}) must be even parity [105]. Raman prohibited odd-parity IR active phonon modes do not appear in Raman spectra for bulk crystals with crystal symmetry [106].

Now turning to the analysis of Raman spectra of the Bi_2Te_3 nanoplates. The Table 3.2 summarizes the Raman band assignments to our manufactured samples. Both of our samples have the active modes A_{1u}^2 and A_{1g}^2 , and the sample 2 M MIPA contains an extra mode E_g^2 at 101.83 cm^{-1} .

The A_{1u}^2 mode, detected at 119.06 and 117.56 cm^{-1} for the samples 1 M MIPA and 2 M MIPA respectively, is composed of longitudinal optical (LO) phonons near the Brillouin

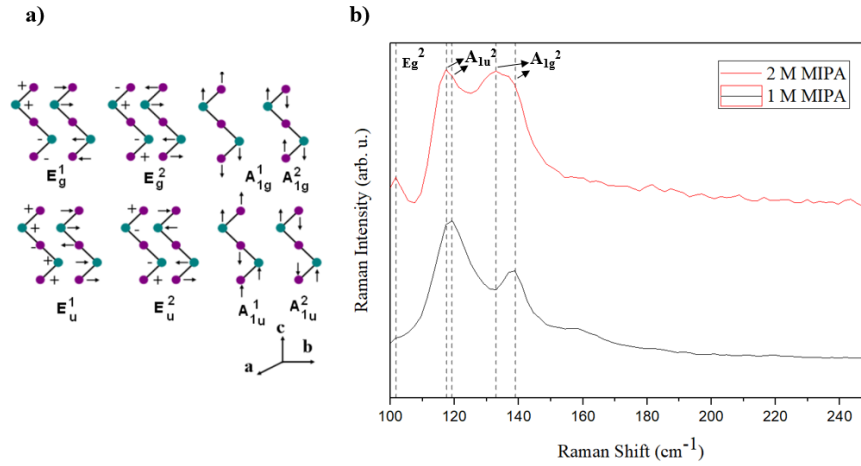


FIGURE 3.5: a) Schematic of the lattice vibrations (12 optical modes) in a Te(1)-Bi-Te(2)-Bi-Te(1) quintuple layer (QL). The subscripts '1' and '2' to the labels E_g , A_{1g} , E_u , and A_{1u} indicate low and high frequency modes, respectively; 'E' and 'A' modes denote in-plane (ab plane) and out-of-plane (c axis) vibrations, respectively. The symbols '+' and '-' represent the atomic displacement towards and away from the observer, respectively. Adapted from [107]. b) Raman spectra of the produced Bi_2Te_3 nanoplates.

TABLE 3.2: Raman vibrational modes of the Bi_2Te_3 nanoplates

Samples	Vibrational Modes		
	E_g^2	A_{1u}^2	A_{1g}^2
1 M MIPA	--	119.06	139.17
2 M MIPA	101.83	117.56	133.14

Zone border (Z point). In bulk Bi_2Te_3 crystals, the A_{1u}^2 mode is IR active but not Raman active [104]. Previous studies suggested that the observed crystal symmetry breakdown is most likely connected to the loss of infinite crystal periodicity due to interfaces and the resulting relaxation of the phonon wave vector $q = 0$ selection rule. As a result, we may safely ascribe the formation of the IR active A_{1u}^2 mode in thin hexagonal nanoplates to the crystal symmetry breaking of nanoplates due to the presence of two interfaces [106]. Thus, Raman measurements of as-grown thin nanoplates unequivocally show that the infrared (IR) active mode (A_{1g}^2) must be odd parity and is Raman prohibited for bulk crystals due to their inversion symmetry [105]. The A_{1u} mode has been reported to correspond to the centrosymmetric Bi_2Te_3 material, with the A_{1g} mode being a Raman forbidden mode, suggesting the presence of nanoscaled components [106, 108].

With increasing MIPA concentration, there is a two-point shift to the left in the mode A_{1u}^2 and a six-point shift to the left in the mode A_{1g}^2 .

The sample 3 M MIPA was unable to be measured since its color had altered to a white tone, suggesting potential oxidation. This modification occurred only after the acquisition of its XRD spectra and SEM images.

3.1.2 Transport Properties

The evaluation of a thermoelectric material's transport properties is essential. Figure 3.6 depicts the outcomes of these properties.

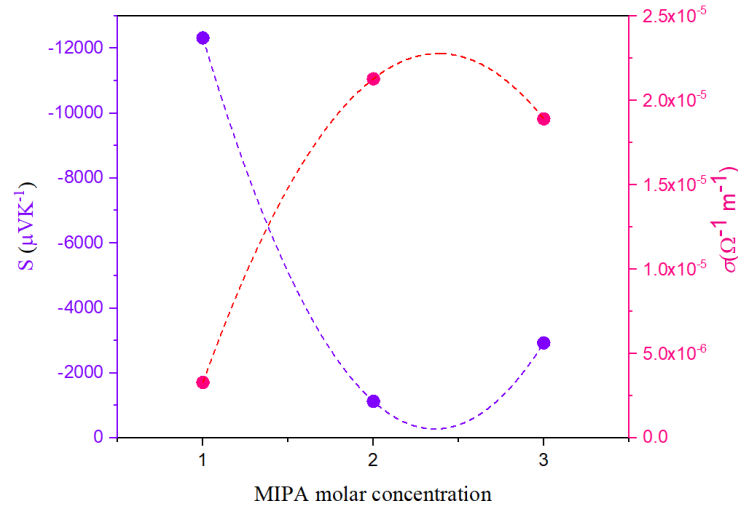


FIGURE 3.6: Seebeck Coefficient and Electrical Conductivity as functions of the molar concentration of MIPA added during the process.

The values of the Seebeck coefficient obtained for all the samples are negative, meaning that the produced Bi_2Te_3 correspond to a n-type semiconductor. In terms of S values, the absolute values of S are quite high, implying that the produced material is very resistive. This is supported by the high resistivity values obtained for each sample (see Table 3.3).

TABLE 3.3: Summary of the transport properties of the produced Bi_2Te_3 nanoplates

Samples	S $\mu V K^{-1}$	ρ Ωm	σ $\Omega^{-1} m^{-1}$	PF $\mu W m^{-1} K^{-2}$
1 M MIPA	-6644.8	303.86	3.291×10^{-6}	0.499
2 M MIPA	-1727.9	47.02	2.126×10^{-5}	0.0635
3 M MIPA	-4943.8	52.93	1.889×10^{-5}	0.462

Concerning the trend of S with MIPA molar concentration, the absolute value of the Seebeck coefficient decreases from 1 to 2, and rises from 2 to 3. Electrical conductivity, on the other hand, reaches its highest point at a MIPA molar concentration of 2.

It is known that the transport properties of these materials depend on the stoichiometry. Thus the excess of Bi for 1 and 3 M could be the main problem for such low conductivity [109].

Also, the microstructure can be another parameter to take into account and a change in the morphology is clearly observed in the SEM images, namely by the appearance of the tubular structure which will benefit the electron transport thus increasing the electron mean free path.

Notice that when considering the practical applications, materials with low resistivity and high Seebeck effect are drawbacks for applications (low power generation).

3.2 Study of the EG substance amount

After properly evaluating the impact of MIPA molar concentration variation in the chemical reduction process used to produce the nanoplates, was also analyzed the effect of the solvent EG used in the Bi_2Te_3 NPs synthesis. To accomplish this, the EG substance amount variation was investigated for the previously studied MIPA concentrations of 1 M, 2 M, and 3 M. The EG substance amounts employed for each MIPA molar concentration were 7.17, 3.59, and 1.79 mol.

Figure 3.7 depicts the labeling of the samples.

3.2.1 Structural and Morphological Characterization

The EG substance amount varied between 1.79, 3.59, and 7.17 for each MIPA molar concentration. Figure 4.1 depicts the XRD spectrum for samples at different EG substance amounts for MIPA molar concentrations 1, 2, and 3. The intensity of the peaks was normalized by dividing by the peak of maximum intensity.

According to the results, the influence of the substance amount of EG does not play an important role on the crystal structure, since all of the samples of the nanoplates generated had a rhombohedral tetradymite-type crystal structure with the space group R-3m (JCPDS 15-0863), which matches the diffractograms reported by Hosokawa et al. [97].

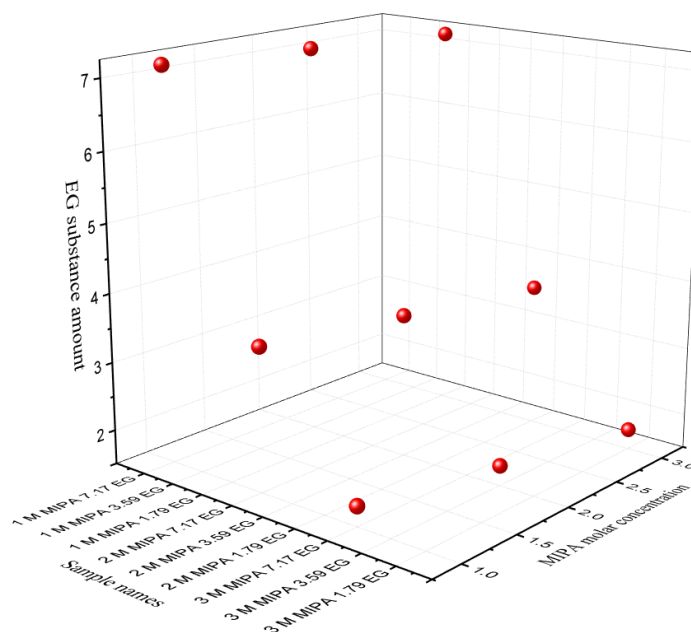


FIGURE 3.7: Labeling of samples, as well as the corresponding MIPA molar concentration and EG substance amount.

When looking at the diffractogram of samples with a MIPA molar concentration of 1, the peak (0111) shifts towards the peak (110) when the EG substance amount is lower. The same is found in samples with an MIPA molar concentration of 2, while the sample with an EG substance amount of 7.17 mol has a stronger defined peak (0111). In the case of samples with an MIPA molar concentration of 3, the peak (0111) does not shift as much as the EG substance amount decreases, but its intensity increases.

Analyzing the diffractogram for each MIPA molar concentration, the width of the peaks diminishes as the EG substance amount decreases. This is supported by the crystalline size results determined by the Debye-Scherrer method shown in Figure 3.9, where it is possible to see a proportionality between the crystallite size and the EG substance amount. This is more noticeable at higher MIPA concentrations where the size changes between 19.25 and 41.3 nm. For the concentration of 2 M, the size variations are not less prominent, thus allowing us to conclude that particle formation at this concentration is solely dependent on MIPA.

Following the XRD analysis, morphological analysis is required to examine the morphological differences between the samples, and the SEM results are depicted in Figure 3.10.

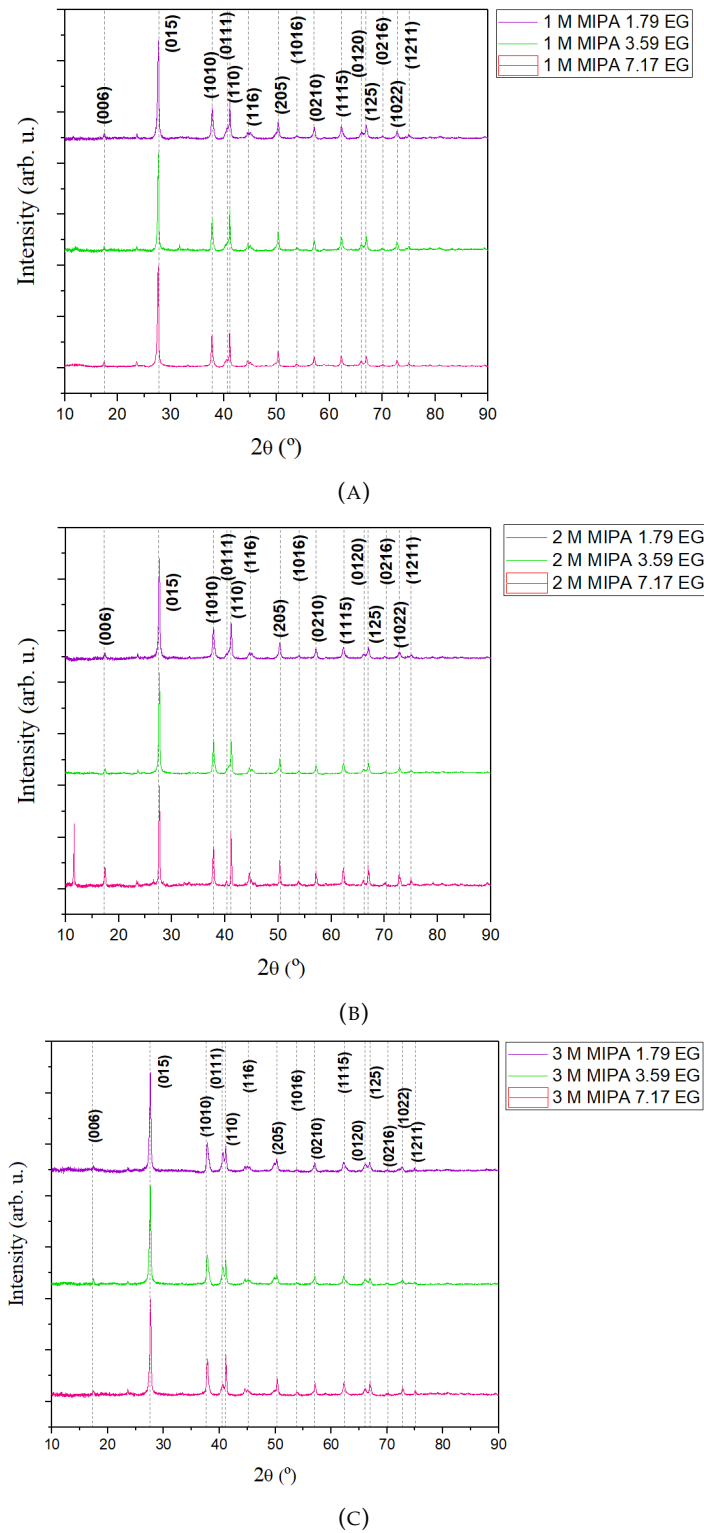


FIGURE 3.8: XRD diffractogram of different Bi_2Te_3 nanoplates samples based on the substance amount of EG added during the chemical reduction process, for samples with a MIPA molar concentration of 1 (A), 2 (B), and 3 (C).

When the appearance of the samples is examined through SEM, it is possible to observe that the tubular structure that was previously noticed when the MIPA molar concentration was investigated is still present.

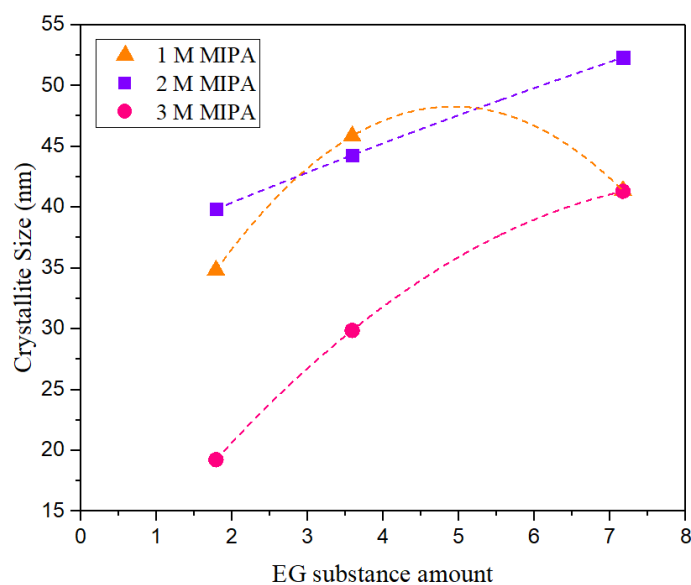


FIGURE 3.9: Crystallite size as a function of the molar concentration of EG added to the process.

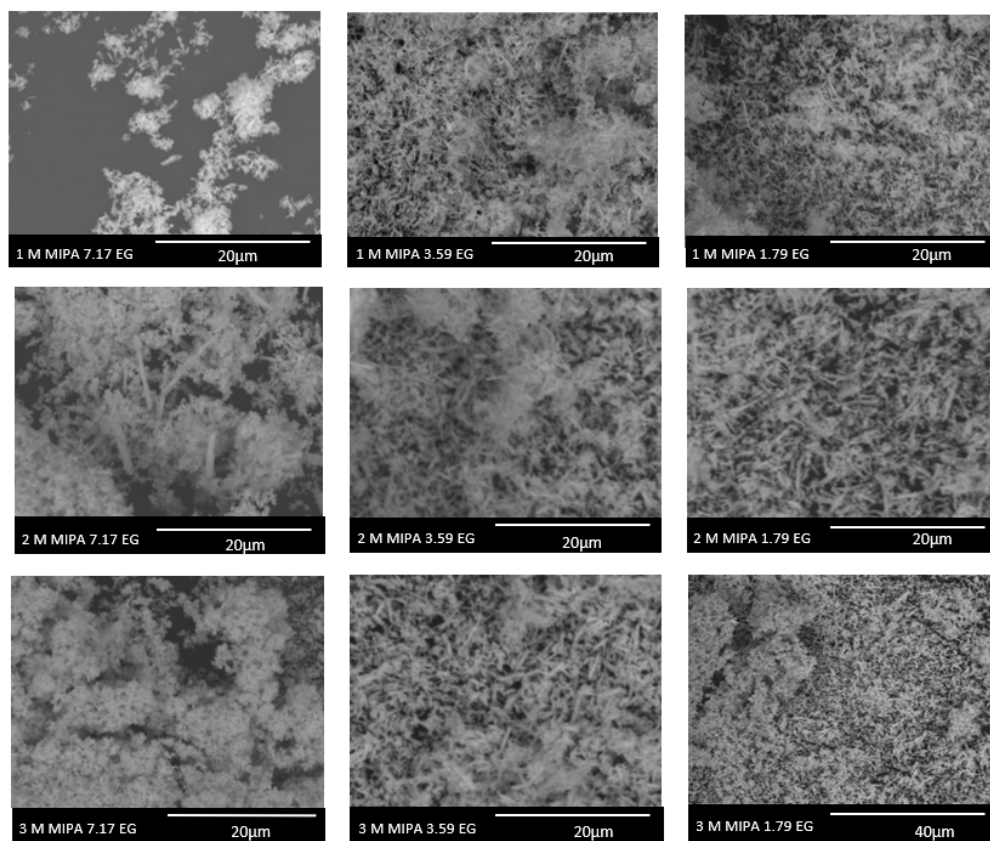


FIGURE 3.10: SEM images of Bi_2Te_3 nanoplates produced with three different MIPA and EG substance amounts.

For samples with a MIPA molar concentration of 1, the particles appear to become more homogenous and with better-defined morphological structure as the EG substance

amount increases. For the three EG substance amounts, the previously reported tubular shape is only found in samples with a MIPA molar concentration of 2.

An EDS analysis was performed in each sample to evaluate its stoichiometry. The results are described in the Table 3.4.

TABLE 3.4: Summary of the EDS analysis of each sample

MIPA molar concentration	EG substance amount	Element	Atomic %	Stoichiometry
1	7.17	Bi Te	43.77 56.22	$Bi_{2.34}Te_3$
	3.59	Bi Te	41.01 58.99	$Bi_{2.08}Te_3$
	1.79	Bi Te	50.39 49.61	$Bi_{3.04}Te_3$
2	7.17	Bi Te	41.63 58.37	$Bi_{2.14}Te_3$
	3.59	Bi Te	40.30 59.70	$Bi_{2.02}Te_3$
	1.17	Bi Te	40.40 59.60	$Bi_{2.03}Te_3$
3	7.17	Bi Te	48.95 51.05	$Bi_{2.88}Te_3$
	3.59	Bi Te	40.71 59.29	$Bi_{2.05}Te_3$
	1.17	Bi Te	45.47 54.53	$Bi_{2.50}Te_3$

When the EDS data are analyzed, it is easy to observe that when the EG substance amount is changed, the stoichiometry changes especially for 1 and 3 M. Notice that the drop in EG substance amount results in a decrease in reaction volume at the time of synthesis. For example, to produce about 3.6 grams of Bi_2Te_3 with the same MIPA molar concentration and an EG substance amount of 7.17, the volume of EG is 400 ml; but, if the EG substance amount is 1.79, the volume of EG is 100 ml. As a result, the concentration of precursors (bismuth and tellurium) in the entire reaction volume is higher, making it easier for the precursors to react with each other. Another explanation for these stoichiometry changes is that lowering the EG substance amount and volume resulted in a larger concentration of MIPA in the reaction. Despite the changes, the substance amount of 3.59 mol appears to be the optimal amount in all 3 M MIPA concentrations, approaching the ideal 2:3 ratio. Furthermore, with the MIPA molar concentration of 2 M, the change in stoichiometry with the EG concentration change is significantly smaller, indicating that 2 M appears to be the ideal MIPA concentration for obtaining the desired stoichiometry.

This is understandable given that MIPA is very alkaline, and a high pH environment is necessary to produce Bi_2Te_3 ; this requirement is corroborated by Lin et al. [101], who employed sodium hydroxide as a base in their synthesis technique.

So, based on the stoichiometry and SEM images, the sample with more accurate stoichiometry is the one with MIPA molar concentrations and EG substance amounts of 2 M and 1.79, respectively.

Following the evaluation of the produced samples by XRD, SEM, and EDS, one may now evaluate and compare the local atomic configurations of the produced Bi_2Te_3 nanoplates with different EG substance amounts. Raman spectroscopy was used for this evaluation (see Figure 3.11, 3.12 and 3.13).

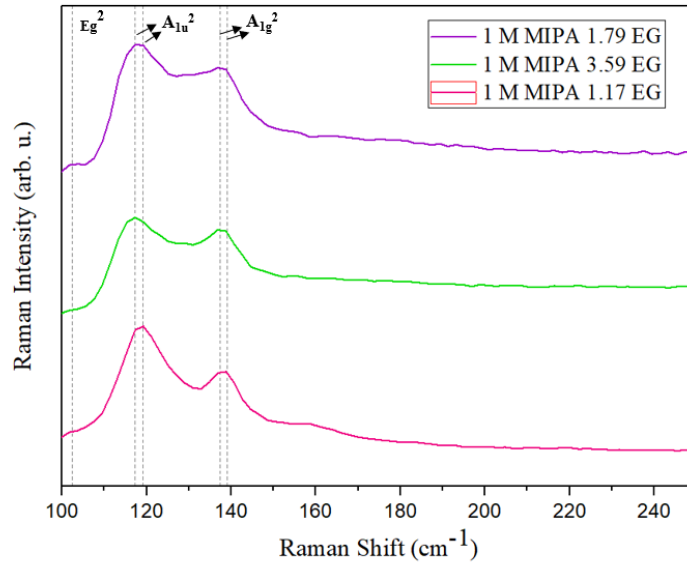


FIGURE 3.11: Raman spectra of Bi_2Te_3 NPs synthesized with a MIPA molar concentration of 1 and varied EG substance amounts.

The Raman band assignments to the materials produced with a MIPA molar concentration of 1 are summarized in Table 3.5. The active modes A_{1u}^2 and A_{1g}^2 are present in all three samples, and the decrease of the EG substance amount promotes the emergence of the mode E_g^2 . Also, with the decrease of the EG substance amount from 7.17 to 3.59 there is a two-point shift in both the modes A_{1u}^2 and A_{1g}^2 .

As previously stated in the MIPA molar concentration investigation, the A_{1u} mode has been shown to correspond to the centrosymmetric Bi_2Te_3 material, with the A_{1u} mode being a Raman prohibited mode in bulk crystals, indicating the existence of nanoscaled components on the prepared samples [106, 108].

TABLE 3.5: Raman vibrational modes of Bi_2Te_3 nanoplates with a MIPA molar concentration of 1 and different EG substance amounts

Samples	Vibrational Modes		
	E_g^2	A_{1u}^2	A_{1g}^2
1 M MIPA 7.17 EG	- -	119.06	139.17
1 M MIPA 3.59 EG	- -	117.49	137.20
1 M MIPA 1.17 EG	101.88	117.49	137.39

The Raman band allocations for samples prepared with a MIPA molar concentration of 2 are reported in Table 3.6. The three vibration modes E_g^2 , A_{1u}^2 , and A_{1g}^2 are present in samples produced with a MIPA concentration of 2. The sole distinction between the three is a three-point shift in the mode A_{1g}^2 when the EG substance amount declines from 7.17 to 3.59.

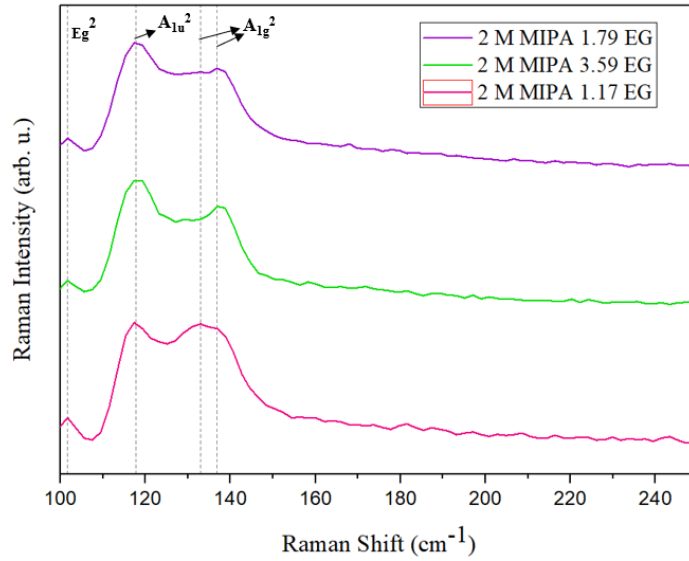


FIGURE 3.12: Raman spectra of Bi_2Te_3 NPs synthesized with a MIPA molar concentration of 2 and varied EG substance amounts.

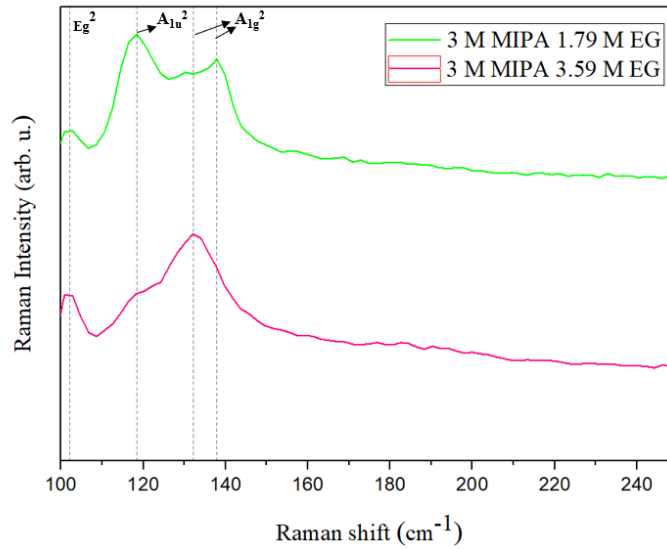
The well-defined peak A_{1u}^2 for all three EG substance amounts indicates that the samples produced are indeed nanoscaled.

Finally, the Raman band allocations for samples produced with a MIPA molar concentration of 3 are displayed in the 3.7 Table. The sample 3 M MIPA 7.17 EG could not be characterized using Raman spectroscopy because it changed to a whitish color after its production and XRD characterization, suggesting potential oxidation.

TABLE 3.6: Raman vibrational modes of Bi_2Te_3 nanoplates with a MIPA molar concentration of 2 and different EG substance amounts

Samples	Vibrational Modes		
	E_g^2	A_{1u}^2	A_{1g}^2
2 M MIPA 7.17 EG	101.83	117.41	133.15
2 M MIPA 3.59 EG	101.83	117.75	136.82
2 M MIPA 1.79 EG	101.83	117.56	136.82

The vibrational modes E_g^2 and A_{1g}^2 are present in both samples, according to the analysis of the spectra displayed in Figure 3.10. However, unlike in the sample 3 M MIPA 1.79 EG, the mode A_{1u}^2 is not clearly defined in the sample 3 M MIPA 3.59 EG. Because the peak A_{1u}^2 is related to the existence of nanoscale components, its absence suggests that the nanoplates are greater in size. When the EG substance amount falls, the peak A_{1g}^2 shifts to the right by 5 points.

FIGURE 3.13: Raman spectra of Bi_2Te_3 NPs synthesized with a MIPA molar concentration of 3 and varied EG substance amounts.TABLE 3.7: Raman vibrational modes of Bi_2Te_3 nanoplates with a MIPA molar concentration of 3 and different EG substance amounts

Samples	Vibration Modes		
	E_g^2	A_{1u}^2	A_{1g}^2
3 M MIPA 3.59 EG	102.11	118.44	132.34
3 M MIPA 1.79 EG	102.30	118.44	137.84

Because of its nanoscale level range, Transmission Electron Microscopy (TEM) was employed at the nanoscale the produced particles that a hexagonal shape was attained. The best sample was selected to inspect by TEM, which corresponds to the one with more accurate stoichiometry which is the sample that was produced with MIPA molar concentrations of 2 and EG substance amount of 1.79, respectively (see Figure 3.14).

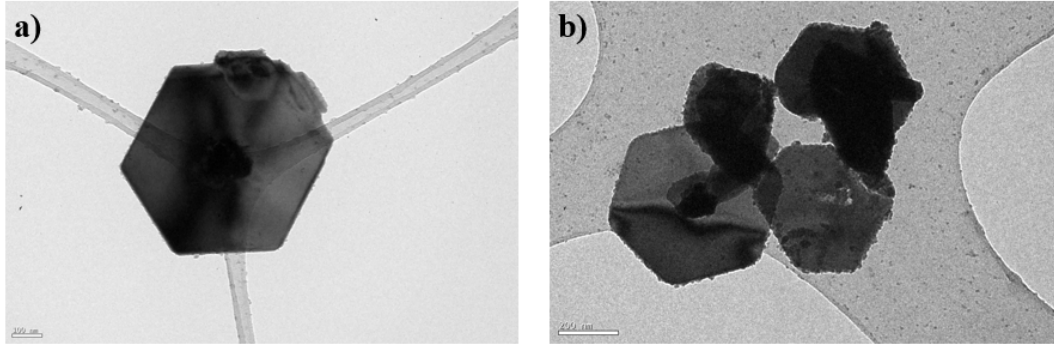


FIGURE 3.14: TEM images of the sample of Bi_2Te_3 synthesized with a molar concentration of 2 MIPA and EG substance amount of 1.79.

The hexagonal shape of the nanoplates can be confirmed; an isolated nanoplate is shown in Figure 3.14 a) at a scale of 100 nm, and its diameter is approximately 650 nm. In Figure 3.14 b), an agglomeration of nanoplates can be seen at a larger scale of 200 nm.

3.2.2 Transport Properties

After morphological and structural characterization of the samples prepared using different amounts of EG added during synthesis, the transport properties, i.e. electrical conductivity and Seebeck coefficient, were determined. The electrical conductivity is displayed in Figure 3.15.

In terms of the relationship between electrical conductivity and EG substance amount variation, for MIPA molar concentrations of 1 M and 2 M, electrical conductivity rises as EG substance amount decreases. This is not the case for the MIPA molar concentration of 3 M. This divergence in the trend to the final concentration of MIPA is justified by the high resistivity of the sample 3 M MIPA 1.79 EG, which, while other samples are also quite resistive, has such a high resistivity that the Seebeck coefficient could not be measured (see Table 3.8).

The samples 1 M MIPA 7.17 EG, 2 M MIPA 7.17 EG, 2 M MIPA 3.59 M EG, 3 M MIPA 7.17 EG, and 3 M MIPA 3.59 M EG show very high absolute values of Seebeck coefficients

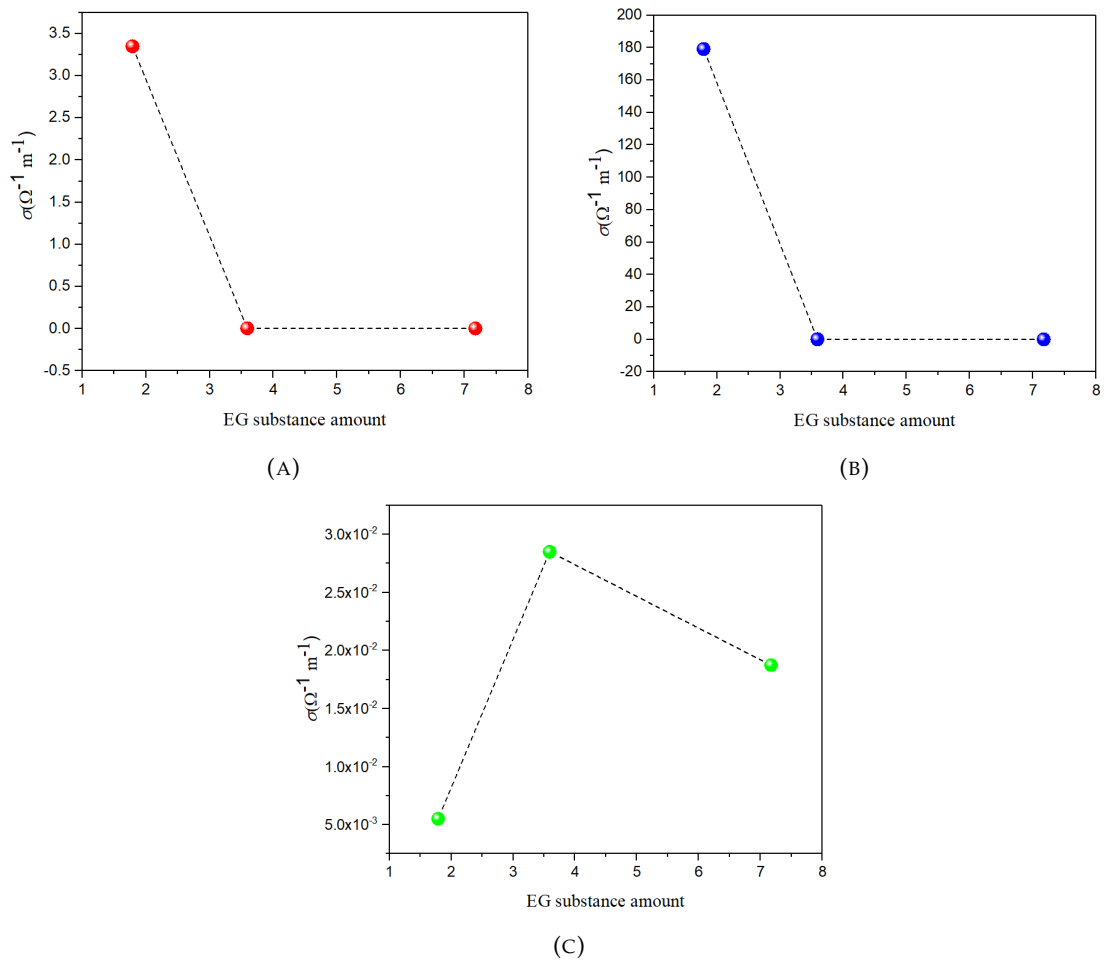


FIGURE 3.15: d Electrical Conductivity of different Bi_2Te_3 nanoplates samples based on the amount of EG added during the synthesis, for samples with a MIPA molar concentration of 1 (A), 2 (B), and 3 (C).

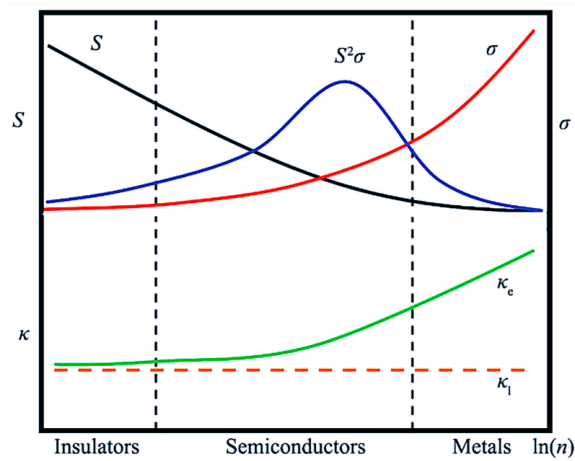


FIGURE 3.16: Correlation of thermoelectric parameters and carrier concentrations. Reproduced from [110].

TABLE 3.8: Summary of the transport properties of the produced Bi_2Te_3 nanoplates with different MIPA and EG molar concentrations

Samples	S μVK^{-1}	ρ Ωm	σ $\Omega^{-1}m^{-1}$	PF $\mu Wm^{-1}K^{-2}$
1 M MIPA 7.17 EG	-12318	303.86	3.29×10^{-3}	4.99×10^{-1}
1 M MIPA 3.59 EG	-35.56	179.99	5.56×10^{-3}	7.03×10^{-6}
1 M MIPA 1.79 EG	-20.22	0.29	3.34	1.37×10^{-3}
2 M MIPA 7.17 EG	-1727.40	47.02	2.13×10^{-2}	6.35×10^{-2}
2 M MIPA 3.59 EG	-9258.20	7.92	1.26×10^{-1}	1.08×10^1
2 M MIPA 1.79 EG	-66.13	5.58×10^{-3}	179.16	7.83×10^{-1}
3 M MIPA 7.17 EG	-4943.8	53.38	1.87×10^{-2}	4.58×10^{-1}
3 M MIPA 3.59 EG	-879.33	35.09	2.85×10^{-2}	2.20×10^{-2}
3 M MIPA 1.79 EG	--	181.45	5.51×10^{-3}	--

and high resistivity. As seen in Figure 3.16, such behavior is characteristic of insulating materials.

After analyzing all of the electrical conductivity data, the sample 2 M MIPA 1.79 EG has the highest value, and while its Seebeck coefficient isn't as high as others, it is in the semiconductor regime, which is our aim.

When the XRD data is compared to the transport characteristics, particularly the electrical conductivity, the increase in the second parameter for the sample 2 M MIPA 1.79 EG may be explained by a decrease in the width of the peaks, indicating a larger crystallite size. This was further supported by SEM images, which showed that the particles were more homogenous and less amorphous, and by Raman spectroscopy analysis, which revealed that the mode that dictates the existence of nanoscaled components ($A1u^2$) was high and well defined. Finally, the TEM images proved the hexagonal shape nanoplates were obtained.

Chapter 4

Planar thermoelectric generator prototype with Bi_2Te_3 nanoplates

To investigate the output of the prepared thermoelectric nanoplates when applied in a device, a printed planar thermoelectric generator (TEG) was manufactured utilizing the screen-printing technique.

The device assembly procedure is thoroughly discussed in section 2.2, but in summary, it consists of transferring a stenciled pattern onto a substrate using a mesh screen, ink, and a squeegee (rubber blade). The device was assembled using treated Kapton, a polyimide film commonly used in flexible printed circuits, the treatment process was fully described in the section 2.2.2.

The ink manufacturing process was also covered in the section 2.2.1. To summarize, the ink must have two main components, the organic binder, poly(vinyl alcohol) (PVA 99%) doped with orthophosphoric acid (H_3PO_4 , 85%), and the prepared inorganic thermoelectric nanomaterials. The sample used for the thermoelectrical ink formulation was the sample prepared with MIPA molar concentrations of 2M and EG substance amount of 1.79 mol, due to its high output. The device's contacts were printed in the Kapton substrate using commercial silver ink.

4.1 Device's characterization

4.1.1 Ink Formulation and characterization

Based on the group experience, PVA doped with H_3PO_4 was chosen as a binder for the ink. The concentration for the ink of polymer wt% versus Bi-Te nanoparticles wt% was

optimized in order to obtain the right printable rheology thus reaching the the wt% of 65 wt% nanoparticles to 35 wt% polymer. The XRD diffractogram of the nanoplates from the sample 2 M MIPA 1.79 M EG utilized in the thermoelectric ink was previously examined in section 3.2.1, but it will be revisited in this part. It is now important to examine the thermoelectric device's XRD spectrum and the difference between the two (see Figure 4.1).

When the two diffractograms are compared, it is feasible to determine that all of the Bi_2Te_3 peaks detected in the XRD spectrum of the sample 2 M MIPA 1.79 EG are also recognized in the device's XRD spectrum. The key distinction between the two is the existence of a peak around 14.34° . When compared to the previously reported diffractogram of H_3PO_4 doped PVA by Alipoori et al. [111], this peak was recognized as the PVA/ H_3PO_4 peak with direction (110).

4.1.2 Output measurements methodology

The performance of the device was measured using a commercial micro-probe system, in which the produced device was placed between two temperature-controlled Peltier's stages (TEC1-12706) and a temperature gradient was applied and controlled by a TC-08 Thermocouple datalogger (PICO Technology) using K type thermocouples. First, using an open circuit the device was connected directly to the nanovoltmeter, and the voltage at open circuit (V_{OC}) was obtained. The device performance was tested using a circuit board and a fixed probe charge at various load resistances ranging from $10\ \Omega$ to $1\ G\ \Omega$ [79]. For voltage and current measurements, the device was tested in two different configurations, displayed in Figure 4.3a and 4.3b respectively.

The current was calculated using Ohm's Law and a probe load of $R = 50$. The output power of the device was established using the output power expression given by,

$$P = VI \quad (4.1)$$

where P is the Power (W), V is the voltage (V), and I the current (A). Figure 4.3 depicts the homemade setup used to conduct the measurements and the produced device, which is composed of ten stripes with 4 mm of width and 16 mm of length.

Figure 4.4 summarizes the device performance with temperature gradients ranging from $\Delta T = 5K$ to $27K$. The heat flow was directed along the length of the thermoelectric composite stripe. First, as illustrated in Figure 4.4a, the device voltage was measured in an

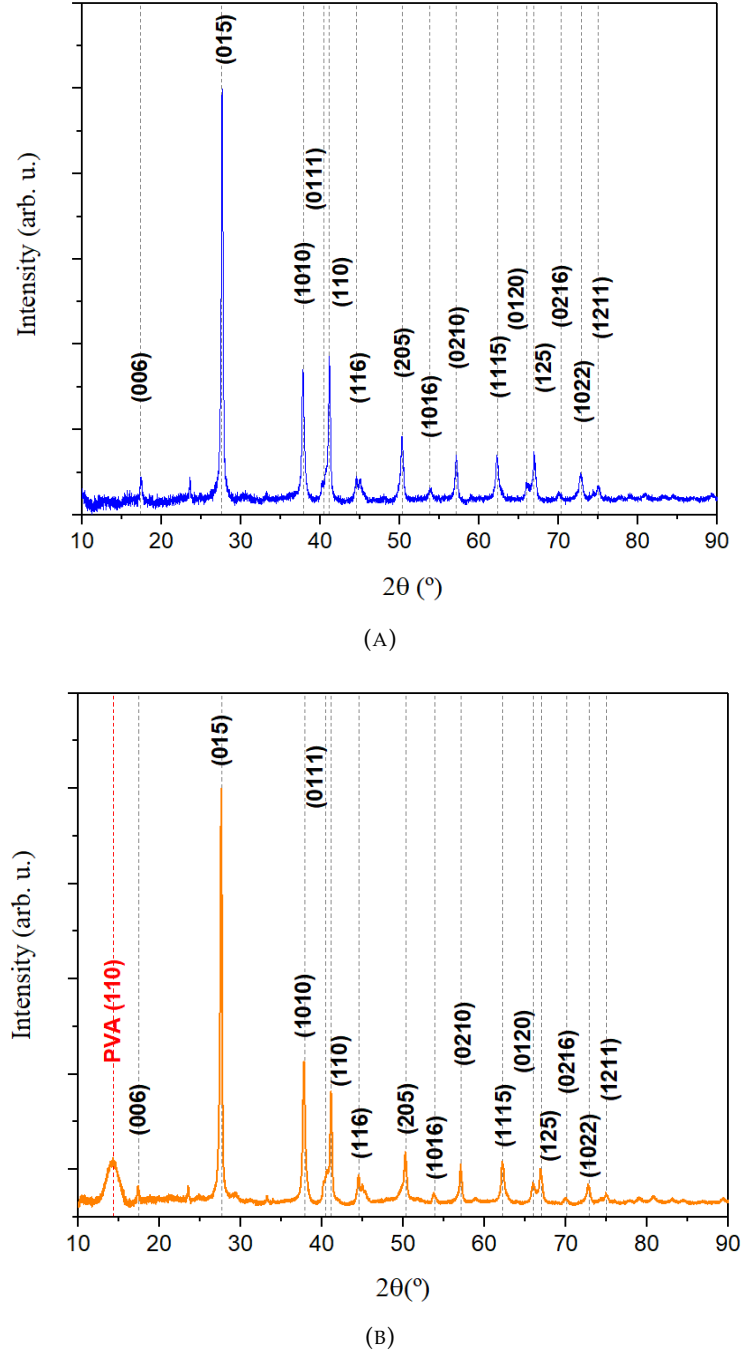


FIGURE 4.1: XRD spectrum of (A) the sample 2 M MIPA 1.79 EG and (B) the thermoelectric device.

open-circuit (V_{OC}). There was a parallel correlation between the V_{OC} and the temperature difference. With a mean value of $361mVK^{-1}$, a linear slope was obtained. Because the stripes are linked in series and each acts as a voltage source, the slope is calculated by adding the Seebeck coefficients of each leg. By dividing the slope by ten legs, a value of $36VK^{-1}$ is obtained.

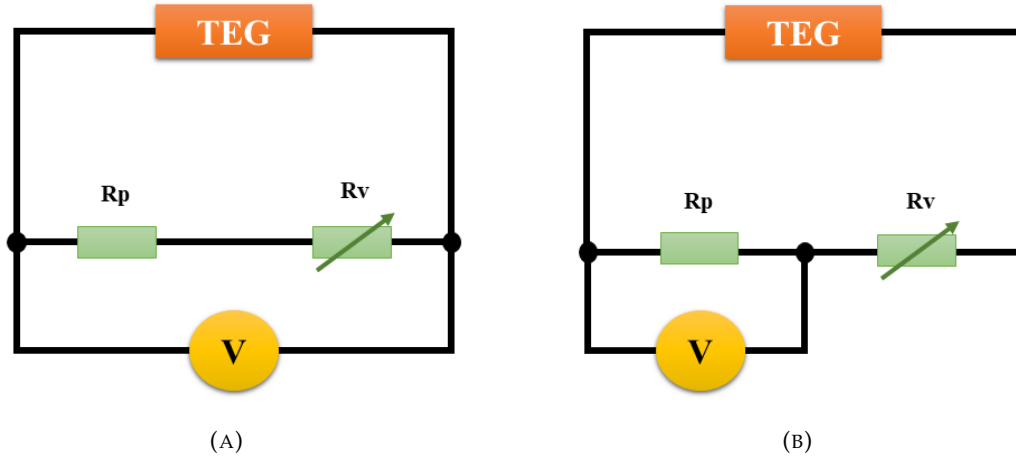


FIGURE 4.2: Circuit configurations for (A) voltage measurement and (B) current measurement.

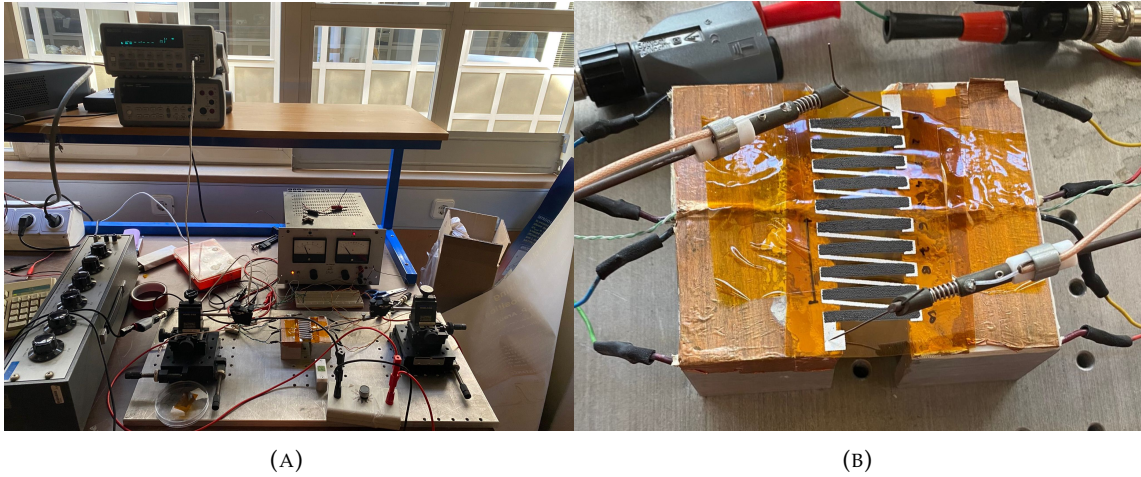


FIGURE 4.3: (A) Overview of the homemade setup used to measure the thermoelectric device. (B) Closer look at the measurement of the device on top of the Peltier stages.

Figure 4.4b depicts the output power as a function of the applied resistance for each of the five temperature gradients. As expected, for low probe resistance the voltage is small either with an increase of resistance probe, the value tends to the output voltages in an open circuit. For the current measurement, it was found that the internal resistance of the device measured directly is higher than $10\text{ M}\Omega$, so the expected current value would be very low (around nV) and therefore impossible to measure. Thus, the power was determined through the maximum power value by the following equation:

$$P_{max} = \frac{V_{max}^2}{4R_{int}} \quad (4.2)$$

with V_{max} being the maximum voltage obtained for each temperature gradient. The results of the P_{max} are depicted in Figure 4.4c.

From this, we can see that the internal resistance value limits the possibility of producing useful energy, due to the great increase of resistance with its inclusion in the PVA/ H_3PO_4 pastes, which typically increases 2 orders of magnitude the resistance [79]. However, this device due to its internal resistance proves to be a good temperature-sensing device.

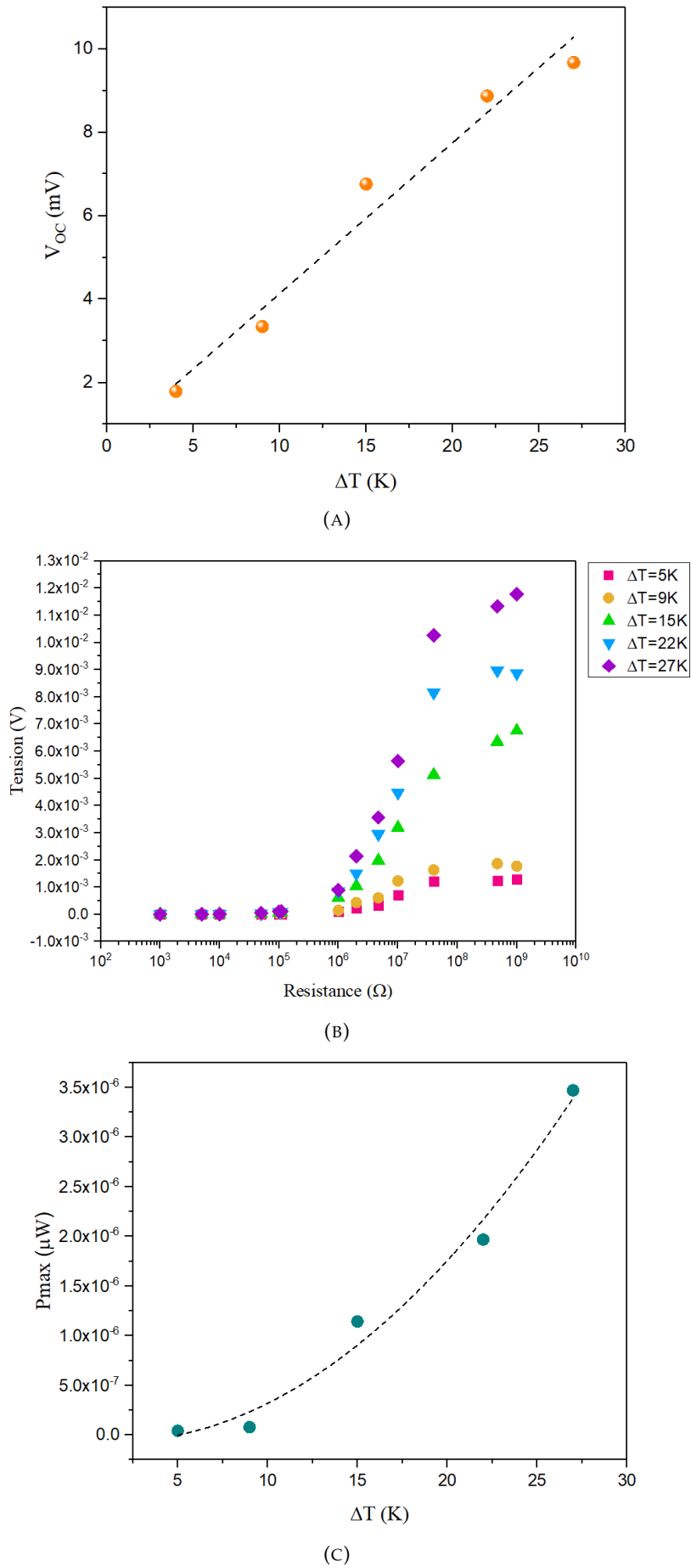


FIGURE 4.4: Characterization of the thermoelectric device. (A) Output voltage at the open circuit as a function of the temperature gradient. (B) Voltage output as a function of the applied resistance for each temperature gradient. (C) Maximum power output measurement as a function of the temperature gradient.

Chapter 5

Final Remarks

Throughout the execution of this dissertation toward the main goal, multidisciplinary research was addressed, ranging from engineering physics and chemistry, printing techniques, thorough materials characterization, and the production of a device prototype as proof of concept. During this route, several accomplishments were achieved and will be detailed described in the next section.

5.1 Conclusions

When this project began, one of the primary aims was to produce nanoplates of Bi_2Te_3 via a chemical reduction process. This goal was achieved and nanoplates with average sizes of roughly 650 nm were obtained.

The variation in the MIPA molar concentration affects the morphology of the nanoplates, particularly the crystallite size, which ranged between 41.30 and 52.30 nm, with the largest value achieved for the sample 2 M MIPA. The results for MIPA molar concentrations below 1 indicate that the reaction environment was not alkaline enough for the formation of Bi_2Te_3 , resulting in the formation of oxides. The stoichiometry of the nanoplates is also affected by the molar concentration of MIPA added to the reaction; the best value was found for the sample 2 M MIPA, whose stoichiometry is $Bi_{2.14}Te_3$. MIPA concentrations less than or equal to 0.5 M result in the formation of no crystalline structures. The Seebeck coefficient of the samples for the three distinct MIPA concentrations proved that they were n-type materials. However, their high resistivity values and absolute magnitude of the Seebeck coefficient indicate that they are insulating materials. The conductivity values varied between 3.29×10^{-6} and $2.126 \times 10^{-5} (\Omega^{-1}m^{-1})$, with the sample 2 M MIPA

achieving the highest value. It should be noted that stoichiometry is an important factor in these measurements.

The amount of EG added to the reaction at the time of the procedure influences the crystallite size as well; reducing it also decreases crystallite size. The SEM images revealed that decreasing the substance amount of EG leads the samples to become more homogenous and morphologically defined. This substance amount decrease also benefits the stoichiometry, as stoichiometry of $Bi_{2.04}Te_3$ was reached for a substance amount of 1.79 and a MIPA molar concentration of 2 M. The TEM technique confirmed the attainment of the nanoplates and their hexagonal shape, with diameters ranging from 400 to 650 nm, for the sample 2 M MIPA 1.79 EG. This sample's nanoplates also had the highest power factor of $0.789 \mu W m^{-1} K^{-2}$, being the most promising candidate.

It was also possible to produce by screen-printing a prototype of a planar geometry device using the nanoplates produced with a molar concentration of MIPA of 2 M and a molar amount of EG of 1.79. With this a Seebeck coefficient of $361 mV K^{-1}$ was obtained.

5.2 Future Work

Given the innovative results obtained in this study, some future guidelines for enhancing the synthesis and production of nanoplates and developing a more efficient thermoelectric device might be considered.

When it comes to the synthesis of materials, a chemical reduction process, measuring and studying the pH of the reaction would be quite interesting since the formation of Bi_2Te_3 demands a very alkaline atmosphere. This research may make it easier to pinpoint the optimal MIPA molar concentration. Because reducing the EG substance amount provided several benefits, it would be advantageous to attempt to produce the Bi_2Te_3 nanoplates without it and to substitute it with another solvent.

For the transport properties, the measurement and analysis of thermal conductivity would be beneficial to characterize the generated sample and determine the zT value. An annealing process can also be used to investigate how this impacts the transport qualities.

Other proportions of PVA/H_3PO_4 and the produced nanoplates of Bi_2Te_3 to produce the ink for screen-printing should be examined when it comes to device assembly, as well as testing the usage of another polymer such as the PEDOT.

The produced thermoelectric prototype can also be tested as a thermal sensor. The radial geometry for thermoelectric generators should also be tested and evaluated.

Appendix A

List of Contributions

This thesis has resulted in one oral presentation and one poster presentation at national conferences during the previous few months.

- **National conferences with oral presentation in the framework of this thesis:**

Isabel Sousa, M. Margarida Maia, Ana L. Pires, Mariana Rocha, André M. Pereira - 'Development and optimization of Bismuth Telluride nanoplates for thermoelectric devices in IoT applications' - 15th Meeting of Young Researchers of the University of Porto - May, 2022.

- **National conferences with poster presentation in the framework of this thesis:**

Isabel Sousa, M. Margarida Maia, Ana L. Pires, Mariana Rocha, André M. Pereira - 'Development and optimization of Bismuth Telluride nanoplates for thermoelectric devices' - FISICA 2022 - 23rd Physics National Conference and 32th Iberian meeting for teaching physics.

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