Preface

We are witnessing rapidly growing demands in high-frequency electronics, wireless communication, and AI-integrated systems, pushing materials science to its limits. As systems become smaller and more integrated, materials must exhibit tunable electromagnetic (EM) properties, thermal stability, mechanical strength, and compatibility with advanced fabrication methods.

Developing materials for such applications requires a precise understanding of their interaction with EM waves, governed by electrical, magnetic, optical, and thermal responses. These interactions are defined by two intrinsic parameters**: permittivity** $(\boldsymbol{\varepsilon})$ **and permeability**$(\boldsymbol{\mu})$. Based on their signs, materials are categorized as double-positive (DPS; $\boldsymbol{\varepsilon > 0; \mu>0}$), epsilon-negative (ENG;$\boldsymbol{\varepsilon < 0}$; $\boldsymbol{\mu > 0}$), mu-negative (MNG; $\boldsymbol{\varepsilon > 0}$; $\boldsymbol{\mu < 0}$), or double-negative (DNG $\boldsymbol{\varepsilon < 0}$; $\boldsymbol{\mu < 0}$). ENG and DNG materials exhibit unique phenomena such as Electromagnetic interference (EMI) shielding, negative refraction, cloaking, and subwavelength confinement. This work focuses specifically on **ENG materials** due to their non-propagating nature and metal-like properties.

ENG materials exhibit negative real permittivity and positive permeability. This behavior arises when the **plasma frequency (**$\boldsymbol{\omega_p}$**)** of free carriers exceeds the frequency of the incident EM wave. As a result, ENG materials exhibit a low characteristic impedance ($\boldsymbol{Z_{ENG}}$) relative to the intrinsic impedance of free space ($\mathbf{Z_0}$), leading to strong impedance mismatch at the material interface. This causes incident EM waves to be mostly reflected, while any transmitted components decay evanescently due to the non-propagating nature of the field within the medium. Such behavior makes ENG materials highly effective for applications requiring **EM shielding**, where the goal is to block or attenuate wave transmission.

EMI is an increasingly important global issue as modern electronic technologies such as 5G/6G, radar, satellite communication, and GPS devices now operate primarily in the 1–18 GHz range, often overlapping with the frequencies used by other instruments. This overlap can cause interference between incoming and outgoing signals, resulting data loss, signal degradation, and malfunction of sensitive equipment under practical conditions. EMI is generally is of two kind, low- and high-frequency EMI. While low-frequency EMI tends to be less harmful, prolonged exposure to high-frequency radiation has been linked to health risks such as DNA damage, skin conditions, and cognitive impairment. Therefore, effective shielding is essential to protect both electronic devices and human health from the impact of EM radiation.

Currently, metals are the primary ENG materials, and due to their high electrical conductivity and strong reflectivity, dominating about 95% of the EMI shielding market. However, their limitations, high weight, corrosion, narrow bandwidth, and high cost also their high charge carrier density pushes their ω_p into the infrared or optical spectrum, limiting their performance in **Radiofrequency systems**. Traditional shielding materials combine ***metals with insulating ceramics*** to reduce effective conductivity and lower their ω_p to the GHz range, but their absorption-based mechanism effective at lower frequencies. However, at higher frequencies, these materials require increased thickness to dissipate EM energy as heat, raising weight and cost.

Ideally, EMI shields should be lightweight, thermally stable, cost-effective, multifunctional, and operate effectively across a broad frequency spectrum. Reflective shielding, based on impedance mismatch, offers a more efficient alternative for modern EMI challenges. These limitations can be addressed by developing alternative materials that mimic metal-like ENG properties. Recently conducting Ceramic oxides with high electrical conductivity and negative permittivity present a promising solution to replace metals in advanced applications.

Prime objective of this work is to explore some new ENG or negative permittivity materials (single-phase ceramic oxides and their composites) and assessing their potential to replace metals for EMI shielding. Based on the literature information we selected two ceramic oxides with the expectation of achieving negative permittivity at room temperature. The study also investigates the influence of external parameters (frequency, temperature) and internal compositional modifications on their dielectric behavior. These materials can also have applications beyond EMI shielding, such as coil-less inductors.

To fulfil above mentioned objectives, in this work we synthesized perovskite oxide **($LaNiO_3$),** layered perovskite oxide or Ruddlesden–Popper phase (**La_2NiO_4**), composites of **SnO_2-$LaNiO_3$,** and **SnO_2-Graphene** composites. Unlike metals, these ceramics allow precise control over free carrier concentration, damping, and plasma frequency while maintaining structural and thermal integrity. Synthesis methods included solid-state reaction, sol–gel, and wet chemical techniques. Structural and morphological analyses were conducted using X-ray diffraction (XRD) and scanning electron microscopy (SEM), while oxidation states were evaluated by X-ray photoelectron spectroscopy (XPS). Dielectric and AC conductivity measurements were performed with an LCR (Inductor-capacitor-resistor) meter over 20 Hz to 2 MHz and temperatures from room temperature to 600 °C

Both $LaNiO_3$ and La_2NiO_4 exhibited negative permittivity across these ranges, explained by plasmonic oscillations of free charge carriers using Drude, Drude-Lorentz, and modified Drude models. The SnO_2-Graphene composite showed epsilon-near-zero (ENZ) behavior, which is promising for advanced technologies such as perfect absorbers. Electrical conductivity measurements evaluated the minimum conductivity thresholds required for ENG behavior across different systems.

EMI shielding effectiveness was tested in the X-band (8–12 GHz) using a vector network analyzer to measure scattering parameters or S parameters (S11, S12, S21, S22). Moreover, these ENG materials showed potential as coil-less inductors, presenting an effective non-metallic alternative to conventional metal coils.

This thesis introduces a new class of **non-metallic ENG ceramics and composites** that exhibit consistent negative permittivity in the RF range. These materials combine **lightweight design**, **broadband response**, and **environmental stability**, making them compelling candidates for **next-generation EMI shielding**, **coil-less inductors**. The findings establish a foundation for further development of ceramic-based multifunctional materials tunable for high-frequency and multifunctional applications.

This research is driven by the following key goals:

- Realize epsilon-negative (ENG) behavior in intrinsically non-metallic, single-phase materials and composites, without relying on metal-based or metamaterial architectures, with stable performance at or above room temperature.
- Experimentally identify the minimum conductivity required to induce negative permittivity, helping guide material selection and future design.
- Investigate the potential of ENG materials in EMI shielding, as well as in device miniaturization such as coil-less inductive components
- The long-term goal is to predict experimental conditions for achieving epsilon-near-zero (ENZ) behavior by tuning the minimum conductivity threshold. This will

facilitate multifunctional ENG materials with versatile properties accessible through minimal compositional adjustments, expanding their application scope

For clarity and convenience, this thesis is structured into eight chapters, each detailing the introduction to the work carried out, the experimental techniques employed, and the research findings:

Chapter 1: This chapter introduces epsilon-negative materials (ENGs), a subclass of metamaterials exhibiting negative permittivity and unique electromagnetic behavior. ENGs hold promise for applications such as electromagnetic interference shielding, antenna miniaturization, and coil-less inductors, outperforming conventional positive-permittivity dielectrics. The research centers on synthesizing and characterizing novel single-phase and composite materials that exhibit stable epsilon-negative response at room temperature and across broad frequency ranges. Key objectives include optimizing electrical conductivity and developing multifunctional materials with epsilon-near-zero properties and tunable electromagnetic responses. This chapter establishes the significance of ENGs, defines the research scope, and frames the thesis goal of addressing current challenges to enable practical, scalable epsilon-negative materials.

Chapter 2: This chapter provides an extensive overview of the synthesis methods and characterization techniques employed throughout the research. It outlines the detailed experimental procedures and sample preparation methods used for microwave and electrical measurements. The chapter begins with a description of the various synthesis routes utilized to synthesis the materials under study. It then delves into the characterization techniques, explaining how each method contributes to the analysis of detailed physics behind material properties. With diagrams and flowcharts are included to illustrate the experimental setups and procedural steps, present a clear visualization of the processes involved.

Chapter 3: The first material system investigated for negative permittivity in ceramics and perovskites is lanthanum nickelate, selected based on theoretical predictions. This study focuses on the synthesis and characterization of the Ruddlesden-Popper phase perovskite La_2NiO_4 as the initial material. La_2NiO_4 synthesised via Solid-state method at 1500 ºC. It also describes the various characterization techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), and dielectric spectroscopy, which are used to investigate its structural, electrical, and dielectric properties. The detailed physics and results are thoroughly analyzed. Consistent trend of negative permittivity was observed from the room temperature up to 600 ºC and attributed to plasma oscillations of free electron. A characteristic trend of semiconductor to metal transition observed at 450 ºC.

Chapter 4: This chapter examines how strontium (Sr) doping affects the negative permittivity and electromagnetic shielding effectiveness of La_2NiO_4. Sr was introduced at concentrations of 0.1, 0.3, and 1 to enhance conductivity and reduce synthesis temperature, chosen for its ionic radius and valence compatibility with lanthanum (La). XRD analysis indicates a solubility limit of Sr at 1. XPS results show nickel in undoped La_2NiO_4 primarily in the +2 oxidation state, but with increasing Sr content, nickel valency shifts from +2 to +3 due to charge compensation. Sr doping systematically increases conductivity and permittivity by at least an order of magnitude. The conduction mechanism is dominated by **small polaron hopping**, supported by reduced binding energies. A semiconductor-to-metal transition is observed, with the transition temperature decreasing as Sr concentration rises. Positive imaginary impedance (Z") confirms the intrinsic inductive behavior of the materials, further supported by simulations showing significant inductance. Microwave shielding tests reveal that the sample with 0.3 Sr doping (LN2) achieves effective shielding of approximately 45 dB, dominated by reflection due to strong impedance mismatch caused by negative permittivity.

Chapter 5: Previous studies showed that, Sr doping in La_2NiO_4 increases conductivity but does not reduce the high synthesis temperature of 1500 ºC. To address this, this chapter introduces $LaNiO_3$, a higher-order perovskite synthesized via the sol-gel method at a lower temperature of 1000 ºC, with the goal of achieving stronger epsilon-negative behavior. The resulting $LaNiO_3$ particles are smaller (~118 nm) and exhibit significantly higher permittivity and conductivity from room temperature to 100 °C, over frequencies from 1 kHz to 1.5 MHz. The negative permittivity is attributed to plasma oscillations of free carriers, analyzed using a **modified Drude model** developed specifically to study epsilon-negative behavior in ceramics. Furthermore, $LaNiO_3$ shows enhanced microwave shielding effectiveness, reaching about 33 dB in the X-band at room temperature. This chapter demonstrates $LaNiO_3$ as a promising alternative that overcomes the limitations of La_2NiO_4.

Chapter 6: This chapter transitions from ceramic-based epsilon-negative materials to composite systems. A new class of composites is introduced using $LaNiO_3$ as the functional phase, aiming to extend electromagnetic performance through compositional design. The synthesis of SnO_2-$LaNiO_3$ (SLN) composites with 10%, 20%, and 30% $LaNiO_3$ via wet mixing method and examined their electrical, dielectric, and shielding effectiveness properties. The results demonstrate that sample SLN10, with the lowest $LaNiO_3$ content, exhibits positive permittivity and primarily absorbs incident electromagnetic waves, resulting in effective absorption-mode shielding. As the $LaNiO_3$ concentration increases, the system transitions to negative permittivity, and the shielding mechanism shifts accordingly from absorption-dominant to reflection-based due to enhanced electrical conductivity and impedance mismatch.

Chapter 7: This chapter investigates the incorporation of graphene into SnO_2 as an alternative to $LaNiO_3$, aiming to reduce synthesis temperatures and improve material performance. Graphene's exceptional electrical conductivity, high surface-to-volume ratio, make it ideal for achieving negative permittivity with minimal filler content. Two composites containing 2%

(SGR2) and 4% (SGR4) graphene were synthesized to evaluate their dielectric and shielding properties. SGR2 exhibits ENZ behavior, with permittivity transitioning from positive to negative near 150 °C, demonstrating potential for **tunable switching applications**. This transition also revealed the **minimum threshold conductivity needed for stable ENG behavior**, confirmed by simulations and earlier work. Shielding in SGR2 is mainly due to absorption, while SGR4's higher conductivity leads to reflection-dominated shielding. This work highlights how adjusting graphene content can fine-tune SnO_2 composites for advanced electromagnetic applications.

Chapter 8: The final chapter reviews the progress in developing ENG behavior across various materials and composites, highlighting its impact on electromagnetic technologies including EMI shielding, antenna miniaturization, and coil-less inductors.