Preface

Permittivity and permeability are two fundamental physical properties of materials that describe how they react to electromagnetic, magnetic and electric fields. Materials are divided into four quadrants based on the permittivity (epsilon, ε) and permeability (mu, μ) sign. These include common materials (both ε and μ are positive), double-negative materials, mu-negative materials, and epsilon-negative materials. The incident electromagnetic waves are transparent to common materials with positive permittivity and permeability, and the electric vector (**E**), magnetic vector (**B**), and wave vector (**k**) correspond to the right-handed rule. Electromagnetic waves can propagate within materials having double negative characteristics, such as metamaterials, but the relationships between **E**, **B**, and **k** are left-handed. In materials with solely negative permittivity or negative permeability, electromagnetic waves fade evanescently. Epsilon-negative materials were initially realised in metamaterials, while mu-negative characteristics were first obtained in ferrites at their magnetic resonance frequency. In recent years, the material having negative permittivity (ε) or/and permeability (μ) have been extensively explored due to their potential applications in optical filters, medical devices, remote aerospace applications, sensor detection, infrastructure monitoring, smart solar power management, crowd control, radoms, high-frequency battlefield communication, lenses for high-gain antennas, improving ultrasonic sensors, and even shielding structures from earthquakes, etc.

The negative permittivity is essential for the meta-performance like negative refraction, negative phase velocity, reverse Doppler effect and Cerenkov effect, etc. Negative permittivity materials have shown great potential in various electromagnetic and electronic applications, such as electromagnetic shielding, wave absorbing, laminated capacitors, and coil-less inductors. The concept of negative permittivity is not new. The permittivity of common metals is always negative when the frequency is below their plasma frequency, ω_p, i.e., all metals below their plasma frequency are negative permittivity materials on their own. However, as frequency falls, the real part of permittivity rapidly declines while the imaginary part substantially increases. As a result, all metals lose their utility as negative permittivity materials in various applications. According to investigations conducted from the standpoint of materials science the negative permittivity can be realised in the radio-frequency band, which is significantly lower than the optical frequency.

In the beginning the concept for achieving/obtaining negative permittivity (ε) or/and permeability (μ) in radio frequency region was solely theoretical. Later it was realised in artificially designed/composed metamaterials, which consists artificially composed periodic arrays of metallic units, rarely seen in natural materials. The recent studies towards the development of metamaterials and realization of negative permittivity (ε) or/and permeability (μ)in natural materials highlighted the necessity of percolating metallic/conducting pathways in ceramic- or polymer-matrix composite(s). The critical percolating structures of building blocks brings challenges for composites to achieve microscopic (at atomic/molecular) level homogeneity that is needed to be used as coatings, film, or even other lower-dimensional materials or devices. This challenge can be overcome by realizing negative permittivity in mono-phase materials which is desirable for the miniaturization of the devices.

Finding a single-phase material showing negative permittivity is a challenging task and very few reports were available. Further, it is reported that negative permittivity depends on external parameters such as frequency and magnitude of the field and temperature. In most of the studies, negative permittivity has been studied as a function of the frequency and magnitude of an applied electric field. Study of negative permittivity as a function of temperature has rarely been made.

From the extensive literature survey, we have come to know that the single-phase materials which have shown negative permittivity in kHz to MHz frequency range are transition metals-based perovskite oxides (ABO_3) such as $PrMnO_3$, $LaSrMnO_3$, $LaCoEuTiO_3$, $LaFeO_3$, $GdFeO_3$, and $LaBaCoO_3$. Except La_2NiO_4, no other system having general A_2BO_4 (Layered Perovskites or Ruddlesden-Popper) has been reported as negative permittivity material. The A_2BO_4 oxide is a two-dimensional perovskite like layer structure, in this structure it is easy to implant ions as dopants into the host lattice and hence manipulate its physical and chemical properties. In Sr_2MnO_4 multivalency of Mn cation offers the opportunity to tune its oxidation state via optimum dopant and its concentration, which may change electrical properties further.

The study of phase diagram of system Sr-Mn-O has shown that Sr_2MnO_4 is a metastable compound, it is stable only between 1350 °C to 1680 °C. Therefore, synthesis of pure Sr_2MnO_4 and its stabilization at low temperature (below 1350 °C) is a challenging task. Attempts have been made to synthesize compositions of La doped $La_xSr_{2-x}MnO_4$, but only synthesis of the compositions in the range $0.25 \leq x \leq 0.7$ could be possible. Therefore, in the view of above-mentioned challenges and to explore the possibility of Sr_2MnO_4 as negative permittivity material, in this thesis work efforts have been made to synthesize doped Sr_2MnO_4 and study phase stability and negative dielectric properties using solid state ceramic route. To tailor observed negative dielectric properties, a few compositions of La (at Sr), Sn (at Mn) and Nb (at Mn) systems for the first time have been synthesized by the same procedure. The effect of selected dopants on phase stability, structure, microstructure and negative permittivity behaviour are studied in detail. Further, it is worth mentioning here that to study explicitly role of the dopant, processing parameters (calcination and sintering temperature and time) were kept same for all the samples. For convenience the introduction to the subject, experimental tools and carried out work in this thesis is presented in theses following seven chapters:

Chapter 1: This chapter briefly presents the introduction of perovskite and layered perovskite oxides. It also describes the scientific and technical investigations carried out on layered perovskite oxides. Various technological applications of A_2BO_4 oxides have also been briefly reviewed in this chapter. The effect of dopants on crystal structure, oxygen stoichiometry and effective carrier concentration are discussed. It is then followed by a brief history towards the development of negative permittivity materials, introduction to negative permittivity & current negative permittivity materials, their concurrent challenges, theoretical models explaining negative permittivity and motivation of work.

Chapter 2: This chapter describes the experimental procedure and techniques used for the preparation & characterization of the samples. The solid-state ceramic route is used for preparation of these materials and described with the help of a flow chart. The physics and methodology of experimental techniques used for characterising synthesized compositions has also been reviewed briefly.

Chapter 3: This chapter presents, the successful synthesis of Sr_2MnO_4using the solid-state reaction technique. Quenching in air from 1500°C to room temperature yielded the pure phase powder of Sr_2MnO_4. The purity of synthesized powder was further examined by FTIR analysis. The Rietveld refinement of XRD data confirmed the tetragonal structure and I4/mmm space group. The band gap, computed from the Tauc's plot, was found to be 1.15 eV. The XPS analysis depicted the presence of Mn^{3+} and Mn^{4+} valence states. Measurement of the AC electrical conductivity over wide temperature (30-500°C) and frequency (0.020 – 2 MHz) ranges were carried out. The conduction mechanism changed from small polaron tunnelling (< 270 °C) to non-overlapping large polaron tunnelling (>270 °C). The frequency versus imaginary part of the impedance (Z'') and modulus (M'') plots exhibited a change in the conduction domain with increase in temperature. This result was further verified by the Ghosh's scaling of the conductivity spectra.

Chapter 4: This chapter presents, the synthesis of few compositions of La doped $La_xSr_{2-x}MnO_4$ (x = 0.3, 0.5, 0.7) system in the air using solid-state ceramic route. Permittivity and AC conductivity studies with respect to frequency and temperature exhibited negative permittivity in the entire range of the measurement (30-300 °C) at all measuring frequency (1 kHz - 2 MHz). The negative permittivity was analysed by the Drude-Lorentz model. It was found that negative permittivity is caused by the plasma oscillations of free charge carriers. The inductive characteristics of the samples has been studied by the modelling of impedance data using various combinations of resistors and inductors. The inductive character of samples shows the prospect of developing synthesized compositions as coil-less inductor.

Chapter 5: This chapter presents, the synthesis of few compositions of the system $Sr_2Mn_{1-x}Sn_xO_4$ (x=0.0, 0.3, 0.5) system in the air using solid-state ceramic route. A change in the sign (positive to negative) of the permittivity above a particular temperature (T_C) is observed at all the measured frequencies. The negative permittivity was analysed by the Drude-Lorentz model. It was found that negative permittivity is caused by the plasma oscillations of thermally excited free charge carriers. Analysis of XPS spectra confirmed the presence of mixed-valence states of both Mn (Mn^{4+} and Mn^{3+}) and Sn (Sn^{4+} and Sn^{2+}) ions. The UV-Vis.-IR spectroscopy results indicated generation of a large number of defect states in the forbidden bandgap region of Sr_2MnO_4 on the substitution of Sn at Mn site. Synthesized samples are promising metamaterials for radio frequency (10 Hz -2 MHz) region applications due to the high-temperature plasmonic behaviour.

Chapter 6: This chapter presents, the synthesis of few compositions of Nb doped $Sr_2Mn_{1-x}Nb_xO_4$ (x = 0.1, 0.2, 0.3, 0.4, 0.5) system in the air using solid-state ceramic route. Out of these, the x=0.4, 0.5 compositions were found to consist of an impurity of $Sr_8Nb_4O_{18}$, which elucidates a solubility limit of Nb in the Sr_2MnO_4. Permittivity and AC conductivity studies with respect to frequency and temperature exhibited negative permittivity in the entire range of the measurement (30-600 °C) for x = 0.1, 0.2 compositions, whereas in the case of x=0.3, 0.4, and 0.5 compositions, the same behaviour was seen above 80°C, 180°C, and 230°C, respectively. The plasmonic oscillations of charge carriers may be responsible for the negative permittivity behaviour, which is analysed by the Drude-Lorentz model. Compositional and temperature dependent sign of the permittivity of the system $Sr_2Mn_{1-x}Nb_xO_4$ makes this system promising materials for switching action in the wide frequency range and temperature range.

Chapter 7: This chapter sums up the overall conclusions of the investigations carried out in the thesis work. A few important suggestions for future scope are also mentioned in this chapter.