Preface

The layered perovskites were first studied by S.N. Ruddlesden and P. Popper in 1958 hence they are known as Ruddlesden Popper (RP) oxides. Ruddlesden–Popper (RP) oxides have shown very attractive and versatile physical properties such as superconductivity, magnetoresistance, and mixed ionic and electronic conductivity, which are potential candidates for energy and electronic devices. The Ruddlesden Popper oxides are represented by general formula $A_{n+1}B_nO_{3n+1}$, where n is a positive integer, for example n=1 A_2BO_4, n=2 $A_3B_2O_7$ and so on. The structure of the first member (n = 1) of this series A_2BO_4 is known as K_2NiF_4 structure, which is built of an alternate stacking of a perovskite slab and a rock-salt slab. In A_2BO_4 structure, the A ion is coordinated by nine oxygen ions and the B ion is coordinated with six oxygen ions. The unit cell is tetragonal having I4/mmm symmetry with lattice parameters a=3.9 Å and c ~ 3 a Å. To obtain this structure, the radius ratio of A and B ions r_A/r_B should be in the range of 1.7 to 2.4 Å. To analyse the stability of the structure of perovskite oxides Goldschmidt suggested a parameter known as Tolerance factor (t), is defined as:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

Where, r_A, r_B and r_O are the ionic radii of cation A, B and anion O respectively. It is reported in the literature that for A_2BO_4 oxides, K_2NiF_4 structure is stable if value of the tolerance factor lies within the limits $0.85 < t < 1.02$. The radius limits for the two cations A and B are 1.0 to 1.9 and 0.5 to 1.2 Å, respectively.

In general ABO_3 oxides are oxygen-deficient perovskites, whereas A_2BO_4 oxides can be both oxygen-deficient and oxygen-excess, depending upon their majority oxygen

defects. In A_2BO_4 system, interstitial sites are present in the AO layer, which can be accommodating excess oxygen as an interstitial oxygen defect. Hence, oxygen ion migration in A_2BO_4 oxides can occur via mechanisms associated with either oxygen vacancies or oxygen interstitials.

In low-dimensional structure (2-D) of A_2BO_4, it is easy to replace ions into the host lattice and create defect states at suitable depths and hence to tune physical properties. A wide variety of chemical substitutions at the A and B sites are possible provided the criteria for ionic radii and the charge neutrality are satisfied. Oxygen interstitial and oxygen vacancies in these oxides can also be formed by selecting suitable dopants for A and B sites. The oxidation states range from +1 to +3 for A-site ions and from +2 to +6 for B-site ions. In addition, different types of oxygen defects affect the oxidation states of metal cations of A_2BO_4 oxides as a result of changes in oxygen stoichiometry. A_2BO_4 oxides have received attention due to their chemical stability and that wide scope of substitution variation to tailor the solid-state properties. From the extensive literature survey on A_2BO_4 oxides it is noticed that electrical and magnetic properties of undoped and doped lanthanide based nicklets, cuperates and cobbaltes have been studied in detail. These materials have shown their potential for various technological applications.

On the other hand, literature on the electrical and magnetic properties of alkaline earth based orthostannate A_2SnO_4 (A=Ca, Sr and Ba) is extremely limited. These orthostannates have been used as host matrix for incorporating the rare earth metals ions (Eu, Dy, Sm etc.) for phosphor application used in various optical devices. Similar to La_2NiO_4, in alkaline earth orthostannate (A_2SnO_4) also has oxygen content and valency of Sn ion can be tune by incorporating suitable dopants at A-site and Sn-site. The cost of lanthanide compounds is more as compared to alkaline earth compounds. Therefore, it is considered worthwhile to investigate properties of alkaline earth orthostannates and

study the effect of substitution on A and B sites of these properties. The study on the effect of substitutions is important for further improvement in their properties.

In this work we have synthesized Sr_2SnO_4 and other new compounds by selecting suitable dopants for both Sr and Sn site. At Sr^{2+} site three dopants Ba^{2+} (isovalent), La^{3+} (hetrovalent, donor), Nd^{3+} (hetrovalent, donor) and at Sn^{4+} only dopant Eu^{3+} (hetrovalent, acceptor) have been incorporated. The effect of incorporation of these dopants on the crystal structure, microstructure, electrical, dielectric, optical and magnetic properties of Sr_2SnO_4 have been investigated. To the best of our knowledge, no report is available on the substituted materials in the literature so far. The results of these investigations are described in chapters 3-7 of the thesis. In this work following systems have been synthesized by solid state ceramic route:

Pure Sr_2SnO_4.

Isovalent Ba^{2+} doped at Sr^{2+} site system $Sr_{2-x}Ba_xSnO_4$ (structural and dielectric).

Donor La^{3+} doped at Sr^{2+} site $Sr_{2-x}La_xSnO_4$ (structural and electrical).

Donor Nd^{3+} doped at Sr^{2+} site, $Sr_{2-x}Nd_x$ SnO4 (structural and magnetic).

Acceptor Eu^{3+} doped at Sn^{4+} site, $Sr_2Sn_{1-x}Eu_xO_4$ (structural and optical).

Chapter 1: This chapter presents the introduction of perovskite and layered perovskite oxides. It describes briefly the scientific and technical investigations carried out on layered perovskite oxides. Various technological applications of A_2BO_4 oxides have been reviewed in this chapter. The effect of different types of substitutions (isovalent, hetrovalent, valence compensated) on structure, electrical, dielectric, optical and magnetic properties of perovskite and layered perovskite oxides are discussed. The end of this concludes with the objectives of the present investigations. From the literature

survey it was noticed that isovalent doping (Sr^{2+} at Ba^{2+} site) and (Sn^{4+} and Ti^{4+}) in $BaTiO_3$ has improved its dielectric properties significantly. Further, it is reported that doping of La^{3+} at Ba^{2+} site in $BaSnO_3$ has increased conductivity by five orders of magnitude. System $Ba_{1-x}La_xSnO_3$ has been widely studied due to its application as optically transparent conducting oxide and humidity sensing material. Therefore, La has chosen to study the effect on the properties of Sr_2SnO_4. Magnetic properties of Nd are interesting; therefore this element has chosen to study its effect on the magnetic properties of Sr_2SnO_4. Optical properties of Eu doped at Sr^{2+} site of Sr_2SnO_4 have already been investigated but in this work we have investigated optical properties by doping of Eu on Sn site.

Chapter 2: This chapter describes the experimental procedure and techniques used for the preparation & characterization of the samples. The solid state ceramic route used for preparation of these materials has been described with the help of a flow chart. To decide the calcination temperature, thermal analysis (TG-DSC) of the mixture of raw materials was carried out using simultaneous TG-DSC set-up (Mettler Toledo). Powder X-ray diffraction (XRD (Rigaku Miniflex II) and scanning electron microscope (Zeiss, model EVO-18 research) have been employed for study of crystal structure and microstructure of the samples. Characteristic bond vibrations present in the structure of the samples has been detected using Fourier transform infrared (Shimadzu; model DF 803) and Raman spectrometer (Renishaw, Leica DM 2500 M). Optical band gap of the samples was determined using the UV- Visible spectrometer (Shimandzu, UV-2600). The photoluminescence and lifetime measurements were recorded by using a spectrometer (HR 320 Jovin Yuvon). Valence states of constituent elements and oxygen vacancies present in the samples have been explored using X-ray photoelectron spectroscopy (PHI 5000 Versa Probe III). Electrical (AC conductivity) and dielectric

properties of selected samples were measured at different temperatures (60-600^{o} C) in the frequency range 20 Hz-2 MHz using high precision LCR meter (Agilent E-4980 A). For magnetic measurements, magnetic properties measurements system (Quantum Design MPMS 3 magnetometer) was used over a temperature range 2-300K and in the applied magnetic field range ±40 kOe.

Chapter 3: This chapter reports, synthesis and characterization of Sr_2SnO_4. Thermal analysis (TG and DSC) of the mixture of raw materials ($SrCO_3$ and SnO_2) and X-ray diffraction (XRD) techniques have been used to study the mechanism of formation for Sr_2SnO_4. The phase pure powder obtained by calcination at 1000^{o}C for 8 h have lattice parameters a=b=4.0508±0.0005 Å, c=12.5904±0.0002 Å and space group I4/mmm are in agreement with the reported literature. The characteristic vibrational and rotational bands active in Sr_2SnO_4 are detected using Fourier Transformed Infra-red (FTIR) and Raman spectroscopy. The Scanning Electron Micrograph (SEM) of the sintered ceramic shows spherical grains with average size (186 ± 20) nm. The absorption and optical band gap of the sample is determined using UV-Vis spectroscopy. Dielectric properties and AC conductivity have been measured in wide frequency and temperature ranges. Dielectric constant and dissipation factor of this material at 10 KHz and 50^{o}C are found to be 280 and 0.6, respectively. Spectroscopic and Complex plane (Nyquist) plots of modulus have confirmed the presence of single Debye-type relaxation process. AC conductivity spectrum of the sample follows universal Johnscher's Power law. By fitting Johnscher's equation to the experimental data of electrical conductivity, parameters σ_{dc}, f_H, n are obtained. Where, σ_{dc}, f_H and n are dc conductivity, hopping frequency and power exponent respectively. Activation energy for DC conductivity has been found to be 0.16 eV almost same as activation energy obtained from the relaxation frequency. The power exponent of AC conductivity (n) is almost constant in the

investigated temperature range, shows that the conduction is takes place due to Quantum Mechanical Tunnelling (QMT) process of electrons between Sn^{2+} to Sn^{4+} sites.

Chapter 4: This chapter results on synthesis and characterization of Ba^{2+} doped at Sr^{2+} system, $Sr_{2-x}Ba_xSnO_4$ (with x = 0.20, 0.40, 0.80, 1.60) have been discussed. All the synthesized compositions have tetragonal structure and I4/mmm space group similar to undoped Sr_2SnO_4. The lattice parameters (a=b and c) increases with increasing concentration of Ba in solid solution which is consistent with Vegard's law for the solid solutions. The transmission electron micrograph (TEM) of calcined powder of a representative sample shows that particles are agglomerated and spherical in shape with average size (76 ± 5) nm. Dielectric and AC conductivity of the sintered ceramics have been studied in the temperature range 50 to 600^oC and frequency range 20 Hz- 2MHz. Further, complex modulus formalism has been applied to understand contribution of interfacial and dipolar polarization in the dielectric properties of the samples. The temperature independent value of dielectric constant and dissipation factor of the samples make them a potential candidate for the thermally stable capacitor and sensor applications.

Chapter 5: This chapter presents results on structural and electrical characterization of system $Sr_{2-x}La_xSnO_4$ (with x=0.01, 0.02, 0.04, 0.06 and 0.10). All the synthesized samples have tetragonal crystal structure and space group I4/mmm like undoped Sr_2SnO_4. The lattice parameters increased up to concentration $x \leq 0.04$ and a decreasing trend observed for > x=0.04 concentration of La. The nature of variation of lattice parameters with x is explained based on charge compensation mechanism. Further, single phase formation of the solid solutions is reconfirmed by their FTIR and Raman spectrum analysis. FE-SEM image of the samples show that variation in average grain

size with concentration x follows same trend as seen for the lattice parameters. The AC conductivity of sintered samples measured as a function of frequency and temperature. The highest electrical conductivity is obtained for sample with x=0.04 which is approximately one orders of magnitude higher than undoped sample Sr_2SnO_4. Further, the conduction mechanism has been studied by QMT model of conduction. The presence of defects such as Sn^{2+} ions, interstitial oxygen and oxygen vacancies (V_O^x) are probed by XPS technique. Also, the results reported in this chapter have been compared with the results reported by earlier works on La doped perovskite oxides.

Chapter 6: The results of investigation on structural and magnetic properties of $Sr_{2-x}Nd_xSnO_4$ (with x=0.01, 0.02, 0.04, 0.06, 0.10) have been reported in this chapter. Rietveld refinement of XRD data is performed to determine the lattice parameters and other structural parameters. The synthesized samples have been further characterized using FTIR, Raman and UV-Vis spectroscopy techniques. Magnetic properties of the samples are measured at room temperature (300 K) and magnetic field range (± 40 kOe). From the room temperature M-H curve of the samples it is noted that compositions x=0.00 (undoped Sr_2SnO_4) is diamagnetic and its diamagnetic nature diminishes with increasing concentration of Nd and become ferromagnetic for x=0.02. The ferromagnetic nature suppresses gradually with further increasing concentration of Nd and become antiferromagnetic. The highest value of saturation magnetization (0.026 emu/gm) is found for sample $Sr_{1.98}Nd_{0.02}SnO_4$. The observed ferromagnetic and antiferromagnetic nature of the samples may be useful for memory devices, electronic chip, transformer, inductor cores, etc.

Chapter 7: This chapter deals with synthesis, electrical and optical characterization of acceptor doped system, $Sr_2Sn_{1-x}Eu_xO_4$ (with x=0.01, 0.02, 0.04, 0.06, 0.10). The single phase of doped samples has been confirmed by XRD analysis. Rietveld refinement of

XRD profile of for the samples are carried out to determine the structural parameters. The absorption and optical band gap of the prepared compositions are determined through UV-Vis spectroscopy. The emission spectrum of all the samples are recorded the wave number range 500-700 nm by exciting with a source of wavelength 466 nm. There are two highest intensity peaks are observed at 572 nm and 614 nm in the emission spectra. The CIE coordinate shifts towards lower wavelength side (red to green) as Eu concentration increases. Optical quenching phenomenon noted in the samples for $x > 0.06$. The observed emission in the visible range of the samples makes them suitable candidates for optical devices and optical imaging applications.

Chapter 8: This chapter sum ups the overall conclusions of the investigations carried out for the thesis. A few important suggestions for future scope are also mentioned in this chapter.