# Preface

Solar energy is a most abundant, free, clean and sustainable energy source which can be directly utilized through the photovoltaic (PV) effect. If technological advancement can utilize only 0.2% of the solar radiation falling on earth every second with 10% efficiency, it will produce 24 terawatts, sufficient to fulfil the societal needs. However, limitation of efficiency in conventional Si-based photovoltaic solar cells, toxic waste and $CO_2$ emission during photovoltaic panel production limit their contribution in the current energy supply market. Emerging photovoltaic technologies such as ferroelectric perovskite solar cells have drawn great attention for their low-cost manufacturing techniques and for possibility of brisk increases of power conversion efficiency up to 25%. Efficiency of conventional PV technologies mainly depends upon the barrier field strength at the p-n junctions which separates the charge carriers, and band gap of the semiconductor. Maximum efficiency of conventional PV technologies that can be achieved is limited by Shockley-Queisser limit. The charge separating electric field i.e., the barrier electric field is formed at the time of manufacture of the p-n junction and cannot be controlled externally. However, a different PV mechanism in ferroelectric photovoltaic materials is present; here photovoltage is not constrained to inbuilt internal barrier fields. In ferroelectric materials, separation of photo-excited charge carriers is done by polarization induced electric field and this field is present throughout the entire crystal and hence also known as the "bulk photovoltaic effect" (BPVE). This property of ferroelectric based solar cells can create above-band gap open-circuit voltages which is not possible in the conventional solar cells. In spite of these attractive properties, there are many challenges in ferroelectric photovoltaic materials like high band gap, low conductivity, device fabrication etc. which restricts their efficiency to remain lower than the conventional solar cells. These challenges demand more research and investigation

on ferroelectric photovoltaic materials. A key challenge is to reduce the wide band gap of ferroelectric material to make suitable for exploring visible range spectrum without compromising the ferroelectric properties. Thus a proper designing of ferroelectric material is required via band gap engineering. The band gap engineering in these systems could potentially be approached through chemical substitution, cation ordering, quantum size effects, lattice mismatch or super lattice formation.

To achieve these goals outlined above, we focused our investigation on the **"Development of Photo-Ferroelectric Materials for Energy Harvesting and Storage"** for this Ph.D. thesis. Our motive is to modify the properties of typical ferroelectrics like $PbTiO_3$, $BaTiO_3$ and Bi-based perovskite materials in such a way that they become useful for ferro-photovoltaic applications. Our detailed investigations on various materials have led to several new findings in the field of ferro-photovoltaic oxide materials. A brief summary of important findings from our investigation on various developed systems in this thesis work is discussed below:

In **Chapter 1**, the requisite fundamental concepts, knowledge and literature survey are discussed in a detailed and systematic way. This chapter starts with illustrating how the energy demand of the world is increasing year by year and still the major source to fulfil this demand is fossil fuels. Then the contribution of renewable energy sources especially the contribution of solar cells is described here. Different types of solar cells along with their efficiencies are compared together and main focus has been paid to ferroelectric photovoltaic solar cells which have great potential to increase the efficiency. The working principle and the advantages of ferroelectric photovoltaic solar cells over conventional solar cells is discussed in detail. Then the physical properties that an ideal photo-ferroelectric material should possess are described. Further, the different type of ferroelectricity and ferroelectric materials are narrated in detail. A brief

review on Pb-based and Pb-free photo-ferroelectric materials has also been carried out in this chapter. In this sequence, we have discussed many interesting photo-ferroelectric materials, which have low band gap and good conversion efficiency. Finally, we have outlined the objective of our research work on ferroelectric photovoltaic oxide materials.

In **Chapter 2,** we have discussed the experimental method of sample preparation and different techniques used to characterize the sample along with their working principle. The TGA-DTA measurement, Scanning electron microscopy, X-ray diffraction measurement and X-ray photoemission spectroscopy have been employed for thermal, morphological, structural, phase, elemental and chemical state analysis. UV-vis spectroscopy and Tauc plots using Kubelka Munk function for the band gap determination has been described. Temperature dependent permittivity and ac resistance were determined from the frequency and temperature dependent complex impedance measurement. At the end of this chapter, polarization (P)-Electric field (E) hysteresis loop measurements are discussed which is performed to see the ferroelectric nature and polarization properties of the sample.

In **Chapter 3,** the results of investigation on $PbTiO_3$ based material is described in detail. Crystal structure, micro-structural, optical, dielectric and ferroelectric properties have been investigated on various compositions of $PbTi_{1-x}Mo_xO_3$ (x = 0.025, 0.050, 0.075, 0.100). All Mo-doped $PbTiO_3$ powder samples were synthesized by solid state method using high energy ball milling process. Structural analysis shows all samples crystallize into tetragonal phase and unit cell parameters change in such a way that c/a ratio increases with increasing substitution concentration. The microstructure of the sintered samples exhibit agglomerated grains leading to non-uniformity in grain size distribution. Temperature dependent permittivity curve reveals that Curie temperature

($T_c$) slightly increases with increasing Mo-substitution concentration which is in consistence with the increase in tetragonality i.e., c/a ratio as revealed by XRD analysis. UV-Vis spectroscopy shows that Mo-substitution in $PbTiO_3$ reduces the band gap significantly without influencing the ferroelectric properties. The P-E hysteresis loops of all the samples show the ferroelectric nature of the material and increasing tetragonal distortion (c/a ratio) with Mo-incorporation implies increase in polarization. So enhanced polarization in Mo-substituted samples will result in more efficient separation of charge carriers. Mo-substitution in $PbTiO_3$ also increases the conductivity which will help the charge carriers, separated by polarization field to reach their respective electrodes.

In **Chapter 4,** we have tried to design a Bi-based novel material compositions $BiY_{(1-x)}Mn_xO_3$ ($x$ = 0.0, 0.10, 0.25, 0.50, 0.75 ) that have low band gap, good conductivity and significant ferroelectric polarization. The samples were synthesized by solid state method using ball milling process. Structural, morphological, optical, dielectric, electrical and ferroelectric properties of $BiY_{(1-x)}Mn_xO_3$ were analyzed using different characterization techniques. XRD analysis shows that most of the samples (except $x$ = 0.75), were indexed with cubic fluorite structure and $Fm3m$ space group. Here, we observed that one of the composition $x$ = 0.50 has sufficiently low band gap (1.76 eV) and significant ferroelectric polarization. Conductivity of the samples were also found to increase with increase in Mn- concentration as well as with increasing temperature showing semiconducting behavior of the developed system.

In **Chapter 5,** we have discussed structural, morphological, dielectric, transport, impedance and ferroelectric properties of polycrystalline lead free material $Ba_{(1-x)}(Bi_{0.5}Li_{0.5})_xTiO_3$ ($x$ = 0.10, 0.12, 0.15, 0.20, 0.25). The material crystallizes into pseudocubic perovskite structure with space group $Pm$-3$m$. Microstructural analysis of

the samples suggests a spheroid shaped non-porous grains with homogeneous grain size distribution. Temperature dependent permittivity curve of all the compositions reveal absence of any high temperature phase transition. This is consistent with XRD analysis results showing the most symmetric cubic crystal structure for all the compositions at room temperature. One of the composition (x = 0.12) is found to have exceptionally high permittivity among all doped compositions. Nyquist plot for all the compositions show a single semicircular curve, the radius of which increases with increasing Bi-Li concentration and decreases with rise in temperature confirming semiconducting behavior. The band gap decreases at first and then starts increasing with increasing Bi-Li co-substituent concentration. Ferroelectric analysis of various compositions showed slim and slanted P-E loops with significant polarization, suitable for energy storage applications. The two compositions of $Ba_{(1-x)}(Bi_{0.5}Li_{0.5})_xTiO_3$ with $x$ = 0.12 and 0.25 have shown extraordinary storage efficiency of ~95% and 96% with good energy storage density which seems to be promising material for energy storage devices.

In **Chapter 6**, a brief summary of the important findings of the present thesis and possibility of future work in this research field, have been discussed.