Preface

The efforts for reducing large consumption of fossil fuels and continuously increasing demand of low-cost photoactive materials for solar energy have stimulated research towards perovskite ferroelectric photovoltaic materials. Even though, the crystalline silicon solar cells are available with high efficiency, but due to its high production cost, the other category of photovoltaic materials have attracted attention, for developing low-cost alternative of silicon solar cells. Various ferroelectric perovskite materials fulfill essential requirements as photovoltaic materials for device applications [Yuan et al (2014)]. The huge interest towards ferroelectric perovskites in photovoltaic area is closely related to their long-term stability and large-scale materials availability, potential for polarization driven charge carriers separation, high open circuit voltages and chemical stability [Butler et al (2015)]. In this direction, various perovskite ceramics such as $BaTiO_3$, $BiFeO_3$ and transition elements doped $PbTiO_3$ have shown considerable promise for ferroelectric photovoltaic applications [Koch et al (1975); Choi et al (2009)]. Emergence of bulk photovoltage, switchable photovoltaic nature, spontaneous polarization driven internal electric field for charge separation and multiferroic character are the key parameters, which can revolutionize optoelectronic technologies [Matsuo et al (2017)]. There are a number of studied highlighting the ferroelectric photovoltaic phenomenon in perovskite materials such as $BaTiO_3$, $PbTiO_3$, and $LiNbO_3$ [Bhatnagar et al (2013)]. Bhatnagar et al have demonstrated the bulk photovoltaic effect in $BiFeO_3$ films [Huang et al (2017)]. Recently, the bulk photovoltaic effect and switchable diode effect in ferroelectrics have been recognized as the most outstanding features that make these materials very promising candidates for solar cells. However, the low photocurrent densities in wide band gap ferroelectric materials have restricted their application in photovoltaic devices, so far. Thus, development of new low band gap ferroelectric materials has drawn great attention of researchers.

The main obstacle in limiting the application of ferroelectric perovskite oxides in photovoltaic cells is their wide band gap and low charge mobility. Due to wide band gap (> 3.0 eV), the ferroelectric photoactive layer cannot absorb visible part of incident solar spectra and thus shows very low photocurrent. The reason behind wide band gap in ABO_3 type perovskite oxides is large difference in electro-negativity between transition metal atoms and oxygen ions in the unit cell. Recently, transition element doped perovskites have shown attractive properties for the ferroelectric photovoltaic applications because of their comparatively lower band gap than other undoped conventional ferroelectric perovskite oxides [Qi et al (2011)]. The Ni and Nb-doped $KNbO_3$ have been widely studied due to its high spontaneous polarization and great promise for application as solar energy harvesting material. Band gap tuning of $KNbO_3$ produced a semiconducting solid solution $[KNbO_3]_{1-x}$-$[Ba(Ni_{0.5}Nb_{0.5})O_3]_x$ (KNBO-BNN) having a lower band gap of 1.1 eV without losing the ferroelectricity [Grinberg et al (2013)]. However, this solid solution exhibited low photo-current [Grinberg et al (2013)]. Another reason for lower photocurrent in these solar cell materials is absorption reduction in photoactive layer due to nano-meter thin film construction for fabrication of solar cell. Different theoretical studies have pointed out that nanostructured materials could improve thin film device efficiency due to their extremely high surface to volume ratio [Tang et al (2014); Ferry et al (2011)]. Variously engineered nanostructures were integrated into the thin films solar cell to increase the absorption in photoactive layer by trapping the light within the surface. The trapping of light inside device is made possible by increasing the optical path length of incident photons. Indeed, multiple studies have already shown the potential application of nanostructured ZnO as the functional element for sensors, photo-diodes, transistors, and light-emitting diodes, but, their light scattering/trapping properties still require in-depth study [Xu et al (2014)]. With the objective of designing and developing new low band gap ferroelectric systems, in the present thesis, we have investigated the optical band gap of transition element doped $PbTiO_3$, $BaTiO_3$, $KNbO_3$ based solid solutions. We have investigated the photovoltaic properties of these new materials in their thin film form also. Our studies have resulted into many new and important findings that can open up new possibilities in the direction of development of low cost photovoltaic materials that can replace silicon based solar cells.

The significant investigations and important findings of the present thesis are listed below:

1. Band gap tuning of $xPbTiO_3$-(1-x)$Bi(Ni_{2/3}Nb_{1/3})O_3$ ceramics, Observation of microscopic domain switching and Photo-voltaic effect in PLD grown thin films

Solid solution of $xPbTiO_3$-(1-x)$Bi(Ni_{2/3}Nb_{1/3})O_3$ [PT-BNN] system with compositions (x= 0.87, 0.77, 0.70, 0.67, 0.66, 0.65, 0.64, 0.63, 0.625, 0.62, 0.60, 0.55 and 0.50) were successfully prepared by solid state ceramic synthesis and characterized for crystal structure, microstructure and optical properties. The PT-BNN shows morphotropic phase boundary (MPB) region in the composition range of x = 0.65 to x =0.60, where tetragonal and rhombohedral phases coexist. The crystallographic structural transitions as a function of composition, in PT-BNN solid solution has been further confirmed by Raman spectroscopy analysis. Composition dependent dielectric properties are also studied. Curie temperature for xPT-(1-x)BNN compositions decreases from 456°C (x = 0.87) to 181°C (x = 0.50). Composition 0.65PT-0.35BNN in the MBP region shows the highest value of dielectric permittivity and remnant polarization (P_r = 25.6 μC/cm^2) and a direct band gap of E_g = 2.3 eV. We have investigated in details the band gap tuning in $x$$PbTiO_3$–(1–x)$Bi(Ni_{2/3}Nb_{1/3})O_3$ (PT-BNN) ceramic by compositional variation in the composition range $0.50 \leq x \leq 0.87$. The absorption spectra of PT-BNN exhibits three absorption shoulders, with one lying in the near-infrared (NIR) region. The presence of absorbance peak in NIR range makes this solid solution applicable in NIR-related fields. The multi-absorbance peaks are originated in absorption spectra due to presence of Ni ions which promotes formation of oxygen vacancies.

The band gap of $PbTiO_3$ is significantly reduced by solid solution formation with $Bi(Ni_{2/3}Nb_{1/3})O_3$. This work provides good insights for the band gap tuning of $PbTiO_3$ by varying the concentration of $Bi(Ni_{2/3}Nb_{1/3})O_3$. The band gap of this solid solution system has been shown to be directly influenced by transition elements (Ni, Co, Cu) doping and altering the stoichiometric ratio of Ni and Nb in $Bi(Ni_{2/3}Nb_{1/3})O_3$ component. The Co-doping in 0.65PT-0.35BNN provides the lowest band gap (E_g = 1.55 eV) but ferroelectric polarization is also decreased. When Ni is replaced by Co, the new solid solution system $0.58PbTiO_3$-$0.42Bi(Co_{2/3}Nb_{1/3})$ shows a lower band gap of 1.3 eV. The reduced band gap is attributed to the extra Co-d_z^2 state and Co-d^2_{x-y} states created between conduction band (CB) and valance band (VB).

We have demonstrated that the multiferroic particulate composites of 0.65PT-0.35BNN with spinel $Ni_{0.65}Zn_{0.35}Fe_2O_4$ (or $Co_{0.5}Zn_{0.5}Fe_2O_4$) also effectively provide a lower band gap. The lowest band gap of E_g = 1.39 eV is obtained for **(**0.25)[0.65PT-0.35BNN]-$0.75Co_{0.5}Zn_{0.5}Fe_2O_4$ composite. CuO doped 0.65PT-0.35BNN also provide a lower band gap and bulk photo-voltaic effect in ceramic pellets form. Ceramic pellets of 0.65PT-0.35BNN composition shows an open circuit voltage (V_{oc}) ~ 4.13V which increases to 5.1 V for 0.3% CuO doped 0.65PT-0.35BNN composition.

The epitaxial PT-BNN films were grown on single crystalline substrate by pulsed laser deposition (PLD) technique and were analyzed using atomic force microscopy, piezoresponse force microscopy (PFM). The photovoltaic effect is studied in PT-BNN thin films prepared by PLD. The temperatures dependent short-circuit current and open circuit voltage is measured and data is analyzed.

2. Band gap tuning of (Co, Bi) doped $PbTiO_3$ ceramics and Observation of Photo-voltaic effect in magnetron sputtered thin films

We have successfully demonstrated the development of $xPbTiO_3$-(1-x)$Bi(Co_{1/2}Ti_{1/2})O_3$ [PT-BCT] (x= 0.80,0.70, 0.65, 0.60, 0.55) solid solution using the conventional solid-state reaction technique. Phase identification and structural characterization of PT-BCT powders were made by X-Ray diffraction technique. Changing the concentration of $Bi(Co_{1/2}Ti_{1/2})O_3$ (BCT) has significant effect on the crystal structure, microstructure, and optical properties of the PT-BCT solid solution. Optical band gap of PT-BCT reduces from 2.9 eV to 1.83 eV with 40% BCT (x = 0.60) concentration. The PT-BCT material shows two direct band gaps. The direct band gap E_{g1} arises from p-d charge-transfer excitations. The band gap at lower energy side E_{g2} arises from hybridization of Co ($3d_z^2$+$O2p_z$) and Co-- 3d excitations The band gap tuning is done by varying the doping percentage of Co (y= 0.45, 0.5, 0.55, 0.60) in $0.60PbTiO_3$-$0.40Bi(Co_yTi_{1-y})O_{3.}$ The optical band gap is found to reduce from 3.2 eV to 1.65 eV as the Co concentration increases in 0.60PT-BCT. The reduced band gap makes the $xPbTiO_3$-(1-x)$Bi(Co_{1/2}Ti_{1/2})O_3$ a promising multiferroic material for ferro-photovoltaics applications. The $0.60PbTiO_3$-$0.40Bi(Co_{0.60}Ti_{0.40})O_3$ (PT-BCT) thin films were deposited on FTO coated glass substrates by magnetron sputtering. The local ferroelectric switching is observed in optimum composition of PT-BCT thin films. The current-voltage (I-V) characteristics of as prepared Ag/PT-BCT/FTO device were measured in dark and under light illumination. The development of switchable electronic devices for future and photo-ferroic solar devices basic understanding of charge transport properties in ferroelectric thin films is crucial. We have analysed different charge transfer mechanism models and the new insight will widen the basic understanding of light induced charge transport process in ferroelectric films deposited on TCO electrode. We also report the strain-gradient induced flexo-photovoltaic effect in PT-BCT/FTO heterostructure measured using conducting Pt-tip. The results of these studies could provide interesting opportunities for designing thin film ferroelectric solar cells and help in analyzing the charge transport mechanism.

3. Development of $xBaTiO_3$-(1-x)$Bi(Ni_{2/3}Nb_{1/3})O_3$ ceramics as new narrow band gap ferroelectric materials for photovoltaic applications

The main obstacle limiting $BaTiO_3$ as photo-absorbing layer in solar cells is its wide band gap which restricts the full absorption of solar spectrum. We have developed and investigated a new low band gap perovskite system $xBaTiO_3$-(1-x)$Bi(Ni_{2/3}Nb_{1/3})O_3$ (BT-BNN) with compositions ($0.50 \leq x \leq 0.92$). Refined structural parameters and bond lengths for xBT-(1-x)BNN solid solutions obtained by Rietveld structure refinement confirms the cubic structure with space group Pm3m for studied compositions. We have carried out detailed investigation to develop lead free semiconducting ferroelectric material. The direct band gap is significantly reduced from 3.2 eV to 2.19 eV for BNN modified $BaTiO_3$. We have chosen Ni^{3+} as non-d_o transition-metal ion ($3d^4$) along with Nb^{5+}($4d^0$) to reduce the band gap and support ferroelectric states. In this work, we have compared the effect of Ni-only substitution and Ni-Nb co-substitution at the Ti-site of $BaTiO_3$ for lowering optical band gap. The presence of Ni-3d states, both at the top of the valence band and at the bottom of the conduction band reduces the overall band gap of BT-BNN. The P-E measurement of BT-BNN samples reveals that the saturation polarization is reduced than $BaTiO_3$ but it retains the ferroelectric nature after BNN substitution. We have demonstrated light intensity dependent, polarization direction dependent photovoltaic behaviour and bulk photo-voltage in BT-BNN ceramics. The current- voltage (I-V) characteristics of as prepared AZO/BT-BNN/Ag/Si device was measured and the PV mechanism in dark and under light illumination is explained using the schematic energy band diagrams. The highest photo-current (J_{sc}~1.5 µA/cm^2) is obtained for 0.70BT-0.30BNN composition. Open circuit voltage V_{oc} highly depends on the polarization of material and it reduced from -3.23 V to -1.38 V with increasing BNN doping concentration in $BaTiO_3$. From obtained experimental results, it can be concluded that V_{oc} directly depends on remnant polarization of material and J_{sc} is related to both band gap and polarization. Our discovery of switchable ferroelectric diode effect in lead free polycrystalline ceramic BT-BNN may provide an opportunity for designing new electronic devices. The observed polarization and band gap dependent photo-current, switchable photovoltaic effect of BT-BNN will be of great interest for future ferroelectric photovoltaic devices.

4. Photovoltaic behaviour of Magnetron Sputtered and Solution processed (1-x)$KNbO_3$-x$Ba(Ni_{1/2}Nb_{1/2})O_{3-\delta}$ Thin Films and Enhancement in photo-current by application of ZnO nano-structures as light trapping layer

The ceramic solid solution of (1-x)$KNbO_3$-x$Ba(Ni_{1/2}Nb_{1/2})O_{3-\delta}$ (KNBNN) with compositions x = 0.05, 0.10,0.15, 0.20, and 0.25 were synthesized by solid state reaction method. The UV-visible absorption spectra of KNBNN reveal that the band gap of KNBNN samples shrink from 3.1 eV to 2.19 eV. A sputtering target of 0.9KNBNN composition was prepared and films were deposited on FTO glass substrates. First time magnetron sputtered and sol-gel based 0.90$KNbO_3$-0.10$Ba(Ni_{1/2}Nb_{1/2})O_{3-\delta}$ thin Films were grown and their photoelectrical properties were measured. We have applied magnetron sputtering and sol-gel techniques to grow KNBNN films as their fabrication process is user friendly cost effective and can be implemented for industrial production. The ferroelectric nature of as deposited films was confirmed by piezoforce microscopy (PFM). A low short circuit photo-current density of 0.026 mA/cm^2 was obtained for Au/KNBN/FTO devices after poling which increased for Ag/KNBN/FTO devices. The low open circuit voltage of device is due to polycrystalline nature of films as polycrystalline films contain defects or grain boundaries that act as recombination centers to trap the photon generated charge carriers. The observed photovoltaic effect in Ag/KNBNN/FTO device can be attributed to depolarization field in KNBNN thin film and Schottky barriers at KNBNN/Ag and KNBNN/FTO interfaces. Further, in this work, we have grown ZnO nanostructures on glass and FTO substrates and explained the growth mechanism using AFM. The surface morphology of the as-grown ZnO nanoparticles, nanowalls and nanorods on glass and FTO coated glass substrates were analyzed using SEM, HRTEM and AFM. It was observed that as grown ZnO nanostructures reduce the reflectance of FTO coated substrates. So, ZnO nanostructures can be sandwiched between an electrode layer and photo-active layer to trap light inside solar cells. Our investigations reveal that a variation in growth geometry of ZnO nanostructures strongly influences their light-harvesting properties as well as the current collection efficiency of devices. The AFM analysis indicated that larger surface area, rougher surface and lower density of interconnected ZnO nanowalls make them a better candidate for light harvesting in solar cells. We have analyzed the possible built-in-field (E_{bi}) at interfaces of different layers in device and depolarization field (E_{dp}) within KNBNN layer. The photocurrent for devices with ZnO nanowalls shows increased J_{sc} = 0.067 mA/cm^2 as compared to devices with ZnO nanorods and nanoparticls. Single layer KNBNN junction solar cell in negative poled condition, shows J_{sc} = 0.01286 mA/cm^2. The photocurrent density of device for ZnO as light trapping layer in the form of nanowalls, nanorods and nanoparticles follows the sequence $J_{NW\text{-}KNBNN} > J_{NR\text{-}KNBNN} > J_{NP\text{-}KNBNN}$, which is consistent with their percentage reflectance. These results indicate that efficient light trapping is the main factor that affected the photocurrent in these devices.

The present findings are not only beneficial to study the growth mechanism of ZnO nanostructures but also provide the clear evidence that optimal geometry of ZnO nanostructures is highly effective in improving the efficiency of solar cells. The results presented in our work can provide a guideline to develop light trapping methodology needed to achieve higher efficiencies in solar cells.

The thesis is organized into **7** chapters.

Chapter 1: gives an introduction to basic concepts of semiconductors and multiferroic materials including the light induced photoelectric phenomenon such as bulk photovoltaic effect, photo-dielectric effect and photo-polarization. A concise review of the recent progress on the understanding of ferroelectric photovoltaic effect, band gap tuning of ferroelectric materials and device design strategies to enhance the photocurrent are also presented.

Chapter 2: describes the preparation methods used for bulk ceramics ferroelectric solid solutions, thin films by PLD, RF sputtering and chemical solution deposition by spin coating method. A brief description of various characterization techniques used in the present thesis is presented. The details of ferroelectric photovoltaic device fabrication and their characterization is also given.

Chapter 3: presents the composition dependent structural, morphological, Dielectric, ferroelectric and optical properties for $xPbTO_3$-(1-x) $Bi(Ni_{2/3}Nb_{1/3})O_3$ solid solutions in the composition range $0.50 \leq x \leq 0.87$. The impact of calcinations and sintering temperature on the structural, morphological and optical properties is also discussed. This chapter also describes the growth procedure, microscopic domain switching and photovoltaic properties of $xPbTO_3$-(1-x)$Bi(Ni_{2/3}Nb_{1/3})O_3$ thin films.

Chapter 4: describe the structural, morphological, ferroelectric and optical properties of $xPbTiO_3$-(1-x)$Bi(Co_{1/2}Ti_{1/2})O_3$ (PT-BCT) samples with composition (x=0.8, 0.70, 0.65, 0.60, 0.55). The mechanism of band gap narrowing in PT-BCT with Co-doping is analyzed. The charge transport mechanisms and photovoltaic effect in the magnetron sputtered PT-BCT thin film based devices are investigated.

Chapter 5: describes the detailed procedure to prepare a new low band gap lead free ferroelectric material $xBaTiO_3$-(1-x)$Bi(Ni_{2/3}Nb_{1/3})O_3$ ($0.50 \leq x \leq 0.97$). The results of structural, morphological, dielectric, ferroelectric and optical properties investigations are presented. Polarization direction dependent photovoltaic behaviour in BT-BNN based devices is studied and anomalous photovoltaic mechanism in this system is explained.

Chapter 6: Describe the growth of (1-x)$KNbO_3$-xBa($Ni_{1/2}Nb_{1/2}$)$O_{3-\delta}$ (KNBO-BNN) thin films using magnetron sputtering and sol-gel based spin coating and their photovoltaic properties. This chapter also presents the growth of ZnO nanostructures, their anti-reflection properties and applications in KNBO-BNN based ferroelectric solar cells as light trapping layer.

Chapter 7: summarizes the main findings of the present work and lists a few suggestions for future investigations.