Chapter 7

Summary and Future Prospects

7.1 Summary and Conclusions

In this chapter, we have summarized the important findings of the present thesis and have suggested future work that needs to be done in this area. The optical properties, ferroelectric, semiconducting nature and photovoltaic properties of transition elements doped $PbTiO_3$, $BaTiO_3$ and $KNbO_3$ based ferroelectric solid solutions have been investigated and reduction of the band gap have been achieved successfully. The phase pure samples were synthesized by conventional solid state reaction route. The phase purity and crystal structures of various compositions were characterized by using x-ray powder diffraction. We have also investigated the photovoltaic behaviour of these ferroelectric materials in their ceramic pellet and thin film forms. Since no detailed light induced physical properties measurements were carried out earlier on these systems, the structural as well as other physical properties, such as, light induced ferroelectric, dielectric, photovoltaic behaviour etc. have investigated in detail. Our detailed investigations on various compositions of these materials have revealed several new important findings that were not reported earlier. The significant outcomes of this thesis work are listed below:

7.2 Significant outcomes of the Present Work

7.2.1. Band gap engineering in xPbTiO$_3$–(1–x)Bi(Ni$_{2/3}$Nb$_{1/3}$)O$_3$ system and detection of photovoltaic behavior in PT-BNN thin film:

In this work, we have systematically investigated the band gap tuning in xPbTiO$_3$–(1–x)Bi(Ni$_{2/3}$Nb$_{1/3}$)O$_3$ (PT-BNN) solid solutions in the composition range $0.50 \leq x \leq 0.87$. The composition dependent morphological, optical, ferroelectric and dielectric properties demonstrated that the highest dielectric permittivity is obtained near MPB region of PT-

BNN ceramics and 0.65PT-0.35BNN composition shows the maximum value of remnant polarization (P_r = 25.6 μC/cm^2). The multi-absorbance peaks in the UV-visible-NIR absorbance spectra are due to presence of Ni-ions which promotes formation of oxygen vacancies. We report that multiple shoulders present in the absorption spectra of PT-BNN correspond to two different band gaps E_{g1} (arising from p-d charge-transfer excitations) and E_{g2} arising from hybridization of Ni ($3d_z^2$+$O2p_z$) and Ni-3d excitations. The BNN doping creates extra energy states between valance band and conduction band which causes lowering of the band gap. Morphotropic phase boundary composition 0.65PT-0.35BNN has the highest P_r value. We further lowered the band gap of 0.65PT-0.35BNN by additional Ni, Co and Cu doping. The direct band gap of 0.65PT-0.35BNN is reduced from 2.3 eV to 2.23 eV by Ni doping (y= 0.07) in $0.65PbTiO_3$-$0.35Bi(Ni_{2/3+y}Nb_{1/3-y})O_3$ solid solutions. Similarly, cobalt ion doping (y =0.1) reduced the band gap of 0.65PT-0.35BNN from 2.3 eV to 1.5 eV. However, the Co-ion doping also degraded the ferroelectric nature of parent material due to extra oxygen vacancies and increased covalent character of bonding. The reduced E_g of Co-ion doped 0.65PT-0.35BNN have motivated us to replace the Ni with Co-ions in $xPbTiO_3$–$(1–x)Bi(Ni_{2/3}Nb_{1/3})O_3$ solid solutions. In this work, we developed a new semiconducting ferroelectric solid solution $xPbTiO_3$–$(1–x)Bi(Co_{2/3}Nb_{1/3})O_3$ for photovoltaic applications. We have obtained lowest band gap (1.3 eV) for 0.58PT-0.42BCN composition of this new system. In another attempt, CuO doped 0.65PT-0.35BNN solid solution with lower band gap (1.8 eV) has been investigated by developing AZO/PT-BNNC/Ag heterostructure which shows bulk photovoltaic response. An open circuit voltage of 5.1V has been achieved for 0.3% CuO doped 0.65PT-0.35BNN thin ceramic pellets. In another attempt, to introduce the multiferroic character, we reduced the band gap of 0.65PT-0.35BNN composition, by particulate composite formation with spinel magnetic system $Ni_{0.65}Zn0_{.35}Fe_2O_4$ & $Co_{0.5}Zn_{0.5}Fe_2O_4$. Further, the epitaxial PT-BNN thin films were successfully grown on LSMO coated STO substrates by pulsed laser deposition (PLD) technique and photovoltaic response has been investigated in AZO/0.65PTBNNO/LSMO/STO heterojunction devices.

7.2.2. Band gap engineering in $xPbTiO_3$-(1 -x)$Bi(Co_{1/2}Ti_{1/2})O_3$ system and Discovery of switchable flexo-photovoltaic behaviour in PT-BCT thin film:

It is found that Co/Ti stoichiometric ratio play a major role in reducing the optical band gap of xPT-(1-x)BCT system and E_g is found to decreased from 3.2 eV to 1.65 eV as the Co concentration increases in 0.60PT-0.40BCT. Thin films of 0.60PT-0.40BCT composition prepared on FTO glass substrates and Ag/PT-BCT/FTO heterostructure showed Schottky diode-like behaviour and the conduction mechanism has been analyzed in this system. A switchable photovoltaic effect has been obtained for this heterostructure which is due to the depolarization field. Using Pt tip as top electrode the I-V of 0.60PT-0.40BCT film has been measured for poled and unpoled samples which showed the switchable photovoltaic response and confirmed the effect of depolarization field on photovoltaic phenomenon.

7.2.3. Development of $BaTiO_3$ based new low band gap perovskite system and observation of Bulk-photovoltaic behavior.

As Ni doping helps to reduce the band gap of ABO_3 type materials and Bi^{3+} and Nb^{5+} support ferroelectric states, we have developed a new ferroelectric system $xBaTiO_3$-(1-x)$Bi(Ni_{2/3}Nb_{1/3})O_3$ by solid state reaction method and its composition dependent structural phase transition has been investigated using Rietveld structural analysis. It is found that all the investigated compositions ($0.50 \leq x \leq 0.92$) have cubic structure with space group Pm3m and Bi-O, Ni-O bond lengths increase with increasing the BNN doping concentrations. In the composition dependent band gap study, it was found that direct band gap of BT-BNN is reduced from 3.2 eV to 2.19 eV with increasing the BNN content to 0.40. There is also a second band gap positioned as E_{g2} ~ 1.32 eV for 0.60BT-0.40BNN. The reduction in band gap is related to sub-band gap formation by Ni3d-states which have their energy levels between C.B. and V.B. states. The band gap reduction in BT-BNN is also related to change in Bi-O bond length. To study the photovoltaic behavior, thin ceramic pellets were used to fabricate the heterostructure. The I-V characterization of AZO/BT-BNN/Ag/Si devices demonstrated the polarization direction dependent photovoltaic response. In composition dependent I-V study, 0.70BT-0.30BNN composition showed higher photocurrent because it has the low band gap as well as sufficient polarization strength. With these outcomes, it can be concluded that both low band gap and appropriate P_r in ferroelectric materials is necessary to get high photovoltaic response. The discovery of switchable ferroelectric diode effect in BT-BNN system will provide an opportunity to design lead free FE-PV devices.

7.2.4. Investigation of photovoltaic behaviour of $0.9KNbO_3$-$0.10Ba(Ni_{1/2}Nb_{1/2})O_{3-\delta}$ Thin Films and Enhancement in photo-current by application of ZnO nano-structures as light trapping layer

We have synthesized several compositions (x = 0.05, 0.10,0.15, 0.20, and 0.25) of ceramic solid solution of $(1-x)KNbO_3$-$xBa(Ni_{1/2}Nb_{1/2})O_{3-\delta}$ (KNBNN) by solid state reaction method and found the lowest band gap (2.1eV) for $0.9KNbO_3$-$0.1Ba(Ni_{1/2}Nb_{1/2})O_{3-\delta}$

composition. Magnetron sputtered and sol-gel based $0.90KNbO_3$-$Ba(Ni_{1/2}Nb_{1/2})O_{3-\delta}$ thin films were grown and their photovoltaic properties has been measured for the first time in our work. The ferroelectric nature of the as deposited films was confirmed by piezo-force microscopy which reveals the photovoltaic response. ZnO nanoparticles, nanorods and nanowalls were grown by chemical route and it was found that ZnO nanowalls have lowest reflectance. The photocurrent density of sol-gel deposited 0.9KN-0.1BNN thin film has increased from 0.0063 mA/cm^2 to 0.067 mA/cm^2 after using light trapping layer of ZnO nanowalls. Our investigations reveal that variations in geometry of ZnO nanostructures strongly influences the light-harvesting properties as well as the current collection in devices. The results presented here will provide a guideline to develop light trapping methodology needed to achieve higher efficiencies in solar cells.

7.3 Key Contributions of this Thesis

To reduce the band gap of wide band gap ferroelectric perovskite oxides, we have designed various new solid solutions and investigated their physical properties. The major contributions of this research work are mentioned as follows:

(1) For the first time, lowest band gap in PT-BNN solid solution is achieved by Co-ion doping. The band gap is reduced to 1.65 eV by compositional engineering.

(2) For the first time, CuO doped PT-BNN solid solutions are prepared and a lower band gap of 1.8 eV is achieved. The bulk photovoltaic response is observed for these solid solutions.

(3) For the first time, epitaxial thin films of PT-BNN are grown using PLD and their photovoltaic behavior is reported.

(4) The detailed analysis of the band gap energies of $xPbTiO_3$-(1-x)$Bi(Co_{1/2}Ti_{1/2})O_3$ solid solutions is studied by changing the Co/Ti stoichiometric ratio. For the first time, PT-BCT based device structure Ag/PT-BCT/FTO is fabricated by growing the polycrystalline 0.60PT-0.40BCT thin films by magnetron sputtering and switchable photovoltaic effect is reported.

(5) We have also investigated the FE-PV behavior in lead free perovskite oxides, as our society is now more concerned about environment friendly technology for energy resources. We developed a new ferroelectric perovskite oxide $xBaTiO_3$-(1-x)$Bi(Ni_{2/3}Nb_{1/3})O_3$ with reduced band gap of E_{g1} = 2.19 eV and E_{g2} = 1.32 eV for x =0.60 composition. We also observed the switchable bulk-photovoltaic response in AZO/BT-BNN/Ag device structure using thin BT-BNN ceramic pellets.

(6) For the first time, 0.9KN-0.10BNN thin films are grown by 'magnetron sputtering and chemical sol-gel process' and their photovoltaic response is investigated.

7.4 Suggestions for Future Work

Our investigations on various ferroelectric solid solutions have revealed many interesting and new aspects linked with structural, optical and photovoltaic behavior of these new materials. However, a number of things are needed to be settled in future investigations. Few important suggestions for future work are given below:

1. To achieve the goal of high efficiency in devices, the PT-BNN thin film deposition process can be optimized further, by using different bottom and top electrodes. A new device design using electron and hole transport layer or light trapping layer can show improved photocurrent and this work can be further extended to reach this goal. Here, we have deposited PT-BNN thin film using PLD. These films can also be deposited using

magnetron sputtering and their photoelectric properties can be compared with PLD grown films. In this work, we were not able to study low temperature and high temperature structural properties for PT-BNN compositions. In a future investigation, it is suggested to study the low and high temperature properties and structural phase transitions in PT-BNN compositions. The structure of various crystallographic phases across MPB region can be investigation in further study of PT-BNN and Co, Ni, Cu doped PT-BNN solid solutions. High temperature neutron and synchrotron diffraction studies should be carried to investigate the phase transitions in PT-BNN for the compositions in range $0.62 \leq x \leq 0.65$. We successfully prepared the 0.65PT-0.35BNN/NZFO and 0.65PT-0.35BNN/CZFO composites. Further studies need to be carried out to explore these materials for various applications. These composites can be further characterized for structural, dielectric and magneto-electric behaviour.

2. The composition dependent low and high temperature XRD, dielectric and ferroelectric properties of PT-BCT compositions should be measured to relate the changes in band gap of this solid solution with increasing the doping concentration. The thin films of all compositions of PT-BCT should be grown to study the systematic change in band gap, ferroelectric and photovoltaic properties. The PT-BCT thin films should also be deposited on STO/LSMO substrates to remove the strain in films due to lattice mismatching. The photovoltaic behavior can be further compared in polycrystalline and epitaxial PT-BCT thin films.

3. We have studied the physical properties of BT-BNN solid solutions and observed that to get more information about crystal structure and phase transitions of this perovskite oxide, there is need of low and high temperature XRD studies of all the compositions. One can

also perform the low temperature dielectric and P-E hysteresis studies of all these compositions. In this work, we have obtained low photocurrent in BT-BNN ceramic pellets based devices, which is mainly due to higher thickness of pellets. In future, thin films of BT-BNN should be grown to improve the photocurrent of devices. It is found that substitution of Ti by transition elements Ni and Nb reduced the band gap of $BaTiO_3$. In place of Ni, other elements like Co, Cu, Fe, Cr and Mn, should be tried to optimally reduce the band gap of $BaTiO_3$ perovskite oxides with better ferroelectric response.

4. The photovoltaic response is observed by us in 0.90KN-0.10BNN thin films. In future, the device efficiency can be increased by optimizing the thickness of these films and by interface engineering. Use of nanostructured materials like ZnO for light trapping requires more optimization process to achieve lowest value of reflectance and thus a greater number of photons trapping inside devices. Further investigations can be done in this direction.

In conclusion, ferroelectric perovskite oxides can be engineered by solid solution formation and doping the transition elements to get the low band gap photovoltaic materials and optimizing the processing conditions. Even though, these perovskite oxides show low photocurrents, various light trapping and interface engineering methods can improve the device efficiency considerably. Therefore, perovskite oxide materials studied in this work can be potential candidates for applications in opto-electronic devices.