Development of Photo-Ferroelectric Materials for Energy Harvesting and Storage

THESIS SUBMITTED IN PARTIAL FULFILLMENT

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Doctor of Philosophy

By

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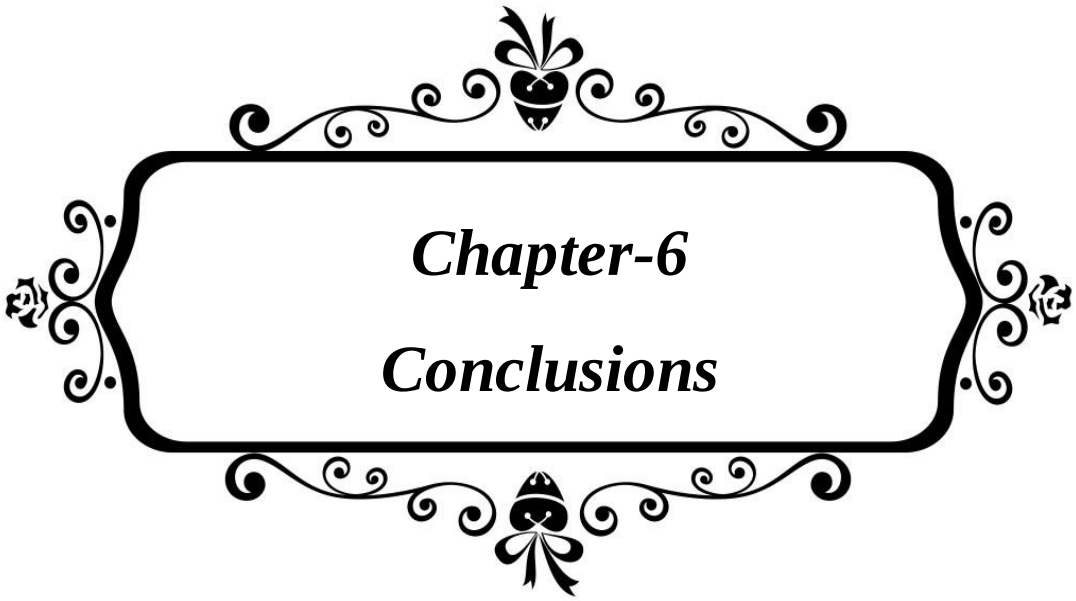

Chapter-6

Conclusions

In this last chapter we have concisely summarized the important findings of this thesis work and have listed some future plans that can be applied in near future.

6.1 Summary of the present work

In the present thesis work, we have explored some typical low cost, easily synthesizable and commercially viable ferroelectric oxide materials. Generally all these investigated materials have good ferroelectricity but wide band gap which restricts their application for photovoltaic applications. Our motive was to modify the composition and properties of typical ferroelectrics like $PbTiO_3$, $BaTiO_3$ and Bi-based ferroelectric perovskites in such a way that they become useful for Ferro-photovoltaic and energy applications. With this objective, we have developed Mo-substituted $PbMo_xTi_{1-x}O_3$ (x = 0.025, 0.05, 0.075 and 0.10) compositions and $BiY_{(1-x)}Mn_xO_3$ (x = 0.0, 0.10, 0.25, 0.50, 0.75) solid solutions with not only significantly reduced band gap, but also having better polarization, absorption and conductivity. Further we have investigated Bi-Li co-substitution effects on a lead-free $BaTiO_3$ based system which is a versatile multifunctional ferroelectric material. In this case, even though, there was not much reduction in the band gap but attractive energy storage properties were observed.

The important results found in the present research work are summarized below-

1. Mo-substituted $PbTiO_3$ samples were prepared by solid state method using both low energy and high energy ball milling process. XRD analysis reveals better solubility of Mo-in high energy ball milling synthesis process than in the low energy milling process. XRD analysis of Mo- substituted $PbTiO_3$ polycrystalline samples reveals tetragonal perovskite crystal structure with $P4mm$ space group. The unit cell parameters ‘a’ and ‘c’ determined by Rietveld structure refinement varies in such a way that tetragonality is enhanced with rising substitution concentration. The microstructure of the sintered samples shows agglomeration of grains leading to non-uniformity in grain size distribution. DC conductivity is

estimated by Nyquist plots, exhibits increasing trend with the increase in Mo-substitution upto 7.5% concentration, the increased conductivity will support the charge carriers to reach their respective electrodes more efficiently. The band gap was successfully reduced from 3.33 eV (pure $PbTiO_3$) to 2.41 eV (7.5 % Mo-substituted $PbTiO_3$) by Mo- substitution in $PbTiO_3$ without supressing the polarization. The composition $PbMo_xTi_{1-x}O_3$ (x = 0.075) having low band gap energy, relatively better conductivity and sufficient polarization appears to be the most useful finding among $PbTiO_3$ based material for photovoltaic applications. A research paper based on these results is published in **Journal of Materials Science: Materials in Electronics 33(5); (2022), pp 2550-2565**.

2. $BiY_{(1-x)}Mn_xO_3$ (x = 0.0, 0.10, 0.25, 0.50 and 0.75) solid solution compositions have been successfully synthesized by solid state method using high energy ball milling. All the developed compositions except x = 0.75, crystallize into cubic fluorite structure with space group Fm-3m and size of the unit cell was found to increases with increasing Mn-concentration. Incorporation of Mn enhances the dielectric permittivity and reduces materials dc resistance resulting into better polarizability and increased conductivity of charge carriers respectively. The conductivity was found to increase with increasing temperature for all the compositions showing semiconductor behaviour. The most interesting finding of this research work is the reduction in band gap and double absorption edges in some samples. The band gap is successfully reduced to 1.76 eV for $BiY_{(1-x)}Mn_xO_3$ with x = 0.50 which is much lower than the band gap of Mn-doped $BiFeO_3$ (1.92 eV). This composition also has an additional absorption edge at 1.46 eV extending the optical absorption to IR region. The composition $BiY_{(1-x)}Mn_xO_3$ with x = 0.75 have even lower absorption edge at 1.33 eV which is near

to ideal band gap (1.1 eV) for maximum efficiency given by Shockley-Queisser Limit. The P-E hysteresis loop measurements confirm the ferroelectric nature for all the developed compositions and polarization increases with increase in Mn-concentration. Concisely, the developed compositions of $BiY_{(1-x)}Mn_xO_3$ solid solution are ferroelectric with low band gap and good conductivity, fairly suitable for solar energy harvesting. A research paper based on these results is published in **Ceramics International journal 48, 17 (2022) 25128-25139.**.

3. Polycrystalline samples of $(Bi_{0.5}Li_{0.5})_xBa_{(1-x)}TiO_3$ (x = 0.10, 0.12, 0.15 , 0.20 and 0.25) novel compositions were again successfully synthesized by solid state method. All samples crystallize into single phase cubic crystal structure with more or less similar lattice constant. The microstructure analysis reveals that average size of grains is getting larger with increasing $(Bi_{0.5}Li_{0.5})^{2+}$ co-substituent concentration. Analysis of temperature dependent dielectric permittivity of all the compositions $(Bi_{0.5}Li_{0.5})_xBa_{(1-x)}TiO_3$ (x = 0.10, 0.12, 0.15) over a wide frequency range yields that permittivity of one composition (x = 0.12) is exceptionally high over whole temperature and frequency range. $(Bi_{0.5}Li_{0.5})^{2+}$ substitution on Ba-site in $BaTiO_3$ prompts conductivity to decrease with increasing substituent concentration. Conductivity were observed to increase with rising temperature and thus showing semiconducting behaviour. This was further confirmed by the band gap values of all samples estimated from the Tauc plot. The band gap of all the developed compositions lies in the UV range (3.09 eV- 3.3 eV) with lowest value (3.09 eV) exhibited by composition with x = 0.12. The P-E hysteresis loop analysis reveals the most interesting results. The two compositions of $(Bi_{0.5}Li_{0.5})_xBa_{(1-x)}TiO_3$ with x = 0.10 and 0.12 have nearly 45° inclined, slim relaxor type P-E loop, ideal for ferroelectric

capacitive storage applications. Storage efficiency calculations yielded that $(Bi_{0.5}Li_{0.5})_xBa_{(1-x)}TiO_3$ with x = 0.10 and 0.12 have extraordinary storage efficiency of 94.5% and 96% with good energy storage density of 0.30 J/cm^3 and 0.44 J/cm^3, respectively. This type of low loss materials are useful to mitigate the heat dissipation problems in advance energy storage devices. Conclusively, we have developed a novel composition of $(Bi_{0.5}Li_{0.5})_xBa_{(1-x)}TiO_3$ with x = 0.12, which possess extraordinary permittivity, high energy storage efficiency with good storage density and semiconductor nature. This material seems to be a potential candidate for energy storage and harvesting application simultaneously. We have applied one Indian patent on energy storage applications based on these results. We have applied one Indian patent on energy storage applications based on these results and thereafter, the manuscript related to this chapter will be communicated to international journal.

6.2 Suggestions for future work

Our investigation on various materials have brought many new aspects linked with band gap engineering of Pb-based, Bi-based and Pb-free perovskite ferroelectric materials. Our investigations on $(Bi_{0.5}Li_{0.5})_xBa_{(1-x)}TiO_3$ (x = 0.10, 0.12, 0.15 , 0.20 and 0.25) have led to discovery of a novel energy storage material. There are various unsettled issues to be investigated in future. Some of the important suggestions for future work are listed below:

1. Thin film preparation of Mo-substituted $PbTiO_3$ and $BiMnO_3$-$BiYO_3$ solid solutions has to be done to investigate the thin film characteristics of the developed materials.

2. Device fabrication and energy harvesting characteristics of the bulk and thin film forms of the developed compositions needs to be done in future.

3. In $BaTiO_3$ based solid solution, it will be interesting to combine the results of Bi,Li co-substitution at Ba-site, with the Mn-Nb substitution on Ti-site, for combinatorial tuning of energy storage and photovoltaic properties.

4. It will be interesting to investigate other Bi-based ferroelectric materials, double perovskite materials with suitable site substitutions to develop high efficiency photo-ferroelectric materials.

5. Theoretical predictions/simulations results need to be exploited suitably to develop new ferro-photovoltaic materials for future energy solutions.