Chapter 7

Summary and Future Scope

This chapter presents the summary of the work presented in this thesis as well as the future scope of the present work.
7.1 Summary of the present work

We have successfully synthesized polycrystalline bulk samples of $\text{A}(\text{Mg}_{0.33}\text{Nb}_{0.67})\text{O}_3$ where $\text{A}= (\text{Ba}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+})[\text{BMN}, [\text{SMN}, [\text{CMN}], \text{Ba}(\text{B}'_{0.33}\text{Nb}_{0.67})\text{O}_3$ where $\text{B}'= (\text{Mg}^{2+}, \text{Co}^{2+}, \text{Cu}^{2+})[\text{BMN}, [\text{BCoN}, [\text{BCuN}], and \text{Sr}(\text{B}'_{0.33}\text{Nb}_{0.67})\text{O}_3$ where $\text{B}'= (\text{Mg}^{2+}, \text{Co}^{2+}, \text{Cu}^{2+}) [\text{SMN}, [\text{SCoN}, [\text{SCuN}]$, by standard solid state reaction technique. The effect of replacement of A- site in $\text{A}(\text{Mg}_{0.33}\text{Nb}_{0.67})\text{O}_3$, B' site in $\text{Ba}(\text{B}'_{0.33}\text{Nb}_{0.67})\text{O}_3$ and B' site in $\text{Sr}(\text{B}'_{0.33}\text{Nb}_{0.67})\text{O}_3$ was studied by means of structural, micro structural, electrical, Conductivity and Optical studies. The following observations have been made on the basis of several experiments performed on the bulk samples.

Work presented in this thesis relates studies on structural, micro structural, dielectric properties (dielectric constant, dielectric loss), Modulus, Impedance studies, conductivity and optical studies of $\text{A}(\text{Mg}_{0.33}\text{Nb}_{0.67})\text{O}_3$, where A stands for $(\text{Ba}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+})$. In $\text{Sr}(\text{D}'_{0.33}\text{Nb}_{0.67})\text{O}_3$ and $\text{Ba}(\text{D}'_{0.33}\text{Nb}_{0.67})\text{O}_3$, D' stands for $(\text{Mg}^{2+}, \text{Co}^{2+}, \text{Cu}^{2+})$. We have synthesized the single phase bulk samples of each of these samples. The thin films of some of the compositions were prepared, i.e. $\text{Ba}(\text{B}'_{0.33}\text{Nb}_{0.67})\text{O}_3$, B' stands for $(\text{Mg}^{2+}, \text{Co}^{2+})$ and $\text{Sr}(\text{Mg}_{0.33}\text{Nb}_{0.67})\text{O}_3$. The thin films of above compositions are prepared by Pulsed laser Deposition (PLD) on ITO coated glass substrates. In addition to this, Swift heavy ion irradiation (SHI) has also been used for material modifications. Since it is well known that SHI irradiation generate different types of controlled defect states namely point defects (Se ~ Seth, Seth is the electronic threshold value of the material), extended point defects (Se ~ Seth) and amorphized latent tracks (Se > Seth), which modify the structural and magnetic properties. Beside these properties, SHI irradiation is also used for engineering the patterns of thin film surface.

Substituting the lower ionic radii at A-site in $\text{A}(\text{Mg}_{0.33}\text{Nb}_{0.67})\text{O}_3$ the structure shifts from higher to lower symmetry, i.e. hexagonal symmetry to Monoclinic symmetry. This structural asymmetry has led to enhanced dielectric properties and introduced the dispersion phenomena but losses also increase as we move from polar (BMN) to non-polar systems (SMN and CMN). All the compositions show the poly dispersive nature. In addition when we replace at the B'-site in Barium series $\text{Ba}(\text{B}'_{0.33}\text{Nb}_{0.67})\text{O}_3$ with 3d elements (Co or Cu), although the ionic radii marginally altered but the structural moves towards better symmetry by Hexagonal structure [BMN, BCoN] becoming Tetragonal [BCuN]. Here the changes in structural symmetry are likely
to be due to the complete Jahn-Teller Distortion in BCuN. Further, our analysis suggest that such a distortion has led to negative effects on dielectric properties as apart from dielectric constant dielectric loss also increased simultaneously. Here conductivity analysis shows the CBH mechanism in BCuN. Now when we carried out B⁺-site substitution with 3d elements (Co or Cu) in Sr(B'_{0.33}Nb_{0.67})O₃, it has led to positive effect of Jahn-Teller distortions. In this case apart from structure moving from lower symmetry to higher symmetry, i.e. from monoclinic to tetragonal, the dielectric constant increases drastically but keeping the dielectric losses low. Further, the relaxor phenomena are also introduced in the system. The conduction mechanism is still predominantly CBH type.

The BMN thin films deposited on different substrates shows that the growth formation on the ITO coated glass substrates is relatively better for film growth and it is also suitable for the dielectric measurements. In comparison to BMN bulk, its thin films show higher values of dielectric constant as well as dielectric loss but overall physical nature are identical to bulk. Frequency and temperature independent behaviour is observed in BCoN sample which was not visible in the bulk sample. All the films grown are of polycrystalline in nature and average grain size is ~50nm, much lower than respective bulk grains. Dielectric measurements show the transition temperature(Tₚ) shifting toward lower temperature suggesting larger flexibility of dipole movements in films. Two step activation energy observed in the SMN film corresponds to shallow traps at low temperatures and at high temperatures it is due to migration of oxygen vacancies.

Analysing the overall effects of irradiation on films dielectric response, it is inferred that Ag¹⁵⁺ irradiation is more helpful then O²⁻ irradiation. This is mainly due to the fact that Ag¹⁵⁺ irradiation due to the type of defects it created is more effective in reducing lattice strain induced dielectric losses along with marginal loss of dielectric constant. Further, frequency independent dielectric nature of BCoN films changes to frequency dependent nature (relaxor like) on irradiation.
Future scope of the Work

It is expected that the Electric field vs. polarization (E-P) plots will give us better understanding regarding the ferroelectric nature of these compositions as well as its relaxor behaviour. The polycrystalline growth of thin films of these materials can be further optimized by optimizing the growth parameters in order to achieve improvement in dielectric parameters. Presently we have carried out irradiation studies on these films only by Ag^{15+}/O^{7+} beams and with limited doses. The studies can be extended to other ion beams with multiple doses in order to get maximum enhancement in dielectric parameters. Further, attempts are on to achieve multi-layer growth of the films for composition which has given us better dielectric response among all the composition studied in the present work.
List of Publications

1. “Ag\(^{15+}\) and O\(^{2+}\) ion irradiation induced improvement in dielectric properties of the Ba(Co\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) thin films” Bhagwati Bishnoi, P.K. Mehta, C.J. Panchal, M.S. Desai, Ravi Kumar, V. Ganesan, Materials Chemistry and Physics 126, 660-664, (2011)

2. “Structural, Optical and Dielectric Properties of A[(Mg\(_{0.32}\)Co\(_{0.02}\)Nb\(_{0.66}\)]O\(_3\) Semiconductor where (A = Ba, Sr or Ca)” Bhagwati Bishnoi, P.K. Mehta, C.J. Panchal, M.S. Desai, R. Kumar, Journal of Nano Electron Phys.3 (1), 698-708, (2011).


4. “Dielectric and Conductivity Studies of Sr[(Mg\(_{0.32}\)Co\(_{0.02}\)Nb\(_{0.66}\)]O\(_3\) Thin Film” P.K.Mehta, Bhagwati Bishnoi, Ravi Kumar, R. J. Choudhary and D. M. Phase Solid State Phenomena 155, 145-149, (2009).

5. “Study of dielectric Relaxation in Sr(Co\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) Compound” Bhagwati S Bishnoi, P.K. Mehta and C. J. Panchal, to be Communicated.

6. “Irradiation Effects On Microstructure and Dielectric Properties of Ba[(Mg\(_{0.32}\)Co\(_{0.02}\)Nb\(_{0.66}\)]O\(_3\) [BMCN] Thin Films” N V Patel, Bhagwati Bishnoi, P. K. Mehta, Ravi Kumar, R. J. Choudhary, D M Phase and V Ganesan, to be Communicated.

7. “High energy Oxygen ion irradiation effects on Sr[(Mg\(_{0.32}\)Co\(_{0.02}\)Nb\(_{0.67}\)]O\(_3\) thin films”, Bhagwati Bishnoi, P. K. Mehta, Ravi Kumar, R J. Choudhary, D. M. Phase and V. Ganesan, to be Communicated.

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List of Publications in Proceedings/Conferences


6. “Dielectric studies of Ba[(Fe$_{1/3}$Co$_{1/3}$)$_{1/2}$Nb$_{1/2}$]O$_3$ Compounds” Devang Shah, Bhagwati Bishnoi and P.K. Mehta, 52$^{nd}$ DAE Solid State Symposium (27$^{th}$ to 31$^{st}$ December 2007, Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore, India) SSPS Proceedings 867 (2007).
7. “Structural and dielectric properties of Ba[(Mg_{1-x}Co_x)_{1/3}Nb_{2/3}]O_3 (X=0.05)” Bhagwati Bishnoi, Devang Shah, P. K. Mehta, Dinesh Shukla and Ravi Kumar, 52nd DAE Solid State Symposium (27th to 31st December 2007, Department of Studies in Physics, University of Mysore, Manasaganagotri, Mysore, India) NSSPS Proceedings 861 (2007)

8. “Dielectric Properties of Sr[(Mg_{0.32}Co_{0.02}) Nb_{0.66}]O_3 [SMCN] thin films” Bhagwati Bishnoi, P.K. Mehta, N.V. Patel and Ravi Kumar 3rd National Seminar on Advances in Material Science (NSAMS 2009) (16th to 17th March 2009, Department of Physics, Manonmaniam Sundaranar University, Tirunelveli, Tamil Nadu, India) NSAMS Proceedings 154, (2009)

9. “Irradiation Effects On Microstructure and Dielectric Properties of Ba[(Mg_{0.32}Co_{0.02}) Nb_{0.66}]O_3 [BMCN] Thin Films”, Bhagwati Bishnoi, P. K. Mehta, N.V. Patel, Ravi Kumar, R. J. Choudhary, D M Phase and V Ganesan, Swift Heavy Ion Multifunctional Engineering Conference (6th to 9th October 2010, at Inter University of Accelerator Centre (IUAC), New Delhi, India)

10. “Structural and dielectric relaxation in Sr(Co_{1/3}Nb_{2/3})O_3” Bhagwati Bishnoi, P. K. Mehta and Ravi Kumar International Conference on Multifunctional Oxide Materials (16th to 18th April 2009, H. P. University, Shimla, India).