Chapter-7

SUMMARY, CONCLUSIONS & RECOMMENDATIONS

7.1 Summary and Conclusions

In the present work, $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin films were prepared using sol gel spin coating process. This technique was selected owing to its simplicity, stoichiometry control and uniform coating over the entire substrate. The selected composition happens to be Morphotropic Phase Boundary (MPB) of PZT, where both tetrahedral and rhombohedral phases coexist. At Zr/Ti ratio of 52/48 both the phases are energetically favorable and fourteen different orientations of spontaneous polarization are present. At this composition, PZT exhibits perovskite structure of ABO_3.

Two different solutions of PZT were prepared by controlling the temperature during sol gel process. The first solution was made at room temperature by stirring the selected precursors (SPZT-1). For the second solution, the temperature was kept at 125^0C during sol gel process (SPZT-2). After aging the solutions for 24 hours, the viscosity of solution SPZT-1 was found to be less than the solution SPZT-2.

In the present work two substrates, alumina and quartz were selected to coat the thin films. These were selected based on extensive literature survey and the ability to withstand the annealing temperature required for perovskite phase formation. Both the substrates were cleaned and measures were taken to avoid any cracks or impressions on the substrates. The films were coated with both solutions using spin coater on bare substrates.

The spin coater was used in a static double mode to obtain homogeneous films. In this mode, the solution placed on a substrate is spun at 500 rpm for 30 sec and 5000 rpm for 50 sec. During the initial stage, the solution occupies the substrate and in next stages, the homogeneous coating along with evaporation of solvent happens.

This spin coating process is followed by proper annealing of thin films to obtain specific thickness and at an annealing temperature of 660^0C, the perovskite phase was formed. Following this method and using two solutions on two different substrates alumina and quartz four PZT thin films were coated. The films on alumina and quartz substrate with a solution at room temperature are named as SA1 and SQ1. The PZT thin films coated with a solution at 125^0C were named as SA2 and SQ2.

This study aimed at observing the effect of solution temperature and type of substrate on various properties of PZT thin films at Morphotropic phase boundary. The synthesized PZT thin films were studied using XRD, HRSEM, UV-Vis, PL, VSM, Nano indenter. Using such characterization tools structural, morphological, optical, luminescence, magnetic and mechanical properties of thin films were analyzed. All characterizations were carried out at room temperature.

- ✓ The structural characterization carried out using XRD reveals that the PZT thin films on alumina and quartz substrate have a perovskite structure at an annealing temperature of 660^0C on both the substrates related to JCPDS (33-0784). There was no evidence of Pyrochlore phase in both films coated with a solution of both temperatures. The variation in the intensity of peak was attributed to change in composition during the transition at MPB.
  The study succeeded in observing the impact of sol temperature and substrate on the structural properties of films. Crystallite size was measured from Debye Scherrer formula depends on sol temperature and increases with a rise in sol temperature. The films have preferred orientation of (100), as the surface energy is minimal at this orientation for PZT thin films. Alumina peaks are observed in SA1 and SA2 films due to diffraction from the substrate.
  Low values of strain and dislocation density indicate the presence of high quality films. The grain size variation was observed to be a function of the substrate. The alumina substrate has high grain size compared to the quartz substrate.

- ✓ The HRSEM images show the good morphology of films on both the substrates. The solution temperature variation has an impact on morphology as tetragonal grains being visible for the films coated with high temperature solution on both the substrates.

The cross sectional views of thin films suggest that the thickness of the films is a function of viscosity which here based on solution temperature than on a number of coatings. The implication is that the 3 layer coated films SA1 and SQ1 have thickness of 1.73µm and 769nm, where as 2 layer coated films SA2 & SQ2 are in the range of 3.37µm and 945nm.

This can also be because of the change in grain size due to rise in solution temperature. The films coated on the bare substrate without seed layer or electrode confirms the effect of substrate on thickness and morphology. The compositional analysis supports the composition of PZT on all the films.

- ✓ The UV-Vis spectroscopy analysis provides an idea that the band gap of the films depends on solution temperature and type of substrate. The change in band gap values was clear from Burstein-Moss effect and Pauli's exclusion principle.

  The film coated with low temperature solution has high band gap as 3.51ev and 3.73eV for SA1 and SQ1 films, where as high temperature solution films SA2 & SQ2 have a band gap of 3.34eV and 3.26 eV. Here again, the effect of the substrate is observed and quartz substrate provides low values of the band gap.

- ✓ The photoluminescence studies of the films suggest that the PL in pure PZT thin films is due to its crystalline structure. The PL spectra observed at same excitation wavelength provides same energy peaks for all the samples, this confirms the compositional symmetry in the films.

  In the present PZT thin films for all the samples, the peak was observed at 408nm confirming the presence of oxygen vacancies. The PL emission at 486nm is due to the hole that is generated as photo process and electron recombines in the radial process, where the electron belongs to a singly ionized oxygen vacancy.

- ✓ The VSM analysis of samples shows a breakthrough behaviour in terms of magnetic properties that is purely dependent on the type of substrate. The PZT films coated on alumina substrate exhibited ferromagnetism at low applied fields and diamagnetism at high fields.

This special property was tried to be justified by monitoring the magnetic properties of PZT powder.

The remanent, saturation magnetization and coercive fields were a function of solution temperature.

The PZT thin films on quartz substrate show diamagnetism due to the high impact of the substrate. Here the ferromagnetic films have squareness ratios that are suitable for recording media and susceptibility of diamagnetic films were suitable for MRI instruments.

✓ The mechanical properties of PZT thin films hinge on solution temperature by showing variations in the young's modulus and hardness values.

Based on the type of substrate these parameters make it clear that the alumina substrate provides better properties compared to quartz. The grain size dependency of parameters can also be observed.

At an outset, this study gives a clear picture of how the type of substrate and temperature variation during sol gel synthesis influences the structure and properties of PZT thin films. This work gave a primary chance to the researcher to focus on magnetic characteristics of PZT thin films which were seldom concentrated. This behaviour was tried to justify through the powders of PZT.

7.2 Recommendations

This study has lead to certain observations which definitely provide a scope for further extension of work. It is believed that the ferroelectricity and magnetism oppose each other, the studies during the early 1960s proved that there is a chance for them to coexist in materials known as multiferroic perovskites.

Multiferroic materials show any of two ferroic order parameters at room temperature. The beauty lies in developing the coupling between them. PZT comes under multiferroic material for which the ferroelectric properties were extensively studied.

The magnetic properties were studied with a dopant inducing magnetism in the material. The literature review gave an idea that the ferromagnetic behaviour which can arise due to oxygen vacancies in perovskite PZT is not concentrated much. Based on this the present work gives a scope to concentrate on d states magnetic property of PZT thin films.

With the extension of this work in this direction, the application areas related to PZT thin films become wide spread and the versatility of PZT can be improvised. Furthermore, the environmental friendly synthesization methods for toxic chemicals that find application areas can be tried and taken care of.