CHAPTER 6

SUMMARY AND CONCLUSIONS

In this chapter the studies conducted on the complex perovskite systems BSN, BHN, SSN, SHN, strontium and calcium doped BSN and BHN are summarized and the conclusions arrived at are presented.

The present work deals with the synthesis and investigation of some complex niobates with rare earths substitution in the B site. Rare earth niobates attract interest due to the diverse physical properties they exhibit. In the present study the rare earths samarium and holmium substituted barium niobates, strontium niobates and their solid solutions with Sr$^{2+}$ and Ca$^{2+}$ are synthesized and investigated. All the compositions are synthesized by high temperature solid state reaction method. To obtain single phase materials each composition is calcined at different temperature for different duration. The phase formation is confirmed by powder X-ray analysis. The microstructural studies are carried out using SEM. Dielectric properties, electrical properties and thermoelectric properties of the systems are studied.

From the XRD patterns all the compositions studied are found to have double cubic perovskite structure. The lattice constant calculated from the XRD peaks for all the compositions is $\sim$ 8Å.

The lattice constant of the solid solutions is found to decrease with the increase in doping concentrations of Sr$^{2+}$ and Ca$^{2+}$ ions. This can be explained as due to the substitution of Sr$^{2+}$ and Ca$^{2+}$ ions of smaller ionic radii in the larger Ba$^{2+}$ sites.
The dielectric constant ($\varepsilon'$) of all the compositions studied are high (>40) and maximum for the BHN sample (>60).

Strontium and calcium doping on BSN and BHN reduces the dielectric constant. This can be due to the decrease in size of the unit cell which reduces the polarization on doping. Calcium doped BSN and BHN have larger dielectric constant than strontium doped BSN and BHN. The unit cell size of calcium doped BSN and BHN is larger than strontium doped BSN and BHN giving rise to the larger dielectric constant.

The dielectric constant of SSN and SHN are comparable to their barium compounds BSN and BHN.

The dielectric constant of all the compositions studied is thermally stable from 373K to 673K.

The temperature coefficient of dielectric constant TC$_\varepsilon$ of all the samples is found to decrease with the increase in frequency and a near zero temperature coefficient of dielectric constant can be expected to be achieved in the microwave region. A minimum value of TC$_\varepsilon$ 4.4ppmK$^{-1}$ is obtained for BHN sample at 1MHz.

Doping of Sr$^{2+}$ and Ca$^{2+}$ ion increases the TC$_\varepsilon$ of BHN and BSN to a small extent.

The holmium substituted compounds have very low value of TC$_\varepsilon$ over a wide range of frequency than the samarium substituted compounds. This can be due to the high degree of B site ordering of holmium compounds.

Dielectric properties of holmium substituted compounds are more thermally stable than the samarium substituted compounds.
The dielectric loss of all the samples are low (~10^{-3}) at higher frequencies and at higher temperatures.

The ac and dc conductivities of all the samples measured in the temperature range of 373K to 673K are low and do not vary much with temperature. This indicates that the electrical conductivities are not thermally activated. The samples exhibit insulating behaviour (Young II Kim 2005). The ordering of B site cations hinders the extended overlap over Nb-O-Nb network. The localized electronic interaction results in the insulating behaviour (Ross Macdonald 1987).

Holmium substituted materials are found to have much lower ac and dc conductivities than samarium substituted materials. Holmium substituted barium compounds and strontium compounds are better insulating materials than samarium substituted compounds due to the high degree of B site ordering of holmium.

Doping of strontium and calcium on BSN and BHN materials result in lower ac and dc conductivities. Addition of Sr^{2+} and Ca^{2+} create scattering centers which reduces the conductivity.

Thermoelectric studies indicate that the charge carriers of all the samples are n type.

The Seebeck coefficient(S) increases with the doping concentration of Sr^{2+} and Ca^{2+} ions on BSN and BHN samples result in the decrease in carrier concentration and conductivity. Comparatively larger increase in the Seebeck coefficient is observed with Ca^{2+} doping on BSN and BHN samples.
Holmium substituted barium and strontium compounds have much lower carrier concentration than the samarium substituted compounds. This indicates the better insulating behaviour of holmium compounds. Similar results are reported in the conductivity studies too.

Calcium substituted BHN are found to be good thermoelectric materials with maximum value of Seebeck coefficient $104\mu\text{VK}^{-1}$ at 303K for $x=0.3$.

The mechanism of conduction for the holmium compounds can be due to the hopping of charge carriers between Nb$^{5+} \leftrightarrow$ Nb$^{4+}$ transition and for samarium compounds conduction can be due to the hopping of charge carriers between Nb$^{5+} \leftrightarrow$ Nb$^{4+}$ and Sm$^{3+} \leftrightarrow$ Sm$^{2+}$ transitions.

- All the samples studied are found to have cubic perovskite structure.

- All the samples have insulating behaviour with high dielectric constant ($> 40$), low dielectric loss, thermally stable, near zero temperature coefficient of dielectric constant and high Seebeck coefficient.

- Substitution of Ho$^{3+}$ ion, in place of Sm$^{3+}$ ion results in better insulating behaviour with high dielectric constant($>60$), very low dielectric loss, thermally stable, near zero temperature coefficient of dielectric constant over a wide range of frequency and high Seebeck coefficient.

The lower tan$\delta$ and near zero TC$_{\epsilon}$ is highly pursued criterion in the current research efforts on microwave and radio frequency devices (Colla et al 1993). The materials BSN, BHN, strontium and calcium
substituted BSN and BHN, SSN and SHN which have high dielectric constant, low tanδ values, near zero TCε and better insulating behaviour are the promising materials for high precision ceramic industry, electronic and microwave applications. The high Seebeck coefficient of these materials makes them suitable for thermoelectric applications.

6.1 FUTURE SCOPE OF THE WORK

Dielectric response of these materials in the high frequency range (GHz) and low temperature range upto liquid nitrogen temperature can give better insight of the dielectric behaviour.

The study of thermal properties like specific heat and thermal conductivity using photo acoustic spectrometer enable to decide the suitability of these materials for thermal applications.

Optical transmittance and absorption study can give the optical characteristics of these materials.

The better insulating behaviour of holmium substituted compounds than samarium substituted compounds can be understood by studying the series of compounds with other rare earths form La to Yb in the B site.

Knowing the dielectric response of isovalent cations substitution (Sr²⁺, Ca²⁺) in the A site, the dielectric response of La³⁺ cation in the A site are the future interest of study.