Chapter 9

SUMMARY

This chapter presents the conclusions based on all the results obtained from the studies on “Physicochemical Investigations on Ceramic Complex Oxides in A-RE-Ti-M-O (A = Li, Ca, Ba or Pb; RE = rare earth; M = Nb or Ta) System”, which has been described in the previous chapters of this thesis.
9.1 SIGNIFICANT CONCLUSIONS

In addition to the specific conclusions presented in the previous chapters, the major conclusions drawn from the work are summarized in this chapter.

A new series of large number of tungsten bronze and pyrochlore type ceramic complex oxides in A-RE-Ti-M-O (A = Li, Ca, Ba or Pb; RE = rare earth; M = Nb or Ta) system have been prepared by using the conventional solid state reaction. The results on characterization of these new oxides are as follows.

1. The structure of the Ba$_3$RE$_2$Ti$_5$M$_5$O$_{30}$ (RE = rare earth; M = Nb or Ta) ceramics is established as tetragonal tungsten bronze (TTB) type structure. This structure is retained even during various substitutions of atoms of similar nature in the above system.

2. The ceramic microstructure analysis of the above ceramics through SEM reveals that the grain morphology influences the dielectric properties. The photographs of Ba$_3$RE$_2$Ti$_5$Ta$_5$O$_{30}$ show usual round type sintered grains which exhibit better dielectric properties except in the case of Ba$_3$La$_3$Ti$_5$Ta$_5$O$_{30}$ sintered ceramics which shows long rod type grains.

3. The dielectric properties of niobium compounds are better than that of the tantalum analogues.

4. Bismuth substitution for rare earth in Ba$_3$RE$_2$Ti$_5$M$_5$O$_{30}$ (RE = La, Nd or Sm) causes little distortion in the structure and changes in the morphology of the sintered grains. These changes might have contributed to significant enhancement of the dielectric properties. The dielectric properties are best only for the partial substitution of Bi. The properties reduce slightly for the fully substituted Bi.

5. The tungsten bronze type structure of the oxides in Ba$_3$RE$_2$Ti$_5$M$_5$O$_{30}$ (RE = rare earth; M = Nb or Ta) can be modified into pyrochlore type structure by replacing Ba by Ca and changing composition to Ca$_3$R$_3$Ti$_7$M$_2$O$_{26.5}$. Thus, again a large number of ceramic complex pyrochlore type oxides could be
prepared under the formula $Ca_3R_3Ti_7M_{26.5}$ ($R =$ rare earth; $M =$ Nb or Ta).

6. As seen in the TTB, niobium based pyrochlore type oxides gave better dielectric properties than the tantalum analogues.

7. The dielectric properties of $Ca_3Sm_3Ti_7Nb_{26.5}$ can be improved by Bi substitution for Sm retaining the pyrochlore type structure of the compound.

8. Lead or lithium replacement for calcium also produced pyrochlore type oxides. These materials have shown dielectric resonance in the microwave frequency region. Further, these materials having low temperature sinterability are potential candidates for use as low-temperature cofired ceramic (LTCC) materials for microwave applications such as multilayer filters and other components.

9. Cerium replacement for the rare earth in both tungsten bronze and pyrochlore type oxides changed the property from insulating to semiconducting. It is assumed that $Ce^{3+}$ is structurally stabilized in both the systems to maintain the oxygen stoichiometry by releasing an electron in the lattice. The semiconducting property can be modified by partial substitution of cerium by other rare earths or by donor substitution e.g. $La^{3+}$ for $Ba^{2+}$ without changing the structure.

10. Partial substitution of bismuth for cerium in the tungsten bronze type semiconducting oxide, $Ba_3Ce_3Ti_5M_3O_{30}$ results in formation of microtubes during the sintering of the ceramics as shown by SEM. The microtubes have grown into rods for the fully bismuth substituted ceramic. The semiconducting property of the ceramic can be altered by partial substitution of the bismuth. Such bismuth substitution in pyrochlore type semiconducting oxide: $Ca_3Ce_3Ti_7M_{26.5}$ did not yield the microtubes but only the rod shaped grains.

11. Structural variations in $Ca_3La_3Ti_7M_{26.5}$ has been observed from mixed phase (pyrochlore and perovskite) to perovskite type by variation in the sintering temperature.
In the ceramic complex oxide system: A-RE-Ti-M-O (A = Li, Ca, Ba or Pb; RE = rare earth; M = Nb or Ta), a large number of phase pure oxides can be produced and their properties can be altered by changing their compositions.

9.2 FUTURE SCOPE OF THIS WORK

Generally, the intrinsic properties of materials such as the microstructure, crystallographic phase, composition, play critical role to determine the electrical and physical properties of materials. The investigated system allows various substitutions of cations, by which the properties can be altered. It will be a great challenge to study these solid-solutions in other form such as in thin films which could present the different interesting facet of these materials. The various processing methods also are of interest.

The dielectric properties of some of the best compositions (Ba$_3$RE$_3$Ti$_5$Nb$_5$O$_{30}$, RE = La, Nd or Sm) can be optimized for useful dielectric materials.

The prepared semiconducting oxides having low band gap may find potential applications in photocatalysts and photolysis of water. Such application oriented studies can be carried out.