Synopsis

The continuing drive towards device miniaturization demands the evaluation of new potential dielectric materials. Enhancement and optimization of dielectric properties is a most challenging topic of research. Dielectrics are required for advanced microelectronic applications. High permittivities are required, permittivities \( \varepsilon_r \) of \( \sim 100 \) with lower losses would be a major advancement in a simple material system. This has been the challenge to the industry and research community for many years. Dielectrics have been investigated in many ceramic oxide systems: \( \text{BaO-TiO}_2 \) [O’Bryan et al. 1974], \( \text{BaO-Nd}_2\text{O}_3-\text{TiO}_2 \) [Guha, 1991; Chen et al. 1995] and \( \text{BaO-TiO}_2-\text{Nb}_2\text{O}_5 \) [Ratheesh et al. 1998]. However, these dielectric materials \( (\varepsilon_r < 100) \) are not sufficient to further decrease the size of microelectronic circuits. Hence, the search for new ceramics with dielectric constant in excess of 100 has become necessary.

On the other side, semiconducting oxides find several applications as in thermistors [Altenburg et al. 2001], PTCR materials [Morrison et al. 2001], gas sensors [Lavenuta 1997], photoelectrolysis of water [Nozik 1975] and ferromagnetics [Nguyen Hoa Hong 2006]. Though the applications are enormous for these oxides, there are not many studies on ceramic complex semiconducting oxides. Among reduced niobates \( A_6\text{Nb}_{10}\text{O}_{30} \) \( (A = \text{Sr, Ba, Eu}) \) compounds with the TTB-type structure were reported for their semiconducting properties [Hessen et al. 1991; Stader et al. 1980] and with a pyrochlore structure, \( \text{CaLnNb}_2\text{O}_7 \) \( (\text{Ln} = \text{Y, Nd}) \) [Ya-Istomin et al. 1997]. Still there is a great demand for semiconducting oxides with specific properties that are suitable for the desired applications.

\( \text{A-RE-Ti-M-O} \) \( (\text{RE} = \text{rare earth}; \text{M} = \text{Nb or Ta}) \) system has been studied in various compositions having tungsten bronze type structure. Their dielectric properties vary from 27 to 260 [Singh et al. 2002; Wakiya 1999]. The proposed stoichiometric compositions in the present thesis has not been investigated before.

Therefore, it will be worthwhile to investigate the Physicochemical Investigations on Ceramic Complex Oxides in \( \text{A-RE-Ti-M-O} \) \( (\text{A} = \text{Li, Ca, Ba or Pb}; \text{RE} = \text{rare earth}; \text{M} = \text{Nb or Ta}) \) system for their structure, ceramic microstructure and electrical properties. The investigating results on the above aspects are presented in this
thesis. The thesis includes eight main chapters and the conclusions and scope of the present work is given in the ninth chapter.

Chapter 1 provides the background needed for the research areas covered in the following chapters. The fundamental ideas about tungsten bronze and pyrochlore type oxides have been described including their dielectric and semiconducting properties. The current knowledge on these systems is also presented.

Chapter 2 gives the general procedure adopted for the preparation of the complex ceramic oxides by the conventional solid state route. A brief description of the instrumentation used for studying the structural, microstructural and electrical characteristics of the prepared ceramic complex oxides is also presented.

Chapter 3 describes the preparation, characterization and properties of \( \text{Ba}_3\text{RE}_3\text{Ti}_5\text{M}_2\text{O}_{30} \) (\( \text{RE} = \text{Y}, \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd} \) or \( \text{Dy}; \text{M} = \text{Nb} \) or \( \text{Ta} \)) ceramics having tetragonal tungsten bronze type structure. The formation of the phase through various rare earth substitutions as well as \( \text{Nb} \) or \( \text{Ta} \) substitution has been discussed. The effect of \( \text{Bi} \) substitution for rare earth in the best dielectric property compositions: \( \text{Ba}_3\text{RE}_{3-x}\text{Bi}_x\text{Ti}_5\text{Nb}_5\text{O}_{30} \) (\( \text{RE} = \text{La}, \text{Nd} \) or \( \text{Sm}; \text{x} = 0.0, 1.0, 2.0, 3.0 \)) were also studied for the enhancement of the dielectric properties. The dielectric constant increases with the increase of \( \text{Bi} \) content, whereas dielectric loss increases.

Chapter 4 deals with the preparation and characterization of a new series of pyrochlore type oxides: \( \text{Ca}_3\text{R}_3\text{Ti}_7\text{M}_2\text{O}_{26.5} \) (\( \text{A} = \text{Pb} \) or \( \text{Li}; \text{R} = \text{Pr}, \text{Sm}, \text{Gd}, \text{Dy} \) or \( \text{Y}; \text{M} = \text{Nb} \) or \( \text{Ta} \)). Apart from XRD analysis, FT-IR is also employed for the structural characterization of these oxides. The ceramic microstructure and dielectric properties are also presented in this chapter.

Chapter 5 probes the microwave dielectric properties of lead or lithium containing pyrochlore type oxides: \( \text{A}_3\text{R}_3\text{Ti}_7\text{M}_2\text{O}_{26.5} \) (\( \text{A} = \text{Pb} \) or \( \text{Li}; \text{R} = \text{Pr}, \text{Sm}, \text{Gd}, \text{Dy} \) or \( \text{Y}; \text{M} = \text{Nb} \) or \( \text{Ta} \)). These materials have shown dielectric resonance in the microwave frequency region. Lead containing pyrochlores have shown better microwave dielectric properties than lithium.

Chapter 6 describes the investigations carried out on a new series of semiconducting oxides: \( \text{Ba}_{3-x}\text{La}_x\text{Ce}_3\text{Ti}_5\text{Nb}_5\text{O}_{30} \) (\( \text{x} = 0.0, 0.5, 1.0 \) or \( 1.5 \)) (tungsten bronze type) and \( \text{Ca}_5\text{Ce}_{3-x}\text{RE}_x\text{Ti}_3\text{Nb}_2\text{O}_{26.5} \) (\( \text{RE} = \text{Y}, \text{Sm} \) or \( \text{Gd}; \text{x} = 0, 1 \) or \( 2 \))
(pyrochlore type). The results on their conductivity studies with respect to temperature are given in this chapter. Effects of donor (La$^{3+}$) substitution for Ba$^{2+}$ or other rare earth substitutions for cerium on their structure, microstructure and electrical conductivity values are also presented in this chapter.

Chapter 7 presents the results obtained for the Bi substitution for cerium in Ba$_3$Ce$_3$Ti$_5$Nb$_5$O$_{30}$ (tungsten bronze type) and Ca$_3$Ce$_3$Ti$_7$Nb$_2$O$_{26.5}$ (pyrochlore type) ceramics. Well grown microtubes with definite edges have been observed during the sintering of Ba$_3$Ce$_{3-x}$Bi$_x$Ti$_5$Nb$_5$O$_{30}$, whereas such microtubes are not seen during the sintering of pyrochlore type oxides: Ca$_3$Ce$_{3-x}$Bi$_x$Ti$_7$M$_{26}$.

Chapter 8 details the results obtained from the structural variations from mixed phase (pyrochlore and perovskite) to perovkite type structure observed for Ca$_3$La$_3$Ti$_7$Ta$_2$O$_{26.5}$ by variation of sintering temperature.

Chapter 9 summarizes the results of the thesis and scope for the future work.