Chapter 1

INTRODUCTION AND LITERATURE REVIEW

In this chapter, the fundamental ideas about tungsten bronze and pyrochlore type oxides have been described including their dielectric and semiconducting properties within the purview of the present investigation. The current status of work on these systems is also presented in this chapter.
1.1 Introduction

Complex oxides exhibit a rich spectrum of properties, including magnetism [Onose and Tokura 2006], ferroelectricity [Sánchez-Andújar et al. 2006], superconductivity [Pathak and Mishra 2005], semiconductivity [Lau et al. 1996], electrical insulation [Park et al. 2006], metallic conductivity [Souza and Jardim 2005], optical behavior [Dawson et al. 2004; De Sande 1996] and ferromagnetism [Kim et al. 2006], which have been research areas of great interest among scientific and technological community for decades. These oxides find wide applications in the modern technology. They also form the basis of communication systems, filter circuits, resonators, circuit protection devices for computers, precision control devices in cameras and automobile suspension systems.

Out of the above, dielectric materials have been studied for decades due to both their applications in important technologies and the fundamentally interesting relationships among their crystal chemistry, crystal structures and physical properties. Recently, dramatic changes in microelectronics and in particular wireless communications technologies have made the materials with the unusual combination of high dielectric constant, low dielectric loss and low temperature dependence of dielectric constant very important and of great interest.

Similarly, semiconducting oxides in complex oxides are studied for widespread applications such as gas sensors [Lora et al. 1992], thermistors [Feltz et al. 1999], photocatalysts [Rafgah et al. 2006], photoelectrolysis of water [Fujishima and Honda 1971], transparent conducting oxides [Sasi et al. 2002] and optoelectronics [Tang 1998]. Semiconducting property is observed in many ceramic complex oxides.

These complex oxides crystallize in large variety of different types of structures such as perovskites, fluorites, pyrochlores, tungsten bronzes, rutiles, garnets, etc. Out of the above structural families, tungsten bronze and pyrochlore type oxides are studied in the present investigation. Hence, it is worthwhile to mention about these type oxides briefly and also about the current status of work on these oxides.
1.2 Tungsten Bronze type Structure

Since the discovery of ferroelectricity in BaTiO$_3$ [Wul and Goldman 1945], there has been an increasing interest in developing and searching for the new materials for different applications. During the process numerous ferroelectric oxides of different structural family were discovered. Among them, tungsten bronze type oxides have been studied extensively owing to their fascinating structural chemistry and technologically relevant physical properties [Lenzo et al. 1967; Itoh and Iwasaki 1972; Liu and Maciolek 1975]. Tungsten-bronze (TB) is a common structure type adopted by many different compounds with a general formula $A_xMO_3$ ($0 \leq x \leq 1$) [Dusek et al. 2002; Roussel et al. 2001]. The tungsten bronze structure consists of a corner sharing framework of MO$_6$ octahedra (M = Ti, Nb, Ta or W) that contain interstitial sites where a variety of metal cations may reside. As reported earlier and extensively discussed, the bronze family can be divided into four groups: perovskite tungsten bronze [Grenthe and Sundberg 2002; Filonenko et al. 2002], tetragonal tungsten bronze (TTB) [Jamieson et al. 1968], hexagonal tungsten bronze [Hussain et al. 2002] and intergrowth tungsten bronze [Kihlborg et al. 2001]. The common types of bronzes are the nonstoichiometric,

![Figure 1.1 Tungsten Bronze structure.](image)
highly colored bronzes; compounds of the type \( (AO)_x(B_2O_5) \) (A = Na, K, Sr, Ba or Pb; B = Nb, Ta, or W) and materials with a general formula \( (A1)_2(A2)_4C_4(B_1)_{2}(B_2)_{0}O_{30} \).

The TTB type structure is also considered the derivative of perovskite. The crystal structure of the TTB-phase is first described by Mangeli (1949). The archetypal structure for the \( (A1)_2(A2)_4C_4(B_1)_{2}(B_2)_{0}O_{30} \) is shown in Figure 1.1. As seen in the above figure, the A, B, and C cations occupy specific sites in the structure and are restricted to certain cations. The cations found in the A site must be able to accommodate large oxide coordination numbers – greater than nine. Thus, this site is restricted to larger alkali, alkaline earth and Pb cations. As shown in the figure, TTB has two kinds of A sites. A1 cations are 12-fold coordination and the coordination polyhedra is identical that in perovskite structure [Wakiya et al. 1999], therefore tolerance factor for A1 site cation \( (t_{A1}) \) can be given by the following equation:

\[
t_{A1} = \frac{(r_{A1} + r_0)}{\sqrt{2(r_B + r_0)}}
\]

On the other hand, A2 cations occupy pentagonal site and their coordination number is 15. In the coordination polyhedra, it is reported that the inter atomic distances between A2 and four O(1), two O(3) and O(4) is shorter than other distances [Sciau et al. 1993; Wakiya et al. 1999]. Therefore from the geometrical consideration, tolerance factor for A2 site cation \( (t_{A2}) \) can be expressed in the following equation:

\[
t_{A2} = \frac{(r_{A2} + r_0)}{\sqrt{23 - 12\sqrt{3}} (r_B + r_0)}
\]

Cations on the B site are in an octahedral coordination environment. Thus, transition metal cations such as Ti\(^{4+}\), Nb\(^{5+}\), Ta\(^{5+}\) and W\(^{6+}\) are commonly observed. Finally, cations on the C site are necessarily small, given the restricted environment and to date only Li\(^+\) and small rare earth ions such as Er\(^{3+}\) and Lu\(^{3+}\) have been observed occupying this site [Benner et al. 1967; Neurgaonakar et al. 1990]. Generally, the smallest interstice is empty, so the general formula is \( A_6B_{10}O_{30} \) for the filled tungsten-bronze structure.

In addition to the rich structural chemistry, tungsten bronzes have a number of interesting physical properties, including second order nonlinear optical behavior
(second-harmonic generation) [Chi et al. 2006; Neurgaonkar and Cory 1986], ferroelectricity and piezoelectricity [Lenzo et al. 1967; Liu and Maciolek 1975; Glass 1969]. These properties are attributable to the noncentrosymmetric, often polar, nature of the materials and more specifically, the intraoctahedral distortion of the B cation (Ti$^{4+}$, Nb$^{5+}$, W$^{6+}$, etc.). The present study deals with the dielectric and semiconducting properties of the ceramic complex oxides. Their current status of work on these systems is presented below.

### 1.2.1 Dielectric properties

From ferroelectricity discovery and related properties in BaTiO$_3$ [Wul et al. 1945], a large amount of research has been addressed to ferroelectric oxides, in the search of new materials having better properties for technological applications. High performance dielectric ceramics act as key materials for resonators and capacitors. Some ferroelectric complex oxides are also very important due to the microwave telecommunications progress involving satellite broadcasting and other related devices [Kolar et al 1980]. Among ferroelectric oxides, oxides with the tetragonal tungsten bronze structure (TTB) type are in the forefront both in the area of research as well as in industrial applications. As described above, TTB structure allows a wide variety of cations substitution due to the presence of several interstices. These substitutions in the structure exhibit a wide spectrum of properties and also sometimes improve the physical properties like ferroelectric, piezoelectric, pyroelectric, electro-optic.

Tungsten bronze type oxides are found in a vast number of compositions in different stoichiometries. The intended work in this thesis is related to tetragonal tungsten bronze type oxides. Hence, the literature review is given below within the purview of the thesis.

During the last decade, extensive research is going on in BaO – RE$_2$O$_3$ – TiO$_2$ – (Nb,Ta)$_2$O$_5$ system, because of their interesting physical properties such as high dielectric constant and low dielectric loss. The above system has been studied in various compositions and generally has tetragonal or orthorhombic TB type structure. Chen et al. 1999, investigated in a number of tetragonal tungsten bronze related compositions in the system BaO – RE$_2$O$_3$ – TiO$_2$ – (Nb,Ta)$_2$O$_5$ such as Ba$_4$Nd$_2$Ti$_4$Ta$_6$O$_{30}$ and Ba$_5$NdTi$_3$Ta$_7$O$_{30}$ for their high dielectric constant (~160) and low
loss ($\sim 10^{-4}$). The typical tetragonal filled tungsten-bronze compounds in the BaO – La$_2$O$_3$ – TiO$_2$ – Nb$_2$O$_5$ quarternary system [Ikeda et al. 1971; Stephenson 1965] were proposed and investigated, for the typical compositions: Ba$_4$La$_2$Ti$_4$Nb$_6$O$_{30}$ and Ba$_5$LnTi$_3$Nb$_7$O$_{30}$. Some more filled tungsten-bronze niobate ceramics have been reported in the quarternary systems containing rare earths, such as that reported by Zheng and Chen 2002, in the BaO – Nd$_2$O$_3$/Sm$_2$O$_3$ – TiO$_2$ – Nb$_2$O$_5$ quarternary system. They have studied for various compositions in the above system, which exhibited high dielectric constant and also relaxor behavior. Shannigrahi et al. 1998, and Palai et al. 2001, reported Ba$_5$RTi$_3$Nb$_6$O$_{30}$ (R = Dy, Sm) and Ba$_4$R$_2$Ti$_4$Nb$_6$O$_{30}$ (R = Y, Sm, Dy) with orthorhombic structure. Ferroelectric phase transition in Ba$_5$LaTi$_{3-x}$Zr$_x$Nb$_7$O$_{30}$ ($x = 0, 1, 2, 3$) ceramics have also been reported by Singh et al. 2002. These compounds showed dielectric constant in the range 27 - 136 and diffuse-type ferroelectric phase transition with transition temperature below room temperature. The compositions Ba$_5$RTi$_3$Nb$_7$O$_{30}$ (R = Eu or Gd) having orthorhombic TB-type structure were reported for their diffuse phase transition and relaxor property [Panigrahi et al. 1999]. Gd compound showed better dielectric constant ($\varepsilon_r = 152$) than Eu substituted compound ($\varepsilon_r = 110$). High permittivity (in the range 193-245) and low dielectric loss has been observed in Ba$_5$LnNiNb$_9$O$_{30}$ (Ln = La, Nd and Sm) ceramics [Fang et al. 2006]. All the three compounds are paraelectric phases adopting the filled tetragonal tungsten bronze (TTB) structure at room temperature. Biju mon et al. 2004, reported some more compositions under the formula Ba$_5$MTi$_3$A$_7$O$_{30}$ (M = Ce, Pr, Nd, Sm, Gd, Dy and Bi; A = Nb, Ta) for their dielectric properties. At 1 MHz, their dielectric constant ($\varepsilon_r$) varies from 164 to 887 and loss tangent (tan$\delta$) from $10^{-3}$ to $10^{-2}$ and the niobates undergo diffuse phase transition above room temperature showing the ferroelectric behavior, the tantalate analogoues exhibit paraelectric behavior. Yuan et al. 2006; and Chen et al. 2005, investigated many compositions by substitution of Ba, Sr and Ca: Ba$_6$Ti$_2$Ta$_8$O$_{30}$, Sr$_6$Ti$_2$Ta$_8$O$_{30}$ and Ca$_6$Ti$_2$Ta$_8$O$_{30}$ [Yuan et al. 2006]. These compounds gave high dielectric constant (170-180) and low dielectric loss (in the order of $10^{-4}$ at 1 MHz) and relatively low temperature coefficient of dielectric constant.

Modifications of the dielectric properties of Ba$_4$Sm$_2$Ti$_4$Ta$_6$O$_{30}$ ceramics by Sr substitution for Ba on the A-sites and Ti substitution for Ta on the B-sites was investigated by Li et al. 2002. The increase in Ti concentration improved significantly
the temperature coefficient of the dielectric constant together with decreased dielectric properties. Ranga Raju and Choudhary 2006, reported the effect of Zr substitution for Ti on structural, dielectric and electrical properties of Sr$_5$SmTi$_3$Nb$_7$O$_{30}$ ceramics. They have orthorhombic crystal structure for all the Zr substitutions. The Zr substitution shifts the curie temperature towards lower side. The effects of La/Sn co-substitution at A and B sites of Ba$_4$Nd$_2$Ti$_4$Ta$_6$O$_{30}$ and Ba$_5$NdTi$_3$Ta$_7$O$_{30}$ ceramics were investigated for their dielectric properties [Zheng et al. 2004 and 2005]. With La/Sn co-substitution in both the compositions, the temperature coefficient was significantly improved to near zero, at the same time, dielectric constant reduced and dielectric loss increased.

The TTB type related compositions have also been investigated in the AB$_2$O$_6$, and A$_3$B$_5$O$_{15}$ stoichiometries. Dielectric ceramics in the system BaO – Nd$_2$O$_3$ – TiO$_2$ have received much attention because of their important applications as microwave dielectric resonators and filters [Kolar et al. 1981; Chen et al. 1995] and the most important compositions fall in the solid solution of Ba$_{6-3x}$Nd$_{8+2x}$Ti$_{18}$O$_{54}$ with the tungsten bronze structure [Cruickshank et al. 1996]. A series of new compounds, Ba$_{1-x}$R$_{2x}$Nb$_2$O$_6$ (R = Nd, Eu, Gd, Tb, Dy, Ho and Er) with tetragonal tungsten bronze (TTB) were reported for their dielectric and ferroelectric properties [Wakiya 1999]. The dielectric constant of these compounds for R = Ho, Er or Y lie between 180 and 260 at room temperature. A new relaxor ferroelectric, Ba$_2$LaTi$_2$Nb$_2$O$_{15}$ having TTB type structure have maximum permittivity of 250-300 at Tc ~ 200 K and frequency-dependent permittivity below Tc, characteristic of relaxor behaviour.

As can be seen from the above, A – R – Ti – M – O system have been investigated extensively for various compositions and substitutions for enhancing the properties. However, the stoichiometry proposed in the present investigation has not been studied by other researchers.

1.2.2 Semiconducting properties

Among reduced niobates A$_6$Nb$_{10}$O$_{30}$ (A = Sr, Ba, Eu) compounds with the TTB-type structure were reported for their semiconducting properties [Hessen et al. 1991; Stader et al. 1980]. The probable reason for this is a rather low charge carrier concentration ~ 0.2e per Nb atom for A$_6^{2+}$ Nb$_{10}$O$_{30}$. Recently, the influence of the
heterovalent substitution of rare earth cations for barium on the crystal structure and conductivity of $\text{Ba}_{6-x}\text{Ln}_x\text{Nb}_{10}\text{O}_{30}$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Nd}$) was studied [D’yachenko et al. 1997; Hwang and Kwon 1995]. Such substitution led to the increase of the charge carrier concentration up to $0.4\,\tilde{\epsilon}$ per Nb atom for the most substituted sample with the nominal composition $\text{Ba}_4\text{La}_2\text{Nb}_{10}\text{O}_{30}$. This value is quite close to that found in $\text{Na}_{0.45}\text{W}_{10}\text{O}_{30}$ ($0.45\,\tilde{\epsilon}$ per Nb atom) with metallic-type conductivity [Muhlenstein and Danielson 1967]. Even superconductivity has been observed in the systems, $\text{M}_x\text{NbO}_2$ ($\text{M} = \text{Li}, \text{Na}$) [Geselbracht and Richardson 1990], $\text{Sr}_{1-x}\text{La}_x\text{Nb}_{2}\text{O}_{6-x}$ [Akimitsu et al. 1991], $\text{A}_x\text{Nb}_{1+x}\text{O}_2$ ($\text{A} = \text{Ca}, \text{Sr}$) [Nakamura 1994], and $\text{Ba} – \text{Nb} – \text{O}$ [Gasparov 1994]. Since then intensive research has been carried out to prepare new non-copper containing superconductors.

Other than TTBs, semiconducting has been observed in many other systems. A few of them are mentioned here just for the sake of information. Shi et al. 1995, reported semiconductor to metallic conductivity in $\text{Ln}_2\text{Mo}_2\text{O}_9$ compounds. The semiconductivity in these compounds is attributed due to clustering of $\text{Mo}_2\text{O}_6$. Spinel-structured semiconductor ceramics (SSSC) are widely used for temperature measurement and in rush current limiting, etc as Negative temperature coefficient (NTC) thermistors [Amin and Newnham 1992].

1.2.3 Optical properties

The various substitutions can improve some physical properties like electro-optic, elasto-optic and pyroelectric found in some compounds of this family. After the discovery of barium sodium niobate (BNN) [Rubbin et al. 1967] as a good electro-optic material, a large number of niobate compounds of this family have been studied such as $\text{Ba}_2\text{Na}_3\text{RNb}_{10}\text{O}_{30}$ [Iwasaki 1971], $\text{K}_2\text{LaNb}_5\text{O}_{15}$ [Ismailzade 1968] and $\text{Ba}_4\text{NaNb}_{10}\text{O}_{30}$ [Subba Rao et al. 1987]. A new compound filled tungsten bronze type structure $\text{Ba}_2\text{Na}_{1-x}\text{RE}_x\text{Nb}_5\text{O}_{15}$ ($\text{RE} = \text{Sc}, \text{Y}, \text{La}, \text{Gd}, \text{Yb}, \text{Lu}; \, x = 0.02$) have been investigated for second harmonic generation [Yoshikawa et al. 2003]. All the samples exhibit an intense second harmonic signal under tunable IR pumping laser source, due to both the high values of the non-linear optical coefficients and the absence of absorption of additional RE ions in the visible range. Recently, luminescent properties have also been reported in $\text{Ba}_{6-x}\text{Eu}_x\text{Ti}_{2+x}\text{Ta}_{8-y}\text{O}_{30}$ and $\text{Ba}_{4-x}\text{K}_x\text{Eu}_2\text{Ti}_{4-y}\text{Ta}_{6+y}\text{O}_{30}$ [Li et al.
2004]. These compounds exhibited typical emission of Eu$^{3+}$ at about 580-620 nm under excitation at 400 nm. Nine tungsten bronze oxides, $A_6M_2M'_{8}O_{30}$ ($A = Sr^{2+}, Ba^{2+}$, or Pb$^{2+}$; $M = Ti^{4+}, Zr^{4+}$ or Hf$^{4+}$; $M' = Nb^{5+}$ or Ta$^{5+}$) have been synthesized and characterized for their structure and second order nonlinear optical behavior.

1.3 Pyrochlore type Structure

Pyrochlore oxides are named after the mineral pyrochlore, (NaCa)(NbTa)O6F/(OH), with which they share a similar structure [JCPDS Card No. 13-254], which can be generalized as $A_2B_2O_7$. The definition of the term pyrochlore is given as a complex oxide mineral composed of niobium, sodium, and calcium (NaCaNb$_2$O$_6$F) that forms brown to black, glassy octahedral crystals and irregular masses. Tantalum atoms replace niobium atoms in the chemical structure, so that pyrochlore forms a solid-solution series with the mineral microlite [(Na, Ca)$_2$Ta$_2$O$_6$(O, OH, F)].

$A_2B_2O_7$ pyrochlores are ternary metallic oxides whose crystal chemistry is complex enough to make them favourable for a wide range of applications. A and B cations are only considered as having charges of $3^+$ and $4^+$ respectively. However, there is another entire series of pyrochlore compounds consisting of $2^+$ and $5^+$ cations.

**Figure 1.2** Unit cell of pyrochlore.
Blue spheres represent $A^{3+}$ cations, yellow $B^{4+}$ and red $O^{2-}$.
The general formula of the oxide pyrochlore structure can be written as $A_2B_2O_6O'$. There are four crystallographically unique atom positions and the space group is Fd3m [Subramanian et al. 1983]. A common way of describing the structure is by fixing its origin on the B site, with atoms located at the following positions (using Wyckoff notation): A at 16d, B at 16c, O at 48f and O' at 8b [Subramanian et al. 1983]. The only internal positional variable of the pyrochlore structure is the oxygen $x$ parameter, which characterizes the 48f oxygen atoms. To better visualize the pyrochlore structure, the convenient, fluorite type description is used [Aleshin and Roy 1962; Longo et al. 1969].

The pyrochlore structure can thereby be considered as an ordered, defective fluorite solid solution. In CaF$_2$, the fluorine anions are located in the tetrahedral sites of a Ca face centered cubic array. In this description of pyrochlore, the A and B cations form the face centered cubic array, but are additionally ordered in the <110> directions such that the A cations are eight coordinate and the B cations are six coordinate with respect to oxygen. This cation ordering means that the tetrahedral anion sites are no longer crystallographically identical. In fact, there are now three distinct tetrahedral sites: the 48f, which has two A and two B nearest neighbours, the 8a, which has four B nearest neighbours and the 8b, which has four A nearest neighbours. In pyrochlore, the 8a positions are vacant. Figure 1.2 depicts one eighth of the pyrochlore unit cell, which is analogous to a single fluorite unit cell. Figure 1.3 depicts a full unit cell of a pyrochlore, with the anions removed in order to better view the two cationic sublattices and the ordering along <110> directions.

The pyrochlore phases can be designated as type 3-4, 2-5 and 1-6 that is $A_2^{3+}B_2^{4+}O_7$, $A_2^{2+}B_2^{5+}O_7$ and $A_2^{1+}B_2^{6+}O_7$ respectively owing to the valencies of A and B cations. Moreover similar to the peroviskites other more complex combinations such as $A_2^+A^{3+}[B^{4+}B^{5+}]$ are feasible. Many of the pyrochlore known in the literature are of the type $A_2^{3+}B^{4+}O_7$. This is due to the fact that a large number of $A^{3+}$ and $B^{4+}$ cations have suitable ionic radius for the formation of pyrochlore structure. The ionic radii of A cations range from 0.09 to 0.15 nm and that of B cations ranges from 0.05 to 0.075 nm. For the formation of any pyrochlore compound, there are two criteria: 1) The ratio of the ionic radius of the cation at the A site to that at the B site must be between 1.46 and
the chemical valences of various ions must make the compound neutral [Subramanian et al. 1983].

![Cationic sub-lattice of pyrochlore](image)

**Figure 1.3** The cationic sub-lattice of pyrochlore.

Identification of systems containing pyrochlore type phase is often extremely difficult because of similarity of the structure to that of fluorite. The cation sublattice of these two structures are identical except for the order of parent in the pyrochlore and unless there is substantial differences in the scattering factors of the two cation types in the pyrochlore, there will little indication of this order in the X-ray diffraction pattern. The only way in which the pyrochlore anion lattice differs from that of fluorite is that one eighth of the anion sites of the latter are vacant and six seventh of the remaining anions are shifted from their ideal fluorite sites. In most relevant systems any contribution from the anion sublattice would be small and not greatly different from that of the fluorite anion array.

The rules regarding the allowed fundamental reflections in the pyrochlore Fd3m space group are available in the International Tables for X-ray Crystallography. However, super lattice or ordering reflections (when supposing the pyrochlore as a fluorite derivative) are (111), (331), and (531) and arise from both cations and anions. The presence of these reflections with h, k, l all odd is indicative of A, B cations and O, O' anions ordering on the 16c, 16d, 48f, and 8a sites respectively in space group Fd3m. In addition, vacant sites will be ordered on 8b sites. However, when pyrochlores have
anion or cation defect structures, the ordering on their individual sites will change although the general ordering (16c, 16d, 48f, 8a) is the same. When the cations in the pyrochlore structure disorder (in this case the pyrochlore crystal structure approaches the defect fluorite structure) [Sleight 1969], these ordering reflections will diminish in intensity [Greedan 1979].

Due to the extensive compositional range of the compounds which exhibit the pyrochlore structure, there are a variety of actual and potential applications for these materials. Examples include: dielectric materials [Cann et al. 1996; Valant and Davies 2000], catalysts [Goodenough and Castellano 1982; Korf et al. 1982], solid electrolytes [Tuller 1992; Kramer et al. 1994; Heremans 1995], thermal barrier coatings [Maloney, 2000 and 2001] as well as actinide host phases for nuclear waste encapsulation [Ewing et al. 1995; Sickfus et al. 2000]. Since pyrochlores have wide spread applications, the literature review with respect to dielectrics and semiconducting oxides is given within the purview of the thesis.

1.3.1 Dielectric Properties

Dielectric ceramics have been extensively studied in bismuth based pyrochlores. Most of the researchers investigated in Bi₂O₃ – ZnO – Nb₂O₅ system.

Bismuth-based pyrochlores have been reported for low-fire high frequency dielectric applications [Yan et al. 1994; Liu et al. 1993]. In contrast to conventional microwave dielectric materials, e.g. Ba(Mg₁/₃Ta₂/₃)O₃ and Zn(Sn, Ti)O₄ that require high sintering temperatures (>1300 °C), the low sintering temperatures of bismuth pyrochlores (<1000 °C) and dielectric properties with low losses (tanδ <10⁻⁴) and dielectric constant up to 150 make them promising candidates for cofired decoupling capacitors in multichip module packaging applications, so-called LTCC packages (low temperature cofired ceramics). Cann et al. (1995), investigated a series of bismuth based pyrochlores of the general formula Bi₂(B²⁺₂/₃ B⁵+₁/₃)O₇ and Bi₂(B³⁺ B⁵+)O₇ where B²⁺ = Mg, Cu, Zn and Ni; B³⁺ = Sc and In; and B⁵⁺ = Nb and Ta. They observed dielectric constant in the range of 67-250 and loss: 0.08 to 0.0001. Bi-pyrochlores and zirconolite dielectrics for integrated passive components was reported by Randall et al. (2003). They focused on embedded capacitor components that fulfill a large range of functions including decoupling, filtering and low-loss termination loads. The improvements of dielectric properties on Bi₂O₃ – ZnO – Nb₂O₅ was observed by V₂O₅.
substitution [Hong et al. 2003]. Du et al. 2002, reported the structure and dielectric properties of $\text{Bi}_2\text{O}_3 - \text{ZnO} - \text{SnO}_2 - \text{Nb}_2\text{O}_5$ quarternary pyrochlores. They could obtain low temperature coefficient of permittivity. Titania addition to $\text{Bi}_2\text{O}_3 - \text{ZnO} - \text{Nb}_2\text{O}_5$ improved the dielectric constant ($\sim 200$) and low dielectric loss ($\tan \delta < 10^{-4}$) at 1 MHz. Effects of Sr substitution on the dielectric characteristics in $\text{Bi}_2\text{O}_3 - \text{ZnO} - \text{Nb}_2\text{O}_5$ was also studied by Du and Yao, 2003. The Sr substitution could increase the temperature coefficient pronouncedly without significant decrease of dielectric constant. Dielectric relaxation in $\text{Bi}_2\text{O}_3 - \text{ZnO} - \text{Nb}_2\text{O}_5$ cubic pyrochlore has been reported by Nino et al. (2001) and observed a broad distribution of relaxation times. Apart from bismuth pyrochlores, lead and calcium pyrochlores were studied extensively for their microwave dielectric properties [Cook and Jaffe 1952; Ubic et al. 2004]. The findings revealed that $\text{Pb}_2\text{Nb}_2\text{O}_7$ does not have the cubic pyrochlore structure. Brusset et al. reported a monoclinic unit cell, however, most later work seems to suggest a trigonal structure [Ubic et al. 2001].

1.3.2 Semiconducting Properties

The first known reduced niobates with a pyrochlore structure, $\text{CaLnNb}_2\text{O}_7$ ($\text{Ln} = \text{Y}, \text{Nd}$) have been studied for their semiconducting properties [Ya Istomin 1994]. The structural refinement of these compounds establishes cubic pyrochlore type structure with space group $\text{Fd}3\text{m}$. Rare earth molybdenum pyrochlores, $\text{Ln}_2\text{Mo}_2\text{O}_9$ ($\text{Ln} = \text{Sm}-\text{Yb}, \text{Y}$) were examined for their electrical properties and they exhibit semiconductivity to metallic behavior [Subramanian et al. 1980].

1.4 Scope of the present work

During this investigation, efforts have been made to prepare and study the properties of new oxide materials in the system “A-RE-Ti-M-O (A = Li, Ca, Ba or Pb; RE = rare earth; M = Nb or Ta)”. Several new oxides having insulating and semiconducting properties could be prepared. The structure, ceramic microstructure and electrical properties of these oxides would depend on their composition. The present investigation involves a detailed study on the structure and properties of a large number of these oxides. Finally, efforts have been made to correlate their properties as well as structure.