Pyroelectric crystals possess the unusual characteristic of being permanently polarized within a given temperature range. Unlike piezoelectric materials which undergo polarization under stress, the pyroelectric materials are polarized spontaneously and form permanent dipoles in the structure. This polarization also changes with temperature, hence, the term pyroelectricity. A subgroup of the spontaneously polarized pyroelectrics is a very special category of materials known as ferroelectrics. Similar to pyroelectrics, materials in this group are spontaneously polarized and possess spontaneous dipoles. However, unlike pyroelectrics, these dipoles are reversible by an electric field smaller than the dielectric breakdown of the material. Thus, the two conditions necessary in a material to classify it as a ferroelectric are:

(i) the existence of spontaneous polarization and
(ii) the ability to reverse the direction of polarization.

Ferroelectricity was discovered in single-crystal materials (i.e. in Rochelle Salt \( \text{KNaC}_4\text{H}_4\text{O}_6\cdot4\text{H}_2\text{O} \)) in 1921 and then in polycrystalline ceramics (i.e. in Barium Titanate \( \text{BaTiO}_3 \)) during the early to mid-1940s. Thereafter, large number of new materials have been discovered which show ferroelectricity that leads to significant number of industrial and commercial applications. The prominent properties of ferroelectric materials such as polarization hysteresis, large dielectric constant and remarkable piezoelectric, pyroelectric and electro-optical effects makes it useful for a number of electronic devices like small size high
capacitance capacitors, piezoelectric sonar, pyroelectric security surveillance devices, medical diagnostic transducers, electrooptic light valves, ferroelectric memories, etc. Because of all these important applications, the field of ferroelectric materials is ever expanding. In this general group of ferroelectric materials, based on the basic structure, the following four types of ceramic ferroelectrics are known:

(i) the Tungsten-Bronze group
(ii) the Perovskites group
(iii) the Pyrochlore group
(iv) the Bismuth Layer-Structured group.

Of these, the Tungsten-Bronze structure ferroelectrics are a large class of technically important materials. These materials belong to an important family of dielectric materials, which display interesting ferroelectric, pyroelectric, piezoelectric and nonlinear optic properties for applications in various electronic devices, such as transducers, actuators, capacitors and ferroelectric random access memory.

**Tungsten Bronze Ferroelectric Ceramic**

The Tungsten Bronze (TB)-type structure having a general formula \((A_1)_4(A_2)_2(C)_4(B_1)_2(B_2)_8O_{30}\) consists of a complex array of distorted \(BO_6\) octahedra sharing corners in such a way that three different types of interstices (i.e., A, B and C) are available for cation substitutions in which a wide variety of substitutions can be made for different applications. It is interesting to observe that some compounds of this family, such as \(K_2LaNb_5O_{15}\), \(Ba_4NaNb_{10}O_{30}\), \(Ba_5RTi_3Nb_7O_{30}\) (\(R = \) rare earth ions) and \(Ba_5YTi_{3-x}Zr_xNb_7O_{30}\) (\(x = 0, 1, 2, 3\)), show
diffuse phase transition and relaxor behaviour. It is now a well – known fact that there is a drastic change in some physical properties of materials on suitable substitutions at different atomic sites of TB structure. After extensive literature survey it was felt that although some work has been reported for both A- as well as B- site substitutions in this TB- structure but a comprehensive study of the changes in physical properties due to systematic substitution at the A-site of these materials is lacking.

With this background in mind, systematic A-site substitution in TB-structured BaO-R_2O_3-TiO_2-Nb_2O_5 (R = Rare Earth) quaternary systems was undertaken. The chemical formulas for the different studied compositions are:

Series 1  Ba_{5-x}Ca_xSmTi_3Nb_7O_{30}; x = 0 to 5

Series 2  Ba_3RTi_3Nb_7O_{30}; R = La, Nd, Sm, Eu, Dy

Series 3  CaBa_4RTi_3Nb_7O_{30}; R = La, Nd, Sm, Eu, Dy

All the samples were prepared by solid state reaction method at the optimized sintering condition of 1300 °C for 10 hours and studied for their structural, dielectric, ferroelectric, piezoelectric, pyroelectric, ac and dc conductivity, impedance and modulus properties. Also Ba_5SmTi_3Nb_7O_{30} have been prepared by Microwave sintering and Mechanical Activation technique by using ball-mill and its properties is compared with that obtained from conventional solid-state reaction method.