Chapter II:
Literature survey and
Statement
of the Problem
2.1 INTRODUCTION

The discovery of BaTiO$_3$ by Ogawa and Waku in 1944 in Japan was unique and independent from those in the U.S and the Soviet Union. Abe and Tanaka had been trying to utilize BaTiO$_3$ ceramics in ultrasonics and developed a Langevin type piezoelectric vibrator as a new electro-acoustic transducer [1]. Several other perovskite and oxide ceramic compositions from the basic constituents of modern piezoelectric ceramics were investigated during early 1950’s. These compositions include Lead Titanate (PbTiO$_3$) [2,3], Lead Zirconate (Pb ZrO$_3$) [4,5] in 1950, Lead metaniobate (PbNb$_2$O$_6$) [6] and Lead Zirconate Titanate Pb(Zr,Ti)O$_3$ [7,8,9] in 1952.

Lead Zirconate Titanate (PZT) is a leading transducer material for more than a quarter century since Jaffe’s patient for Pb(Zr,Ti)O$_3$ was established, many researchers have diverted their attention towards the morphotropic phase boundary compositions of PZT. Isupov [10] reported existence of an extended region of MPB compositions where tetragonal and rhombohedral phases are both stable. Kakegawa et al [11] prepared PZT samples with MPB compositions from aqueous solutions of TiCl$_4$ and ZrOCl$_2$ and they found no co-existence of two phases over the entire range of PZT compositions and confirmed that the co-existence behavior was caused by a compositional fluctuation in PZT samples prepared from raw oxide powders. Line et al [12] have reported in this Pb(Zr$_{1-x}$Ti$_{x}$)O$_3$ work that powders prepared
from the hydro thermal method are all cubic in external shape and crystal structure. While PZT powders from solid state reaction method at \( x = 0.52 \) are tetragonal in crystal structure, Tandon et al [13] have reported low temperature, sintering of PZT ceramics using glass additive systems. Sammas and Cao [14] have reported the preparation of a new dielectric ceramic based on \( \text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3 \) which could be useful in communications. Shi, G. et al [15] have reported excellent dielectric and pyroelectric properties of \( \text{PbTiO}_3 \) (PT), \( (\text{Pb},\text{La})\text{TiO}_3 \) and \( \text{Pb}(\text{Zr,Ti})\text{O}_3 \) thin films. The pyroelectric coefficients of PT, PLT and PZT thin films are \( 2.9 \times 10^{-8} \text{ C/cm}^2\text{K}, \) \( (3.37-5.25) \times 10^{-8} \text{ C/cm}^2\text{K}, \) and \( 6.10 \times 10^{-8} \text{ C/cm}^2\text{K}, \) respectively.

Snow [16,17] has developed methods of atmospheric sintering for the fabrication of PLZT ceramics for optical applications. Biggers and Schulze[18-20] have reported relatively high dielectric constant low \( \tan \delta \) and low sensitivity to D.C bias. The temperature coefficient of capacitance broadens [21] with slight addition of PLZT in the antiferroelectric region, but the dielectric constant decreases slightly. First data on electro optic properties of \( \text{SrBaCaNb}_2\text{O}_6 \) (SBN) single crystal were reported by Kopylov and Kravchenko in 1982 [22]. Who measured the electro optic effect by polarization method at \( \lambda = 633 \text{ nm} \) and found that temperature dependence of half-wave voltage was linear. The single crystals of \( \text{Sr}_4\text{NaLiNb}_{10}\text{O}_{30} \) were grown by Czochkalski technique by Zhu Yong and Zhangdao Fan [23] and studied electro optic, pyroelectric properties. They reported pyroelectric
coefficient $7 \times 10^{-4}$ C/m$^2$.k which is nearly equal to SBN. Trutomu Yano et al [24] had grown colorless single crystals from metals of $\text{Sr}_4\text{NaLiNb}_{10}\text{O}_{30}$ by Czochralski method and found that the crystal spontaneous polarization is $18 \mu\text{C/cm}^2$ by pulse method. Zhong Weili et al [25] reported the dielectric and Pyroelectric properties of $\text{Sr}_{2-x}\text{Ca}_x\text{NaNb}_5\text{O}_{15}$ in the temperature range 300-10K. Single crystals of SBN, SKN and PBN were grown and their ferroelectric properties were studied by Neurgaonkar et al [26] who found that dielectric, piezoelectric and electromechanical coupling coefficients are significantly large. In 1990, Neurgaonkar et al [27] proposed a classification of tungsten bronze materials into four groups based on their structures, and ferroelectric and optical properties. They found that dopants would control the speed of response and coupling strength as well as spectral range. The best performance was established for $\text{Ce}^{3+}$ and $\text{Cr}^{3+}$ doped SBN: 60 crystals in the visible and IR regions respectively. Borchardt et al [28] reported that hysteresis loops obtained with liquid electrodes on SBN exhibit good saturation, not dependent on the remnant polarization on the maximum field and higher values of spontaneous polarization. The primary pyroelectricity measurements in Strontium Barium Niobate single crystals were reported by Liu and Cross [29]. A very large Pyroelectric coefficient at room temperature was reported by Glass [30] for $x=0.25$ and 0.50 in $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ and the author constructed a pyroelectric a detector for $x=0.33$ and used at 300 k to detect single pulses of 10.6 micro radiations from Q-switched carbon-dioxide laser with a rise time,
less than 30 nano seconds. Francombe [31] reported that properties of 
\( \text{Ba}_{1-x}\text{Sr}_x\text{Nb}_2\text{O}_6 \) were broadly similar to the material \( \text{PbBaNb}_2\text{O}_6 \) series except at 
a barium which end of the systems, i.e., \( x<0.2 \).

Modified SBN and Lead Potassium Niobate ceramics were prepared and 
studied the effect of various dopants on the physical properties was studied by 
Bhanumathi et al [32] Thin films with n-type and P-type conductivity 
indoped and undoped PZT, SBN and PBN were processed on a silicon 
substrate by Sol-gel method by Yuhuanxu et al [33].

Mander [34] reported that the dielectric, ferroelectric properties of
Strontium Barium Niobate (SBN) thin films. In our laboratory Tungsten 
Bronze Ceramics have been extensively studied. Work on SBN ceramics was 
reported by Chandra Mouli et al [35] who studied the effect of alkali metal 
dopants on the Curie temperature and dielectric behavior of Strontium Barium 
Niobate ceramics. Padmaja Rani et al [36] studied the effect of \( \text{Ag}^+ \) and \( \text{K}^+ \) on 
the piezoelectric properties of \( \text{PbBaNb}_2\text{O}_6 \) and reported an increase in the 
thickness of the coupling coefficient and an increase in the Curie temperature 
with increase in the silver concentration.

PBN was first discovered around 1960 [37-39] and was considered very 
promising for electro optic and photo refraction applications. The most 
interesting solid solution in the family of tungsten bronze ferroelectrics that 
between \( \text{PbNb}_2\text{O}_6 \) and a hypothetical member \( \text{BaNb}_2\text{O}_6 \) namely lead barium 
niobate \( \text{Pb}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6 \) [38-43]. tungsten bronze ferroelectrics with a
morphotropic phase boundary (MPB) can have a number of enhanced properties compared with other conventional ferroelectric compounds because of the proximity in free energy of an alternative ferroelectric structure [44]. The earlier research before 1980 on PBN was based on measurements on polycrystalline form, primarily due to the lack of single crystals. Lane et al [45] reported that the pyroelectric coefficient of Pb₀.₆Ba₀.₄Nb₂O₆ ceramic sample near MPB is 270 μC/m².K. Shrout et al [46] reported pyroelectric coefficients of PBN crystals of several compositions.

Oliver et al [47] worked extensively on the ferroelectric properties of tungsten bronze morphotropic phase boundary systems and discussed the potential advantages and limitations of these boundary systems. Neurgaonkar et al [48] the reported structure and ferroelectric properties of potassium, lanthanum and bismuth doped in lead meta niobate. They explained that introduction of K⁺ with either La³⁺ or Bi³⁺ would produce similar results. In lead Barium Niobate Curie temperature first decreases with increasing of barium concentration and then increases in tetragonal phase. This is unique among all the tungsten bronze structural materials.

Shrout et al [46] studied the dielectric and piezoelectric properties of lead barium niobate crystals and reported a strong enhancement of dielectric and piezoelectric coefficients at the MPB. A maximum d₃₃ of 185 PC/N for Pb₀.₆Ba₀.₄Nb₂O₆. Neuragaonkar et al [49] reported a high electro optic figure of merit for lead barium niobate crystals, which makes PBN an attractive material
for electro optic and photorefractive applications such as holographic data storage. A limiting factor, reported by Oliver et al [47] and Shrout et al [50] in the development of lead barium niobate single crystals was the volatility of lead oxide at the melting temperature, and although it was possible to grow PBN crystals of up to several millimeter cross section using the Czochralski method, the rapid loss of PbO from the melt has led to poor control over stoichiometry and compositional homogeneity. Guo et al [51] reported the polarization mechanism in tungsten bronze ferroelectric lead barium niobate near the MPB for both ceramics and bulk crystals by means of both electrical and optical methods.

Subba Rao et al [42] reported out a ferroelectric phase formation and a minimum Curie point at about 35 mole% of barium niobate in lead barium niobate and hence concluded the existence of a phase boundary at this compositions separating the lead niobate solid solutions from lead barium niobate type ferroelectrics. Fig 2.1 is taken from Jaffe, Cook and Jaffe [44] summarises the dielectric studies of lead barium niobate by Goodman, Isupov and Kosiakov and Subba Rao et al [42].

Myeongkyu Lee et al [52] studied the photo refractive properties of tungsten bronze ferroelectric lead barium niobate crystals and reported an increase in the both photo refractive sensitivity and gain coefficient with decreasing wavelength.
Fig. 2.1. PHASE DIAGRAM FOR PbNb$_2$O$_6$-BaNb$_2$O$_6$ SYSTEM
Isupov and Kosiakov [43] reported a saturation in the hysteresis loop when the barium composition in lead barium niobate concentration from 40 to 60 mole%. There was a decrease in the spontaneous and remnant polarization while there was a significant increase in Ec which was observed only when barium niobate concentration was decreased to 30 mole%. On comparing piezoelectric resonance frequency temperature characteristics of lead barium niobate with that of barium titanate, Isupov and Kosiakov felt that lead barium niobate with 50% of barium niobate is stable over a broad temperature range from -80 to 250°C which is very desirable for the piezoelectric resonator applications.

Transparent ferroelectric ceramics of hot pressed lanthanum modified PBN are reported Yokosuka and Marutake [53]. They have determined lattice parameters over a wide range of temperatures. A comparison with dielectric, piezoelectric, pyroelectric and optical properties reveals the existence of successive phase transitions i.e from tetragonal(para) – tetragonal(ferro) – orthorhombic(ferro) for Pb₀.₆Ba₀.₄Nb₂O₆. The tetragonal – orthorhombic transition is shown to be a typical type of diffuse phase transitions characterized by a wide dispersion.

Baxter and Hellicar [40] studied electrical properties of lead meta niobate and barium niobate of solid solutions. They observed a rise in room temperature dielectric constant as the barium niobate content is increased from zero to 40 mole% and the curie temperature decreased over the same range of
compositions. Further increase of barium content reduced the dielectric constant and raised the Curie temperature. The coupling coefficients increased as the barium content is increased to 40 mole% and then decreased with further replacement of lead by barium. Lane at al [45] reported a minimum value of piezoelectric voltage coefficient near the MPB.

Nagata et al [56] studied the properties of grain-oriented transparent lead barium lanthanum niobate (PBLN) hot pressed ceramics. In their study the \((\text{Pb}_x\text{Ba}_{1-x})_y\text{La}_4\text{Nb}_2\text{O}_6\) samples were hot pressed and their permittivity, piezoelectric and optical properties were measured for compositions of \(y=0.4\) to 0.8 and \(y=0.0\) to 0.10 and their grain orientation behavior was discussed. Neurgaonkar et al [55] reported piezoelectric and ferroelectric properties of modified lanthanum and pure \(\text{Pb}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6\) dense hot pressed ceramics and found a maximum \(d_{33}\) of 275 PC/N for PBLN: 60 when electric field was applied in a direction parallel to the hot pressing direction. Considerable c-axis grain-orientation in the plane normal to the pressing axis in their work was evident with corresponding isotropic, dielectric, piezoelectric and polarization properties.

2.1 Statement of Problem:

The focus of the present study is to explore the Electrical studies on pure and modified rare earth elements such as Cerium (Ce) at different phases. The ceramic compositions were prepared following the solid state synthesis method. They were then characterized in detail x-ray diffraction and
the lattice parameters were determined to identify their phases. Measurement of dielectric, piezoelectric and pyroelectric coefficients and its dependence on temperature was done to determine, the curie temperature ($T_c$) and the relationship with dopant concentrations.

From the pioneering work of Fran Combe [38] and Subba Rao [39,42], it is well known that by substitution of barium in lead metaniobate in place of lead, morphotropic phase boundary occurs at $\text{Pb}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$. When Ba concentration is increased above 40 mole % the structure is tetragonal and with the barium concentration below 40 mole% structure exhibits orthorhombic distortion. As in PBN also exhibits a peak in pyroelectric properties at the MPB. This is because near MPB polar vectors have a greater number of directions to orient when compared with the other phases. R.Lane et al [45] who did pioneering work PBN ceramic composition near MPB and Myeogkyu Lee et al [54] also did the work on PBN single crystal at different phases. Yokosuka and Murutake [53] have studied dielectric, piezoelectric, pyroelectric and optical properties of Lanthanum doped $\text{Pb}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ Ceramic compositions near MPB region.

In contrast to the works reported by researchers who might have extensively used lanthanum as dopant in PBN ceramic compositions at different phases, in the present study rare-earth elements, such as Cerium has been chosen as dopant as the atomic radius of cerium nearly equal to that of lead. The general formula used for the preparation of all the compositions
depending on the compositions of the amounts of the constituents is given by

\[ \Phi_{(1-z/2)Ba_{(1-z)}Ce_xNb_2O_6} \] where \( y = 0 \) to 0.1 and \( 1-x = 0.35, 0.40, \) and 0.45. The usual high temperature technique consisting of steps of powder

Experiments are divided into three series.

1) Effect of cerium on PBN in orthorhombic side of phase boundary for varying concentrations of Cerium (0.02 to .1) mentioned as A-series, Barium concentration (35 mole%) kept constant.

2) Effect of cerium on PBN near morphotropic phase boundary for varying concentrations of Cerium (0.02 to .1) mentioned as B-series, Barium concentration (40 mole%) kept constant.

3) Effect of cerium on PBN in the tetragonal phase boundary for varying concentrations of Cerium (0.02 to .1) mentioned as C-series, Barium Concentration (45 mole%) kept constant.

The aim of the present work is to study the Electrical properties of pure and cerium doped PBN ceramic compositions at different phases.
Referances

19. Schulzer W Dielectric properties of PbZrO$_3$-PbJ$_{103}$-La$_2$O$_3$ Ph.D., Thesis
27. R.R. Neurgaonkar, W.K. Lory, J.R. Oliver and M. Khoshnevisan and E.J.
Sharp, Ferroelectrics 102, 3 (1990).
34. Mander R.G. Ceramica (Sao paulo braz),(port) 47 (302) 72 (2001)


