

**PHASE DIAGRAM, CRYSTAL STRUCTURE AND  
STRUCTURE PROPERTY CORRELATIONS IN  
(1-x)Ba(Cu<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-(x)PbTiO<sub>3</sub> CERAMICS**



**Thesis submitted in partial fulfillment for the  
Award of degree**

**Doctor of Philosophy**

**By**

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**2023**

***Dedicated to...***

***My Beloved Parents***

*(Smt. Rajkumari & Shri Sanver Lal Prajapti)*

***&***

***Parents-In-Law***

*(Smt. Lalita & Shri Govind Lal Prajapat)*

विवेकख्यातिरविप्लवा हानोपायः।

निरंतर अभ्यास से प्राप्त निश्चल और निर्दोष विवेकज्ञान, हान (अज्ञानता) का उपाय है।

**“Uninterrupted practice of discrimination (between real and unreal) is the means to liberation and the cessation of ignorance.”**

(Source - Patanjali's Yog Sutra 2.26)



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## PREFACE

Compositional tuning and defect engineering are important tools in the development of functional materials with good physical properties. In the present scenario, the piezoelectric device market is still dominated by traditional Lead based materials such as  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ,  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $(x)\text{PbTiO}_3$  due to their excellent dielectric, piezoelectric and ferroelectric properties. The properties of these materials are finely related to the crystal structure and maximum response is achieved for the compositions tuned near the morphotropic phase boundary (MPB) regions. MPB region is a composition range where the crystal structure changes from one type of symmetry to the other, with a nearly vertical phase boundary, which is mostly temperature independent, in the temperature-composition diagram.

Finding new materials with reduced toxicity and without compromising the desired piezoelectric properties is the motivation of this thesis. Since MPB is a key for obtaining good responses with compositional tuning, an effort has been made to develop a new ferroelectric solid solution and explore its compositions for finding MPBs and testing physical properties near them. In this thesis, a previously unexplored ferroelectric solid solution with formula  $(1-x)\text{Ba}(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $(x)\text{PbTiO}_3$  has been investigated for its crystal structure, phase transitions and phase stabilities. The present work also comprises a comprehensive study of the crystal structure at temperatures ranging from cryogenic (14K) to very high temperatures (1073K) and its entanglement with various physical properties. These studies have led to the discovery of many compositions possessing different crystal structure than the end components  $\text{Ba}(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3$  and  $\text{PbTiO}_3$ . Several intermediate crystallographic phases, such as, cubic, coexisting cubic and tetragonal phases, coexisting two tetragonal phases,

coexisting tetragonal and monoclinic phases etc., are observed while changing composition at room temperature. Due to the presence of several distinct phases and phase coexistence regions, multiple phase boundaries are found in the phase diagram of the solid solution. Composition dependence of the physical properties like dielectric, ferroelectric, piezoelectric etc. and their correlation with the microstructure, crystal structure has been investigated for various compositions of the solid solution.

In this thesis, the first-ever construction of the phase diagram has been done for  $(1-x)\text{Ba}(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$  ceramics. For the very first time in this work, a phenomenon of phase separation is noticeably observed, predominantly in a small composition region of the solid solution. The MPBs have been observed for relatively low Pb-content compositions of the solid solution with negligible thermal expansion below pseudocubic phase transition, showing its potential as low-level fatigue ferroelectric ceramics. Different advanced characterization techniques like XRD, XPS, SEM and EDS have been used to characterize the samples. Compositional controlling of different structures and the chemistry of the resulting phases of the solid solution have been done.

The comprehensive investigations on the  $(1-x)\text{Ba}(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$  solid solution in the present thesis are listed below:

- Room temperature crystal structural solutions for the entire solid solution at close compositional intervals.
- Temperature-dependent crystal structure solution of selected representative compositions near phase boundaries.
- First ever construction of temperature versus composition phase diagram of the solid solution.

- Investigation of compositional content for confirmation of stoichiometric integrity and homogeneity of the as-prepared samples of the solid solution.
- Inclusive studies of microstructure, ferroelectric, dielectric and piezoelectric properties of the solid solution.
- Studies of the tailoring effect of MnO<sub>2</sub> as an additive on the crystal structure, microstructure, dielectric, ferroelectric and piezoelectric properties of a selected composition of the solid solution.

The thesis is organized in 7 different chapters. A brief description of these chapters and their important results are as follows:

**Chapter 1:** A foundation for basic definitions, terms and concepts driving piezoelectricity and ferroelectricity in perovskites has been given in this chapter. The origin of high responses of physical properties has been given attention along with recent development in MPB ceramics comprising similar solid solutions and defect-engineered materials. A brief literature review of previous investigations on Ba(Cu<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> compound and its solid solutions are also included in this chapter. The objectives of the thesis are listed at the end.

**Chapter 2:** This chapter proceeds with a brief introduction to the physical property characterization techniques and instruments. The chapter then, unfolds the details of the solid solution synthesis process in ceramic form and optimizations of calcination and sintering conditions at various compositions. A pure perovskite phase has been obtained for almost all the investigated compositions of (1-x)Ba(Cu<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-(x)PbTiO<sub>3</sub> solid solution.

**Chapter 3:** This chapter divulges the evolution of room temperature crystal structure as composition varies. The crystal structural solutions of the different compositions with distinct crystallographic structures are critically comprehended using comparative studies of Rietveld Refinement of the structure from XRD patterns considering plausible crystal structures and variations in the lattice parameters and unit cell volume. Both the end components of the solid solution ( $x = 0, 1$ ) crystallize in a tetragonal crystal structure. The crystal structure of these end components quickly transforms to different symmetry in the solid solution, even with the addition of 0.05 concentration variation. Various other crystal structures viz., cubic structure ( $Pm-3m$  for  $0.05 \leq x \leq 0.55$ ), coexistence of cubic and tetragonal structures ( $'Pm-3m + P4mm'$  for  $0.59 \leq x < 0.62$ ), coexistence of two tetragonal structures ( $'P4mm + P4mm'$  for  $0.62 \leq x < 0.65$ ), coexistence of monoclinic and tetragonal structures ( $'Pm + P4mm'$  for  $0.65 \leq x \leq 0.85$ ), coexistence of two tetragonal structures ( $'P4mm + P4mm'$  for  $0.90 \leq x < 0.975$ ) have been observed at room temperature across the compositional series. Including the phenomenological differences between the phase coexistence of monoclinic and tetragonal structures, the composition region  $0.65 \leq x \leq 0.85$  is further divided in two regions and one more phase boundary is assigned in the region. This way, a total of seven phase boundaries have been observed at room temperature between these different crystal structure combinations.

**Chapter 4:** This chapter is focused on the exploration of the crystal structure from cryogenic temperatures (14K) to very high temperatures (1075K) for some selected representative compositions having distinct crystal structural configurations in the solid solution. The nature of phase coexistence was evaluated based on the temperature dependent phase stabilities of the compositions near the phase boundaries.



Fascinatingly, two types of phase coexistence have been observed in the solid solution. One is predominantly found in the composition regions  $0 \leq x \leq 0.65$  and  $0.95 \leq x \leq 1$  and is the usual first-order thermodynamic phase transition induced, commonly found in the perovskites. The dominance of the second type of phase coexistence was observed in the  $0.75 \leq x \leq 0.90$  composition region, which exhibits a typical phase separation and finds its similarities with quenched and compositionally disordered complex perovskite solid solutions. Although small scale phase separation has been spotted many times in similar Pb-based ferroelectric solid solutions, but in this solid solution a clear visualization of this phenomenon is observed for the very first time. These separated phases are believed to be driven by the large strain variation and subsequent accommodation of stress. The chapter illustrates the first ever construction of a composition versus temperature phase diagram for this solid solution using crystal structural and temperature dependent dielectric permittivity studies on various compositions. The interpretation of the phase dynamics and phase stabilities of the solid solution is included in this chapter.

**Chapter 5:** In this chapter, the compositional homogeneity and integrity of some selected compositions of the solid solution has been verified by EDS and XPS studies. For the entire composition range, several physical characterizations, including microstructure, dielectric, ferroelectric and piezoelectric, are described in detail. This chapter emphasizes on the establishment of co-relations of these physical properties with their crystal structure and microstructure. In the as-prepared conditions the composition region  $0.70 \leq x \leq 1$ , exhibit good ferroelectric properties having the highest responses for the composition lying near the morphotropic phase boundaries.

**Chapter 6:** In this chapter, the effect of the  $\text{MnO}_2$  additive on a selected composition  $(0.38)\text{Ba}(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3-(0.62)\text{PbTiO}_3$ , of the solid solution has been explored. The tailoring in the crystal structure, microstructure, dielectric, ferroelectric and piezoelectric properties have been observed along with the establishment of a correlation between the structure and physical properties of these  $\text{MnO}_2$  modified ceramics. The observed high responses in piezoelectric and ferroelectric properties have been demonstrated as a result of formation of defect-engineered ceramics and is investigated for defect chemistry based modifications in compositional content and valences. An increase in direct piezoelectric strain coefficient from  $2.5\text{pC/N}$  to  $72\text{pC/N}$  has been observed for a typically 1 weight percent of  $\text{MnO}_2$  additive in  $(0.38)\text{Ba}(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3-(0.62)\text{PbTiO}_3$ .

**Chapter 7:** This chapter summarizes the main findings of the research work carried out for the present PhD thesis and lists a few important suggestions for future investigations.

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## ABBREVIATIONS

|                                |  |
|--------------------------------|--|
| $T_C$                          | Curie Temperature  |
| MPB                            | Morphotropic Phase Boundary  |
| PPB                            | Polymorphic Phase Boundary   |
| BCN                            | $\text{Ba}(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3$                        |
| PT                             | $\text{PbTiO}_3$   |
| RT                             | Room Temperature   |
| XRD                            | X-Ray Diffraction  |
| NPR                            | Nano polar region  |
| $(1-x)\text{BCN}-(x)\text{PT}$ | $(1-x)\text{Ba}(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3-(x)\text{PbTiO}_3$ |

# NOTATION

## Symbols

|                 |                              |
|-----------------|------------------------------|
| $G_{\text{tf}}$ | Goldschmidt tolerance factor |
| K               | Kelvin                       |
| Å               | Angstrom                     |
| Hz              | Hertz                        |
| $\chi^2$        | Chi-square                   |
| $\epsilon$      | Dielectric Permittivity      |