PHASE DIAGRAM, CRYSTAL STRUCTURE AND STRUCTURE PROPERTY CORRELATIONS IN $(1-x)Ba(Cu_{1/3}Nb_{2/3})O_3-(x)PbTiO_3$ CERAMICS

Thesis submitted in partial fulfillment for the Award of degree

Doctor of Philosophy

By

Krishna Prajapati

SCHOOL OF MATERIALS SCIENCE AND TECHNOLOGY
INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI – 221005
INDIA

Roll No. 17111006

2023

Dedicated to…

My Beloved Parents

(Smt. Rajkumari & Shri Sanwer 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)

भारतीय प्रौद्योगिकी संस्थान
काशी हिन्दू विश्वविद्यालय
INDIAN INSTITUTE OF TECHNOLOGY
BANARAS HINDU UNIVERSITY

CERTIFICATE

It is certified that the work contained in the thesis titled "***Phase Diagram, Crystal Structure and Structure Property Correlations in*** $(1\text{-}x)Ba(Cu_{1/3}Nb_{2/3})O_3\text{-}(x)PbTiO_3$ ***Ceramics***" by "***Krishna Prajapati***" has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy and SOTA for the award of Ph.D. Degree.

Date: 21-06-2023
Place: Varanasi

Signature:
(Dr. Akhilesh Kumar Singh)
Supervisor
(Associate Professor & Coordinator)
School of Materials Science & Technology,
IIT(BHU), Varanasi

Associate Professor/सह-आचार्य
School of Materials Science & Technology/पदार्थ विज्ञान एवं प्रौद्योगिकी स्कूल
Indian Institute of Technology/भारतीय प्रौद्योगिकी संस्थान
(Banaras Hindu University), Varanasi/काशी हिन्दू विश्वविद्यालय, वाराणसी

भारतीय प्रौद्योगिकी संस्थान
काशी हिन्दू विश्वविद्यालय

INDIAN INSTITUTE OF TECHNOLOGY
BANARAS HINDU UNIVERSITY

UNDER TAKING BY THE CANDIDATE

I, Krishna Prajapati, a research scholar under the supervision of Dr. Akhilesh Kumar Singh, Associate Professor, School of Materials Science and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi, give undertaking that the thesis titled "*Phase Diagram, Crystal Structure and Structure Property Correlations in* $(1\text{-}x)Ba(Cu_{1/3}Nb_{2/3})O_3\text{-}(x)PbTiO_3$ *Ceramics*" submitted by me for the degree of Doctor of Philosophy is a record of first-hand research work done by me during the period of study.

I avail myself to responsibility such as, an act will be taken on behalf of me, mistakes, errors of facts, and misinterpretations are of course entirely my own.

Date. 21-06-2023

Place: Varanasi

Krishna Prajapati
(Krishna Prajapati)

भारतीय प्रौद्योगिकी संस्थान
काशी हिन्दू विश्वविद्यालय

INDIAN INSTITUTE OF TECHNOLOGY
BANARAS HINDU UNIVERSITY

DECLARATION OF THE CANDIDATE

I, **Krishna Prajapati**, certify that the work embodied in this Ph.D. thesis is my own bona fide work and carried out by me under the supervision of Dr. Akhilesh Kumar Singh for a period from July 2017 to June 2023 at the School of Materials Science and Technology, Indian Institute of Technology, (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc. reported in the journals, books, magazines, reports, dissertations, thesis, etc., or available at websites and included them in this Ph. D. thesis and have not cited as my own work.

Date: 21-06-2023
Place: Varanasi

Krishna Prajapati
Signature of the Student
(Krishna Prajapati)

CERTIFICATE BY THE SUPERVISOR

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

(Dr. Akhilesh Kumar Singh)
Supervisor
Associate Professor/सह-आचार्य
School of Materials Science & Technology/पदार्थ विज्ञान एवं प्रौद्योगिकी स्कूल
Indian Institute of Technology/भारतीय प्रौद्योगिकी संस्थान
(Banaras Hindu University), Varanasi/काशी हिन्दू विश्वविद्यालय, वाराणसी

Coordinator
Coordinator/समन्वयक
School of Materials Science & Technology/पदार्थ विज्ञान एवं प्रौद्योगिकी स्कूल
Indian Institute of Technology/भारतीय प्रौद्योगिकी संस्थान
(Banaras Hindu University), Varanasi/काशी हिन्दू विश्वविद्यालय, वाराणसी

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis: **"Phase Diagram, Crystal Structure and Structure Property Correlations in $(1-x)Ba(Cu_{1/3}Nb_{2/3})O_3-(x)PbTiO_3$ ceramics"**

Name of the Student: **Krishna Prajapati**

Copyright Transfer

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University) all rights under copyright that may exist in and for the above thesis submitted for the award of the "Ph. D. degree".

Krishna Prajapati
Signature of the Student
(Krishna Prajapati)

Date: 21-06-2023
Place: Varanasi

Note: However, the author may reproduce or authorize others to reproduce materials extracted verbatim from the thesis or derivative of the thesis for author's personal use provided that the source and the Institute's copyright notices are indicated.

ACKNOWLEDGEMENTS

It is simply impossible to imagine this odyssey of getting a doctoral degree without the assistance, guidance and support of my teachers, colleagues, family and friends. Although my adequate expression of gratitude for their contribution is also equally impossible to summarise in a few pages, I would still try to do that by mentioning their names. At this moment of accomplishment, first of all, I would like to pay homage to the founder of Banaras Hindu University, Pandit Madan Mohan Malvia ji, who made this glorious temple to appreciate spiritual, technical and scientific knowledge about this vast existing universe.

I am extremely grateful to my mentor and supervisor, Dr. Akhilesh Kumar Singh, Asso. Prof. and Co-ordinator, School of Materials Scirnce and Technology [SMST], Indian Institute of Technology (Banaras Hindu University) [IIT(BHU)] for his guidance throughout the journey. I am very thankful for his scholarly suggestions, which will remain with me as an inexhaustible source of scientific learning throughout my life. His approach of encouragement and the stress-free environment he created in the laboratory have made me a far more confident and independent scientist than I was a few years ago.

I want to thank my RPEC committee members, Dr. Amritanshu Pandey, Asso. Prof., Department of Electronics and Dr. Sanjay Singh, Asst. Prof., SMST for their advice and instructions along the way. I would like to express my gratitude to Dr. Chandan Upadhyay, Asst. Prof. SMST for extending his laboratory facilities. I would also like to thank the faculty members of the School (SMST) Prof. Rajiv Prakash, Prof. Pralay Maiti, Dr. Chandana Rath, Dr. Bhola Nath Pal, Dr. Ashish Kumar Mishra, Dr. Shrawan Kumar Mishra, Dr. Nikhil Kumar and Dr. Ravi Panwar for the valuable discussions and suggestions given by them during seminars and otherwise. I would also like to thank former faculty of the School, Prof. Dhananjay Pandey (Institute Prof.), Prof. Jitendra Kumar (Visiting Prof.), Dr. Sri Ram Singh (Visiting Prof.) and Dr. Ashish Kumar Singh (DST INSPIRE Faculty) for their teachings.

I gratefully acknowledge my Institute IIT(BHU), Varanasi for providing me with the necessary funding and fellowship to pursue the research work. I acknowledge Central Instrument Facility, IIT(BHU) for providing various instrumental facilities for research work. I am also thankful to Saha Institute of Nuclear Physics, West Bengal and Jawaharlal Nehru Centre for Advanced Scientific Research, Bengaluru, for facilitating the synchrotron diffraction facility at Photon Factory (PF), High Energy Accelerator Research Organization (KEK), Japan and the Department of Science and Technology, India for financial support in doing so. I would like to acknowledge Dr. Gouranga Manna, Mr. Pintu, Mr. Sabhyasachia and Mr. Shubhadip for helping in the high temperature synchrotron XRD expeminents at the synchrotron facility, PF, KEK, Japan.

I would also like to acknowledge my seniors, Dr. Parmanand Jena (ex-Institute Post-Docterate Fellow), Dr. Vijyeta Pal (Chanakya Post-Docterate Fellow) and Dr. Dinesh Kumar (ex-RA), Dr. Shushil Kumar, Dr. Narendra Kumar Singh, Dr. Chandra Bhal Singh, Dr. Monika Singh, Mr. Pragyanand Prajapati and Mr. Ankit Dwivedi for scientific discussions. I am indebted to my friends, Ms. Pooja Sonkar, Dr. Shanu Mishra and Dr. Debarati Pal, for always being there and bearing the good and bad times with me during my PhD. I am thankful to my colleagues Dr. Priya Singh, Dr. Shweta Pal, Dr. Shubhajit Jana, Dr. Shivam Tiwari, Mr. Manish Yadav, Mr. Abhay Narayan Singh, Mr. Pravesh Yadav, Dr. Nila Pal, junior work fellows Mr. Rajnikant and junior labmates Mr. Satyendra Kumar Satyarthi, Mr. Vishwa Pratap Singh, Ms. Srishti Paliwal, Ms. Deep Mala, Mr. Prosun Mondal, Ms. Sadhna Yadav and M.tech project

students Mr. Satnam Singh Khanuja, Mr. Kamlesh Choudhary, Jai Kishan Pratap Singh and Praveen Jais for providing an encouraging and friendly environment. I am thankful to all non-teaching staff of the School for their cooperation at all levels.

I am very grateful for being loved and brought up by my grandparents Late Smt. Godavri Devi and Late Shri Bansilal Prajapati. I express my indebtedness to my parents, Smt. Rajkumari Prajapati (who has loved me unconditionally) and Shri Sanwer Lal (who has been the source of my inspiration), and my parents in-law Smt. Lalita Prajapat (who stood by my side in every situation and was sure of my PhD persuasion when no one was) and Sri Govind Lal Prajapat (whose affection and care have been incredible). I want to express my deep gratitude to my wonderful husband, Dr. Manish Kumar Prajapat, who has shown me nothing but love and support throughout my life and made my doctorate journey seem like walking on roses. I cannot imagine having completed my PhD without being supported by a father figure, my bother Dr. Rohit Prajapati, who also started his PhD journey at IIT Madras in the same period as mine. He constantly had my back in all the ups and down of PhD and guided and suggested me whenever I needed (be it 3 AM or 3 PM). Without thanking my sister in-laws, Mrs. Kiran Prajapati and Mrs. Madhu Prajapati, for their support, this recognition would be lacking. I am thankful to my entire family, including all my brothers and sisters and their spouses, especially my brothers-in-law, Mr. Arun Kumar Prajapat and Mr. Sanket Kumar Prajapat. I would like to thank Mr. Dayamay Roy, Mrs. Sheela Roy, Dr. Shilpi Roy, Dr. Vipul Srivastawa, Mr. Deborshi Roy, Mr. Munnu Lal, Mrs. Pratibha Singh, Ms. Kanchan Singh, Mr. Neeraj Singh, Ms. Isha Singh and Mr. Aditya Singh for making this journey beautiful by being the family I needed at Varanasi.

I am also thankful to all whom I could not mention here and who helped me directly or indirectly throughout the PhD duration.

Finally, I am grateful to the Almighty God Shiva and his Kashivishwanath Dham for giving me the strength to face all the challenges along the journey.

(Krishna Prajapati)

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 $Pb(Zr_xTi_{1-x})O_3$, $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-(x)PbTiO_3$ 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 $(1-x)Ba(Cu_{1/3}Nb_{2/3})O_3-(x)PbTiO_3$ 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 $Ba(Cu_{1/3}Nb_{2/3})O_3$ and $PbTiO_3$. 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)$Ba(Cu_{1/3}Nb_{2/3})O_3$-(x)$PbTiO_3$ 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)$Ba(Cu_{1/3}Nb_{2/3})O_3$-(x)$PbTiO_3$ 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_2 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 $Ba(Cu_{1/3}Nb_{2/3})O_3$ 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 $(1-x)Ba(Cu_{1/3}Nb_{2/3})O_3-(x)PbTiO_3$ 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*-3*m* for $0.05 \leq x \leq 0.55$), coexistence of cubic and tetragonal structures ('*Pm*-3*m* + *P*4*mm*' for $0.59 \leq x < 0.62$), coexistence of two tetragonal structures ('*P*4*mm* + *P*4*mm*' for $0.62 \leq x < 0.65$), coexistence of monoclinic and tetragonal structures ('*Pm* + *P*4*mm*' for $0.65 \leq x \leq 0.85$), coexistence of two tetragonal structures ('*P*4*mm* + *P*4*mm*' 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 MnO_2 additive on a selected composition (0.38)$Ba(Cu_{1/3}Nb_{2/3})O_3$-(0.62)$PbTiO_3$, 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 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 2.5pC/N to 72pC/N has been observed for a typically 1 weight percent of MnO_2 additive in (0.38)$Ba(Cu_{1/3}Nb_{2/3})O_3$-(0.62)$PbTiO_3$.

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.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

T_C	Curie Temperature
MPB	Morphotropic Phase Boundary
PPB	Polymorphic Phase Boundary
BCN	$Ba(Cu_{1/3}Nb_{2/3})O_3$
PT	$PbTiO_3$
RT	Room Temperature
XRD	X-Ray Diffraction
NPR	Nano polar region
(1-x)BCN-(x)PT	$(1-x)Ba(Cu_{1/3}Nb_{2/3})O_3-(x)PbTiO_3$

NOTATION

Symbols

G_{tf}	Goldschmidt tolerance factor
K	Kelvin
Å	Angstrom
Hz	Hertz
χ^2	Chi-square
ε	Dielectric Permittivity