Development of Bi-Based Lead-Free Piezoelectric Ceramics for High Temperature Applications

THESIS SUBMITTED IN PARTIAL FULFILLMENT

FOR THE AWARD OF DEGREE

DOCTOR OF PHILOSOPHY

By

Srishti Paliwal

School of Materials Science and Technology
Indian Institute of Technology
(Banaras Hindu University)
Varanasi - 221005, India

Roll No: 19111005 **2024**

"The important thing is not to stop questioning. Curiosity has its own reason for existing".

ALBERT EINSTEIN

DEDICATED TO.....

MY LOVING FAMILY

& FRIENDS

भारतीय
प्रौद्योगिकी
संस्थान
काशी हिन्दू विश्वविद्यालय

IIT INDIAN INSTITUTE OF TECHNOLOGY
BANARAS HINDU UNIVERSITY

CERTIFICATE

It is certified that the work contained in the thesis titled **"Development of Bi-Based Lead-Free Piezoelectric Ceramics for High Temperature Applications"** by **"Srishti Paliwal"** 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: 29/June/2024
Place: Varanasi

Signature: AKSingh

(Dr. Akhilesh Kumar Singh)
Supervisor
(Professor & Coordinator)
School of Materials Science & Technology,
IIT(BHU), Varanasi-221005

Professor/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

IIT INDIAN INSTITUTE OF TECHNOLOGY
BANARAS HINDU UNIVERSITY

DECLARATION OF THE CANDIDATE

I, Srishti Paliwal, certify that the work embodied in this Ph.D. thesis is my own bonafide work and carried out by me under the supervision of Professor Akhilesh Kumar Singh for a period from July 2019 to June 2024 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 wilfully 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: 29/June/2024
Place: Varanasi

(Srishti Paliwal)

CERTIFICATE BY THE SUPERVISOR

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

AKSingh

(Dr. Akhilesh Kumar Singh)
Supervisor
(Professor & Coordinator)
School of Materials Science & Technology,
IIT(BHU), Varanasi-221005

Professor/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

AKSingh

Coordinator of the School

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: "Development of Bi-Based Lead-Free Piezoelectric Ceramics for High Temperature Applications"

Name of the Student: Srishti Paliwal

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 "Doctor of Philosophy".

Date: 29/June/2024
Place: Varanasi

Signature of the Student
(Srishti Paliwal)

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

Firstly, I extend my deepest gratitude to my esteemed supervisor, Professor Akhilesh Kumar Singh, for his invaluable guidance, insightful suggestions, and unwavering encouragement throughout my Ph.D. journey. His faith in my ability to work independently and his support in selecting research problems aligned with my interests have significantly boosted my confidence as a researcher. His enthusiasm, patience, and kindness have been pivotal during challenging times.

I am sincerely thankful to the faculty members of the School of Materials Science and Technology, including Prof. Dhananjai Pandey, Prof. Rajiv Prakash, Prof. Pralay Maiti, Prof. Chandana Rath, Dr. Chandan Upadhyay, Dr. Bhola Nath Pal, Dr. Ashish Kumar Mishra, Dr. Shrawan Kumar Mishra, Dr. Sanjay Singh, Dr. Nikhil Kumar, Dr. Ravi, and Dr. Udayshankar, for their invaluable suggestions and support. Special thanks to Prof. Rajeev Kumar Singh, Department of Electrical Engineering, IIT (BHU), for his encouragement and support as an external RPEC member.

I acknowledge the Central Instrument Facility (CIF) at IIT (BHU) for providing access to essential experimental facilities.

I am deeply grateful to my labmates, Dr. Vijeyta Pal, Dr. Monika Singh, Dr. Pragyan Prajapati, Dr. Krishna Prajapati, Dr. Vishwa Pratap Singh, Mr. Ankit Dwivedi, Ms. Pooja Sonkar, Mr. Satyendra Kumar Satyarthi, Ms. Deep Mala, Mr. Prosun Mondal, and Ms. Sadhana Yadav, for their unwavering cooperation and camaraderie.

My heartfelt thanks go to my friends and colleagues, Ms. Sudepta Bauri, Ms. Swikriti Tripathi, Mr. Sudarshan Sarkar, Mr. Ravi Singh, Mr. Akhilesh Yadav, Mr. Rohit Jha and Mr. Amit Bar for their moral support and suggestions.

I owe a profound debt of gratitude to my beloved parents (Mrs. Mukta Paliwal and Mr. Rajesh Paliwal), my grandparents (Late Shri Haribhau Paliwal, Smt. Sushila Devi, Late Shri Maheshanand Kala and Smt. Raji Dev), my siblings (Mrs. Megha Paliwal, Ms. Anjali Paliwal, Mr. Aditya Paliwal) and my brother-in-law (Mr. Rakesh Dhoundiyal) for their unconditional love and support. I am extremely grateful to Mr. Sushant Batra for his patience, unwavering support, and love throughout this journey. I also appreciate Mr. Piyush Nainwal and Manisha Chauhan for their constant encouragement.

I express my appreciation to all technical and non-technical staff at IIT (BHU) for their assistance during my stay on the campus.

I acknowledge the financial assistance provided by the Government of India through the Prime Minister's Research Fellowship. I am also thankful to the Department of Science and Technology, India, and IIT (BHU) for additional financial support.

In conclusion, the journey towards my doctoral degree has been made possible by the invaluable assistance, guidance, and support of my mentors, colleagues, family, and friends. Though words may fall short, this acknowledgment is a humble attempt to express my deep appreciation to each one of you and also to all those not mentioned here.

Sincerely

Srishti Paliwal

TABLE OF CONTENTS

List of Figures

List of Tables

List of Symbols and Abbreviations

α	Absorption coefficient
λ	Wavelength
T_C	Curie temperature
$\tan\delta$	Loss tangent (Dielectric loss)
ε'	Real part of the permittivity
ε''	Imaginary part of the permittivity
d_{33}	Piezoelectric charge coefficient measured along poling direction
E	Electric field
E_a	Activation energy
E_c	Coercive field
E_g	Optical band gap
γ	Diffusivity constant
Ω	Resistance
θ	Theta (degrees)
$\chi 2$	Chi square (Goodness of Fit)
k_B	Boltzmann constant
T	Temperature
T_m	Transition Temperature at the maxima of temperature dependent dielectric constant plot
T_{VF}	Vogel Fulcher temperature

τ	Relaxation time
VFT	Vogel Fulcher Tammann
XRD	X-ray Diffraction
FTIR	Fourier Transform Infrared
Vis	Visible light
UV	Ultraviolet radiation
DRS	Diffuse Reflectance Spectroscopy
SEM	Scanning Electron Microscope
EDS	Energy Dispersive X-ray Spectroscopy
XPS	X-ray Photoemission Spectroscopy
PUND	Positive Up Negative Down
PL	Photo Luminescence
MPB	Morphotropic Phase Boundary
FE	Ferroelectric
DC	Direct Current
PZT	Lead Zirconate, $PbZr_xTi_{1-x}O_3$
BFO	Bismuth Ferrite, $BiFeO_3$
BT	Barium Titanate, $BaTiO_3$
BF-BT	Bismuth Ferrite-Barium Titanate, $BiFeO_3$ -$BaTiO_3$
KNN	Potassium Sodium Niobate, $K_{0.5}Na_{0.5}NbO_3$
BNT	Bismuth Sodium Titanate, $Bi_{0.5}Na_{0.5}TiO_3$
BIT	Bismuth Titanate, $Bi_4Ti_3O_{12}$
PNR	Polar Nano Region
ε	Permittivity

P_s	Saturated Polarization
P_r	Remnant Polarization
E_c	Coercive Electric Field