

भारतीय  
प्रौद्योगिकी  
संस्थान  
काशी हिन्दू विश्वविद्यालय



INDIAN  
INSTITUTE OF  
TECHNOLOGY  
BANARAS HINDU UNIVERSITY





# **LiNbO<sub>3</sub> based Environmental - friendly high T<sub>c</sub> Ceramics for Electrical Energy Storage and Device Applications**



**Thesis Submitted in partial fulfillment for the  
Award of Degree**

***Doctor of Philosophy***

**By**

***Satyendra Kumar Satyarthi***

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

**Roll No. 17031503**

**2024**



*Dedicated*

*to*

*“My Family”*



*“Nation Builders”*



ॐ ॐ ॐ ॐ ॐ, ॐ ॐ ॐ ॐ ॐ ।  
ॐ ॐ ॐ ॐ ॐ, ॐ ॐ ॐ ॐ ॐ ॥

कोनू हासो कि मानन्दो, निच्चं पज्जलिते सति ।  
अंध कारेन ओनद्धा, पदीपं न गवेसथ ॥

अर्थात्

जहाँ प्रतिक्षण सब कुछ जल (नष्ट हो रहा ) रहा हो,  
वहां कैसा आमोद कैसा प्रमोद (हसीं, आनंद ) ?  
ऐ (अविद्या रूपी) अन्धकार से घिरे भोले लोगों,  
तुम (ज्ञानरूपी ) प्रकाश (प्रदीप) की खोज क्यों नहीं करते ?



सन्दर्भ : भगवान गौतम बुद्ध (सुकिती ) की वाणी, गाथा संख्या १४६ (146), धम्मपद





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 "*LiNbO<sub>3</sub> based Environmental-friendly high T<sub>c</sub> Ceramics for Electrical Energy Storage and Device Applications*" by "*Satyendra Kumar Satyarthi*" 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, Candidacy and SOTA for the award of Ph.D. degree.

Date. 31/07/2024

Place: Varanasi

(Dr. Akhilesh Kumar Singh)

Supervisor

Professor

School of Materials Science & Technology

IIT (BHU), Varanasi

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



INDIAN  
INSTITUTE OF  
TECHNOLOGY  
BANARAS HINDU UNIVERSITY

## DECLARATION BY THE CANDIDATE

I, **Satyendra Kumar Satyarthi**, certify that the work embodied in this Ph.D. thesis is my own bonafide work carried out by me under the supervision of **Professor Dr. Akhilesh Kumar Singh** for a period from **December 2017** to **July 2024** at the **School of Materials Science and Technology**, Indian Institute of Technology (Banaras Hindu University), Varanasi. The matter embodied in this Ph.D. 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 journals, books, magazines, reports dissertations, thesis, *etc.*, or available at websites and have not included them in this thesis and have not cited as my own work.

Date: 31/07/2024

Place: Varanasi

(Satyendra Kumar Satyarthi)

## 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  
Professor

School of Materials Science & Technology  
IIT (BHU), Varanasi

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

School of Materials Science & Technology  
IIT (BHU), Varanasi

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



## COPYRIGHT TRANSFER CERTIFICATE

**Title of the Thesis:** "LiNbO<sub>3</sub> based Environmental-friendly high T<sub>c</sub> Ceramics for Electrical Energy Storage and Device Applications".

**Candidate's Name:** Satyendra Kumar Satyarthi

### Copyright Transfer

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

Date: 31/07/2024

Place: Varanasi

(Satyendra Kumar Satyarthi)

**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 notice are indicated.



## ACKNOWLEDGMENTS

---

Very firstly, I would like to express my heartfelt thanks and gratitude to my supervisor **Prof. Dr. Akhilesh Kumar Singh**, School of Materials Science & Technology, IIT (BHU), Varanasi, for his guidance and support throughout my Ph.D. journey. I would also like to be thankful to him for providing me the opportunity to join his lab and also provide a free environment and freedom of the selection of research work as well. He always supported me whenever I needed him to, sort out academic and non-academic issues, and encouraged me. I would also be thankful to him for providing the freedom to access the lab whenever I need other than institute timing. Further, I would like to thank my previous supervisor, **Dr. Akansha Dwivedi**, former assistant professor of ceramic engineering at IIT (BHU), for her support and guidance during the initial phase of my Ph.D. journey.

I would also like to thank the faculty members of the SMST, Prof. Rajiv Prakash, Prof. Pralay Maiti, Prof. Chandana Rath, Dr. Bhola Nath Pal, Dr. Chandan Upadhyay, Dr. A. K. Mishra, Dr. S. K. Mishra, Dr. Sanjay Singh, Dr. Nikhil Kumar, Dr. Ravi Panwar and Dr. Uday Shankar for discussion and guidance during seminars and coursework studies. I am sincerely thankful to my RPEC members, Dr. Ashutosh Dubey (Associate Prof and Head, Ceramic Engineering, IIT (BHU) and Dr. Shrawan Kumar Mishra (Associate Prof, SMST), for their kind support, encouragement, and guidance.

I would also like to thank the faculty members of Ceramic Engineering, Prof. Devendra Kumar, Prof. Om Prakash, Dr. Santanu Das, Dr. M. R. Majhi, and others. I would like to thank Prof. RamaNand Rai (Department of Chemistry, Institute of Science, Banaras Hindu University), Dr. Satish Kanaujia (Asst. Prof. Department of Humanistic Studies, IIT-BHU), Dr. Kesheo Prasad, (Asst. Prof. Department of Civil engineering, IIT-BHU), Dr. Bhanu Pratap Singh, (Senior Principal Scientist & Professor, CSIR-NPL, New Delhi), for their kind motivation, support and encouragement in the research work as well as in life.

I would like to thank My M.Tech thesis supervisor **Prof. Dr. Nitin Kumar Puri**, (Professor, DTU (DCE and Director NIELIT, Patna), New Delhi and My B.Tech thesis supervisor **Dr. Amit Kumar Rai**, (Research Professor at Intelligent System Laboratory, Busan, South Korea) and Prof. Dr. Sanjeev Kumar, (Head, Department of Applied Physics,

PEC, Chandigarh), Dr. Shobhna Dhiman, (Associate Professor, PEC, Chandigarh) for their support in my academic journey.

I gratefully acknowledge all CIF, IIT (BHU) and Department of Metallurgical Engineering, IIT (BHU), Varanasi, for providing various instrumental facilities, especially Lalit Kumar Singh, Senior Technical Superintendent, Department of Metallurgical Engineering, IIT (BHU).

On this occasion, I would like to pay tribute to my teacher, Respected Satyadev Trigunayat (He was not my first teacher, but I don't remember any teacher before him), Principle B.N.B.T Convent School, Gorakhpur, and his family, whose teachings still play an important role in my life. On this occasion, I would like to pay tribute to my last school class teacher, Respected Shashi Bhushan Srivastava (My last class teacher and my school senior), Lecturer of Physics, Mahatma Gandhi Inter College, Gorakhpur.

I would also like to thank the BHU Healthcare Care Center for its facility and medication and Dr. Surjit Singh (RDSO, LKO) for providing medical help whenever I needed it.

I take this opportunity to express my heartfelt thanks to my seniors Dr. Prem Prakash (Ceramic Engineering, IIT BHU), Dr. Chandrabhal Singh, Dr. Dinesh Kumar, Dr. Ankit Dwivedi and Dr. Vinod Kumar (Chemistry, IIT-BHU) for their technical support, emotional support, and encouragement from time to time whenever I required it. I would also like to thank my B. Tech and M. Tech seniors like Dr. Kamal Arora (Researcher at University of Missouri, United States), Dr. Vinay Kumar (Associate Professor, Graphic Era University, India), Dr. Ratneshwar Kumar Ratnesh (Asst. Prof.), Sunil Kumar (Manager at Larsen & Toubro) for their support in my life.

I would like to thank to one of my as a younger brother Dr. Vishwa Pratap Singh, (Research Associate at Bilkent University, Ankara), (who is also my Engineering degree junior) for his continuous support and encouragement in every aspect of my life from 2011, I would also like to thanks Manish Meena (SVNIT, Immigration officer, New Delhi) for their motivation encouragement and support in my life, I would also like to thanks Dipesh Jadhav (SVNIT, Dy. Engineer, GSECL), Bharat (SVNIT, Dy. Exc. Engineer, at GoG.), some of my others very close friends like Hemant Kumar (Project Engineer, Universidad de Tarapaca, Chile), Hemant Kumar (PhD, ICAR), Anil Kumar (Co-Founder, Sologix energy), Vivek Kumar Singh (PhD Scholar at MNIT, Allahabad.), Sudhansu Gautam (JE, AIIMS Delhi),

Jayendra Pratap (M.G.I.C.), Mukesh Kumar, Surya Kant Sharma (M.G.I.C.), Jaikishan (Sandip) Sonkar, Avinash Srivastav, Deshraj Sanawar and Vijaya Guguloth, Diksha and Soniya Gautam and her husband, for being in my life and providing support whenever needed.

I am indebted to my parents, Respected Gyanti Devi and Respected Sudarshan Prasad Satyarthi (Ret. Teacher) and my elder brothers, Dr. Sangh Priy Satyarthi (M.O. NRHM) and Respected Satya Prakash Satyarthi, (J.E. UPRVNL), whose many sacrifices and never-give-up attitude prepared me mentally to succeed at this level. On this occasion, I want to pay my deepest respects to my late grandfather, Respected Swami Nath (Neta Ji, whom I never got to meet) and late grandmother Respected Piyari Devi. They fought through many obstacles and firmly established the foundation of education in our family. At this moment, I also pay tribute to my forefathers, great-grandfather Respected Mallu and great-great-grandfather Respected Sahagun. I would like to express my heartfelt appreciation to Respected Arti (Didi) and Late. Respected Rajendra Prasad (Jija ji) and their family for support throughout my life. I would like to thank Amreen for her continuous support in the ups and downs of my life.

I would like to thank Institute seniors, Juniors, PhD batch mates, and lab mates like Dr. Vijyeta Pal, Dr. Pragyan Prajapati, Dr. Krishna Prajapati, and Deep Mala, Pooja Sonkar, Srishti Paliwal, Prosun Mondal, Sadhana, Harish Verma (Physics), Gaurav Singh (Pharma), Dr. Harsh Jain (Ceramic), Abhay Kumar (Civil), and all belonging to SMST and Ceramic Engineering, IIT-BHU, Varanasi, for providing their words of inspiration and encouragement. I would like to thank IIT-BHU Gymkhana family members like Gautam Rai (Coach-Cricket), Kishan Kumar and others.

I am also thankful to all, whom I could not mention here, who helped me directly or indirectly throughout the work. I am grateful to all the institute's non-teaching staff for their cooperation at all levels.

I take great pleasure in conveying my indebtedness to IIT-BHU, Varanasi, and MHRD for granting me an Institute Fellowship and providing all the facilities of the Departments/Schools/Centers to accomplish this research work.

Varanasi, Uttar Pradesh, India

(Satyendra Kumar Satyarthi)



<b>LIST OF FIGURES.....</b>	<b>xxiii</b>
<b>LIST OF TABLES.....</b>	<b>xxix</b>
<b>LIST OF SYMBOLS &amp; ABBREVIATIONS.....</b>	<b>xxxii</b>
<b>PREFACE.....</b>	<b>xxxiii</b>
<b>Chapter 1: Introduction and literature review.....</b>	<b>1</b>
1.1 Energy requirement.....	1
1.2 Benefits of stored energy.....	2
1.3 Motivation (Electrical energy storage and consumptions) .....	3
1.4 Foundation.....	7
1.5 What is Perovskite?.....	8
1.5.1 The historical background of Perovskite.....	8
1.5.2 Distorted Perovskite Structure.....	10
1.5.3 Applications of Perovskite Oxides.....	11
1.6 Electro Ceramic Materials.....	12
1.7 Composite ceramic material.....	14
1.7.1 Characteristics of Ceramic composites.....	14
1.7.2 Types of composite Ceramic materials.....	15
1.7.3 Applications of composite ceramics.....	15
1.8 Capacitors.....	16
1.9 Dielectric Materials.....	17
1.10 Polarization.....	18
1.10.1 Electronics Polarization.....	20
1.10.2 Ionic polarization.....	21
1.10.3 Orientation polarization.....	22
1.10.4 Space Charge Polarization.....	22
1.11 Ferroelectric Materials.....	23
1.11.1 Origin of Ferroelectricity.....	25

1.11.2 Saturation Polarization.....	26
1.11.3 Remnant Polarization.....	27
1.12 Electrical Energy storage.....	27
1.13 Photoluminescence materials.....	29
1.13.1 Intrinsic and Extrinsic luminescent materials.....	30
1.14 Properties of Lithium Niobate.....	32
1.14.1 General Structure of Lithium Niobate.....	32
1.14.2 Literature Survey related to LiNbO <sub>3</sub> materials.....	33
1.15 Objectives of the Present work.....	49
1.16 Scope of this Thesis.....	52
References.....	53
<b>Chapter 2: Experimental and Characterization techniques.....</b>	<b>61</b>
2.1 Introduction.....	61
2.2 List of Precursor/Chemical .....	62
2.3 Synthesis of materials.....	63
2.3.1 Solid state reaction method via High energy ball mill (Mechanochemical process)..	63
2.3.2 Calcination Process.....	65
2.3.3 Pellets formation (Pressing) and Sintering of Samples.....	65
2.3.4 Schematic diagram for the Synthesis and Sintering of materials.....	67
2.4 Characterization Techniques.....	67
2.4.1 Powder X-ray diffraction (XRD) .....	68
2.4.2 X-ray photoelectron spectroscopy (XPS) .....	70
2.4.3 Scanning Electron Microscopy.....	72
2.4.4 Ultra Violet- Visible spectroscopy.....	73
2.4.5 Fourier transform infrared spectroscopy.....	76
2.4.6 Electric and Dielectric Measurement.....	78
2.4.7 Polarization-Electric field hysteresis loop characterization.....	79
2.4.8 Photoluminescence spectroscopy.....	80
2.4.9 Thermogravimetric analyzer.....	81

2.5 Conclusion.....	83
---------------------	----

**Chapter 3: Enhanced Dielectrics, Ferroelectric and Optical Properties of Lithium Niobate for High Temperature Applications Using Potassium Oxide (K<sub>2</sub>O) Additive...85**

3.1 Introduction.....	85
3.2 Experimental.....	88
3.3 Characterizations.....	89
3.4 Results and discussion.....	90
3.4.1 Crystal structure analysis.....	90
3.4.2 Morphological analysis.....	94
3.4.3 X-ray Photoelectron Spectroscopy Study.....	99
3.4.4 Fourier Transform Infrared spectroscopy.....	102
3.4.5 Thermogravimetric analysis.....	103
3.4.6 Optical Properties and band gap analysis.....	105
3.4.7 Photoluminescence properties.....	107
3.4.8 Dielectrics analysis.....	109
3.4.9 Polarization electric field analysis.....	112
3.5 Conclusions.....	116
References.....	117

**Chapter 4: Electrical and Optical Properties of Environmental Friendly Li<sub>(1-x)</sub>Sm<sub>x/3</sub>NbO<sub>3</sub> Ceramics for High Temperature Energy Storage Applications.....123**

4.1 Introduction.....	123
4.2 Experimental.....	125
4.3 Characterizations.....	126
4.4 Result and Discussion.....	127
4.4.1 Structural Analysis.....	127
4.4.2 Morphological Study.....	132
4.4.3 X-ray Photoelectron Spectroscopy Analysis.....	136

4.4.4 Fourier Transform Infrared Spectroscopy Analysis.....	139
4.4.5 Thermogravimetric analysis.....	140
4.4.6 UV-Vis Spectroscopy Analysis.....	142
4.4.7 Photoluminescence Analysis.....	144
4.4.8 Dielectric Analysis.....	148
4.4.9 Polarization and electric field characteristics Analysis.....	151
4.5 Conclusions.....	154
References.....	155

**Chapter 5: Investigation of Multifaceted Properties for Environment friendly (1-x)LiNbO<sub>3</sub>-x(Li<sub>0.5</sub>Dy<sub>0.5</sub>)TiO<sub>3</sub> Solid Solution.....161**

5.1 Introduction.....	161
5.2 Experimental.....	163
5.3 Results and discussion.....	165
5.3.1 Crystal structure analysis.....	165
5.3.2 Morphological analysis.....	168
5.3.3 Thermogravimetric analysis.....	171
5.3.4 X-ray Photoelectron Spectroscopy Study.....	172
5.3.5 Fourier transform infrared spectroscopy spectra (FTIR) analysis.....	174
5.3.6 UV-Vis Spectroscopy Analysis.....	176
5.3.7 Photoluminescence Spectroscopy Analysis.....	178
5.3.8 Dielectric analysis.....	181
5.3.9 Polarization-Electric field analysis.....	184
5.4 Conclusions.....	188
References.....	188

**Chapter 6: Conclusion and Future scope.....193**

6.1 Summary of the present work.....	193
6.2 Future Scope of this research work.....	196

List of Publications (Research Articles) .....	199
List of Publications (Book Chapters) .....	201
List of Attended Conference/Seminar/Workshop.....	203



## LIST OF FIGURES

Figure No.	Captions	Page No.
<b>Chapter 1</b>	<b>Introduction and literature review</b>	1
Figure 1.1	Various types of Energy and energy storage	1
Figure. 1.2	Various electrical energy sector based industries	3
Figure 1.3	Generation of estimated revenue in different years	4
Figure 1.4	Consumption percentage of electrical energy storage devices and applications in different part of globe	5
Figure 1.5	Simple Perovskite Stuructre	9
Figure 1.6	Classification of all type of Perovskite materials	10
Figure 1.7	Distroted Perovskite Stuructre (Orthorhombic)	11
Figure 1.8	A prototype of Parallel plate capacitor	17
Figure 1.9	Dielectric material in two different state (a) UnPolarized state of dielectric material (b) Polarized by an applied electric field	18
Figure 1.10	Phenomenon of Electronic polarization for $E = 0$ and $E \neq 0$ for a dielectric material	21
Figure 1.11	Phenomenon of Ionic polarization for $E = 0$ and $E \neq 0$ for a dielectric material	21
Figure 1.12	Phenomenon of Orientation polarization for $E = 0$ and $E \neq 0$ for a dielectric material	22
Figure 1.13	Phenomenon of Space Charge polarization for $E = 0$ and $E \neq 0$ for a dielectric material	23
Figure 1.14	Phenomenon of Ferroelectricity and Polarization-Electric Field loop in a dielectric material	26
Figure 1.15	Electric Displacement-Electric Field (D-E) loop	28
Figure 1.16	Stages of Charging and Discharging of capacitors	29
Figure 1.17	Phenomenon of photoluminescence in a photo-luminescent material	31
Figure 1.18	(a-b) Dielectric constant, (a) as a function of temperature at different frequencies, (b) Variation of ac conductivity with frequency	35
Figure 1.19	(a) Photoluminence spectra at room temperature of mesoporous and nonporous lithum niobate, (b) Magnetization as a function of magnetic	37

	field curve at different temperatures for mesoporous lithium niobate, (c) Variation of magnetization as a function of temperature under ZFC and FC conditions	
Figure 1.20	(a) Frequency dependent dielectric constant plots of LiNbO <sub>3</sub> in the temperature, (b) Range 403°–613°K. Arrhenius plot of LiNbO <sub>3</sub> showing two thermally activated conduction processes	38
Figure 1.21	(a) Various properties of ceramics, dielectric constant of at 10 kHz in the range of (b) –60–180 °C and (c) 280–580 °C.	39
Figure 1.22	Interdigital electrode transducer for surface acoustic wave (SAW) generation in lithium niobate	40
Figure 1.23	Histograms of distribution of piezo response signals for LiNbO <sub>3</sub> /SiO <sub>x</sub> /Si (line 1) and LiNbO <sub>3</sub> /Pt/Si (line 2) heterostructures	41
Figure 1.24	XRD patterns of doped and pure LiNbO <sub>3</sub> powders doped with different concentration of magnesium and calcined at 600 C for 3 h.	42
Figure 1.25	(a) Emission spectra of LN doped with Sc <sub>2</sub> O <sub>3</sub> at an excitation wave length of 370 nm. (b) Emission spectra of LN doped with Sc <sub>2</sub> O <sub>3</sub> at an excitation wavelength of 289 nm. (c) Variation of intensities in emission spectra of LN with Sc <sub>2</sub> O <sub>3</sub> . (d) Variation of intensities in emission spectra of LN with Lu <sub>2</sub> O <sub>3</sub> doping.	43
Figure 1.26	(a) Photoluminescence spectra for Cr-doped LiNbO <sub>3</sub> crystals, (b) Transmission spectra for undoped and Cr-doped LiNbO <sub>3</sub> crystals	44
Figure 1.27	Schematic configuration of a high temperature transducer and experimental setup.	45
Figure 1.28	(a) Piezoelectric ceramic transformer proposed by Rosen, (b) Piezoelectric transformer using a rotated Y-cut LiNbO <sub>3</sub> single crystal	46
Figure 1.29	Proposed model for apatite formation on LiTaO <sub>3</sub> powders in SBF	47
Figure 1.30	(a) Frequency dependent Dielectric constant, (b) Frequency dependent tangent loss, (c) Temperature dependent Dielectric constant, (d) Temperature dependent tangent loss, (e) Temperature dependent AC conductivity.	47
Figure 1.31	Schematic of the LN photonic-crystal EOM.	48
<b>Chapter 2</b>	<b>Experimental and characterization techniques</b>	61
Figure: 2.1	(a) High energy planetary ball mill Retsch PM400, (b) Horizontal section of High energy ball mill, (c) Schematic diagram of the mechanism inside the high energy ball mill.	65
Figure. 2.2	(a) Hydraullic Press Pellet Maker, (b)Green Pellet, (c) MgO Sealed Alumina Crucible, (d) Finale sintered Pellets.	66
Figure. 2.3	Schematic diagram of solid state reaction method for the materials sysntehsis.	67
Figure. 2.4.	(a) Regaku Miniflex Benchtop XRD Machine, (b) XRD Phenomenon based on Braggs Law, (c) XRD Pattern of a ceramic material.	70
Figure. 2.5	(a) XPS Instrument, (b) Schematic diagram of mechanism of XPS, (c) XPS Graph of a ceramic material.	71

Figure. 2.6	(a) FESEM Instrument (EVO - Scanning Electron Microscope MA15 / 18 CARL ZEISS Microscopy ltd), (b) Ray diagram for SEM, (c) The FESEM image of a Ceramic Material	73
Figure. 2.7	(a) UV Instrument (Jasco v-650), (b) Schematic diagram of UV-Visible spectroscopy, (c) UV Spectrum of Ceramic Materials.	75
Figure. 2.8	(a) FTIR Instrument (ThermoScientific Nicolet summit), (b) FTIR Pattern of ceramic materials, (c) Schematic Diagram of FTIR Instrument.	77
Figure. 2.9	(a) Impedance Analyzer (Keysight), (b) Ceramic sample with electroding, (c)Equivalent Circuit, (d) Dielectric Constant of ceramic materials.	79
Figure 2.10	(a)PE Analyzer Instrument (Radiant Technology), (b)Sample Holder with Si oil, (c) Schematic diagram of PE Analyzer, (d) PE Loop of ceramic materials.	80
Figure 2.11	(a)PL Instrument, (b)Schematic diagram of Photoluminescence spectroscopy, (c) PL Spectra of Ceramic materials.	81
Figure 2.12	(a) TGA Instrument, (b) Schematic diagram of TGA analyzer, (c) TGA Curve of a ceramic material.	82
<b>Chapter 3</b>	<b>Enhanced Dielectrics, Ferroelectric and Optical properties of Lithium Niobate for High Temperature Applications Using Potassium Oxide (K<sub>2</sub>O) Additive</b>	85
Figure. 3.1	Schematic unit cell of the pure lithium niobate drawn by VESTA software using the structural parameters obtained from Rietveld structure refinement	88
Figure. 3.2	(a-b) X-Ray diffraction pattern of LiNbO <sub>3</sub> (a) for Calcined powder at 750 °C (b) for sintered pellet at 1050 °C.	91
Figure. 3.3	X-Ray diffraction pattern of LiNbO <sub>3</sub> + x (wt%)K <sub>2</sub> O with varying composition of x	92
Figure. 3.4	(a-e) Le Bail structural Refinement fitting for LN + x (wt%)K <sub>2</sub> O	93
Figure. 3.5	(a-f) Scanning electron microscopic images of LN + x (wt%)K <sub>2</sub> O calcined powder, (d-f) Particle size distribution.	95
Figure. 3.6	(a-c) Energy-Dispersive X-ray Spectroscopy (EDS) spectra of LN + x (wt%)K <sub>2</sub> O calcined powder.	96
Figure 3.7	(a-e) Scanning electron microscopic images of LiNbO <sub>3</sub> with different concentration of K <sub>2</sub> O additive and histogram of the grain sizes (inset), (f) Bar diagram comparison of average grain sizes for various compositions.	98
Figure 3.8	(a-c) EDS Spectrum analysis of LiNbO <sub>3</sub> with different concentration of K <sub>2</sub> O additive	99
Figure 3.9	(a-k) X-ray photo electron spectra of various elements for pure LN, and LN with 2.72 wt% and 5.44 wt % K <sub>2</sub> O additive concentration.	101
Figure 3.10	FTIR Spectra for the pure LN, and LN with 2.72 wt% and 5.44 wt % K <sub>2</sub> O additive concentration.	102

Figure 3.11	(a) Thermograph of pure LN, and LN with 2.72 wt% and 5.44 wt% K <sub>2</sub> O additive, (b) Plot of ln(ln(1/Y)) vs 1000/T for, pure LN, (c) x = 2.72 wt% K <sub>2</sub> O, (d) x = 5.44 wt% K <sub>2</sub> O (d).	104
Figure 3.12	Histogram of activation energy in different temperature range for (a) LiNbO <sub>3</sub> (b) LN with 2.72 wt% K <sub>2</sub> O (c) LN with 5.44 wt% K <sub>2</sub> O.	105
Figure 3.13	(a) Absorption spectra; (b) Indirect band gap; (c) Direct band gap of LN with various concentration of K <sub>2</sub> O additive in the range (0.0 ≤ x (wt%) ≤ 5.44). (d) Variation of direct band gaps as a function of K <sub>2</sub> O additive concentration.	106
Figure 3.14	Photoluminescence spectra for LN with different concentration of K <sub>2</sub> O additive.	108
Figure 3.15	Photoluminescence spectra for LN with different concentration of K <sub>2</sub> O additive in 3D form.	109
Figure 3.16	(a-f) Temperature and frequency (100Hz to 100kHz) dependent dielectric behaviour of LN with different K <sub>2</sub> O additive concentration.	112
Figure 3.17	(a-e) Polarization-Electric field ferroelectric hysteresis loops for LN with different concentration of K <sub>2</sub> O additive, (f) Composition dependence of polarization at 70 kV/cm field.	115
<b>Chapter 4</b>	<b>Electrical and Optical Properties of Environmental Friendly Li<sub>(1-x)</sub>Sm<sub>(x/3)</sub>NbO<sub>3</sub> Ceramics for High Temperature Energy Storage Applications</b>	123
Figure 4.1	(a-b) X-Ray diffraction pattern of Li <sub>(1-x)</sub> Sm <sub>(x/3)</sub> NbO <sub>3</sub> (a) for Calcined powder at 800 °C for 12 hours (b) for sintered pellet at 1050 °C for 8 hours.	128
Figure 4.2	XRD patterns of Li <sub>(1-x)</sub> Sm <sub>(x/3)</sub> NbO <sub>3</sub> ceramics.	129
Figure 4.3	(a-f) Rietveld refinement of Li <sub>(1-x)</sub> Sm <sub>(x/3)</sub> NbO <sub>3</sub> .	130
Figure 4.4	(a-c) Crystal structure of Li <sub>(1-x)</sub> Sm <sub>(x/3)</sub> NbO <sub>3</sub> for x =0, 0.03, 0.05.	131
Figure 4.5	(a-f) Morphological SEM images of Li <sub>(1-x)</sub> Sm <sub>(x/3)</sub> NbO <sub>3</sub> .	133
Figure 4.6	(a-k) Elemental mapping and, (l) Grain size variation, of Li <sub>(1-x)</sub> Sm <sub>(x/3)</sub> NbO <sub>3</sub> with varying composition of x	134
Figure 4.7	(a-d) EDS Spectrum analysis of Li <sub>(1-x)</sub> Sm <sub>(x/3)</sub> NbO <sub>3</sub> with different concentration x.	135
Figure 4.8	(a-s): XPS elemental Analysis of Li <sub>(1-x)</sub> Sm <sub>(x/3)</sub> NbO <sub>3</sub> ceramics.	138
Figure 4.9	FTIR Spectra of Li <sub>(1-x)</sub> Sm <sub>(x/3)</sub> NbO <sub>3</sub> Ceramics.	140
Figure 4.10	Weight loss versus Temperature variation for Li <sub>(1-x)</sub> Sm <sub>(x/3)</sub> NbO <sub>3</sub> ceramics.	141
Figure 4.11	(a) Variation of absorption spectra of Li <sub>(1-x)</sub> Sm <sub>(x/3)</sub> NbO <sub>3</sub> for various compositions. (b) Indirect band gap of Li <sub>(1-x)</sub> Sm <sub>(x/3)</sub> NbO <sub>3</sub> (c) Direct band gap of Li <sub>(1-x)</sub> Sm <sub>(x/3)</sub> NbO <sub>3</sub> (d) Indirect band gaps of Li <sub>(1-</sub>	143

	$x$ ) $\text{Sm}_{(x/3)}\text{NbO}_3$ with composition variation (e) Direct band gaps of $\text{Li}_{(1-x)}\text{Sm}_{(x/3)}\text{NbO}_3$ with composition variation.	
Figure 4.12	(a) Photoluminescence spectra for $\text{Li}_{(1-x)}\text{Sm}_{(x/3)}\text{NbO}_3$ with composition (b) Variation of peak intensity of green, yellow and red band with varying composition of $\text{Li}_{(1-x)}\text{Sm}_{(x/3)}\text{NbO}_3$ (c) Variation of peak position of Green, Yellow and Red band with varying composition of $\text{Li}_{(1-x)}\text{Sm}_{(x/3)}\text{NbO}_3$ ceramics.	145
Figure 4.13	Intensities of Photoluminescence spectra for $\text{Li}_{(1-x)}\text{Sm}_{(x/3)}\text{NbO}_3$ with composition variation in 3D form.	146
Figure 4.14	(a-e) Permittivity vs Temperature and, (f-j) Tangent loss vs Temperature, with varying composition of $\text{Li}_{(1-x)}\text{Sm}_{(x/3)}\text{NbO}_3$ in the frequency range 100 Hz – 1MHz.	150
Figure 4.15	(a) Polarization to Electric field and (b) Remnant Polarization and Saturated Polarization with varying composition of $\text{Li}_{(1-x)}\text{Sm}_{(x/3)}\text{NbO}_3$ .	153
Figure 4.16	(a-e) P-E hysteresis loop showing the energy storage density and energy loss density and (f) Energy efficiency (%) with varying composition of $\text{Li}_{(1-x)}\text{Sm}_{(x/3)}\text{NbO}_3$ ceramics.	153
<b>Chapter 5</b>	<b>Investigation of Multifaceted Properties for Environment friendly (1-x)LiNbO<sub>3</sub>-x(Li<sub>0.5</sub>Dy<sub>0.5</sub>)TiO<sub>3</sub> Solid Solution</b>	161
Figure 5.1	XRD Pattern of (1-x)LiNbO <sub>3</sub> -x(Li <sub>0.5</sub> Dy <sub>0.5</sub> )TiO <sub>3</sub> ceramic for different composition (x)	166
Figure 5.2	Rietveld structure refined fits for (a) LiNbO <sub>3</sub> and (b) (1-x)LiNbO <sub>3</sub> -x(Li <sub>0.5</sub> Dy <sub>0.5</sub> )TiO <sub>3</sub> where x = 0.1.	167
Figure 5.3	Crystal structure of (1-x)LiNbO <sub>3</sub> -x(Li <sub>0.5</sub> Dy <sub>0.5</sub> )O <sub>3</sub> with mix phases; (a) Rhombohedral phase and (b) cubic phase.	168
Figure 5.4	Scanning electron microscopic images of (1-x)LiNbO <sub>3</sub> - x(Li <sub>0.5</sub> Dy <sub>0.5</sub> )TiO <sub>3</sub> , where (a) x = 0, (b) x = 0.00625, (c) x = 0.0125, (d) x = 0.05, (e) x = 0.1, (f) x = 0.2.	170
Figure 5.5	Thermogravetric analysis of Pure Lithium Niobate and (1-x)LiNbO <sub>3</sub> -xLi <sub>0.5</sub> Dy <sub>0.5</sub> TiO <sub>3</sub> for x = 0.1	172
Figure 5.6	X-ray photo electron spectra of (1-x)LiNbO <sub>3</sub> -x(Li <sub>0.5</sub> Dy <sub>0.5</sub> )TiO <sub>3</sub> for x = 0.1, (a) Fitting of Nb 4s, Li 1s spectra, (b) Fitting of O1s spectra (c) Fitting of Nb 3d spectra, (d) Fitting of Dy 3d spectra, (e) Fitting of Ti 2p spectra	174
Figure 5.7	Fourier transform infrared spectroscopy spectra of (1-x)LiNbO <sub>3</sub> -x(Li <sub>0.5</sub> Dy <sub>0.5</sub> )TiO <sub>3</sub> for different value of x at room temperature	175
Figure 5.8	(a) Variation of absorption spectra of (1-x)LiNbO <sub>3</sub> -x(Li <sub>0.5</sub> Dy <sub>0.5</sub> )TiO <sub>3</sub> solid solutions for various compositions in the range (0.0 ≤ x ≤ 0.2). (b) Indirect band gap of (1-x)LiNbO <sub>3</sub> -x(Li <sub>0.5</sub> Dy <sub>0.5</sub> )TiO <sub>3</sub> solid solutions (c) Direct band gap of (1-x)LiNbO <sub>3</sub> -x(Li <sub>0.5</sub> Dy <sub>0.5</sub> )TiO <sub>3</sub> (d) Direct band gaps for (1-x)LiNbO <sub>3</sub> -x(Li <sub>0.5</sub> Dy <sub>0.5</sub> )TiO <sub>3</sub> solid solution with composition variation, (e) Direct band gap showing exact tangential point.	177
Figure 5.9	(a) Photoluminescence spectra of LiNbO <sub>3</sub> solid solution (b) Photoluminescence spectra for (1-x)LiNbO <sub>3</sub> -xLi <sub>0.5</sub> Dy <sub>0.5</sub> TiO <sub>3</sub> solid solutions with composition variation.	180

Figure 5.10	(a) Photoluminescence spectra of $\text{LiNbO}_3$ solid solution showing cyan colour emission spectrum peak fitting, (b) Photoluminescence spectra of $(1-x)\text{LiNbO}_3-x\text{Li}_{0.5}\text{Dy}_{0.5}\text{TiO}_3$ ( $x = 0.025$ ) solid solution showing blue and cyan colour emission spectrum peak fitting, (c) Variation of peak position of cyan and yellow band with varying $x$ in $(1-x)\text{LiNbO}_3-x\text{Li}_{0.5}\text{Dy}_{0.5}\text{TiO}_3$ solid solutions, (d) Variation of peak intensity of cyan and yellow band with varying $x$ in $(1-x)\text{LiNbO}_3-x\text{Li}_{0.5}\text{Dy}_{0.5}\text{TiO}_3$ solid solutions.	180
Figure 5.11	Dielectrics behavior of $(1-x)\text{LiNbO}_3+x(\text{Li}_{0.5}\text{Dy}_{0.5})\text{TiO}_3$ for different value of $x$ (a) Permittivity at varying temperature at 1 kHz, (c) at 100 kHz (e) at 1MHz, Tangent loss at varying temperature at (b) 1 kHz, (d) 100 kHz and (f) 1MHz.	184
Figure 5.12	(a) Ferroelectric behavior and (b) Composition vs Polarization, of $(1-x)\text{LiNbO}_3-x(\text{Li}_{0.5}\text{Dy}_{0.5})\text{TiO}_3$	186
Figure 5.13	(a-e) P-E Energy hysteresis loop showing the are representing storage energy density and energy loss density and (f) Energy efficiency (%) with varying composition of $(1-x)\text{LiNbO}_3-x(\text{Li}_{0.5}\text{Dy}_{0.5})\text{TiO}_3$ .	187

## LIST OF TABLES

<b>Chapter 2</b>	<b>Experimental and characterization techniques</b>	61
Table 2.1	List of used precursor and chemicals for the synthesis of the samples.	62
<b>Chapter 3</b>	<b>Enhanced Dielectrics, Ferroelectric and Optical properties of Lithium Niobate for High Temperature Applications Using Potassium Oxide (K<sub>2</sub>O) Additive</b>	85
Table 3.1	Crystal lattice parameters and unit cell volume for various compositions of LN with K <sub>2</sub> O additive, obtained from Le Bail refinement.	94
Table 3.2	Percentage of elemental composition for pure LN and with 2.72 wt% and 5.44 wt% K <sub>2</sub> O additive as determined from EDS studies.	99
Table 3.3	Density of sintered LN with various concentration of K <sub>2</sub> O additive.	99
<b>Chapter 4</b>	<b>Electrical and Optical Properties of Environmental Friendly Li<sub>(1-x)</sub>Sm<sub>x/3</sub>NbO<sub>3</sub> Ceramics for High Temperature Energy Storage Applications</b>	123
Table 4.1	Crystal structure parameters obtained from Rietveld Structural refinement	131
Table 4.2	Percentage of elemental composition, Atomic percentage and Error percentage for Li <sub>(1-x)</sub> Sm <sub>(x/3)</sub> NbO <sub>3</sub> .	135
Table: 4.3	Electrical energy storage density and energy efficiency for Li <sub>(1-x)</sub> Sm <sub>x/3</sub> NbO <sub>3</sub> ceramic with varying compositions x.	154
<b>Chapter 5</b>	<b>Investigation of Multifaceted Properties for Environment friendly (1-x)LiNbO<sub>3</sub>-x(Li<sub>0.5</sub>Dy<sub>0.5</sub>)TiO<sub>3</sub> Solid Solution</b>	161
Table 5.1	Lattice parameters and unit cell volume of primary phase (1-x)LiNbO <sub>3</sub> -x(Li <sub>0.5</sub> Dy <sub>0.5</sub> )O <sub>3</sub> of samples	167
Table 5.2	Lattice parameters and unit cell volume of secondary phase of (1-x)LiNbO <sub>3</sub> -x(Li <sub>0.5</sub> Dy <sub>0.5</sub> )O <sub>3</sub> samples	168
Table 5.3	Electrical energy density and energy efficiency for (1-x)LiNbO <sub>3</sub> -x(Li <sub>0.5</sub> Dy <sub>0.5</sub> )TiO <sub>3</sub> with varying compositions	187



## LIST OF SYMBOLS & ABBREVIATIONS

---

$\eta$	Energy efficiency
$\alpha$	Polarizability
$h\nu$	Photon energy
$E_g$	Band gap
$\nu$	frequency
$h$	Plank constant
$k$	Boltzmann Constant
$K$	Kelvin
$E_a$	Activation Energy
$U$	Energy density
$\text{\AA}$	Angstrom
$\psi$	Electric potential barrier
Hz	Hertz
$T$	Temperature
$T_c$	Curie temperature
$\chi$	Susceptibility
$\sigma$	Conductivity
$L_d$	Debye length
$V_{oc}$	Open-circuit voltage
$\theta$	Angle
eV	Electron Volt
$\lambda$	Wavelength
$E_i$	Applied electric field specific value
$\mu\text{m}$	Micrometer
$\epsilon$	Dielectric Permittivity
$\tau$	Dielectric Relaxation Time
$\rho$	Total charge per unit area in electrode
$P$	Ferroelectric polarization

$E_c$	Coercive field
$P_{max}$	Maximum polarization
$P_s$	Spontaneous polarization
$P_r$	Remnant polarization
$E_b$	Breakdown strength
XPS	X-ray spectroscopy
AFM	Atomic force microscopy
C.B.	Conduction band
V.B.	Valence band
DW	Domain wall
FESEM	Field emission scanning electron microscopy
HRTEM	High resolution transmission microscopy
FTIR	Fourier transform infrared
XRD	X-Ray diffraction
XPS	X-ray photoelectron spectroscopy
PL	Photoluminescence spectroscopy
UV-Vis.	Ultra Violet visible spectroscopy
AFM	Atomic force microscopy

## **PREFACE**

---

The rapid increases in urbanization, high adaptability of portable electronic devices, daily increase in Internet on things, limitation of conventional energy sources, and rapid increases in pollution make the crisis of energy supply, and conventional fossil fuel energy sources cannot fulfill the demand energy supply. For a few decades, technologists, Researchers, and scientists have started thinking and developing new electrical energy sources in which energy materials always play a crucial role. As in this area of research developed, researchers started thinking about developing energy materials with various properties such as electrical energy materials should be highly useful in various kinds of applications, electrical energy materials exist with high energy-related properties, electrical energy materials should be environmentally friendly like it must be Lead (Pb) and Bismuth (Bi) free with nontoxic nature, materials should be applicable for a different kind of odd environmental condition like in the low temperature and high temperature that means highly thermally stable. In today, portable electronic devices have become a necessary part of everyone's life in many forms with different kinds of applications worldwide, therefore. The alternatives to fossil fuels are so much needed as batteries, sensors, optical displays, and sensing devices. Supply electrical energy in various kinds of electronic devices; dielectric-based batteries have played an important role for many decades in this kind of energy sector for portable devices, sensors, and home-made appliances. Dielectrics-based capacitors are the key components that make a great contribution to energy storage in energy applications. When we started studying this, it came to the knowledge that most of the energy materials are associated with non-ecologically unfriendly and also not very suitable for high-temperature applications in the form of batteries or other sensing and display devices. It has been proven that the energy density of dielectric-

based capacitors is lower than conventional batteries, but the research scope in this area is very wide with positive results. The capacitors are associated with their unique importance as well as an important domain of applicability in the energy storage sectors because of their fast charging with fast discharging phenomenon, which is not found in batteries.

There are a lot of ceramic dielectric materials are generally in use, and those are also reported in various research papers, materials like  $\text{PbTiO}_3$ ,  $\text{BiFeO}_3$ ,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ,  $\text{Bi}_4\text{Si}_3\text{O}_{12}$ ,  $\text{BaTiO}_3$ ,  $\text{BaZr}_{1-x}\text{Ti}_x\text{O}_2$  (BZT),  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  and many other solid solutions are used as energy storage dielectrics in the capacitors from the past many decades and are still very useful in various area of applications but when the environmentally friendly and high-temperature stability comes in the discussion, the alternatives of these materials are also a crucial need. Above all listed materials associated with good dielectric constant but they exist with below  $500^\circ\text{C}$  of curie temperature that's means high-temperature applications are very limited at but not at too high temperatures is observed at industries, mining's, space and other places. Rather than these materials, many solid solutions are also useful for dielectrics applications, but again, when high temperatures come into discussion, the same limitations come to the front. Several decades ago, Bellman synthesized  $\text{LiNbO}_3$  in their laboratory with excellent Dielectric, Ferroelectric, Piezoelectric, and Photorefractive properties, and after that, they published an article in 1965 about the single crystal development of  $\text{LiNbO}_3$  (LN) by using Czochralski method. Ashkin et al reported the photorefractive properties of  $\text{LiNbO}_3$  (LN) in 1966. From the first development of  $\text{LiNbO}_3$  to now, much research has been done for the synthesis of different kinds of LN, like ceramics, Nanofibers, thin films, and single crystals, for applications in various fields like sensor actuators, and energy storage, but many huge areas are still not filled and vacant for the extensive research work.

In this present work, we have selected LiNbO<sub>3</sub> ceramic as a base material for the whole research work, and we used different additive and doping materials to enhance properties like sintering and related to electrical energy storage like Dielectric, ferroelectric, and optical properties. LN was reported as a Rhombohedral structure with R3c space group with a very high curie temperature of about 1210 °C for the ceramic form. The addition and the doping in LiNbO<sub>3</sub> have been done using K<sub>2</sub>O, Sm<sub>2</sub>O<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>, respectively. Where the K<sub>2</sub>O is used as an additive in weight-by-weight percentage form, Sm<sup>3+</sup> was doped at the Li site with different stoichiometric ratios, and Dy<sup>3+</sup> and Ti<sup>4+</sup> were co-doped in LN in different solid solutions. Our investigations on LiNbO<sub>3</sub> ceramics have obtained several important findings, which are as follows.

### **1. Enhanced Dielectrics, Ferroelectric and Optical properties of Lithium Niobate for High Temperature Applications Using Potassium Oxide (K<sub>2</sub>O) Additive**

Dielectrics, Ferroelectric, and Optical properties of Lithium Niobate have been examined using Potassium Oxide (K<sub>2</sub>O) as an additive on the samples prepared by solid-state reaction using high-energy ball milling. The crystal structure analysis by Rietveld structure refinement confirms that the LiNbO<sub>3</sub> (LN) with K<sub>2</sub>O additive also exhibits the rhombohedral structure with the R3c space group. The SEM characterization of the microstructure reveals that the samples sintered at a temperature of 1050 °C have regular and uniform grain morphology and better density. The average grain size decreases for the K<sub>2</sub>O added compositions in the beginning and increases later for higher concentrations of additive. Thermal study with TGA suggests that as the activation energy decreases, the polarization is enhanced, and the LN composition with 2.72 wt% K<sub>2</sub>O additive shows the best thermal stability. The frequency and temperature-dependent dielectric properties were investigated in

a wide range of frequencies, and a substantial enhancement in the dielectric constant of LN was obtained by K<sub>2</sub>O addition. A significant enhancement in permittivity is obtained with an increase in temperature. The band gap values for the various compositions' direct and indirect band gaps are also determined. The least direct band gap is discovered to be 2.36 eV for the composition with 2.72 wt% K<sub>2</sub>O additive. The composition-dependent photoluminescence (PL) emission studies reveal that the emission spectra for both the pure LiNbO<sub>3</sub> and K<sub>2</sub>O-added LiNbO<sub>3</sub> compositions lie in the UV-visible region. All the investigated compositions exhibit distinct green, yellow, and red emission peaks. The LN with 2.72 wt% K<sub>2</sub>O additive shows the best dielectric, thermal stability, and polarization response with maximum polarization P<sub>s</sub> ~1.16 μC/cm<sup>2</sup>. The present investigations suggest that the properties of LN can be significantly improved by using K<sub>2</sub>O additive for sustainable, low-cost, environmentally friendly energy storage material for high-temperature applications.

## **2. Electrical and Optical Properties of Environmental Friendly Li<sub>(1-x)</sub>Sm<sub>(x/3)</sub>NbO<sub>3</sub> Ceramics for High Temperature Energy Storage Applications**

This research work delves into the synthesis and characterization of Li<sub>(1-x)</sub>Sm<sub>(x/3)</sub>NbO<sub>3</sub> ceramic, employing a high-energy ball milling process. The investigation explores the incorporation of Sm<sup>3+</sup> at the Li<sup>1+</sup> site across a range of compositions (x = 0, 0.01, 0.02, 0.03, 0.04, 0.05). Structural analysis, using X-ray diffraction (XRD) and Rietveld structural refinement, establishes that within the investigated composition range, no significant changes in the crystal structure are evident. The X-ray photoelectron spectroscopy revealed the presence of oxygen vacancies as well as the stable oxidation state of different elements like O<sup>2-</sup>, Nb<sup>5+</sup>, Sm<sup>3+</sup>, Li<sup>1+</sup>. At sintering temperature 1050°C, the average grain sizes vary approximately from 1.5 μm to 3.8 μm for different compositions with regular grain

morphology. The UV-Vis analysis reveals a noteworthy reduction in the band gap to  $3.09 \pm 0.003$  eV for the  $x = 0.01$  composition. Photoluminescence studies exhibit distinct green, orange, and red bands, with the highest intensity observed for  $x = 0.01$ , showcasing promising optical properties. The dielectric permittivity of Sm-substituted compositions surpasses the response of pure  $\text{LiNbO}_3$ , demonstrating an increasing trend with temperature in the frequency range 100 Hz to 1 MHz intriguingly, no Curie temperature is observed up to  $500^\circ\text{C}$  for any composition. The polarization versus electric field hysteresis loop response highlights better polarization characteristics at the room temperature and maximum polarization is  $0.66 \mu\text{C}/\text{cm}^2$  for the composition  $x = 0.05$ . The energy storage response of the developed compositions is investigated, which reveals a maximum efficiency of 46.64% for  $x = 0.04$  in  $\text{Li}_{(1-x)}\text{Sm}_{(x/3)}\text{NbO}_3$ . The tunable optical properties, enhanced dielectric response, and notable energy efficiency of this high  $T_C$  ceramics suggest their utility across diverse applications. These findings not only contribute to the understanding of functional ceramic materials but also pave the way for their optimized utilization in advanced technological applications, particularly in energy storage devices under non ambient conditions at high temperatures.

### **3. Investigation of Multifaceted Properties for Environment friendly $(1-x)\text{LiNbO}_3$ - $x(\text{Li}_{0.5}\text{Dy}_{0.5})\text{TiO}_3$ Solid Solutions**

This research work presents experimental data on the development of environmentally friendly ceramics based on the solid solution  $(1-x)\text{LiNbO}_3$ - $x(\text{Li}_{0.5}\text{Dy}_{0.5})\text{TiO}_3$  prepared through high-energy ball milling with varying compositions. Structural analysis, employing Rietveld structure refinement, reveals a consistent presence of a mixed phase, encompassing cubic and Rhombohedral phases for compositions up to  $x = 0.1$ . Sintering at  $1050^\circ\text{C}$  yields varied average grain sizes ( $3.46 \mu\text{m}$  to  $1.09 \mu\text{m}$ ) with distinct compositions, displaying regular and

consistent grain morphology. X-ray photoelectron spectroscopy indicates the presence of oxygen vacancies and reveals the oxidation states of elements such as  $O^{1-}$ ,  $O^{2-}$ ,  $Nb^{5+}$ ,  $Dy^{3+}$ ,  $Ti^{4+}$ , and  $Ti^{3+}$ . Dielectric properties are investigated across a wide frequency range (1 kHz to 1 MHz) and temperatures up to 500 °C, revealing a frequency-dependent reduction in both dielectric constant and dielectric loss for all compositions. Ferroelectric properties show enhancement at room temperature, with the maximum polarization reaching approximately  $0.8 \mu C/cm^2$  for  $x = 0.1$ . A band gap reduction is observed in  $LiNbO_3$  with increasing  $(Li_{0.5}Dy_{0.5}TiO_3)$  contents, and a minimum direct band gap of  $2.95 \pm 0.002$  eV is obtained for  $x = 0.05$  composition. Photoluminescence analysis demonstrates the presence of Yellow, Cyan, and Blue bands, which are valuable for Yellow laser and Light light-emitting diodes (LEDs) applications. The dielectric permittivity of  $(1-x)LiNbO_3-x(Li_{0.5}Dy_{0.5})TiO_3$  ceramics shows a better response with an increase of temperature in the frequency range of 1 kHz to 1 MHz for all compositions than Pure  $LiNbO_3$  and there is also no curie temperature observed up to 500°C for any composition this makes it a candidate material for high-temperature applications. We achieved a maximum recoverable energy storage density of  $17.96$  mJ/cm<sup>3</sup> and a maximum energy efficiency of 34.00 %. Overall, these findings provide valuable insights into the structural, electrical, and optical properties of the studied ceramics, suggesting their potential for the development of high-temperature phosphor materials for white LEDs, yellow lasers, energy storage, and other diverse high-temperature technological applications.