

**ELECTRICAL AND ELECTROMECHANICAL
STUDIES OF COMPLEX OXIDE MATERIALS AT
MORPHOTROPIC PHASE BOUNDARY**

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by

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Submitted

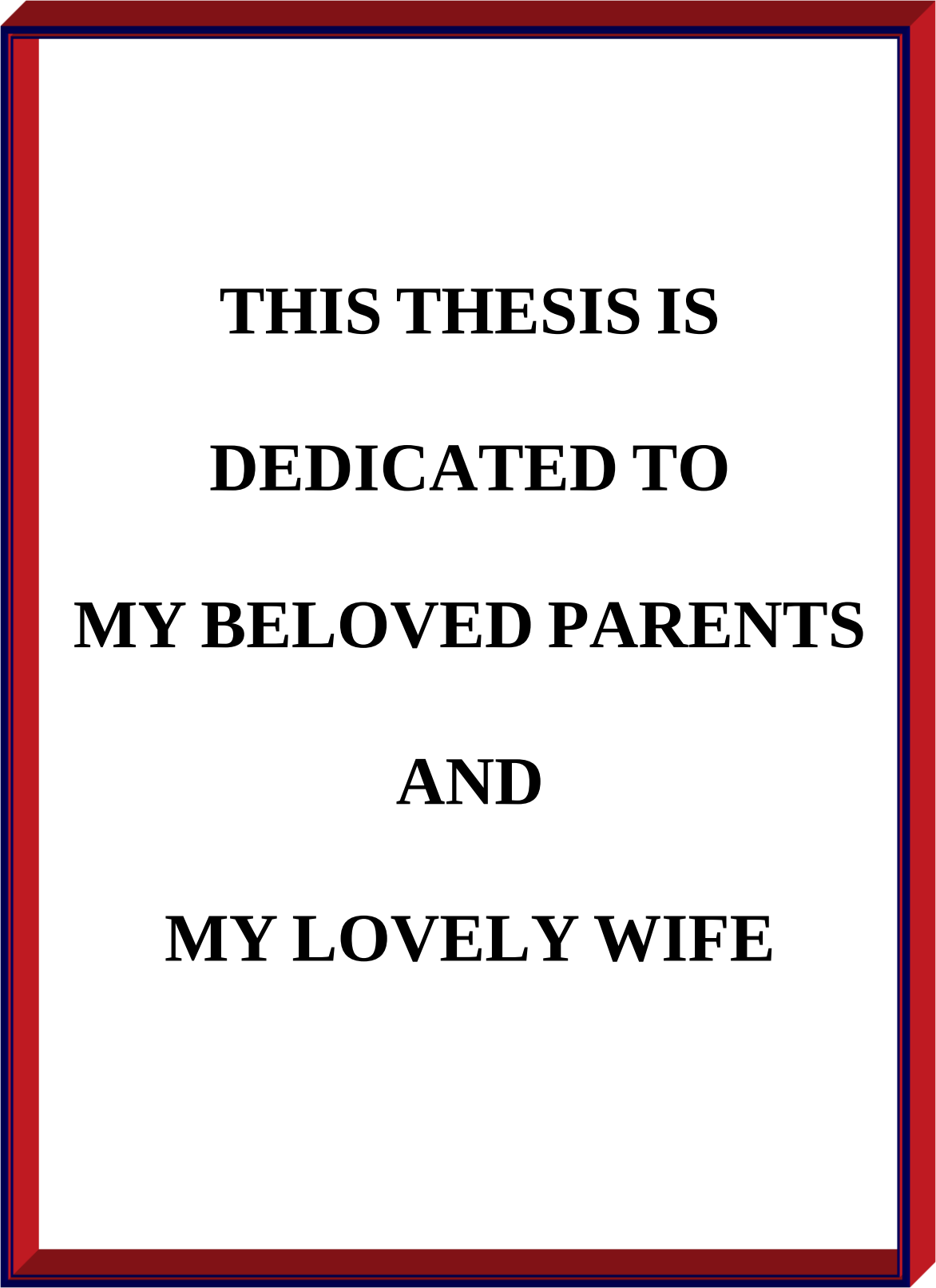
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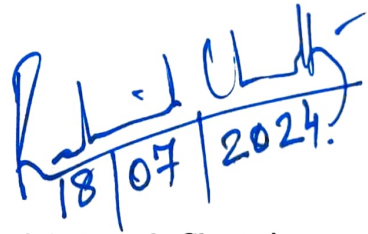


**THIS THESIS IS
DEDICATED TO
MY BELOVED PARENTS
AND
MY LOVELY WIFE**

CERTIFICATE

This is to certify that the Thesis entitled “**ELECTRICAL AND ELECTROMECHANICAL STUDIES OF COMPLEX OXIDE MATERIALS AT MORPHOTROPIC PHASE BOUNDARY**” being submitted by **Mr. Hitesh Kumar** to the Department of Physics, Indian Institute of Technology Delhi for the award of the degree of ‘**Doctor of Philosophy**’ is a record of bonafide work carried by him. He has worked under my supervision and guidance and has fulfilled the requirement for the submission of this Thesis.

The results contained in this work have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.



Prof. Ratnamala Chatterjee

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Hitesh Kumar

ABSTRACT

Smart materials remember their original shape on removal of external parameters (like temperature, electric field, magnetic field, etc.), and are said to exhibit the shape memory effect. Our work is mainly focused on converse piezoelectric ceramics (e.g., $\text{Pb}(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$ etc.) in which appreciable value of remnant strain observed even when applied electric field is removed, and an electric field in opposite polarity is required to get initial state, which is the characteristic of shape memory materials. The maximum value of field induced strain/remnant strain is observed at the composition with coexistence of ferroelectric and antiferroelectric phases known as morphotropic phase boundary (MPB) composition in these oxides. Shape memory oxides (SMO) with a remnant strain of $\sim 0.1\text{-}0.25\%$ have been reported in literature and PZST is a well-studied SMO with maximum remnant strain $\sim 0.06\%$ at morphotropic phase boundary (MPB) composition ($\text{Zr}:\text{Sn}=7:3$) reported by Pathak et. al.. This makes interest to study these PZST-based SMO for various applications such as actuators, memory, and transducer devices. In this regard, we perform a detailed study on lead-based oxides (in bulk and thin-film form) with modification at A-site and B-site (i.e., by composition variation) to achieve shape memory behaviour with improved remnant strain value.

Focus of the present work is to look for the compositions at the Antiferroelectric (AFE) and ferroelectric (FE) phases Morphotropic Phase Boundary (MPB) with objective to enhance strain and energy storage properties due to the unique crystal structures and the coexistence of two phases with minimal energy difference. In view of different literature survey and title of my thesis, present work will focus on the study the *lead-based smart complex perovskite oxides (in bulk and thin film form)*. The main aim of this

investigation is to examine the behavior of *lead-based smart complex perovskite oxides (in bulk and thin film form)* under doping and to develop a new processing method that will improve the properties of these ceramics.

In this thesis work, polycrystalline Bi-doped PZST series namely, $\text{Pb}_{(1-3y/2)}\text{Bi}_y[(\text{Zr}_{0.7}\text{Sn}_{0.3})_x\text{Ti}_{1-x}]\text{O}_3$ (with $x=0.938, y=0.00, 0.01, 0.02$ and $y=0.01, x=0.930, 0.931, 0.932, 0.933$ and 0.934), prepared using the conventional ceramic method and we demonstrate a remnant strain of $\sim 0.27\%$ in Bi doped PZST bulk ceramics at MPB composition ($x=0.933, y=0.01$). Moreover, thin films (thickness ~ 250 nm) compositions close to MPB of bismuth-doped PZST series with the stoichiometric formula $\text{Pb}_{0.985}\text{Bi}_{0.01}[(\text{Zr}_{0.7}\text{Sn}_{0.3})_x\text{Ti}_{1-x}]\text{O}_3$, by varying the (Zr, Sn)/Ti ratios ($x=0.935, 0.940, 0.945, 0.950$) were deposited on a Pt/TiO₂/SiO₂/Si substrate using pulsed laser deposition technique. The highest piezoelectric coefficient ($d_{33}\sim 330$ pm/V) and remnant strain ($S_{\text{rem}}\sim 0.33\%$) values at the MPB composition ($x=0.945$ film) indicates good ferroelectric and piezoelectric properties.

The comprehensive outline of thesis including all chapters is as given below.

Chapter 1 (Introduction) contains aim, motivation, scope, and organization of the present thesis with a brief description of electrical and electromechanical studies performed on lead-based (A and B-site doped $\text{Pb}(\text{Zr},\text{Sn})\text{TiO}_3$) smart/intelligent perovskite oxides (bulk ceramics and thin film form). Some technical terminologies such as perovskite structure, ferroelectricity, piezoelectricity, converse piezoelectricity, shape memory effect (SME), and morphotropic phase boundary (MPB) were explained. The detailed recent progress including literature survey of maximum shape memory

(recoverable remnant strain) obtained in these systems at around MPB composition (with mixed FE and AFE phases) are also reviewed in present chapter.

Chapter 2 (Processing and characterization techniques): is divided into two sections including detailed description on the experimental methods (used to produce bulk ceramics and thin films) and techniques to characterize them. In first section, starting from the detailed optimization process for preparation of Bulk ceramics (Bi doped PZST) oxides using conventional solid state reaction route, their thin film device preparation using pulsed laser deposition technique in different compositions is being reported here. Second section describes about characterization techniques utilized for the detailed electrical and electromechanical studies of prepared oxide samples.

Chapter 3 (Bismuth as antiferroelectric phase-stabilizer in $\text{Pb}(\text{ZrSn})\text{TiO}_3$: Designing a new material with large strain and shape memory effect): contains AFE phase stabilizing effect of Bi substitution at A-site in $\text{Pb}[(\text{Zr}_{0.7}\text{Sn}_{0.3})_{0.938}\text{Ti}_{0.062}]\text{O}_3$. A detailed structural, dielectric, ferroelectric, current, and shape memory studies performed on bulk PZST system (around MPB composition) with A-site Bismuth modification, $\text{Pb}_y\text{Bi}_{1-(3/2)y}[(\text{Zr}_{0.7}\text{Sn}_{0.3})_{0.938}\text{Ti}_{0.062}]\text{O}_3$ ($y=0.00, 0.01, 0.02$). The composition $\text{Pb}_{0.985}\text{Bi}_{0.01}(\text{Zr}_{0.7}\text{Sn}_{0.3})_{0.938}\text{Ti}_{0.062}\text{O}_3$ with 1% Bi substitution lies just outside the MPB towards the AFE side and allows an electric field driven atomic rearrangement for disordered state. The disorder and randomness introduced through this substitution is seen to impact the electromechanical property like strain, quite drastically ($S_{\max} \sim 0.3\%$). Keeping the optimal Bi inclusion and Zr: Sn as 70:30, the B-site of $\text{Pb}_{0.985}\text{Bi}_{0.01}[(\text{Zr}_{0.7}\text{Sn}_{0.3})_x\text{Ti}_{1-x}]\text{O}_3$, is varied between $x=0.930$ to 0.934 . I-E measurements confirms that the system is brought back to MPB for $x = 0.933$, which is in well

agreement with our P-E/S-E measurements. The strain values of $S_{max} \sim 0.44\%$ and a remnant strain $S_{rem} \sim 0.27\%$ are obtained for the optimized MPB composition $Pb_{0.985}Bi_{0.01}[(Zr_{0.7}Sn_{0.3})_{0.933}Ti_{0.067}]O_3$. This value is larger than the value found for other Pb-based, BNT-based, BT- based, KNN-based, BiFeO₃, NaNbO₃ and AgNbO₃ based ceramics [26,27].

Chapter 4 (Optimization of MPB for Sn substituted Lead Bismuth Zirconate Titanate thin films by the electromechanical behavior related to energy storage capacity) examines the electromechanical behaviour of Sn substituted Lead Bismuth Zirconate Stannate Titanate (PBZST) thin films at MPB. Using PLD technique, the thin film growth parameters of bismuth-doped PZST close to MPB were adjusted by varying the (Zr, Sn)/Ti ratios. Thin films (~250 nm) with the stoichiometric formula $Pb_{0.985}Bi_{0.01}(Zr_{0.7}Sn_{0.3})_xTi_{1-x}O_3$, ($x = 0.935, 0.940, 0.945$, and 0.950) were grown on a Pt/TiO₂/SiO₂/Si substrate using PLD technique at optimized conditions. P-E loops confirm that MPB is near to $x = 0.945$, and further PFM measurements also confirmed the same. Analyzing the PFM phase and amplitude hysteresis loops, local piezoelectric coefficient (d_{33}) and remnant strain (S_{rem}) values computed as ~330 pm/V and 0.33 % at the MPB composition ($x = 0.945$).

Chapter 5 (Conclusions and Future Scope) focus on the key findings and drawn conclusions of the current study and provides a summary of the entire thesis's work of research. This chapter also provide recommendations for further studies in this area.

सारांश

बुद्धिमान पदार्थ बाहरी मापदंडों (जैसे तापमान, विद्युत क्षेत्र, चुंबकीय क्षेत्र, आदि) को हटाने पर अपने मूल आकार को याद रखते हैं, और कहा जाता है कि यह आकार स्मृति प्रभाव प्रदर्शित करते हैं। हमारा काम मुख्य रूप से कन्वर्स पीजोइलेक्ट्रिक सिरेमिक (उदाहरण के लिए, $\text{Pb}(\text{Zr}, \text{Sn}, \text{Ti})\text{O}_3$ इत्यादि) पर केंद्रित है, जिसमें लागू विद्युत क्षेत्र को हटा दिए जाने पर भी अवशेष तनाव का सराहनीय मूल्य देखा जाता है, और प्रारंभिक अवस्था प्राप्त करने के लिए विपरीत ध्रुवता में एक विद्युत क्षेत्र की आवश्यकता होती है, जो आकार स्मृति पदार्थ की विशेषता है। इन ऑक्साइडों में क्षेत्र प्रेरित तनाव/अवशेष तनाव का अधिकतम मूल्य मोर्फोट्रोपिक चरण सीमा (एमपीबी) संरचना के रूप में जाने जाने वाले फेरोइलेक्ट्रिक और एंटीफेरोइलेक्ट्रिक चरणों के सह-अस्तित्व के साथ संरचना में देखा जाता है। साहित्य में $\sim 0.1\text{-}0.25\%$ के अवशेष तनाव के साथ आकार मेमोरी ऑक्साइड (एसएमओ) की सूचना दी गई है, और PZST एक अच्छी तरह से अध्ययन किया गया एसएमओ है जिसमें मोर्फोट्रोपिक चरण सीमा (एमपीबी) संरचना (Zr: Sn = 7: 3) पर अधिकतम अवशेष तनाव $\sim 0.06\%$ पाठक एट अल. द्वारा प्रतिवेदित किया गया है। यह एक्चुएटर्स, मेमोरी और ट्रांसड्यूसर उपकरणों जैसे विभिन्न अनुप्रयोगों के लिए इन PZST-आधारित एसएमओ का अध्ययन करने में रुचि पैदा करता है। इस संबंध में, हम बेहतर अवशेष तनाव मूल्य के साथ आकार स्मृति व्यवहार प्राप्त करने के लिए ए-साइट और बी-साइट (यानी, संरचना भिन्नता द्वारा) पर संशोधन के साथ सीसा-आधारित ऑक्साइड (थोक और पतली-फिल्म के रूप में) पर एक विस्तृत अध्ययन करते हैं।

वर्तमान कार्य का फोकस अद्वितीय क्रिस्टल संरचनाओं और न्यूनतम ऊर्जा अंतर के साथ दो चरणों के सह-अस्तित्व के कारण तनाव और ऊर्जा भंडारण गुणों को बढ़ाने के उद्देश्य से एंटीफेरोइलेक्ट्रिक (एएफई) और फेरोइलेक्ट्रिक (एफई) चरणों मोर्फोट्रोपिक चरण सीमा (एमपीबी) में रचनाओं की तलाश करना है। विभिन्न साहित्य सर्वेक्षण और मेरे शोध ग्रंथ के शीर्षक को ध्यान में रखते हुए, वर्तमान कार्य सीसा-आधारित बुद्धिमान जटिल पेरोव्स्काइट ऑक्साइड (थोक और पतली फिल्म के रूप में) के अध्ययन पर केंद्रित होगा। इस जांच का मुख्य उद्देश्य डोपिंग के तहत सीसा-आधारित बुद्धिमान जटिल पेरोव्स्काइट ऑक्साइड (थोक और पतली फिल्म के रूप में) के व्यवहार की जांच करना और एक नई प्रसंस्करण विधि विकसित करना है जो इन सिरेमिक के गुणों में सुधार करेगी।

इस शोध ग्रंथ के कार्य में पॉलीक्रिस्टलाइन Bi-डॉपड PZST श्रृंखला अर्थात्, $\text{Pb}_{(1-3y/2)}\text{Bi}_y[(\text{Zr}_{0.7}\text{Sn}_{0.3})_x\text{Ti}_{1-x}]\text{O}_3$ ($x=0.938$ के साथ $y=0.00, 0.01, 0.02$ और $y=0.01, x=0.930, 0.931, 0.932, 0.933$ और 0.934), पारंपरिक

सिरेमिक विधि का उपयोग करके तैयार किया गया और हम एमपीबी संरचना ($x=0.933$, $y=0.01$) पर Bi-डोपड PZST थोक सिरेमिक में $\sim 0.27\%$ का अवशेष तनाव प्रदर्शित करते हैं। इसके अलावा, पतली फिल्मों (मोटाई ~ 250 nm) स्टोइकोमेट्रिक सूत्र $\text{Pb}_{0.985}\text{Bi}_{0.01}[(\text{Zr}_{0.7}\text{Sn}_{0.3})_x\text{Ti}_{1-x}]\text{O}_3$ के साथ बिस्मथ-डॉपड PZST श्रृंखला के एमपीबी के करीब की रचनाएँ, $(\text{Zr, Sn})/\text{Ti}$ अनुपात ($x=0.935, 0.940, 0.945, 0.950$) को परिवर्तन करके स्पंदित लेजर जमाव तकनीक का उपयोग करके $\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$ सबस्ट्रेट पर जमा किया गया था। एमपीबी संरचना ($x=0.945$ फिल्म) पर उच्चतम पीजोइलेक्ट्रिक गुणांक ($d_{33} \sim 330$ pm/V) और अवशेष तनाव ($S_{\text{rem}} \sim 0.33\%$) मान अच्छे फेरोइलेक्ट्रिक और पीजोइलेक्ट्रिक गुणों को इंगित करते हैं।

सभी अध्यायों सहित शोध ग्रंथ की व्यापक रूपरेखा नीचे दी गई है।

अध्याय 1 (परिचय) में वर्तमान शोध ग्रंथ का उद्देश्य, प्रेरणा, दायरा और संगठन शामिल है, जिसमें सीसा-आधारित (ए और बी-साइट डोपड $\text{Pb}(\text{Zr,Sn})\text{TiO}_3$ बुद्धिमान पेरोव्स्काइट ऑक्साइड (थोक सिरेमिक और पतली फिल्म के रूप में) पर किए गए विद्युतीय और विद्युत यांत्रिक अध्ययनों का संक्षिप्त विवरण है। कुछ तकनीकी शब्दावली जैसे पेरोव्स्काइट संरचना, फेरोइलेक्ट्रिसिटी, पीजोइलेक्ट्रिसिटी, कन्वर्स पीजोइलेक्ट्रिसिटी, आकार स्मृति प्रभाव (एसएमई), और मॉर्फोट्रोपिक चरण सीमा (एमपीबी) को समझाया गया। लगभग एमपीबी संरचना (मिश्रित एफई और एएफई चरणों के साथ) में इन प्रणालियों में प्राप्त अधिकतम आकार मेमोरी (पुनर्प्राप्ति योग्य अवशेष तनाव) के साहित्य सर्वेक्षण सहित विस्तृत हालिया प्रगति की भी वर्तमान अध्याय में समीक्षा की गई है।

अध्याय 2 (प्रसंस्करण और लक्षण वर्णन तकनीक): प्रयोगात्मक तरीकों (थोक सिरेमिक और पतली फिल्मों का उत्पादन करने के लिए प्रयुक्त) और उन्हें चिह्नित करने की तकनीकों पर विस्तृत विवरण सहित दो खंडों में विभाजित किया गया है। पहले खंड में, पारंपरिक ठोस अवस्था प्रतिक्रिया मार्ग का उपयोग करके थोक सिरेमिक (Bi-डॉपड PZST) ऑक्साइड की तैयारी के लिए विस्तृत अनुकूलन प्रक्रिया से शुरू करके, विभिन्न रचनाओं में स्पंदित लेजर जमाव तकनीक का उपयोग करके उनकी पतली फिल्म डिवाइस की तैयारी यहां बताई जा रही है। दूसरा खंड तैयार ऑक्साइड नमूनों के विस्तृत विद्युत और विद्युत यांत्रिक अध्ययन के लिए उपयोग की जाने वाली लक्षण वर्णन तकनीकों के बारे में वर्णन करता है।

अध्याय 3 ($\text{Pb}(\text{ZrSn})\text{TiO}_3$) में एंटीफेरोइलेक्ट्रिक चरण-स्थिरीकरणकर्ता के रूप में बिस्मथ: बड़े तनाव और आकार स्मृति प्रभाव के साथ एक नया पदार्थ डिजाइन करना): $\text{Pb}[(\text{Zr}_{0.7}\text{Sn}_{0.3})_{0.938}\text{Ti}_{0.062}]\text{O}_3$ में ए-साइट पर Bi

प्रतिस्थापन का एफई चरण स्थिरीकरण प्रभाव शामिल है। ए-साइट बिस्मथ संशोधन, $Pb_yBi_{1-(3/2)y}[(Zr_{0.7}Sn_{0.3})_{0.938}Ti_{0.062}]O_3$ ($y=0.00, 0.01, 0.02$) के साथ थोक PZST प्रणाली (एमपीबी रचना के आसपास) पर एक विस्तृत संरचनात्मक, परावैद्युत, लोहवैद्युत, धारा और आकार स्मृति अध्ययन किया गया। रचना $Pb_{0.985}Bi_{0.01}(Zr_{0.7}Sn_{0.3})_{0.938}Ti_{0.062}O_3$ 1% Bi प्रतिस्थापन के साथ एफई पक्ष की ओर एमपीबी के ठीक बाहर स्थित है और अव्यवस्थित स्थिति के लिए एक विद्युत क्षेत्र संचालित परमाणु पुनर्व्यवस्था की अनुमति देता है। इस प्रतिस्थापन के माध्यम से शुरू की गई अव्यवस्था और अनियमितता को तनाव जैसे विद्युत यांत्रिक गुण को काफी हद तक प्रभावित करते देखा गया है ($S_{max} \sim 0.3 \%$)। युक्ततम Bi समावेशन और Zr: Sn को 70:30 के रूप में रखते हुए, $Pb_{0.985}Bi_{0.01}[(Zr_{0.7}Sn_{0.3})_xTi_{1-x}]O_3$ की बी-साइट, $x=0.930$ से 0.934 के बीच भिन्न-भिन्न ली जाती है। I-E माप यह पुष्टि करता है कि प्रणाली को $x = 0.933$ के लिए एमपीबी में वापस लाया जाता है, जो हमारे P-E/S-E मापों के साथ अच्छी तरह से मेल खाता है। अनुकूलित एमपीबी संरचना $Pb_{0.985}Bi_{0.01}[(Zr_{0.7}Sn_{0.3})_{0.933}Ti_{0.067}]O_3$ के लिए S_{max} का तनाव मान $\sim 0.44\%$ और एक अवशेष तनाव $S_{rem} \sim 0.27\%$ प्राप्त होता है। यह मान अन्य Pb-आधारित, BNT-आधारित, BT-आधारित, KNN-आधारित, $BiFeO_3$, $NaNbO_3$ और $AgNbO_3$ आधारित सिरामिक के लिए पाए गए मान से बड़ा है [26,27]।

अध्याय 4 (ऊर्जा भंडारण क्षमता से संबंधित विद्युत यांत्रिक व्यवहार द्वारा Sn प्रतिस्थापित लेड बिस्मथ जिर्कोनेट टाइटेनेट पतली फिल्मों के लिए एमपीबी का अनुकूलन) एमपीबी पर Sn द्वारा प्रतिस्थापित लेड बिस्मथ जिर्कोनेट स्टैनेट टाइटेनेट (PBZST) पतली फिल्मों के विद्युत यांत्रिक व्यवहार की जांच करता है। पीएलडी तकनीक का उपयोग करते हुए, एमपीबी के करीब बिस्मथ-डॉप्ड पीजेडएसटी के पतले फिल्म विकास मापदंडों को (Zr, Sn)/Ti अनुपात को अलग-अलग करके समायोजित किया गया था। अनुकूलित परिस्थितियों में पीएलडी तकनीक का उपयोग करके Pt/TiO₂/SiO₂/Si सबस्ट्रेट पर स्टोइकोमेट्रिक सूत्र $Pb_{0.985}Bi_{0.01}(Zr_{0.7}Sn_{0.3})_xTi_{1-x}O_3$, ($x = 0.935, 0.940, 0.945$, और 0.950) के साथ पतली फिल्में (~ 250 nm) तैयार की गईं। P-E लूप पुष्टि करते हैं कि एमपीबी $x = 0.945$ के करीब है, और आगे पीएफएम माप ने भी इसकी पुष्टि की है। एमपीबी संरचना ($x = 0.945$) पर पीएफएम चरण और आयाम हिस्टैरिसिस लूप का विश्लेषण करने पर, स्थानीय पीज़ोइलेक्ट्रिक गुणांक (d_{33}) और अवशेष तनाव (S_{rem}) मान की गणना ~ 330 pm/V और 0.33% के रूप में की जाती है।

अध्याय 5 (निष्कर्ष और भविष्य का दायरा) वर्तमान अध्ययन के प्रमुख निष्कर्षों और निकाले गए निष्कर्षों पर ध्यान

केंद्रित करता है और संपूर्ण शोध ग्रंथ के शोध कार्य का सारांश प्रदान करता है। यह अध्याय इस क्षेत्र में आगे के अध्ययन के लिए अनुशंसा भी प्रदान करता है।

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LIST OF SYMBOLS

ε	: Real Part of Dielectric Constant
ε_0	: Permittivity of Free Space
T	: Temperature
E	: Electric Field
E_C	: Coercive Electric Field
T_C	: Ferroelectric Curie Temperature
d	: Lattice Spacing
C	: Capacitance
V	: Voltage
f	: Frequency
P	: Polarization
P_s	: Saturation Polarization
P_r	: Remnant Polarization
S	: Strain
S_{max}	: Maximum Strain
S_{rem}	: Remnant Strain
A	: Area of Electrode
t	: Thickness of Sample
R_{rms}	: Root-Mean-Square Surface Roughness
λ	: Wavelength
d_{33}	: Piezoelectric Coefficient
t	: Goldsmith tolerance factor

R_A : Avarage radius of A-site

γ : Diffusitivity factor

LIST OF ABBREVIATIONS

PZT	: Lead Zirconate Titanate
PZST	: Lead Zirconate Stannate Titanate
PBZST	: Lead Bismuth Zirconate Stannate Titanate
BT	: Barium Titanate
BNT	: Bismuth Sodium Titanate
KNN	: Potassium Sodium Niobate
BFO	: Bismuth ferrite
PLD	: Pulsed Laser Deposition
MPB	: Morphotropic Phase Boundary
XRD	: X-Ray Diffraction
AFM	: Atomic Force Microscopy
PFM	: Piezoresonse Force Microscopy
SEM	: Scanning Electron Microscopy
EDXS	: Energy Dispersive X-ray Spectroscopy
FE	: Ferroelectric
PE	: Paraelectric
AFE	: Antiferroelectric
SME	: Shape Memory Effect
SMA	: Shape Memory Alloy
SMO	: Shape Memory Oxide
P-E	: Polarization vs. Electric Field Hysteresis Loop
I-E	: Current vs. Electric Field Hysteresis Loop

S-E : Strain vs. Electric Field Hysteresis Loop