"LEAD-FREE PIEZOELECTRIC MATERIALS: A STUDY ON SILK FIBROIN-ZnO HYBRID FILMS FOR FLEXIBLE SENSING APPLICATIONS"

A MAJOR PROJECT REPORT SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF THE DEGREE OF

MASTER OF SCIENCE

IN

CHEMISTRY

Submitted by

VIJITA SINGH

(23/MSCCHE/62)

Under the supervision of

PROF.ROLI PURWAR

DEPARTMENT OF APPLIED CHEMISTRY

DELHI TECHNOLOGICAL UNIVERSITY

(Formerly Delhi College of Engineering)

Bawana Road, Delhi-110042

JUNE,2025

DELHI TECHNOLOGICAL UNIVERSITY

(Formerly Delhi College of Engineering)

Bawana Road, Delhi-110042

CANDIDATE'S DECLARATION

I, Vijita Singh (23/MSCCHE/62), student of M.Sc. Chemistry hereby declare that the project Dissertation titled **"Lead-Free Piezoelectric Materials: A Study on Silk Fibroin-ZnO Hybrid Films for Flexible Sensing Applications"** which is submitted by me to the department of Applied Chemistry, Delhi Technological University, Delhi, in the partial fulfilment of the requirement for the award of the degree of Master of Science, is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma, Associateship, Fellowship, or other similar title or recognition.

Title of the Paper: Lead-Free Piezoelectric Materials: A Study on Silk Fibroin-ZnO Hybrid Films for Flexible Sensing Applications

Author names: Vijita Singh and Roli Purwar

Name of the Journal: Springer Book Chapter (SCOPUS-INDEXED)

Status of the Paper: Under Review

Date of paper publication: Yet to be published

Place: Delhi

Date: June 2025

VIJITA SINGH

(23/MSCCHE/62)

Department of Applied Chemistry

DELHI TECHNOLOGICAL UNIVERSITY

(Formerly Delhi College Of Engineering)

Bawana Road, Delhi-110042

CERTIFICATE

I, hereby certify that the Project Dissertation titled **"Lead-Free Piezoelectric Materials: A Study on Silk Fibroin-ZnO Hybrid Films for Flexible Sensing Applications"** which is submitted by Vijita Singh (23/MSCCHE/62), Department of Applied Chemistry, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the degree of Master of Science, is a record of the project work carried out by the student under my supervision. To the best of my knowledge, this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere.

Place: Delhi

Date: June 2025

PROF.ANIL KUMAR	PROF.ROLI PURWAR
(HEAD OF THE DEPARTMENT)	(SUPERVISOR)

ACKNOWLEDMENT

The success and outcome of this project required a great deal of guidance and assistance from many people, and I am extremely fortunate to have received this support throughout its completion.

My heartfelt gratitude towards my project supervisor, Prof. Roli Purwar, Department of Applied Chemistry, Delhi Technological University, for providing me with the guidance and advice I needed to complete this project on time.

I would also like to thank Prof. Anil Kumar, Head of the Department of Applied Chemistry, Delhi Technological University, for his constant support during the project work. I would like to express my special thanks to my PhD scholars, Manu Dhiman and Megha Bhoj, for their constant motivation.

Last but not least, I would like to express my special thanks to my parents and my friends who have endured these long working days and whose motivation kept me moving ahead in this project.

VIJITA SINGH

(23/MSCCHE/62)

ABSTRACT

The widespread use of lead and its derivatives as piezoelectric materials has been causing immense environmental and notable public health issues. Herein, we are principally going to review lead-free piezoelectric materials. It is well known that Lead zirconate titanate (PZT) is prominent for its dominating piezoelectric qualities, but the primary cause of lead's extended environmental persistence is its non-biodegradable nature. Presently, several materials are being explored as potentially appealing PZT substitutes for particular uses. This study examines recent advances in lead-free materials, including ZnO nanostructures, inorganic ceramics such as barium titanate (BT), sodium potassium niobate (KNN), sodium bismuth titanate (BNT), bismuth layer-structured ferroelectrics (BLSFs), and polymers like PVDF and PVDF-TrFE. It focuses on their biocompatibility, high electromechanical coupling factor, and stable electrical properties, focusing on preparation, structure–property correlation, and finding promising applications in bioengineering, military, optoelectronic information, and energy. Lastly, the difficulties and viewpoints surrounding lead-free piezoelectric materials and devices are discussed.

Keywords: piezoelectric, lead-free materials, polymers, inorganic ceramics

CONTENTS

LIST OF TABLES & FIGURES

CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1. Introduction

The hazardous effects of lead on human health and the government have raised significant concerns over the continued use of lead-containing piezoelectric materials like lead zirconate titanate (PZT). Although PZT is known for its exceptional piezoelectric material efficiency, its toxicity has prompted a global shift towards safer, eco-conscious alternatives. As a result, scientists have introduced a new generation of lead-free materials that offer comparable performance while being environmentally benign. These include perovskite ceramics such as barium titanate and potassium sodium niobate, as well as materials from other categories like zinc oxide semiconductors and flexible organic polymers like PVDF and biopolymers.

At the same time, innovations in processing techniques-such as electrospinning, low-temperature fabrication, and 3D printing-have made it possible to tailor these materials for advanced uses. This has opened up exciting opportunities in the development of flexible electronics, energy-harvesting systems, medical sensors, and smart environmental monitors, marking a major step forward in sustainable material science.

1.2. Research Gaps in Lead-Free Piezoelectric Materials

Despite the considerable strides made in developing lead-free piezoelectric materials, their widespread commercial deployment still faces significant challenges. Although materials such as potassium sodium niobate (KNN), bismuth sodium titanate (BNT), barium titanate (BT), and polyvinylidene fluoride (PVDF) have demonstrated promising properties, critical limitations persist that hinder their ability to fully replace conventional lead-based systems like lead zirconate titanate (PZT).

1.2.1. Performance Gap Compared to PZT

A major barrier to the adoption of lead-free piezoelectrics lies in their inferior functional properties compared to PZT. While some lead-free ceramics, particularly KNN, have achieved piezoelectric coefficients (d_{33}) exceeding 400 pC/N through advanced doping and grain orientation methods, these outcomes are typically confined to laboratory-scale studies and are difficult to replicate under industrial conditions. Moreover, BNT-based materials often exhibit instability at elevated temperatures, including depolarization, which restricts their operational range in high-temperature applications. These performance inconsistencies continue to limit their practical viability in demanding environments.

1.2.2. Processing and Fabrication Challenges

Producing high-density, defect-free microstructures remains a critical challenge, especially in lead-free ceramics like KNN. Conventional sintering methods frequently result in porosity and heterogeneous grain structures, which negatively impact piezoelectric response. Although advanced approaches such as reactive template grain growth (RTGG) have been proposed to address these microstructural issues, such methods are often too complex or costly for large-scale implementation. In the case of polymers like PVDF and its copolymers PVDF-TrFE, reliable induction of the electroactive β-phase is essential for optimal performance. However, processes such as mechanical stretching and electrical poling have yet to be standardized for consistent and scalable outcomes.

1.2.3. Thermal and Electrical Stability

Lead-free piezoelectrics generally exhibit inferior thermal and electrical endurance compared to their lead-based counterparts. For example, barium titanate (BT) has a relatively low Curie temperature (~ 130 °C), which confines its utility in applications involving high thermal loads. Similarly, PVDF-based materials tend to degrade under prolonged exposure to heat and ultraviolet light, resulting in compromised performance.

1.2.4. Limited Understanding of Domain Dynamics

A comprehensive grasp of the domain switching, phase transformation, and fatigue characteristics in lead-free piezoelectric materials remains underdeveloped. In particular, materials based on BNT display complex phase transitions, especially between rhombohedral and tetragonal structures near the morphotropic phase boundary (MPB), which are not yet thoroughly clarified. This lack of clarity hampers the ability to accurately model and tailor material compositions for improved functional performance. Compared to the extensive studies on PZT, investigations into aspects such as domain wall motion, resistance to fatigue, and long-term aging behaviour in lead-free alternatives are still relatively limited.

1.2.5. Scalability and Cost-Efficiency

The commercial scalability of lead-free piezoelectric materials is another pressing gap. Many high-performing materials are synthesized using techniques such as sol-gel processing, hydrothermal synthesis, or spark plasma sintering, which are either cost-prohibitive or not scalable. For industrial adoption, more cost-effective and robust processing routes must be developed without compromising material performance.

1.2.6. Underexplored Biopolymer Systems

Though the paper discusses the potential of natural materials such as chitin, collagen, and gelatin, these systems remain vastly underexplored. Their inherent biocompatibility and biodegradability make them ideal for transient biomedical applications, yet their piezoelectric properties are relatively weak, and synthesis protocols are still in early stages. Exploring molecular modifications, cross-linking strategies, and composite formation with ceramic nanoparticles may open new frontiers in bio-piezoelectronics.

1.3. Research Objectives

1. To identify environmentally sustainable piezoelectric materials with high performance.
2. To improve synthesis techniques for better material quality and uniformity
3. To strengthen thermal and electrical reliability under operating conditions
4. To facilitate the integration of lead-free materials into functional devices
5. To explore naturally derived piezoelectric biomaterials

CHAPTER 2

LITERATURE REVIEW

Over the past decade, researchers have made significant strides in discovering and optimizing lead-free piezoelectric compounds. The evolution from PZT to green materials is motivated by international regulations such as the EU's Restriction of Hazardous Substances (RoHS), which limits the use of lead in electronic devices.

2.1. Piezoelectricity Concept

The piezoelectric effect is the phenomenon whereby piezoelectric materials produce an electric charge in response to mechanical stress[2]. The Curie brothers discovered this effect for the first time in 1880. The word "piezo" comes from the definition of mechanical tension or pressure. The direct effect, in which mechanical strain results in an electric charge, and the converse effect, in which an electric field causes mechanical deformation, are the two modes of operation of the piezoelectric effect (Fig.1). Because of these characteristics, piezoelectric materials can be employed in two main applications: actuators, which use the opposite effect, and sensors, which rely on the direct effect[3]. The development of sensors and actuators based on this phenomenon was made possible by the discovery of piezoelectricity.

Piezoelectric materials exhibit two effects: the **direct effect** (mechanical stress inducing electric charge) and the **converse effect** (electric field causing mechanical deformation). These effects are exploited in sensors and actuators, respectively.

Two key operation modes are:

- **d33 Mode (Longitudinal):** Polarization and applied force are parallel, yielding higher charge density.
- **d31 Mode (Transverse):** Polarization and applied force are perpendicular.

The efficiency of energy conversion depends on factors such as the material's crystalline structure, electromechanical coupling coefficient, and design architecture.[4][5]

2.2. Notable advancements include:

- Barium titanate (BT) and its solid solutions for enhanced piezoelectric responsiveness and Curie temperatures.
- KNN-based systems with improved performance through texturing and dopant engineering.
- Promising actuator behavior is provided by bismuth sodium titanate (BNT), particularly in multicomponent solid solutions.
- Organic polymers that offer mechanical flexibility and biocompatibility, such as PVDF and PVDF-TrFE.
- Piezoelectrics based on biopolymers (such as gelatin and chitin) for biodegradable, self-powered sensors.

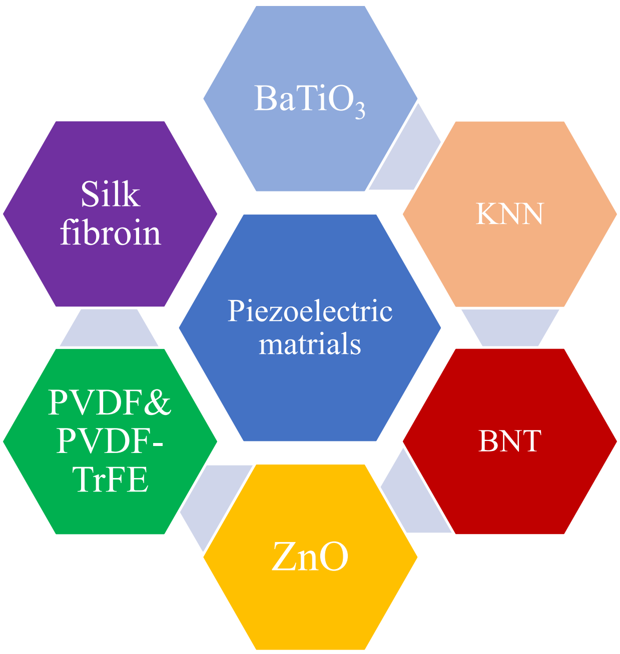


Fig.1. **Schematic diagram showing different piezoelectric materials**.

.2.3. Conventional Lead-Based Piezoelectric Materials

PZT remains the benchmark for piezoelectric performance due to its high d_{33} values and tunable phase boundaries[6]. However, its toxic lead oxide content leads to serious environmental accumulation and health hazards like neurotoxicity and developmental impairments.[7] Thus, the shift towards lead-free alternatives is not only strategic but imperative[8].

2.4. Lead-Free Piezoelectric Materials: Progress and Challenges

2.4.1. Barium Titanate (BT)-Based Systems

Barium titanate ($BaTiO_3$, BT) was among the first perovskite-structured materials discovered to exhibit significant piezoelectric and ferroelectric properties. While historically recognized for its use in capacitors, its piezoelectric behavior has garnered substantial attention for eco-friendly device applications[9]. BT offers several advantages, including a relatively high dielectric constant, strong electromechanical coupling, and ease of fabrication through various ceramic processing methods.

However, the primary limitation of pure BT lies in its low Curie temperature (approximately 120°C), which restricts its operational range in high-temperature applications. To overcome this challenge, extensive efforts have been directed toward modifying the BT structure through compositional engineering. Strategies such as doping with elements like calcium, zirconium, and bismuth have been employed to enhance both thermal stability and piezoelectric response[10].

For instance, binary systems such as $BaTiO_3$–$(Bi_{0.5}K_{0.5})TiO_3$ (BKT) have demonstrated a significant increase in Curie temperature, reaching values around 380°C. Furthermore, Praveen et al. [11] reported successful synthesis of barium zirconate titanate-barium calcium titanate (BZT–BCT) ceramics using sol-gel techniques, achieving superior phase control, smaller particle sizes, and enhanced piezoelectric properties. Their optimized compositions exhibited a high remanent polarization (12.2 $\mu C/cm^2$), a piezoelectric coefficient (d_{33}) of 637 pC/N, and an electromechanical coupling factor (k_p) of 0.0596, illustrating BT-based systems' potential to rival traditional PZT ceramics.

Recent investigations have also explored ternary systems, such as $BaTiO_3$–$BiFeO_3$–$Bi(Mg_{0.5}Ti_{0.5})O_3$ (BF–BT–BMT), which exhibit morphotropic phase boundaries (MPBs) analogous to those in PZT. The formation of MPBs between pseudocubic and rhombohedral phases leads to a substantial enhancement in piezoelectric performance. An optimal composition achieved in this system exhibited a piezoelectric coefficient of 154 pC/N and a Curie temperature exceeding 480°C, offering a promising route for high-temperature piezoelectric applications.[12]

2.4.2. Potassium Sodium Niobate (KNN)-Based Systems

Potassium sodium niobate ($K_{0.5}Na_{0.5}NbO_3$, commonly referred to as KNN) has emerged as one of the most promising candidates to replace lead-based piezoelectrics, particularly PZT, owing to its excellent piezoelectric properties, high Curie temperature, and environmentally benign nature[13]. KNN-based ceramics exhibit a Curie temperature around 400°C, significantly higher than that of barium titanate, thus offering superior thermal stability for high-temperature device applications.

Despite these advantages, unmodified KNN typically demonstrates a moderate piezoelectric constant (d_{33} in the range of 80–160 pC/N), which initially limited its practical competitiveness against PZT[14]. To overcome this, extensive research has focused on compositional tailoring and microstructural engineering. Methods such as texturing, doping with aliovalent ions, and forming solid solutions have been shown to significantly enhance the piezoelectric response.

A notable advancement was achieved by Saito et al., who utilized reactive template grain growth (RTGG) to fabricate highly textured (K, Na, Li) (Nb, Ta, Sb) O_3 ceramics, attaining a piezoelectric coefficient as high as 416 pC/N—comparable to commercial PZT[15]. Further enhancements have been realized through careful doping strategies; for example, the incorporation of $(Bi_{0.5}K_{0.5})HfO_3$ and $CaZrO_3$ into KNN matrices has led to piezoelectric coefficients surpassing 550 pC/N, demonstrating the flexibility of KNN-based systems to achieve superior functional properties[16].

Beyond enhancements in piezoelectric properties, compositional modifications of KNN have also led to higher mechanical quality factors and better polarization stability-both essential for applications such as actuators and energy harvesting. According to Li et al., KNN ceramics with significant texturing achieved a d_{33} value as high as 700 pC/N along with a Curie temperature of 242 ℃, establishing them as some of the most efficient lead-free piezoelectric materials to date [17].

In summary, KNN-based materials have shown remarkable potential through continuous innovations in composition and processing. Their high Curie temperature, combined with tunable piezoelectric properties, makes them strong contenders for next-generation, eco-friendly piezoelectric applications, particularly in biomedical implants, high-temperature transducers, and flexible energy harvesting devices[18][19].

2.4.3. Bismuth-Based Systems

Bismuth-based compounds have gained substantial attention as lead-free piezoelectric materials due to their distinctive layered structures, high depolarization temperatures, and intrinsic environmental friendliness. Among them, bismuth sodium titanate ($Bi_{0.5}Na_{0.5}TiO_3$, BNT) and bismuth layer-structured ferroelectrics (BLSFs) represent two key families offering unique advantages for actuator and sensor applications.

BNT, a perovskite material, demonstrates notable ferroelectric and piezoelectric characteristics and possesses a relatively high depolarization temperature nearing 290 °C, though its native (d_{33} ~75 pC/N) is moderate. Performance enhancements through its lithium and strontium doping have led to materials like BNLST, which show improved d_{33} values exceeding 170 pC/N and stable functionality at temperatures beyond 300 °C [20], making them excellent ctes for high-temperature applications in actuators, precision positioning systems, and biomedical ultrasound devices.

(BLSFs), such as $Bi_4Ti_3O_{12}$ and $BiNbTiO_9$ stand out for their remarkable thermal endurance, often functioning effectively at temperatures above 600 °C. Although their piezoelectric output is relatively modest (typically between 20-30 pC/N), their robustness in extreme thermal and mechanical environments makes them ideal for sensor applications and deep-well drilling.

Furthermore, to address inherent limitations such as low polarization and weak piezoelectric sensitivity, BLSFs have been modified through rare-earth doping-using elements like lanthanum or cerium-to boost piezoelectric response and reduce coercive fields [21].These strategies continue to advance the potential of BLSFs for operation in demanding conditions.

Table 1. Piezoelectric materials and their properties

Materials	Composition	Preparation method	Tc(C)	d33	*Ref.*
PVDF	B-phase PVDF	Phase transition technique	_	-49.6	[22]
Biopolymers	Fish gelatine nanofibers	Electrospinning		-20	[23]
BLSFs	$BaBi_4T_4O_{15-x}CeO_2$	High Temperature Solid-State method	407	242	[24][25]
KNN-based ceramic	$_{0.96}(K_{0.5}Na_{0.5})_{0.95}Li_{0.05}Nb_{(1-x)}Sb_xO_3\ _{0.04}BaZrO_3$	Normal Sintering	197	425	[26]
	$(Na,K)(Nb,Ta)O_3$	TSSG	291	200	[27]
BT-based ceramics	$xBa(Zr_{0.2}Ti_{0.8})O_3\ _{(1-x)}(Ba_{0.7}Ca_{0.3})TiO_3$	Sol-gel method	_	637	[11]
	BF–BT–xBi(Mg ½ Ti ½)O_3	High Temperature Sintering	482	184	[12]
BNT-based ceramic system	$_{0.94}(Bi_{0.5}Na_{0.5})TiO_3–_{0.06}BaTiO_3-xBi_4Ti_3O_{12}$(BNT–BT–xBiT)	Conventional Solid-State method	675	152	[28]
	$_{0.95}$(Na ½ Bi ½) $TiO_3–_{0.05}$ BaTiO	TSSG	_	360	[29]

2.4.4. Zinc Oxide (ZnO) Nanostructures

ZnO is a wide-bandgap semiconductor with intrinsic piezoelectric characteristics stemming from its non-centrosymmetric wurtzite structure[30]. In addition to its common use in electronics and optoelectronics, zinc oxide (ZnO) nanowires and nanobelts have gained attention for generating mechanical energy using piezoelectric nanogenerators (PENGs)[31]. The vast surface area, high flexibility, and ease of fabrication of ZnO nanostructures make them ideal for application in wearable and flexible energy devices. However, their piezoelectric performance can be affected by free charge carriers that reduce efficiency through internal screening. To overcome this, recent improvements like doping with elements such as chlorine and modifying the surface of ZnO have helped increase their energy conversion capabilities.

2.4.5. Bismuth Ferrite ($BiFeO_3$)

Bismuth ferrite ($BiFeO_3$) is a unique multiferroic oxide that displays both ferroelectric and antiferromagnetic properties at room temperature, a combination that is uncommon in such materials. Its high Curie temperature (~830°C) and substantial spontaneous polarization make it a strong candidate for high-temperature piezoelectric applications. Although challenges related to leakage current and phase stability persist, progress in nanostructuring $BiFeO_3$ thin films and creating solid solutions (e.g., $BiFeO_3$–$BaTiO_3$ composites) has demonstrated enhanced piezoelectric responses and electrical reliability. The multifunctional nature of $BiFeO_3$ also opens prospects for devices that combine mechanical energy harvesting with magnetic field sensing, broadening its appeal for smart systems.

In summary, emerging inorganic systems like ZnO, $ZnSnO_3$, and $BiFeO_3$ expand the landscape of lead-free piezoelectrics by offering distinctive mechanical, electronic, and multifunctional properties. Their compatibility with flexible platforms and potential for integration into wearable, biomedical, and environmental monitoring technologies make them attractive targets for future research and development.

2.4.6. Polyvinylidene Fluoride (PVDF) and Its Copolymers

Polyvinylidene fluoride (PVDF) is one of the piezoelectric polymers that has attracted a lot of interest because of its comparatively high piezoelectric performance in organic materials. Apart from its electromechanical characteristics, PVDF has strong chemical stability, low acoustic impedance, and great flexibility, which make it suitable for a variety of uses [32]. Under mechanical stress, aligned molecular dipoles in PVDF's β-phase crystal structure produce detectable polarization, which is the main cause of the piezoelectric effect. PVDF is usually subjected to electrical poling and mechanical stretching, which raises the percentage of the desired β-phase, in order to improve this piezoelectric characteristic. PVDF can exhibit piezoelectric coefficients ranging from 24 to -34 pC/N even in the absence of significant treatment, hence facilitating its application in cutting-edge technologies such as flexible sensors and nanogenerators[33]. PVDF is becoming more and more popular in applications such as wearable electronics, biomedical implants, and miniature robotic systems because of its low weight and mechanical versatility [34]. By encouraging the β-phase to emerge spontaneously, the copolymer PVDF-TrFE (polyvinylidene fluoride–trifluoroethylene) improves on PVDF's functionality. Trifluoroethylene (TrFE) increases remanent polarization and improves electromechanical coupling by lowering the energy barrier for the formation of polar crystalline areas. Because of this, PVDF-TrFE is more effective than regular PVDF in applications such as energy scavengers, motion-actuated devices, and flexible pressure sensors.[35]

Modern processing techniques like electrospinning and nanoimprinting have shown promise in aligning polymer chains, greatly boosting the material's piezoelectric output. Further improving their functionality in cutting-edge electronic devices, PVDF-TrFE has been combined with inorganic fillers, such as barium titanate ($BaTiO_3$) nanoparticles, to create composite systems with better piezoelectric and dielectric qualities.

2.4.7. Biopolymer-Based Piezoelectrics

Natural biopolymers such as cellulose[36], chitin, collagen[37], and gelatin have also demonstrated intrinsic piezoelectric behavior, offering biodegradable and biocompatible alternatives to synthetic polymers. These materials possess hierarchical molecular structures with oriented dipoles, leading to mechanical-electrical coupling under deformation.

For example,[23] electrospun gelatin nanofibers derived from fish sources have been shown to generate detectable piezoelectric signals, paving the way for their use in self-powered biomedical sensors. Similarly, chitin films extracted from squid pens have exhibited notable piezoelectric outputs, making them promising candidates for eco-friendly, flexible energy harvesting devices[38].

Biopolymer-based systems are especially appealing for transient electronics, implantable devices, and green technologies, where biodegradability and minimal environmental impact are critical requirements. While their piezoelectric coefficients are generally lower compared to PVDF or inorganic ceramics, ongoing research into hybrid structures and molecular alignment strategies is rapidly improving their performance.

In conclusion, organic lead-free materials, encompassing synthetic polymers like PVDF and PVDF-TrFE and naturally derived biopolymers, represent a versatile and sustainable class of piezoelectric materials. Their unique combination of flexibility, light weight, and compatibility with soft interfaces positions them at the forefront of innovation in wearable electronics, medical implants, and flexible energy systems.

Table 2. Parameters of Lead-Free Piezoelectric Materials

Materials	d_{33}(pC/N)	Tc(°C)	K
KNN	80-160 [39],[40]	400 [14]	0.51 [39]
ZnO	9.2,12.4 [41],[42]	-	-
$BaTiO_3$	191[43]	130 [43]	0.49 [44]
$LiNbO_3$	6 [45]	1150 [45]	0.23 [45]
BNT	75 [46]	<290 [47]	~0.21 [48]
AlN	5 [49]	>2000 [50]	0.23 [51]
PVDF	-24 to -34 [34]	75-80 [34]	0.20 [52]
PVDF-TrFE	-25 to -40 [45]	~110 [52]	~0.29 [52]

2.5. Applications of Lead-Free Piezoelectric Materials

Numerous opportunities for their practical application have been made possible by the exceptional electromechanical qualities of lead-free piezoelectric materials as well as advancements in fabrication techniques. They are perfect candidates for new technologies in the consumer electronics, healthcare, energy, and industrial sectors because of their inherent flexibility, biocompatibility, and environmental sustainability. The main application areas where lead-free piezoelectrics are having a revolutionary effect are covered in this section.

2.5.1 Energy Harvesting Systems

For remote or wearable devices in particular, mechanical energy harvesting is an essential method for powering portable and autonomous electronics. Body movements, vibrations, and environmental forces are examples of ambient mechanical deformations that can be transformed into useful electrical energy via lead-free piezoelectric nanogenerators (PENGs).

The development of flexible PENGs has made extensive use of ZnO nanostructures because of their simplicity of production and suitability for soft surfaces. The construction of lightweight, stretchable harvesters that can power low-energy devices like fitness trackers and medical sensors has also been made possible by PVDF and PVDF-TrFE-based flexible films.

With improved output voltages and energy conversion efficiencies, recent hybrid designs that combine polymers and lead-free ceramics like $BaTiO_3$ are interesting options for integration into wearable electronics, smart fabrics, and the Internet of Things (IoT) nodes. Furthermore, with the development of ultra-sensitive lead-free piezoelectric materials, energy harvesting from biomechanical sources, like human walking or heartbeats, has become more and more possible.

2.5.2 Wearable and Implantable Sensors

For wearable and implantable sensor technologies, many lead-free piezoelectrics are perfect due to their flexibility, low weight, and biocompatibility. Applications include blood pressure, breathing, joint movement, heart rate, and other physiological indicators that allow for continuous health tracking without the use of external power sources.
For real-time motion detection and posture monitoring, PVDF-based films have been integrated into smart clothing and patches when arranged into pressure-sensitive matrices. Biodegradable and environmentally safe alternatives for short-term biomedical implants that spontaneously disintegrate after their useful life are provided by biopolymer sensors manufactured from chitin and gelatin. Furthermore, lead-free piezoelectric sensors that are implantable and based on BNT or KNN ceramics have been investigated for internal body monitoring. These sensors provide less invasive options for patient care and rehabilitation without the hazardous risk that comes with lead-containing systems.

2.5.3. MEMS and NEMS Devices

Actuators, resonators, switches, and filters are among the quickly expanding sectors of microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS), which use piezoelectric materials. In addition to meeting environmental regulations, lead-free piezoelectrics provide excellent performance at small scales when incorporated into MEMS/NEMS devices.

For instance, because of their strong mechanical characteristics and suitability for semiconductor production, aluminium nitride (AlN) thin films have been effectively used in high-frequency resonators and filters. The usage of lithium niobate ($LiNbO_3$) thin films in MEMS sensors for high-temperature and high-frequency applications is also growing.

Developments in 3D microfabrication, lithographic patterning, and thin-film deposition have made it possible to precisely manage lead-free piezoelectric MEMS/NEMS systems, opening the door to new developments in energy-efficient computing, wireless communication, and biological sensing.

In summary, lead-free piezoelectric materials have transcended traditional applications, finding new roles in energy harvesting, flexible and wearable sensing, and miniaturized electromechanical systems. Their adaptability, environmental friendliness, and compatibility with advanced manufacturing techniques position them at the forefront of sustainable technological development across multiple domains.

Table 3. Summary of Inorganic, Organic, and Biopolymer Lead-Free Piezoelectric Materials.

Material	**Type**	**Key Properties**	**Applications**	**Enhancements / Notes**
Barium Titanate ($BaTiO_3$)	Inorganic – Perovskite oxide	Exhibits a high dielectric constant and strong electromechanical coupling	Used in capacitors, actuators, and multilayer ceramic devices	Performance enhanced with BKT or BMT to increase Curie temperature
Potassium Sodium Niobate (KNN)	Inorganic – Perovskite oxide	Shows piezoelectric coefficient up to 700 pC/N with doping; biocompatible	Ideal for high-temperature sensors and implantable medical devices	Improved by doping with elements like Li and Ta
Bismuth Sodium Titanate (BNT)	Inorganic – Perovskite oxide	Provides large strain response suitable for actuators	Applied in actuators and micro-electromechanical systems (MEMS)	Performance enhanced by doping with Sr, Li, or La
Zinc Oxide (ZnO)	Inorganic – Wurtzite semiconductor	Forms nanowires, exhibits flexibility, suitable	Utilized in nanosensors, energy harvesters,	Nanostructuring enhances sensitivity and performance

		for nanoscale piezoelectric use	and flexible electronics	
$LiNbO_3$ / AlN	Inorganic – Non-centrosymmetric	Stable at high temperatures, MEMS-compatible, lower d_{33}	Used in RF filters, optical systems, and MEMS components	Well-suited for extreme environments due to thermal stability
PVDF / PVDF-TrFE	Organic – Synthetic polymer	Highly flexible, shows piezoelectricity in the β-phase	Applied in wearable electronics, sensors, and flexible devices	β-phase alignment improves piezoelectric effect
Chitin / Collagen / Gelatin	Biopolymer – Natural origin	Naturally piezoelectric, biodegradable, compatible with biological systems	Used in health-monitoring sensors and self-powered biomedical devices	Blends allow tailoring; eco-friendly alternatives to synthetics
Silk Fibroin – ZnO Composite	Hybrid – Biopolymer + Inorganic	Combines silk's flexibility with ZnO's piezoelectric features; easy to cast into films	Ideal for wearable biosensors, targeted drug delivery, and soft electronics	Performance relies on crystal orientation and ZnO distribution

CHAPTER-3

EXPERIMENTAL ANALYSIS

3.1. Materials

Silk cocoons from mulberries (Bombyx mori) were provided by the Central Sericulture Research and Training Institute in Mysore, India. Calcium chloride fused LR was supplied by Thomas Baker (Chemicals) Pvt. Ltd. A 99.5% pure form of glycerol was provided by Thermos Fisher Scientific India Pvt. Ltd. Avantor Performance Materials India Ltd. provided 98% pure methanol (AR) and formic acid (AR). Sisco Research Laboratories Pvt. Ltd. supplied the Type I zinc oxide nanopowder (average particle size: 30 nm). Milli-Q water was employed in the coagulation process.

3.2. Degumming Process of silk fibroin

Degumming of silk cocoons was done as shown in the fig.2. In the degumming process, the silk cocoon (*Bombyx mori*) was cut into small parts and placed in a 1 L (1000 ml) of boiling solution of Na_2CO_3 (0.02 M) for 3-4 hours to remove sericin or other impurities completely. The obtained silk fibroins were dried in an oven set to 70 degrees Celsius for the entire night after being rinsed three to four times in hot water (2 L) for 30 minutes. The degummed silk fibroin was stored in a dry place.

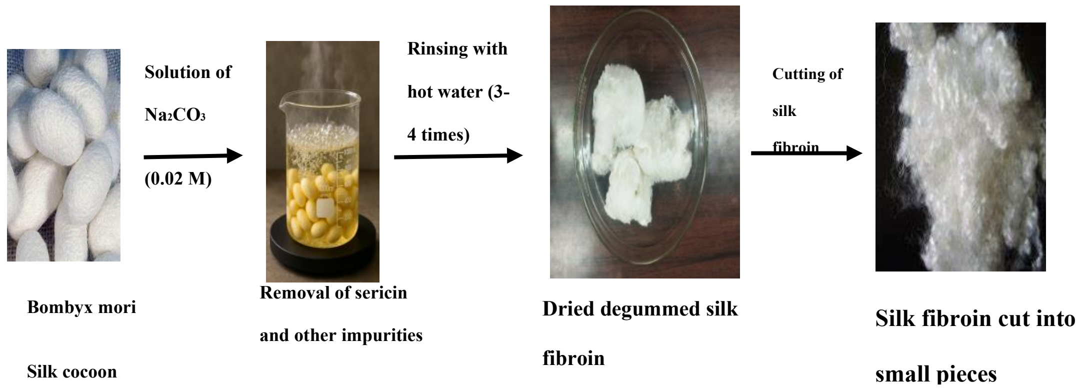


Fig.2. Degumming Process of *Bombyx mori* Silk Fibroin

3.3. Preparation of silk fibroin solutions

The degummed silk was slowly dissolved in a solution of 10 ml of formic acid (98-100 %)-calcium chloride (2 wt% (w/v)) at room temperature by continuous stirring for up to 3-4 hours. The final concentration was kept at 10 wt% (w/v). After continuous stirring of 3-4 hours, plasticizer Dextrose anhydrase (15%(w/v)) was added to the solution to induce flexibility in the films. After that, the solution was again stirred for another 2-3 hours to get a homogenous solution.

$CaCl_2$ is essential for dissolving silk in formic acid (FA) because it breaks the fibroin structure's hydrogen bond. As soon as formic acid causes the silk fibroin structure to swell, $CaCl_2$ enters it and breaks it up into fibrils that are nm in size.

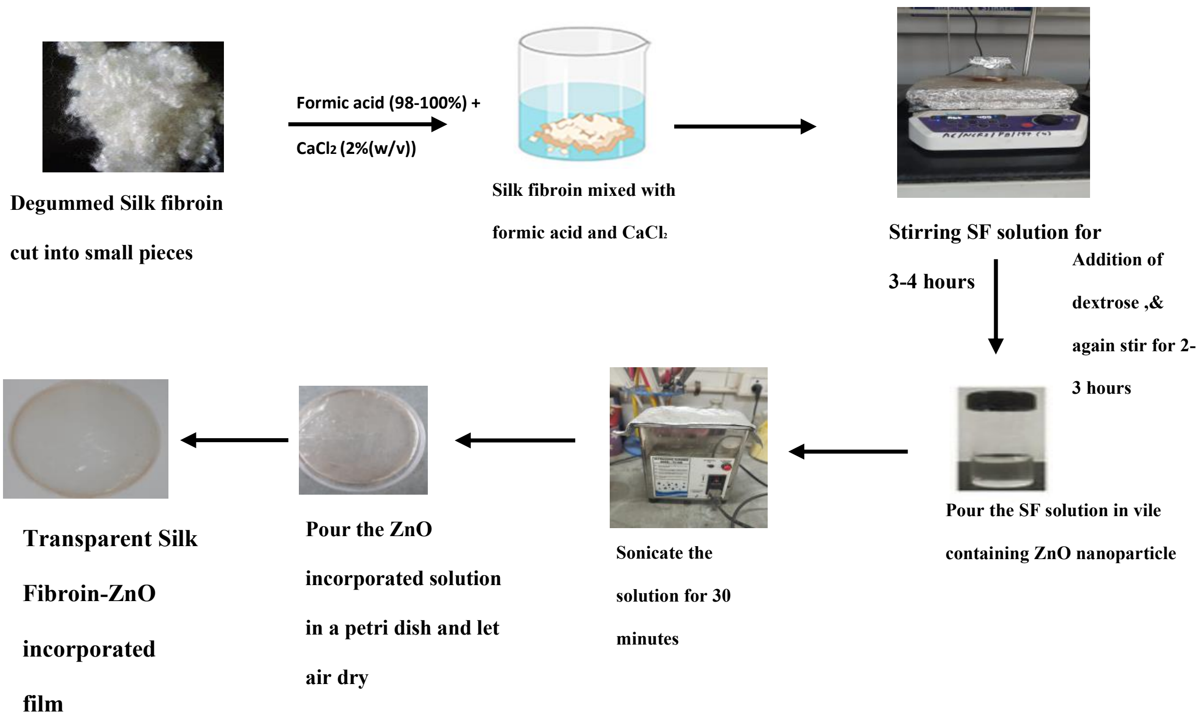


Fig.3. Preparation of pure silk fibroin film

3.4. Formulation of Silk Fibroin films with Metal Oxide Nanoparticles

To begin, Zinc Oxide nanoparticles were dispersed in a solution containing 2% (w/v) calcium chloride dissolved in formic acid. This dispersion was subjected to sonication for 30 minutes to ensure thorough mixing. The resulting nanoparticle-containing solution was then used to dissolve silk fibroin at room temperature. This dissolution process was carried out under continuous stirring at 500 revolutions per minute(rpm) for approximately 3 to 4 hours. The silk fibroin concentration in the solution was adjusted to 10 % (w/v).

In order to impart flexibility to the films, Dextrose anhydrase (plasticizer) was incorporated into the silk fibroin solution at a concentration of 15% (w/v). The amount of metal oxide nanoparticles added to the fibroin solution was varied systematically, with the concentration set at 0.75% and 1.0% (w/w), to examine the influence of nanoparticle content on the characteristics of the composite films.

3.5. Film Fabrication via the Solvent Casting Technique

The films were fabricated using the solvent casting method. Different volumes of the prepared solution were dispensed into petri dishes to obtain films with target thicknesses of approximately 3ml and 5ml. After casting, the films were left to dry under ambient conditions overnight to allow solvent evaporation and film formation.

In **Figure 3**, the degumming and fabrication of silk fibroin nanocomposite solutions and films have been presented.

Table 4. Fabrication process of Silk Fibroin solutions and films

Sample	Fabrication and treatment Conditions
Pure Silk fibroin (SF)	Degummed silk fibroin dissolved in $CaCl_2$/formic acid (2 wt% (w/v)) solvent and the pure silk fibroin solutions.
Silk fibroin/ZnO	Zinc Oxide nanoparticles (0.75% w/w) incorporated silk fibroin bio-nanocomposite solution.
Silk fibroin/ZnO	Zinc Oxide nanoparticles (1% w/w) incorporated silk fibroin bio-nanocomposite solution

CHAPTER- 4

RESULTS AND DISCUSSION

4.1. Conductivity Analysis

The graph shows the variation of electrical conductivity over time for pure silk fibroin and ZnO-incorporated SF films (0.75% and 1% w/w). The ZnO (0.75 %) film exhibits the highest conductivity, followed by pure SF and then the 1% ZnO film. The enhancement in conductivity for the 0.75 % ZnO sample suggests optimal dispersion and effective charge transport pathways. In contrast, the slight decrease in conductivity for the 1 % ZnO sample may result. Overall, the incorporation of ZnO nanoparticles significantly improves the electrical performance of silk fibroin, particularly at optimized concentrations.

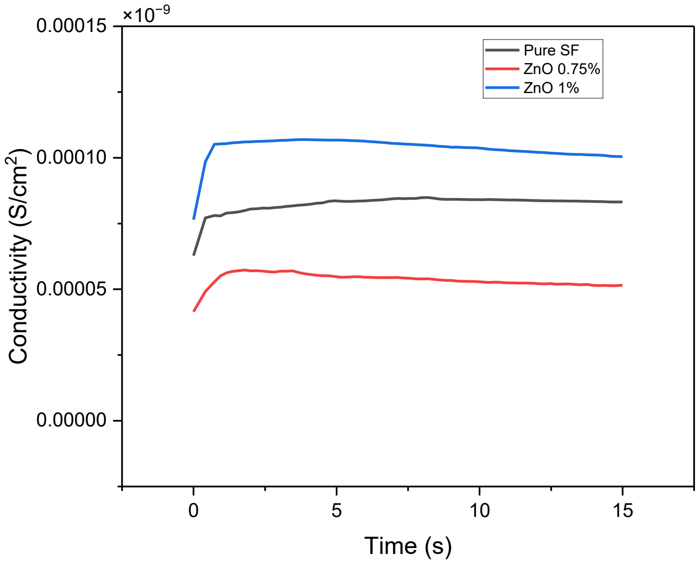


Fig 4. Conductivity analysis of Pure SF and ZnO incorporated films

4.2 FTIR Analysis of. Pure SF and ZnO incorporated films

FTIR spectra of pure silk fibroin of pure silk fibroin and ZnO-incorporated silk fibroin films (0.75 % and 1 % w/w ZnO) showing the characteristics of Amide I, Amide II, and Amide III bands. The spectral shifts and intensity changes indicate alterations in the secondary structure of silk due to ZnO nanoparticle incorporation. Spectra in the range of 1800-1200 cm^{-1} highlight the Amide I, Amide II, and Amide III bands characteristic of silk fibroin's secondary structure. The Amide I shows a peak shifting in the range of (~ 1620 -1650 cm^{-1}), associated with C=O stretching, shows a noticeable decrease in intensity upon ZnO incorporation, indicating disruption of β-sheet content. The Amide II band shows a peak shifting in the range of (~ 1500 -1600 cm^{-1}), representing N-H bending and C-N stretching, also shifts and becomes less intense in the ZnO-loaded samples. The Amide III band shows a peak shifting in the range of (~ 1220 -1300 cm^{-1}), linked to C-N stretching and N-H deformation, displays slight broadening and intensity changes. Overall, the spectral changes suggest that ZnO nanoparticles interact with the silk matrix, reducing crystallinity and enhancing molecular disorder, which supports improved flexibility of the films.

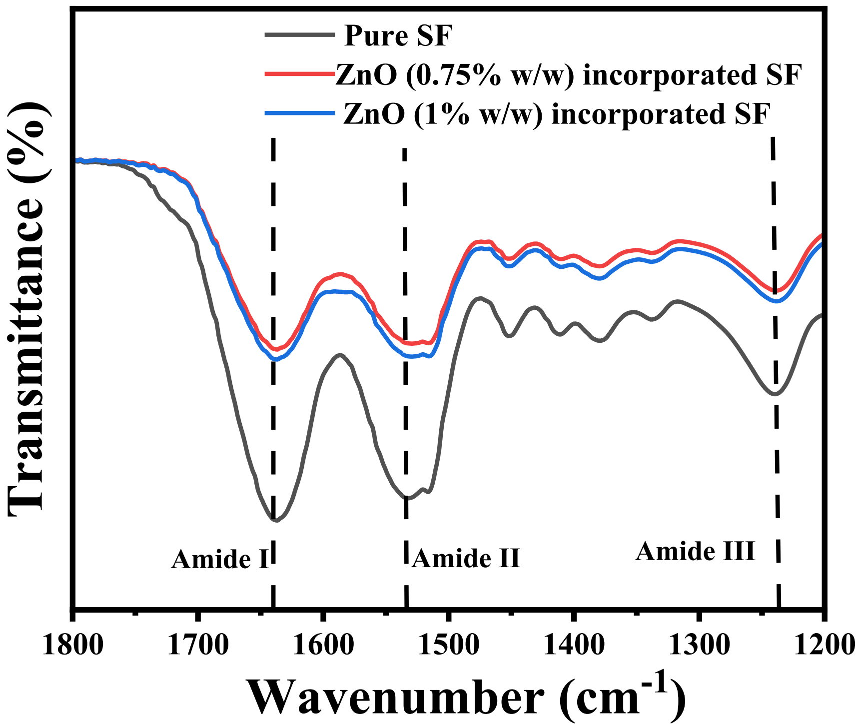


Fig 5.. FTIR Spectra of Pure SF and ZnO Incorporated Films

CHAPTER -5

CONCLUSIONS & FUTURE SCOPE OF WORK

This study explored the potential of lead-free piezoelectric materials with a special focus on silk fibroin-ZnO hybrid films for flexible electronic applications. Through a thorough literature review and experimental evaluation, it was demonstrated that the incorporation of ZnO nanoparticles into silk fibroin significantly enhances its piezoelectric and electrical properties. The fabricated SF/ZnO determined how the conductivity of the silk fiber matrix was affected by metal oxide nanoparticles. Silk fibroin nanocomposite films' conductivity was improved by the addition of ZnO nanoparticles. The structural characteristics of silk fibroin/metal oxide nanocomposite films revealed that the inclusion of metal oxide nanoparticles decreased the crystal size, crystallinity, and β-sheet content. The Silk-ZnO hybrid films presented in this study offer a strong foundation for future developments in flexible piezoelectric devices. Upcoming research can focus on integrating these films into wearable sensors and energy-harvesting systems, while also evaluating their durability under real-world conditions. Enhancing functionality through the addition of other nanomaterials and employing advanced fabrication techniques like inkjet printing could enable miniaturized and patterned devices.

REFERENCES

[1] M. D. Maeder, D. Damjanovic, and N. Setter, “Lead Free Piezoelectric Materials,” *J Electroceram*, vol. 13, no. 1–3, pp. 385–392, Jul. 2004, doi: 10.1007/s10832-004-5130-y.

[2] P. K. Panda, “Review: environmental friendly lead-free piezoelectric materials,” *J Mater Sci*, vol. 44, no. 19, pp. 5049–5062, Oct. 2009, doi: 10.1007/s10853-009-3643-0.

[3] M. Habib, I. Lantgios, and K. Hornbostel, “A review of ceramic, polymer and composite piezoelectric materials,” *J Phys D Appl Phys*, vol. 55, no. 42, p. 423002, Oct. 2022, doi: 10.1088/1361-6463/ac8687.

[4] K. S. Ramadan, D. Sameoto, and S. Evoy, “A review of piezoelectric polymers as functional materials for electromechanical transducers,” *Smart Mater Struct*, vol. 23, no. 3, p. 033001, Mar. 2014, doi: 10.1088/0964-1726/23/3/033001.

[5] W. Tian, Z. Ling, W. Yu, and J. Shi, “A Review of MEMS Scale Piezoelectric Energy Harvester,” *Applied Sciences*, vol. 8, no. 4, p. 645, Apr. 2018, doi: 10.3390/app8040645.

[6] A. Tawfik, O. M. Hemeda, A. M. A. Henaish, and A. M. Dorgham, “High piezoelectric properties of modified nano lead titanate zirconate ceramics,” *Mater Chem Phys*, vol. 211, pp. 1–8, Jun. 2018, doi: 10.1016/j.matchemphys.2018.01.073.

[7] T. Fujii, S. Watanabe, M. Suzuki, and T. Fujiu, “Application of lead zirconate titanate thin film displacement sensors for the atomic force microscope,” *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena*, vol. 13, no. 3, pp. 1119–1122, May 1995, doi: 10.1116/1.587914.

[8] Z. Butt, R. A. Pasha, F. Qayyum, Z. Anjum, N. Ahmad, and H. Elahi, “Generation of electrical energy using lead zirconate titanate (PZT-5A) piezoelectric material: Analytical, numerical and experimental verifications,” *Journal of Mechanical Science and Technology*, vol. 30, no. 8, pp. 3553–3558, Aug. 2016, doi: 10.1007/s12206-016-0715-3.

[9] T. Takenaka, H. Nagata, and Y. Hiruma, “Current Developments and Prospective of Lead-Free Piezoelectric Ceramics,” *Jpn J Appl Phys*, vol. 47, no. 5S, p. 3787, May 2008, doi: 10.1143/JJAP.47.3787.

[10] A. Khokhar, M. L. V. Mahesh, A. R. James, P. K. Goyal, and K. Sreenivas, “Sintering characteristics and electrical properties of BaBi4Ti4O15 ferroelectric ceramics,” *J Alloys Compd*, vol. 581, pp. 150–159, Dec. 2013, doi: 10.1016/j.jallcom.2013.07.040.

[11] J. P. Praveen, T. Karthik, A. R. James, E. Chandrakala, S. Asthana, and D. Das, “Effect of poling process on piezoelectric properties of sol–gel derived BZT–BCT ceramics,” *J Eur Ceram Soc*, vol. 35, no. 6, pp. 1785–1798, Jun. 2015, doi: 10.1016/j.jeurceramsoc.2014.12.010.

[12] L.-F. Zhu, B.-P. Zhang, S. Li, L. Zhao, N. Wang, and X.-C. Shi, “Enhanced piezoelectric properties of Bi(Mg1/2Ti1/2)O3 modified BiFeO3–BaTiO3 ceramics near the morphotropic phase boundary,” *J Alloys Compd*, vol. 664, pp. 602–608, Apr. 2016, doi: 10.1016/j.jallcom.2016.01.003.

[13] H.-C. Thong *et al.*, “Technology transfer of lead-free (K, Na)NbO3-based piezoelectric ceramics,” *Materials Today*, vol. 29, pp. 37–48, Oct. 2019, doi: 10.1016/j.mattod.2019.04.016.

[14] J. Rödel, W. Jo, K. T. P. Seifert, E. Anton, T. Granzow, and D. Damjanovic, “Perspective on the Development of Lead-free Piezoceramics,” *Journal of the American Ceramic Society*, vol. 92, no. 6, pp. 1153–1177, Jun. 2009, doi: 10.1111/j.1551-2916.2009.03061.x.

[15] Y. Saito *et al.*, “Lead-free piezoceramics,” *Nature*, vol. 432, no. 7013, pp. 84–87, Nov. 2004, doi: 10.1038/nature03028.

[16] P. Li *et al.*, “High-performance potassium-sodium niobate lead-free piezoelectric ceramics based on polymorphic phase boundary and crystallographic texture,” *Acta Mater*, vol. 165, pp. 486–495, Feb. 2019, doi: 10.1016/j.actamat.2018.12.024.

[17] P. Li *et al.*, “Ultrahigh Piezoelectric Properties in Textured (K,Na)NbO $_3$ -Based Lead-Free Ceramics,” *Advanced Materials*, vol. 30, no. 8, Feb. 2018, doi: 10.1002/adma.201705171.

[18] L. Qiao, G. Li, H. Tao, J. Wu, Z. Xu, and F. Li, "Full characterization for material constants of a promising KNN-based lead-free piezoelectric ceramic," *Ceram Int*, vol. 46, no. 5, pp. 5641–5644, Apr. 2020, doi: 10.1016/j.ceramint.2019.11.009.

[19] A. Safari and M. Hejazi, "Lead-Free KNN-Based Piezoelectric Materials," in *Lead-Free Piezoelectrics*, New York, NY: Springer New York, 2012, pp. 139–175. doi: 10.1007/978-1-4419-9598-8_5.

[20] X. Zhang *et al.*, "Enhancement of recoverable energy density and efficiency of lead-free relaxor-ferroelectric BNT-based ceramics," *Chemical Engineering Journal*, vol. 406, p. 126818, Feb. 2021, doi: 10.1016/j.cej.2020.126818.

[21] S. Mahboob, G. Prasad, and G. S. Kumar, "Impedance spectroscopy and conductivity studies on B site modified (Na0.5Bi0.5)(NdxTi1 − 2xNbx)O3 ceramics," *J Mater Sci*, vol. 42, no. 24, pp. 10275–10283, Dec. 2007, doi: 10.1007/s10853-006-1122-4.

[22] N. Soin *et al.*, "Novel '3-D spacer' all fibre piezoelectric textiles for energy harvesting applications," *Energy Environ. Sci.*, vol. 7, no. 5, pp. 1670–1679, 2014, doi: 10.1039/C3EE43987A.

[23] S. K. Ghosh and D. Mandal, "Bio-assembled, piezoelectric prawn shell made self-powered wearable sensor for non-invasive physiological signal monitoring," *Appl Phys Lett*, vol. 110, no. 12, Mar. 2017, doi: 10.1063/1.4979081.

[24] C. L. Diao, J. B. Xu, H. W. Zheng, L. Fang, Y. Z. Gu, and W. F. Zhang, "Dielectric and piezoelectric properties of cerium modified BaBi 4 Ti 4 O 15 ceramics," *Ceram Int*, vol. 39, no. 6, pp. 6991–6995, Aug. 2013, doi: 10.1016/j.ceramint.2013.02.036.

[25] I. Coondoo, N. Panwar, H. Amorín, V. E. Ramana, M. Algueró, and A. Kholkin, "Enhanced Piezoelectric Properties of Praseodymium-Modified Lead-Free $(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$ Ceramics," *Journal of the American Ceramic Society*, vol. 98, no. 10, pp. 3127–3135, Oct. 2015, doi: 10.1111/jace.13713.

[26] B. Zhang *et al.*, "Lead-free Piezoelectrics Based on Potassium–Sodium Niobate with Giant d_{33}," *ACS Appl Mater Interfaces*, vol. 5, no. 16, pp. 7718–7725, Aug. 2013, doi: 10.1021/am402548x.

[27] L. Zheng, X. Huo, R. Wang, J. Wang, W. Jiang, and W. Cao, “Large size lead-free (Na,K)(Nb,Ta)O3 piezoelectric single crystal: growth and full tensor properties,” *CrystEngComm*, vol. 15, no. 38, p. 7718, 2013, doi: 10.1039/c3ce40658j.

[28] P. Li, B. Liu, B. Shen, J. Zhai, L. Li, and H. Zeng, “Large strain response in Bi 4 Ti 3 O 12 modified BNT-BT piezoelectric ceramics,” *Ceram Int*, vol. 43, no. 1, pp. 1008–1013, Jan. 2017, doi: 10.1016/j.ceramint.2016.10.033.

[29] L. Zheng *et al.*, “Complete set of material constants of 0.95(Na0.5Bi0.5)TiO3-0.05BaTiO3 lead-free piezoelectric single crystal and the delineation of extrinsic contributions,” *Appl Phys Lett*, vol. 103, no. 12, Sep. 2013, doi: 10.1063/1.4821853.

[30] A. Kurihara, K. Nomura, K. H. Ken-ichi Hirota, and T. I. Takuro Ikeda, “Piezoelectricity and Electrostriction in Ferroelectric Actuators,” *Jpn J Appl Phys*, vol. 31, no. 9S, p. 3085, Sep. 1992, doi: 10.1143/JJAP.31.3085.

[31] X. Wang, J. Song, and Z. L. Wang, “Nanowire and nanobelt arrays of zinc oxide from synthesis to properties and to novel devices,” *J Mater Chem*, vol. 17, no. 8, p. 711, 2007, doi: 10.1039/b616963p.

[32] H. Kawai, “The Piezoelectricity of Poly (vinylidene Fluoride),” *Jpn J Appl Phys*, vol. 8, no. 7, p. 975, Jul. 1969, doi: 10.1143/JJAP.8.975.

[33] K. K. Sappati and S. Bhadra, “Piezoelectric Polymer and Paper Substrates: A Review,” *Sensors*, vol. 18, no. 11, p. 3605, Oct. 2018, doi: 10.3390/s18113605.

[34] J. Gomes, J. Serrado Nunes, V. Sencadas, and S. Lanceros-Mendez, “Influence of the β-phase content and degree of crystallinity on the piezo- and ferroelectric properties of poly(vinylidene fluoride),” *Smart Mater Struct*, vol. 19, no. 6, p. 065010, Jun. 2010, doi: 10.1088/0964-1726/19/6/065010.

[35] L. Persano *et al.*, “High performance piezoelectric devices based on aligned arrays of nanofibers of poly(vinylidenefluoride-co-trifluoroethylene),” *Nat Commun*, vol. 4, no. 1, p. 1633, Mar. 2013, doi: 10.1038/ncomms2639.

[36] Md. M. Alam and D. Mandal, "Native Cellulose Microfiber-Based Hybrid Piezoelectric Generator for Mechanical Energy Harvesting Utility," *ACS Appl Mater Interfaces*, vol. 8, no. 3, pp. 1555–1558, Jan. 2016, doi: 10.1021/acsami.5b08168.

[37] M. Minary-Jolandan and M.-F. Yu, "Nanoscale characterization of isolated individual type I collagen fibrils: polarization and piezoelectricity," *Nanotechnology*, vol. 20, no. 8, p. 085706, Feb. 2009, doi: 10.1088/0957-4484/20/8/085706.

[38] V. Nguyen, R. Zhu, K. Jenkins, and R. Yang, "Self-assembly of diphenylalanine peptide with controlled polarization for power generation," *Nat Commun*, vol. 7, no. 1, p. 13566, Nov. 2016, doi: 10.1038/ncomms13566.

[39] L. EGERTON and D. M. DILLON, "Piezoelectric and Dielectric Properties of Ceramics in the System Potassium—Sodium Niobate," *Journal of the American Ceramic Society*, vol. 42, no. 9, pp. 438–442, Sep. 1959, doi: 10.1111/j.1151-2916.1959.tb12971.x.

[40] H. Du, Z. Li, F. Tang, S. Qu, Z. Pei, and W. Zhou, "Preparation and piezoelectric properties of (K0.5Na0.5)NbO3 lead-free piezoelectric ceramics with pressure-less sintering," *Materials Science and Engineering: B*, vol. 131, no. 1–3, pp. 83–87, Jul. 2006, doi: 10.1016/j.mseb.2006.03.039.

[41] E. Broitman, M. Y. Soomro, J. Lu, M. Willander, and L. Hultman, "Nanoscale piezoelectric response of ZnO nanowires measured using a nanoindentation technique," *Physical Chemistry Chemical Physics*, vol. 15, no. 26, p. 11113, 2013, doi: 10.1039/c3cp50915j.

[42] J. Cardoso, F. F. Oliveira, M. P. Proenca, and J. Ventura, "The Influence of Shape on the Output Potential of ZnO Nanostructures: Sensitivity to Parallel versus Perpendicular Forces," *Nanomaterials*, vol. 8, no. 5, p. 354, May 2018, doi: 10.3390/nano8050354.

[43] J. Gao, D. Xue, W. Liu, C. Zhou, and X. Ren, "Recent Progress on BaTiO3-Based Piezoelectric Ceramics for Actuator Applications," *Actuators*, vol. 6, no. 3, p. 24, Jul. 2017, doi: 10.3390/act6030024.

[44] D. Xue, Y. Zhou, H. Bao, C. Zhou, J. Gao, and X. Ren, “Elastic, piezoelectric, and dielectric properties of $Ba(Zr_{0.2}Ti_{0.8})O_3$-50$(Ba_{0.7}Ca_{0.3})TiO_3$ Pb-free ceramic at the morphotropic phase boundary,” *J Appl Phys*, vol. 109, no. 5, p. 054110, Mar. 2011, doi: 10.1063/1.3549173.

[45] J. F. Tressler, S. Alkoy, and R. E. Newnham, “Piezoelectric Sensors and Sensor Materials,” *J Electroceram*, vol. 2, no. 4, pp. 257–272, 1998, doi: 10.1023/A:1009926623551.

[46] N. P. Maria Joseph Raj, A. KS, G. Khandelwal, N. R. Alluri, and S.-J. Kim, “A lead-free ferroelectric $Bi_{0.5}Na_{0.5}TiO_3$ based flexible, lightweight nanogenerator for motion monitoring applications,” *Sustain Energy Fuels*, vol. 4, no. 11, pp. 5636–5644, 2020, doi: 10.1039/D0SE00963F.

[47] K. Reichmann, A. Feteira, and M. Li, “Bismuth Sodium Titanate Based Materials for Piezoelectric Actuators,” *Materials*, vol. 8, no. 12, pp. 8467–8495, Dec. 2015, doi: 10.3390/ma8125469.

[48] E. Taghaddos, H. Charalambous, T. Tsakalakos, and A. Safari, “Electromechanical properties of flash sintered BNT-based piezoelectric ceramic,” *J Eur Ceram Soc*, vol. 39, no. 9, pp. 2882–2888, Aug. 2019, doi: 10.1016/j.jeurceramsoc.2019.03.050.

[49] I. L. Guy, S. Muensit, and E. M. Goldys, “Extensional piezoelectric coefficients of gallium nitride and aluminum nitride,” *Appl Phys Lett*, vol. 75, no. 26, pp. 4133–4135, Dec. 1999, doi: 10.1063/1.125560.

[50] R. Hou, D. Hutson, and K. J. Kirk, “Development of sputtered AlN thin-film ultrasonic transducers for durable high-temperature applications,” *Insight - Non-Destructive Testing and Condition Monitoring*, vol. 55, no. 6, pp. 302–307, Jun. 2013, doi: 10.1784/insi.2012.55.6.302.

[51] S. Tadigadapa and K. Mateti, “Piezoelectric MEMS sensors: state-of-the-art and perspectives,” *Meas Sci Technol*, vol. 20, no. 9, p. 092001, Sep. 2009, doi: 10.1088/0957-0233/20/9/092001.

[52] K. Koga and H. Ohigashi, “Piezoelectricity and related properties of vinylidene fluoride and trifluoroethylene copolymers,” *J Appl Phys*, vol. 59, no. 6, pp. 2142–2150, Mar. 1986, doi: 10.1063/1.336351

APPENDIX

PLAGIARISM REPORT

turnitin Page 2 of 27 - Integrity Overview Submission ID trn:oid:::27535:100583916

8% Overall Similarity

The combined total of all matches, including overlapping sources, for each database.

Filtered from the Report

- Bibliography
- Quoted Text
- Cited Text
- Small Matches (less than 8 words)

Match Groups

- **41** Not Cited or Quoted 8%
  Matches with neither in-text citation nor quotation marks
- **0** Missing Quotations 0%
  Matches that are still very similar to source material
- **0** Missing Citation 0%
  Matches that have quotation marks, but no in-text citation
- **0** Cited and Quoted 0%
  Matches with in-text citation present, but no quotation marks

Top Sources

- 2% Internet sources
- 5% Publications
- 4% Submitted works (Student Papers)

Integrity Flags

0 Integrity Flags for Review

No suspicious text manipulations found.

Our system's algorithms look deeply at a document for any inconsistencies that would set it apart from a normal submission. If we notice something strange, we flag it for you to review.

A Flag is not necessarily an indicator of a problem. However, we'd recommend you focus your attention there for further review.

AI REPORT

turnitin Page 2 of 42 - AI Writing Overview Submission ID trn:oid:::27535:99824008

*% detected as AI

AI detection includes the possibility of false positives. Although some text in this submission is likely AI generated, scores below the 20% threshold are not surfaced because they have a higher likelihood of false positives.

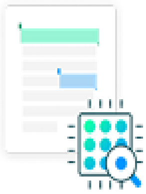
Caution: Review required.

It is essential to understand the limitations of AI detection before making decisions about a student's work. We encourage you to learn more about Turnitin's AI detection capabilities before using the tool.

Disclaimer
Our AI writing assessment is designed to help educators identify text that might be prepared by a generative AI tool. Our AI writing assessment may not always be accurate (it may misidentify writing that is likely AI generated as AI generated and AI paraphrased or likely AI generated and AI paraphrased writing as only AI generated) so it should not be used as the sole basis for adverse actions against a student. It takes further scrutiny and human judgment in conjunction with an organization's application of its specific academic policies to determine whether any academic misconduct has occurred.

Frequently Asked Questions

How should I interpret Turnitin's AI writing percentage and false positives?
The percentage shown in the AI writing report is the amount of qualifying text within the submission that Turnitin's AI writing detection model determines was either likely AI-generated text from a large-language model or likely AI-generated text that was likely revised using an AI-paraphrase tool or word spinner.



False positives (incorrectly flagging human-written text as AI-generated) are a possibility in AI models.

AI detection scores under 20%, which we do not surface in new reports, have a higher likelihood of false positives. To reduce the likelihood of misinterpretation, no score or highlights are attributed and are indicated with an asterisk in the report (*%).

The AI writing percentage should not be the sole basis to determine whether misconduct has occurred. The reviewer/instructor should use the percentage as a means to start a formative conversation with their student and/or use it to examine the submitted assignment in accordance with their school's policies.

What does 'qualifying text' mean?
Our model only processes qualifying text in the form of long-form writing. Long-form writing means individual sentences contained in paragraphs that make up a longer piece of written work, such as an essay, a dissertation, or an article, etc. Qualifying text that has been determined to be likely AI-generated will be highlighted in cyan in the submission, and likely AI-generated and then likely AI-paraphrased will be highlighted purple.

Non-qualifying text, such as bullet points, annotated bibliographies, etc., will not be processed and can create disparity between the submission highlights and the percentage shown.

CERTIFICATE OF PARTICIPATION

ATMA RAM SANATAN DHARMA COLLEGE

UNIVERSITY OF DELHI

Accredited Grade 'A++' By NAAC || All India 5th Rank in NIRF (Ministry of Education)

3rd International Conference on

Advanced Functional Materials and Devices (AFMD-2025)

for Sustainable Development

Under the aegis of IQAC and supported by Department of Biotechnology (GoI)

Certificate of Participation

This is to certify that Prof./Dr./Mr./Ms.

VIJITA SINGH

Delhi Technological University

has participated in the 3rd International Conference on "Advanced Functional Materials & Devices for Sustainable Development" (AFMD-2025) organised by Department of Physics under the aegis of IQAC ARSD College, University of Delhi, India during March 03-05, 2025 in hybrid mode.

He/She has presented **Poster** entitled:

PP-48:-Lead free Piezoelectric Materials

Dr. Shankar Subramanian	Dr. Anjali Sharma	Prof. Vinita Tuli	Prof. Gyantosh Kumar Jha
Convener, AFMD-2025	Convener, AFMD-2025	Coordinator, IQAC	Principal/Patron AFMD-2025

Certificate No: ARSD/AFMD25/PP/049

Fwd: Notification of Shortlisting for Springer Book Chapter – AFMD 2025 Inbox ×

roli purwar <roli.purwar@dtu.ac.in> Fri, May 2, 5:26 PM

to me

Professor, Polymer Science and Chemical Technology,
Department of Applied Chemistry
Delhi Technological University, Shahbad Daulatpur
Delhi, India-110042

---------- Forwarded message ---------
From: <afmd2025@arsd.du.ac.in>
Date: Wed, 30 Apr, 2025, 21:44
Subject: Notification of Shortlisting for Springer Book Chapter – AFMD 2025
To: <roli.purwar@dtu.ac.in>

Paper No. Title & : PP-48 Lead-free Piezoelectric Material

Dear **Prof./Dr./Mr./Ms. Roli Purwar**

Delhi Technological University

Greetings,

We are delighted to inform you that your paper, submitted to the AFMD 2025 conference, has been shortlisted for potential publication in the **Springer Book Chapter** following the initial screening by the AFMD 2025 Technical Committee.

Paper No. Title & : PP-48 Lead-free Piezoelectric Material

Dear **Prof./Dr./Mr./Ms. Roli Purwar**

Delhi Technological University

Greetings,

We are delighted to inform you that your paper, submitted to the AFMD 2025 conference, has been shortlisted for potential publication in the **Springer Book Chapter** following the initial screening by the AFMD 2025 Technical Committee.

Please note that shortlisting does not guarantee acceptance for the book chapter. Your submission will undergo a rigorous and thorough review by our expert panel, after which you will be notified of the final decision.

For any further inquiries, please feel free to contact the AFMD 2025 Editorial Team at afmd2025@arsd.du.ac.in.

Warm regards,

AFMD 2025 Committee

afmd2025@arsd.du.ac.in (mailto:afmd2025@arsd.du.ac.in)