PREFACE

From the intricate working of everyday electronics to the forefront of medical technologies, piezoelectric materials have profoundly influenced modern science and industry. These materials, known for their remarkable ability to convert mechanical energy into electrical energy and vice versa, are integral to the development of sensors, actuators, and energy harvesting devices. However, the widespread use of lead-based piezoelectrics, such as lead zirconate titanate (PZT), poses significant environmental and health risks due to lead's toxicity. This has spurred a global quest for sustainable and eco-friendly alternatives. This thesis, titled "Development of Bi-based Lead-Free Piezoelectric Ceramics for High-Temperature Applications," addresses this critical challenge. The research presented herein explores the synthesis and optimization of novel Bi-based lead-free piezoelectric ceramics. By leveraging site engineering techniques, we have developed compositions that not only mitigate the environmental hazards associated with lead but also exhibit superior performance under high-temperature conditions.

The primary objective of this research is to create materials with enhanced functional properties suitable for high-temperature energy harvesting applications. This involves not only developing new Bi-based compositions but also optimizing fabrication techniques to improve their structural, morphological, dielectric, and ferroelectric properties. The extensive experimental work documented in this thesis includes the use of advanced characterization techniques to validate the performance and stability of these materials.

A brief summary of important findings from our investigation on various developed systems in this thesis work is discussed below:

Chapter 1, provide a comprehensive overview of the fundamental concepts and advancements in the field of piezoelectric materials, focusing on Bi-based lead-free ceramics. We discussed the principles of dielectrics, piezoelectricity, and ferroelectricity, emphasizing the differences between normal and relaxor ferroelectrics, crucial for tailoring materials to specific applications. We explored the unique structure and properties of perovskites, highlighting their adaptability for developing advanced piezoelectric materials. Recent advancements in Bi-based lead-free materials, particularly the $BiFeO_3$-$BaTiO_3$ system and $Bi_4Ti_3O_{12}$ Aurivillius ceramics, were reviewed for their high Curie temperatures and excellent dielectric and ferroelectric properties. The importance of synthesis and characterization methods was underscored, as processing techniques critically impact material properties. In a nutshell this chapter has provided an overview of the background and importance of developing lead-free, Bi-based piezoelectric ceramics for high-temperature applications.

Chapter 2 detailed the experimental methods and characterization techniques employed in this research. We described the synthesis of Bi-based lead-free piezoelectric ceramics using solid-state reactions, emphasizing the importance of precise control over processing conditions such as air quenching and closed sintering. The chapter outlined the comprehensive suite of characterization techniques used, including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), dielectric spectroscopy, ferroelectric and piezoelectric measurements, to analyze the structural, morphological, and electrical properties of the synthesized materials. The detailed experimental setup and procedural rigor ensured the reliability and reproducibility of the results, laying a strong foundation for the subsequent analysis and interpretation of the functional properties of the developed ceramics.

Chapter 3 presents the impact of processing methods on the structural and functional properties of Sc, Ga-modified $BiFeO_3$-$BaTiO_3$ (BF-BT) piezoceramics. We compared two distinct sintering techniques: air quenching (AQ) and closed sintering (CS). Our findings demonstrated that the air-quenched samples exhibited superior electrical and ferroelectric properties, including higher resistivity, improved remnant and spontaneous polarization, reduced dielectric loss, and enhanced dielectric permittivity across a wide temperature range. The structural analysis confirmed the formation of pure perovskite phases with small grain sizes, while the ferroelectric studies revealed relaxor-like behavior, characterized by broad frequency-dependent dielectric peaks and reduced hysteresis. These improvements underscore the significant influence of the air quenching method on enhancing the material's functional properties, making them suitable for high-temperature applications. Chapter 3 concludes by highlighting the crucial significance that processing methods have in maximizing the performance of BF-BT-based piezoelectric ceramics and proving that air quenching is a useful strategy for attaining better electrical and dielectric characteristics.

Chapter 4 explores the isovalently substituted lead-free binary solid solution, $0.67(Bi_{1-x}La_xFe_{0.97}Ga_{0.03}O_3)$-$0.33(BaTiO_3)$ (BF-BT) ($x \leq 0.07$), synthesized by solid state ceramic method via air quenching sintering. FTIR and XRD along with Rietveld structure refinement confirmed a pure perovskite phase with a pseudocubic structure (space group $Pm\bar{3}m$) for developed compositions. SEM revealed a dense microstructure with fine grain size (<1.5 μm) and minimal porosity. XPS analysis reveals predominant Fe^{+3} states, along with oxygen vacancies. Ferroelectric studies demonstrated a maximum remnant polarization (P_r) of 12.3 $\mu C/cm^2$ and coercive field E_c of 30.95 kV/cm for La^{3+} concentration of x=0.03. Overall decrement in P_r can be attributed to dipolar defectinduced random fields reducing the activation barrier for domain nucleation. Leakage current measurement reveals improved resistivity (~10^8 Ω cm) up to an applied field of 30 kV/cm. Dielectric measurements unveiled two frequency-dependent anomalies in temperature dependence above room temperature, indicative of diffuse phase transitions. The Vogel-Fulcher model depicted an increasing freezing temperature (from 465 K for x=0.01 to 551 K for x=0.07) and decreasing activation energy (from ~0.61 eV to 0.07 eV) with increasing La^{3+} concentration. The estimated diffuseness parameter around ~2 suggested relaxor behavior. Doping with La resulted in increased dielectric permittivity at 10 kHz (from 4100 to 24066), showcasing the efficacy of site engineering in augmenting the functional properties of BF-BT for high-temperature dielectric and transducer applications.

Chapter 5 focuses on site engineering as a strategy to introduce and enhance the functionalities of $BiFeO_3$-$BaTiO_3$ (BF-BT) based relaxor piezoceramics for high-temperature applications. The chapter explores the effect of substituting specific elements at the A and B sites of the perovskite structure to optimize the material's optical, dielectric, and ferroelectric properties. Site engineering is used to introduce the functionality by substituting A/B sites in $0.67BiFe_{0.97-x}Ga_{0.03}Sc_xO_3$-$0.33BaTiO_3$ and $0.67(Bi_{1-x}La_yFe_{0.97}Ga_{0.03}O_3)$-$0.33(BaTiO_3)$ abbreviated as BFSBT-x and BLFBT-y respectively where x, y ≤ 0.07, respective solid solutions. To better understand its effect, crystal structural, dielectric, optical, and ferroelectric properties were characterized and compared for different compositions. The X-ray diffraction pattern suggests the formation of pure perovskite structure with pseudocubic phase as the major phase present in both BFSBT-x and BLFBT-y series. The indirect band gap of 1.81 eV and 1.93 eV lying in visible range was obtained for x=0.03 and y=0.03 composition, respectively. The temperature-dependent dielectric studies reveal frequency-dependent dielectric anomalies in permittivity corresponding to diffuse phase transitions stipulating relaxor-like behavior, which was further confirmed by modified Curie-Weiss law fitting. The enhanced temperature stability, good dielectric properties, and lower band gap suggest that site engineering is an efficient way to enhance the functional properties of $BiFeO_3$-$BaTiO_3$ based samples for high-temperature applications.

Chapter 6 delves into the investigation of the functional properties of $(Bi_{4-x}Sm_{0.5})(Ti_{3-0.01}Ta_{0.01})O_{12}$ (BITST) Aurivillius ceramics sintered at 950 ℃ , 1050 ℃ , and 1150 ℃ in comparison with the pure $Bi_4Ti_3O_{12}$ (BIT) counterpart, synthesized via the conventional solid-state route. By incorporating Sm/Ta additives and adjusting the sintering temperature, various electrical properties such as dielectric behavior, leakage current, ferroelectric, optical and piezoelectric performance were tailored. Analysis using XRD confirmed the formation of pure phases, with degree of lattice distortion increased on Sm/Ta incorporation. Fourier Transform Infrared spectroscopy further validated the formation of perovskite structure. Microstructural evaluation revealed platelet- like formations across samples sintered at different temperatures. Ferroelectric investigations at room temperature demonstrated slim hysteresis loops and increased remnant polarization with elevated sintering temperatures in BITST, as corroborated by PUND measurements. Leakage current measurements indicated a notable enhancement in leakage current density, ranging from 10^{-3} to 10^{-7}, with increasing sintering temperatures from 950 to 1150 ℃. BITST S1150 exhibited a high Curie temperature of 617 ℃, accompanied by reduced dielectric losses across a wide temperature range up to 400 ℃. The resistivity significantly increased from 10^5 to the order of 10^{10} on increasing the sintering temperature of the BITST, suggesting an expanded sintering window obtained on Sm/Ta incorporation which enables the application of higher electric fields during the poling process. The reduced oxygen vacancies as a result of donor doping and rare earth ion doping is confirmed by XPS studies. Notably, BITST demonstrated an outstanding piezoelectric charge coefficient (d_{33}) and high Curie temperature of 39 pC/N and 617 ℃ respectively, rendering it suitable for high-temperature applications.

Chapter 7 summarizes the key findings of this research, demonstrating that site engineering and optimized fabrication techniques significantly enhance the structural, dielectric, and ferroelectric properties of Bi-based ceramics, making them suitable for high-temperature applications. The incorporation of La, Sc, Ga, Sm, and Ta additives led to high resistivity, improved polarization, reduced dielectric loss, and enhanced dielectric permittivity. The chapter also proposes future research directions, including advanced characterization techniques, detailed mechanistic studies, further composition optimization, practical device integration, environmental impact assessments, and exploration of Bi-based ceramics as multiferroic materials. In conclusion, this thesis advances the development of high-performance, environmentally friendly Bi-based lead-free piezoelectric ceramics, paving the way for their broader adoption and commercialization in advanced technological applications.