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

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By

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7.1 Summary of the Thesis

The research presented in this thesis has focused on the development of Bi-based lead-free piezoelectric ceramics for high-temperature applications. The following key findings summarize the significant contributions and outcomes of this study:

1. We have successfully synthesized novel lead-free Sc, Ga- modified BF-BT polycrystalline piezoceramics and systematically investigated the impact of closed sintering and air quenching methods on their functional properties. The ceramics prepared using the air quenching method exhibited significant improvements in resistivity, P_r, P_s, T_m, and E_C, along with reduced dielectric loss, and enhanced dielectric permittivity across a wide temperature range as compared to closed sintered samples. The broad frequency-dependent dielectric behavior and reduced values of P_r and E_C further support the relaxor-like characteristics. The decreased P_r values make these materials suitable for energy storage applications, while the reduced hysteresis benefits actuation purposes. Overall, this study emphasizes the importance of understanding ceramic processing methods for the development of high-performance lead-free BF-BT based piezoceramics.
2. We have successfully synthesised high-temperature lead-free La and Ga modified BF-BT ceramics. The analysis of dielectric constant and loss as a function of temperature and frequency demonstrated significant frequency dispersion, indicating relaxor-like behavior. This behavior is attributed to the introduction of La^{+3} ions, which disrupt the long-range ordering and introduce centrosymmetry in the material. The presence of La ions affects the relaxation mechanisms and leads to a decrease in the energy barrier for dipole reorientation. The dielectric constant was significantly enhanced, when

compared at a frequency of 10 kHz, as the concentration of La^{+3} dopant increased from x=0.01 to 0.07. All in all, this work demonstrates the effectiveness of simultaneous site engineering, by incorporating La and Ga ions, to enhance the dielectric and ferroelectric properties of the BF-BT based system.

3. In BFSBT and BLFBT ceramics the La^{+3} doping helps in pure phase formation while Sc^{+3} doping helps in increasing the resistivity and ferroelectric behavior. The room temperature dielectric constant has increased from 578 to 661 for BFST and 803 to 1393 for BLFT with increasing doping concentration from 1 to 7 mol%. The temperature dependent dielectric constant curves show broad frequency dependent peaks which indicates the relaxor like behavior which was further confirmed by modified Curie-Weiss law fitting giving the value of diffusivity constant close to 2. From the calculation of energy storage density, the maximum W_{rec} value of ~ 0.34 J/cm^3 for x=0.03 and ~ 0.25 J/cm^3 for y=0.05 were obtained. Irrespective of the doping site the optical band gap has reduced (~1.8 eV) with respect to pure BFO and BT, which can be beneficial for photovoltaics and optoelectronics applications. Optimizing doping strategies using site engineering is crucial for enhancing the material's polarization capabilities while mitigating the negative effects of domain wall pinning and defect formation.
4. Through strategic A/B site engineering, the dielectric, ferroelectric, and piezoelectric properties of BITST ceramics, particularly those sintered at 1150 (BITST S1150), were significantly enhanced. The incorporation of Sm and Ta effectively lowers the concentration of inherent oxygen vacancies, consequently reducing leakage current and enhancing resistivity. The ferroelectric measurement shows that the P-E loops become slim on increasing the sintering temperature indicating reduction in lossy behavior due to increased grain size, density and reduced oxygen vacancies. BITST S1150

demonstrated a piezoelectric charge coefficient (d_{33}), significantly higher than that of pure BIT, which illustrates a substantial improvement in piezoelectric properties. The BITST S1150 ceramics exhibited an increased T_C, improved dielectric constants, and reduced dielectric losses, validating their suitability for high-temperature applications. Notably, the resistivity of the ceramics was markedly enhanced, for BITST S1150 compared to pure BIT. Additionally, optical property enhancements, including a narrowing of the band gap (3.12 eV to 3.06 eV) and increased luminescence suggest improved light absorption capabilities, facilitating potential applications in optoelectronic devices. The findings elucidate the significant role of dopant selection and sintering temperature in optimizing the microstructural and functional properties of BIT ceramics. This investigation underscores the potential of tailored BITST ceramics for high-performance applications in environments demanding robust electrical and optical properties.

In conclusion, in this research we successfully developed novel Bi-based lead-free compositions using site engineering techniques, yielding promising electrical properties suitable for high-temperature applications. The optimization of fabrication techniques, particularly air quenching and closed sintering methods, significantly enhanced the functional properties of ceramics, with air quenched samples demonstrating superior electrical and ferroelectric properties. Comprehensive structural and morphological analyses, including XRD, FTIR, and SEM, confirmed the formation of pure perovskite phases and dense microstructures with fine grain sizes. The developed ceramics exhibited strong frequency-dependent dielectric permittivity with broadened transition peaks and ferroelectric relaxor-like behavior. The dielectric measurements revealed high dielectric constants and reduced dielectric loss over a wide temperature range. Site engineering through isovalent substitution notably improved the dielectric and ferroelectric properties, with La-doped compositions showing enhanced dielectric permittivity, higher resistivity, and improved ferroelectric characteristics. Additionally, the incorporation of Sm/Ta additives and the adjustment of sintering temperatures in $Bi_4Ti_3O_{12}$ Aurivillius ceramics resulted in enhanced dielectric, ferroelectric, and piezoelectric performance, underscoring their potential for high-temperature applications.

7.2 Future Scope

Further exploration of these materials could lead to significant advancements in the development of devices capable of operating under extreme conditions, thereby extending the functional limits of piezoelectric and optoelectronic materials. A deeper understanding of these microscopic interactions can guide the development of materials with tailored ferroelectric properties, enhancing their application potential in technology. The future scope of study in these areas includes advancing characterization techniques (such as PFM and TEM), theoretical modeling of materials properties (like d_{33}^* and d_{33}), and practical applications (such as energy harvesting devices using polymer nanocomposites). These endeavors aim to push the boundaries of piezoelectric materials research towards more efficient and sustainable energy solutions.

1. **PFM (Piezoresponse Force Microscopy)**: PFM is a technique used to study the local piezoelectric properties of materials at the nanoscale. Future studies could focus on enhancing the sensitivity and resolution of PFM techniques, exploring noval materials, and understanding the fundamental mechanisms of piezoelectricity at the nanoscale.
2. **TEM (Transmission Electron Microscopy)**: TEM is an imaging technique that allows researchers to study the microstructure of materials at very high resolution, down to atomic scale. Future studies might involve using TEM to characterize the microstructure of piezoelectric materials, study defects and interfaces that affect their properties, and correlate structure-property relationships.

3. **Piezoelectric Strain Coefficient** (d_{33}*): d_{33}* is a key parameter that quantifies the piezoelectric response of a material, specifically the strain generated per unit electric field along a particular direction (often the thickness direction in ceramics). Theoretical studies could focus on predicting d_{33}* for new materials, optimizing crystal orientations or domain structures to maximize d_{33}*, and understanding how it affects the performance of piezoelectric devices.
4. **BIT (Bismuth Titanate) Based Samples**: BIT is a well-known piezoelectric material with potential applications in sensors, actuators, and energy harvesting. Theoretical studies on BIT could include computational modelling of its crystal structure, electronic properties, phase transitions, and predicting its piezoelectric performance under different conditions.
5. **Device Fabrication Using Polymer Nanocomposites for Piezoelectric Energy Harvesting**: This involves integrating piezoelectric materials into polymer matrices to create nanocomposites that can harvest mechanical energy (e.g., vibrations) and convert it into electrical energy. Future research could focus on optimizing the composition of these nanocomposites (e.g., filler concentration, polymer matrix type), improving processing techniques (e.g., solution casting, 3D printing), and enhancing the energy conversion efficiency of resulting devices.

The findings from this research open several avenues for future exploration and development in the field of lead-free piezoelectric materials. Advanced characterization techniques, such as transmission electron microscopy (TEM) and in-situ X-ray diffraction, can provide deeper insights into the microstructural and phase evolution mechanisms. Detailed mechanistic studies on the role of various dopants and the effects of different processing conditions can help in understanding the fundamental principles governing the observed enhancements in properties. Further optimization of compositions by exploring other dopants and their combinations can achieve even higher piezoelectric coefficients and better thermal stability. Future research should also focus on integrating these developed materials into practical devices, such as sensors, actuators, and energy harvesters, to evaluate their performance in real-world applications. Conducting comprehensive environmental impact assessments of the developed lead-free ceramics compared to traditional lead-based materials can highlight the benefits and promote their adoption in various industries. Efforts towards scaling up the fabrication process and addressing the challenges associated with large-scale production will be crucial for commercialization. Additionally, investigating the potential of Bi-based lead-free ceramics as multiferroic materials, which exhibit coupled ferroelectric and magnetic properties, could open new dimensions for multifunctional applications. In conclusion, the development of Bi-based lead-free piezoelectric ceramics presents a promising pathway for achieving high-performance, environmentally friendly materials suitable for high-temperature applications. Continued research and development in this area hold the potential to significantly impact various technological fields and contribute to sustainable advancements in material science.