Abstract

Piezoelectric materials can interconvert mechanical energy into electrical energy, this property makes the piezoelectric materials a potential candidate for their usage in energy harvesting applications. Devices exploiting the piezoelectric effect functionality of materials have become an indispensable part of everyday life, such as cell phones, lighters, microphones, etc. Recent advancements in materials technology, such as the evolution of low−power electronic devices, have led to remarkable growth in demand for piezoelectric materials. The synthetic piezoelectric material, lead zirconate titanate (($Pb(Zr_xTi_{1-x})O_3$, PZT), finds overwhelming usage across broad fields of application due to its superior piezoelectric performance. However, the toxicity of lead and its alarming consequences on nature and human health has emphasized the need for environmentally benign alternatives. Potassium sodium niobate ($K_xNa_{1-x}NbO_3$, KNN) and bismuth ferrite ($BiFeO_3$, BFO) are two materials that carry the promise of replacing lead−based materials.

In this thesis, performed within the European Union funded H2020−MSCA−ITN−2016 ENHANCE project, KNN and BFO materials have been strategically tailored for their composition, morphology, and structure to explore their applicability in vibrational energy harvesting applications. To this end, a facile electrospinning technique was employed to prepare one-dimensional (1D) piezoelectric nanofibers (PNFs). The preparation of nanofibers and the integration of PNFs in energy harvesting units were iteratively optimised to correlate and enhance materials characteristics and piezoelectric performance. In the case of KNN, an instance for enhancing the harvestable energy has been made through engineering the phase boundary by modifying at the A− and B− site of the perovskite unit cell with the incorporation of Li^+ and Ta^{5+} ions. Subsequent characterisation of the PNFs with piezoresponse force microscopy showed that the piezoelectric response of the material modified with Li (4 mol%)

and Ta (20 mol%) had twice the piezoelectric response as compared to pristine KNN. As a proof-of-concept, energy harvesting units were fabricated by embedding 3 wt.% of the PNFs in a polyvinylidene fluoride (PVDF) polymer matrix. The piezoelectric nanogenerators (PENGs) based on Li and Ta modified PNFs exhibited higher power output of 5.6 V vs 0.92 V of PENG based on pristine KNN PNFs. The reason for such an enhanced power output arises from the amplified polarization rotation of the dipoles induced by the structural distortion of the perovskite unit cell upon incorporating Li^{+} and Ta^{5+} ions in the KNN lattice. Temperature vs *in-situ* Raman spectra measurements confirmed the lowering of the Curie temperature of the Li and Ta modified PNFs on account of induced structural distortion due to the size discrepancy of substitutional ions in the KNN lattice.

In the case of BFO, the significance of high anisotropic grain morphologies for energy harvesting applications has been elucidated. For this purpose, the synthesis parameters for obtaining monolithic, phase pure BFO have been thoroughly discussed. Phase characterisation studies by XRD and the subsequent Rietveld refinement confirmed the formation of a non−centrosymmetric, ferroelectric unit cell. The industrious performance of the PENGs based on BFO PNFs has been demonstrated through exceptional long−term stability of the voltage output recorded after storing the samples under atmospheric conditions for 4 months, which showed very little attenuation of the voltage signal while delivering an average output voltage of 2.95±1.02 V.

This work presents a cutting−edge demonstration of tailoring a material from the bottom−up, through synthesis−function−high energy density device fabrication for vibrational energy harvesting application. The results obtained significantly contribute to the understanding of the tailored anisotropic morphologies of lead−free ceramic oxides for their piezoelectric and vibrational energy harvesting characteristics. In the process of investigations, the work also brings forth new findings that will expand the understanding of KNN and BFO systems towards achieving the goal of lead–free piezoelectric devices.