

## ABSTRACT

Piezoelectric materials have gained increased attention in the recent times due to their significant technological applications. These materials are widely used to make ultrasound transducers, sensors, actuators and others are used for energy harvesting. Due to its brilliant piezoelectric properties, Lead Zirconate Titanate (PZT) is mostly used with a piezoelectric constant of  $d_{33} = 374 \text{ pC/N}$  from experimental reports and  $306 - 314 \text{ pC/N}$  from theoretical studies. However, due to the toxic nature of lead oxide which is formed when PZT is being manufactured, there is increased effort in development of lead-free materials. Several classes of materials have recently been studied and are now being considered as potential alternatives to PZT. Lead free perovskite systems such as Bismuth Sodium Potassium Titanate (BNKT) have been developed, with a piezoelectric constant  $d_{33} = 157 \text{ pC/N}$ . However, the main drawback of this system is that it is highly corrosive and has a low piezoelectric constant compared to PZT. In the quest to provide suitable alternatives, dopants such as zirconium have been used, which improved the piezoelectric constant of BNKT up to  $203 \text{ pC/N}$ . Hf which possesses similar physico-chemical properties as zirconium has led to an improvement in the piezo electric constant of other piezoelectric systems such as in hafnium doped Barium Titanate (BT). It has an added advantage of being extremely resistant to corrosion, which is expected to mitigate the corrosive nature of BNKT. In this study, hafnium has been incorporated in BNKT so as to engineer an alternative material suitable for piezoelectric applications. Density Functional Theory (DFT) method was used to predict the structural and piezoelectric properties of hafnium doped BNKT, starting with those of Bismuth Sodium Titanate (BNT) and BNKT. The exchange and correlation was taken as the Generalized Gradient Approximation (GGA). The optimal lattice parameters for BNT were found to be  $a = 5.57 \text{ \AA}$  and  $c/a$  ratio of 2.50 for the conventional cell, having space group R3c space group number 161. Piezoelectric constant for this system was found to be  $97.67 \text{ pC/N}$ . This structure was adopted for doping and further calculations. Potassium doped bismuth sodium titanate was modelled using VESTA software and its optimized lattice parameter was found to be  $a = 5.60 \text{ \AA}$ . Piezoelectric constant for this system was found to be  $147.42 \text{ pC/N}$ . Hafnium doped BNKT had an improved piezoelectric constant of  $205.52 \text{ pC/N}$  for 3% hafnium doping, which decreased to  $163.22 \text{ pC/N}$  at the level of 6% doping. The results shows that small amounts of hafnium improved the piezoelectric constant of BNKT from  $147.42 \text{ pC/N}$  to  $205.52 \text{ pC/N}$ . Elastic and elastic compliance full tensors for these systems was also generated with elastic constants of  $C_{33} = 286.48 \text{ Gpa}$ ,  $282.13 \text{ Gpa}$ ,  $257.193 \text{ Gpa}$  and  $276.43 \text{ Gpa}$  for BNT, BNKT, 3% Hf doped BNKT and 6% Hf doped BNKT respectively. This study concludes that doping BNKT with hafnium indeed improves the piezoelectric properties of BNKT. This makes this material more useful in energy generation since high piezoelectric constant leads to efficient mechanical – electrical energy conversion in the piezoelectric materials.