Mechanisms of Thermal Depolarization in Lead-free Relaxor/Semiconductor Composites

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Lead containing piezoceramics dominate the commercial market due to their exceptional piezoelectric and ferroelectric properties, low cost and ease of preparation [1]. In the past two decades, the driving force for innovation to develop new piezoceramics has been the growing concern due to environmental toxicity imposed by the use and disposal of lead-based materials [2]. Of the several lead-free systems that have been proposed, the lower manufacturing cost and good piezoelectric properties make (1-*x*)$Na_{1/2}Bi_{1/2}TiO_3$-*x*$BaTiO_3$ (NBT-*x*BT) solid solution, a key candidate as a low cost lead-free alternative to lead containing materials. One of the major issues limiting the use of this material is the thermal depolarization, wherein the material loses its macroscopic ferroelectricity. Zhang *et al*. [3] recently demonstrated that the inclusion of semiconductor ZnO particles into the NBT-6BT matrix leads to an increase in the depolarization temperature (T_D). The present study investigates the underlying mechanisms that result in enhanced thermal stability of the composites.

The composites of NBT-*x*BT with ZnO inclusions were prepared by conventional solid state synthesis. An increase in T_d of ~40–60 ^oC was observed for the composites with NBT-6BT and NBT-9BT. In the case of composites with non-ergodic relaxor NBT-6BT, a ferroelectric long range order was found to be induced, which is attributed to the residual thermal stresses arising from the mismatch in the coefficient of thermal expansion of the constituent phases. This was also evidenced from Nuclear Magnetic Resonance of sodium (^{23}Na NMR), which exhibited a decrease in the cubic content characterizing the relaxor phase. The thermal depolarization behavior of the composites is rationalized based on two competing mechanisms - an increase in the transition temperature from ferroelectric to relaxor state ($T_{F\text{-}R}$), thereby enhancing T_D and a stress induced shift in T_D that results in a broadened depolarization behavior. The results signify the use of the composite approach in inducing ferroelectric order and enhancing the thermal stability of lead-free relaxor piezoelectrics in a significant manner.

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