Processing of Lead-free Piezoelectrics

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The last decade has seen a considerable effort in development of lead-free alternatives to lead zirconate titanate (PZT) based piezoelectric materials. Several approaches to enhance the piezoelectric properties of lead-free ceramics have been investigated, categorized as either compositional engineering (*e.g.* doping) or microstructural engineering (*e.g.* grain texture or oriented films) to enhance the piezoelectric properties. Here we present development of environmental friendly aqueous solution-based processing routes to microstructural engineered lead-free piezoelectrics ($K_{0.5}Na_{0.5}NbO_3$ (KNN), $Ba_{0.92}Ca_{0.08}TiO_3$ (BCT) and $Bi_{0.5}Na_{0.5}TiO_3$ (BNT)) in the form of bulk textured ceramics and thin films.

The preferred crystallographic orientation of the texture is rarely justified for grain texture and the mechanisms by which texturing improve the performance are not well understood. We therefore investigated the effect of <100> and <111> texturing on the piezoelectric properties of (BCT) with the aim of engineering high-performance lead-free piezoceramics. We demonstrate how broadening of the stable temperature range of the tetragonal phase can cause extender ferroelectricity over a wide temperature range, supported by observations of increased piezoelectric response with <100> texture and decreased response with <111>-texture. In addition to processing of stable, high-performance lead-free piezoelectric ceramics by wet chemical approach, we also demonstrate that consideration of the extender/rotator nature of piezoelectric properties are imperative for improving the piezoelectric response through texturing.

In addition, the enhancement of piezoelectric properties of oriented thin films will be highlighted with the focus on KNN and BNT-based materials on different types of substrates. We report on successful fabrication of KNN and BNT thin films by a simple environmental friendly aqueous chemical solution deposition. Highly oriented and epitaxial lead-free piezoelectric $(Na_{0.5}K_{0.5})NbO_3$ (KNN) thin films were fabricated on (100)-, (110)- and (111)-oriented $SrTiO_3$ substrates. To aid texturing of the KNN-based films, a molten salt dissolution/reprecipitaion method was used and NaCl/KCl was added to the precursor solution. The prepared films were highly oriented following the orientation of the substrates. Further, deposited thin films of BNT prepared from a solution of bismuth citrate stabilized by ethanolamine, $NaOH$, and titanium tetraisopropoxide stabilized by citric acid were single phase, and the microstructure of the films were shown to be homogeneous and dense. Decomposition of the gel was a critical step of the synthesis, and the conditions resulting in phase pure materials will be discussed. These new aqueous solution deposition routes are low cost, robust, and suitable for implementation of lead-free materials in different applications. The piezo- and dielectric properties will be discussed in relation to the texture, epitaxy as well as type and orientation of the substrate.