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Advances in Development and Applications of Pb-Free Piezoelectric Materials for Transducer Applications

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Pb-based ferroelectrics and piezoelectrics in the form of bulk ceramics, single crystals, composites, and thin films have been used in sensors, actuators, and other electromechanical devices. In addition, Pb-based antiferroelectric materials are an excellent candidate for energy storage applications. However, the toxicity of these materials and their exposure to the environment during processing steps such as calcination, sintering, machining, as well as problems in recycling and disposal have been major concerns around the globe for the past few decades. The report of high piezoelectric activity in the ternary lead-free ($K_{0.44}$, $Na_{0.52}$, $Li_{0.04}$)($Nb_{0.84}$, $Ta_{0.10}$, $Sb_{0.06}$)O_3[1)], ($Bi_{0.5}$,$Na_{0.5}$)TiO_3-($Bi_{0.5}$,$K_{0.5}$)TiO_3-$BaTiO_3$ /($B_{0.5}$i,$Li_{0.5}$)TiO_3[2)], and Ba($Ti_{0.8}Zr_{0.2}$)O_3-($Ba_{0.7}Ca_{0.3}$)TiO_3[3)] systems have given high hope for alternatives to Pb-based materials. Recent modifications of KNN-based compositions with $BaZrO_3$ in combination with ($Bi_{0.5}$,$K_{0.5}$)HfO_3 results in excellent electromechanical properties.[4)] In addition, a few compositions in Pb-free antiferroelectric materials show promising energy density, efficiency, and breakdown strength (BDS) for dielectric energy storage applications.[5)] Therefore, increased research and developments in Pb-free materials brings hope for practical applications close to reality. The organization of this talk is as follows:

First, Pb-based piezoelectric/ferroelectric and antiferroelectric materials will be reviewed in view of their flexibility on a wide range of compositions, processing/reproducibility, and outstanding properties. Examples of low- and high-T_c Pb-based materials are presented. Processing of novel ceramic and composite designs for transducer applications will be presented. In addition, design and fabrication of novel piezoelectric ceramics and composites by an additive manufacturing process developed and patented at Rutgers will be discussed.

In the second part of the talk, the latest developments on BNT-based composition will be reviewed, with an emphasis on the development of reproducible hard piezoelectric composition with high and low Q and moderate electromechanical properties. The BNT-based hard composition outperformed the Pb-based piezoelectric in high power applications due to the higher coercive field and more stable Q with vibration velocity.[6)] Our research on low-temperature sintering of BNT-based ceramics with Cu electrodes using a combination of sintering aids and a controlled atmosphere opens an excellent opportunity for Pb-free multilayer actuators.

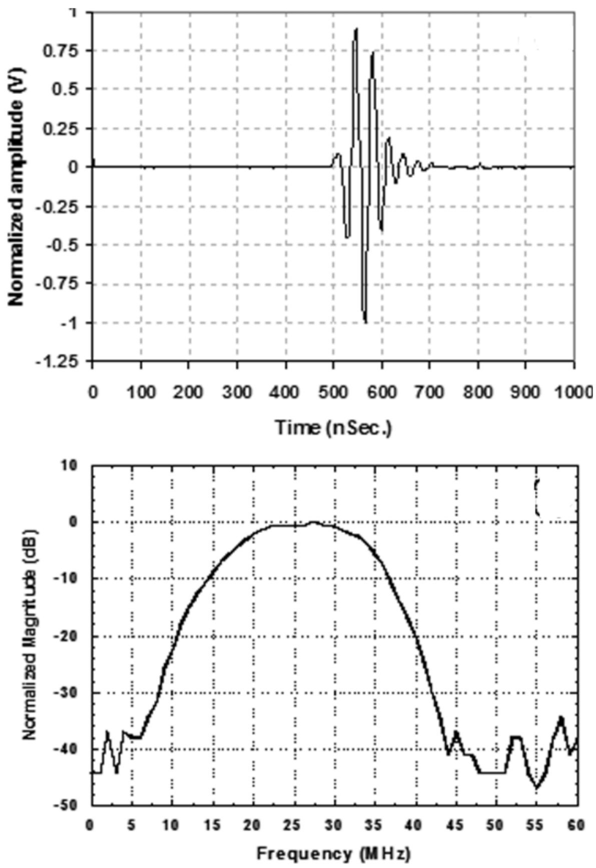

Fig. 1: Time and frequency domain responses of KNN-LT-LS transducer with matching and backing layers.

In part three, electromechanical properties and acoustic characteristics of various Pb-free materials , including the most promising compositions for medical imaging and high-power applications, will be discussed, and compared to Pb-based transducers. For example, **Fig. 1**. shows the time echo responses and associated frequency spectra of the KNN-LS-LT transducer with and without matching

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layer with -6db band width of about 70% which is comparable to those of the PZT transducer.[7)] In addition, transducers developed with a BNT-based composition showed superior performance compared to PZT in high power applications.[8)] **Fig. 2** shows the acoustic pressure vs. peak-to-peak voltage (V_{pp}) behavior of the $(BiNa_{0.88} K_{0.08}Li_{0.04})_{0.5}(Ti_{0.985}Mn_{0.015})O_3$ (BNKLT88-1.5Mn) BNKLT88-1.5 Mn and PZT 841 (hard composition) transducers. The rarefactional acoustic pressure of BNT-based transducer shows linear response up to 105 V where the acoustic pressure was measured to be about 1.13 MPa. The PZT transducer shows nonlinearity after 70 V with an acoustic pressure of 1.01 MPa. One can conclude that the peak rarefaction pressure of the BNT-based transducer can reach a higher value than the PZT-based transducer. The results demonstrate that BNKLT88-1.5 Mn composition is a promising candidate for high intensity focused transducer application.

The design of effective piezoelectric and dielectric composite systems has proven to be a decisive factor in the advancement of key technologies in the past, such as in hydrophones and ultrasonic medical imaging applications. Recently, PVDF-based polymers have been regarded as the preferred matrix material for development of composites for energy harvesting and storage applications. Composites consisting of PVDF with various oxide fillers having different particle morphologies and dielectric constants have been developed with high energy storage density and efficiency.[9)] Historical and recent methods of effective composite design, development, and their excellent performance for ultrasound imaging, energy harvesting and storage, and high-power applications will be presented.

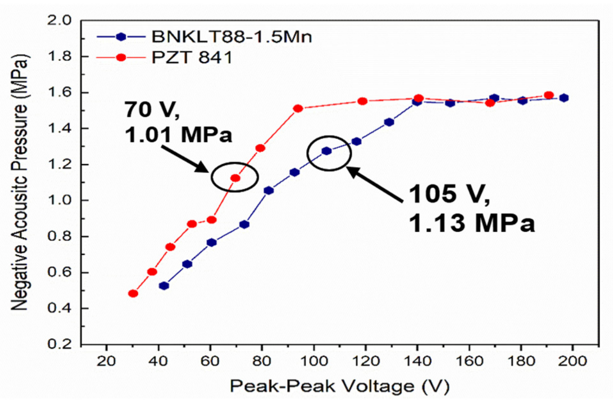

Fig. 2: Acoustic pressure vs. peak to peak voltage of 3.5 MHz for BNT-based *and* PZT-based transducer.

Lastly, silver niobate perovskite, $AgNbO_3$ (ANO), has recently been of interest as a material for capacitors with large recoverable energy density. This is due to the high field antiferroelectric (AFE) to ferroelectric (FE) transition first reported by Fu, *et al.* in 2007.[10)] Significant improvements in preparation of ANO have been realized through chemical substitution and strain engineering. Challenges to the preparation of high-quality ANO ceramics include instability of the oxide and volatility of Ag during high-temp processing leading to increased leakage current. Development of pure $AgNbO_3$ ceramic powder and densification by conventional sintering (CS) and cold sintering process (CSP) and the effect of processing parameters on perovskite phase formation and microstructure will be highlighted.[11)]

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