Lead-free Piezoelectric Ceramics for High-frequency Ultrasound Transducers

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ABSTRACT - This paper presents the latest development of lead-free piezoelectric ceramics and their application to the high frequency ultrasound transducers. Three kinds of lead-free piezoelectric ceramics $[(K_{0.5}Na_{0.5})_{0.97}Li_{0.03}(Nb_{0.9}Ta_{0.1})O_3$, $K_{0.5}Na_{0.5}(Nb_{0.94}Sb_{0.06})O_3 + 0.5mol\%MnO_2$ and $K_{0.5}Na_{0.5}NbO_3 + 0.5mol\%MnO_2]$ were fabricated and characterized. High frequency (40MHz) ultrasound transducers were successfully fabricated with these ceramics. The performance of the transducers were evaluated and compared with transducers fabricated from lead-based materials. The results suggest that lead-free piezoelectric materials in some degree may serve as an alterative to lead-based piezoelectric materials for high-frequency ultrasonic transducer applications.

INTRODUCTION

Lead-based piezoelectric materials such as lead zirconium titanate (PZT) exhibit excellent piezoelectric performance and thus have been widely used in ultrasonic transducers in past decades. However, due to environment concern, many countries and organizations are now restricting the use of lead-containing materials. Development of alternative high-performance lead-free piezoelectric materials to those lead-based materials thus has generated much interest in recent years [1-3]. Among the lead-free piezoelectric materials, alkali niobates and modified bismuth titanates have attracted major interest [4-6]. In this study, we will report fabrication and characterization of newly developed lead-free piezoelectric materials, which includes $(K_{0.5}Na_{0.5})_{0.97}Li_{0.03}(Nb_{0.9}Ta_{0.1})O_3$, $K_{0.5}Na_{0.5}(Nb_{0.94}Sb_{0.06})O_3 + 0.5mol\%MnO_2$ and $K_{0.5}Na_{0.5}NbO_3 + 0.5mol\%MnO_2$, and their application in high frequency ultrasonic transducers. In addition, performances of the transducers have been evaluated and compared with transducers fabricated from lead-based material PMN-PT single crystal.

MATERIAL FABRICATION AND CHARACTERIZATION

A conventional ceramic fabrication technique was used to prepare $(K_{0.5}Na_{0.5})_{0.97}Li_{0.03}(Nb_{0.9}Ta_{0.1})O_3$, $K_{0.5}Na_{0.5}(Nb_{0.94}Sb_{0.06})O_3 + 0.5mol\%MnO_2$ and $K_{0.5}Na_{0.5}NbO_3 + 0.5mol\%MnO_2$ ceramics using analytical-grade metal oxides or carbonate powders: Na_2CO_3 (99.8%), K_2CO_3 (99.9%), Li_2CO_3 (99%), Sb_2O_5 (99%), Ta_2O_5 (99.99%), Nb_2O_5 (99.959%) and MnO_2 (99%). The powders in the stoichiometric ratio of the compositions were mixed thoroughly in ethanol using zirconia balls for 8 hours, and then dried and calcined at 880℃ for 6 hours. After the calcinations, the mixture was ball-milled again and mixed thoroughly with a PVA binder solution, and then pressed into disk samples. The disk samples were finally sintered at 1070-1140℃ for 4 hours in air. Silver electrodes were applied on the top and bottom surfaces of the samples. The samples were poled under a dc field of 4-5kV/mm at 180℃ in a silicone oil bath for 30 minutes.

Piezoelectric and dielectric properties of the lead-free materials and PMN-PT single crystal were carefully characterized and summarized in Table 1. Those measured data were then used in KLM model simulation software (PiezoCAD) to predict performance of the transducers. As shown in the table, the lead-free ceramics exhibit a piezoelectric constant $d_{33} \geq 109$ pC/N, relative dielectric constant $\varepsilon_r \geq 327$, while maintaining a low dielectric loss $tan\theta(\%) \leq 4.5\%$. Especially, as presented, all three kinds of lead-free ceramics exhibit excellent electromechanical coupling ($k_t > 0.4$), which is one

of the most important parameters in ultrasound transducer application, normally yielding wide bandwidth and high sensitivity of the transducers. The relative high dielectric constant of some of the ceramics make them candidates for small aperture single element transducers such as needle transducers or ultrasound arrays.

Table 1: Piezoelectric and dielectric properties of the lead-free ceramics and PMN-PT

Materials	d_{33} (pC/N)	k_p	k_t	ε_r	tanθ (%)
1	245	0.42	0.44	1426	4.5
AAT	166	0.49	0.47	586	1.69
AAI	109	0.45	0.42	327	0.86
PMN-PT	2200	0.7	0.56	800*	0.5

1: $(K_{0.5}Na_{0.5})_{0.97}Li_{0.03}(Nb_{0.9}Ta_{0.1})O_3$
AAT: $K_{0.5}Na_{0.5}(Nb_{0.94}Sb_{0.06})O_3 + 0.5mol\%MnO_2$
AAI: $K_{0.5}Na_{0.5}NbO_3 + 0.5mol\%MnO_2$
*clamped dielectric cosntant

TRANSDUCERS FABRICATION AND MEASUREMENTS

In order to compare the performance of the lead-free ceramics in ultrasound transducer application to that of conventional lead-based materials, single element transducers were fabricated with three lead-free materials discussed above and lead based piezoelectric material PMN-PT. To build 40*MHz* transducers, the bulk ceramics were first lapped to half-wavelength thickness, and tuned to desired diameters to obtain the transducer 50*Ohms* electric impedance. For medical application, which requires wide bandwidth as well as high sensitivity of the transducers, two matching layers with a light backing strategy is employed [7]. In this design, 2-3*μm* silver epoxy (7.3*MRayls*) and parylene (2.5*MRayls*) were selected as the first and second front-face matching materials respectively. Conductive epoxy (Esolder-3022) with an acoustic impedance of 5.9*MRayls* was used as backing material. Before fabrication, simulations were carried out with PiezoCAD software, which is based on the KLM model, to predict performance of the transducers. Simulation data were summarized in Table 2.

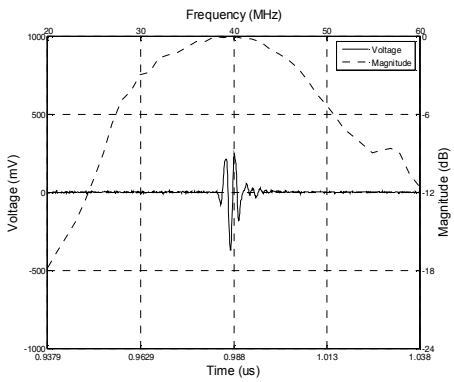
Table 2: Simulation parameters for PiezoCAD

Ceramics	1	AAT	AAI	PMN-PT
Density (kg/m^3)	4544	4528	5444	8000
Velocity (*m/s*)	4000	6522	5609	4646
Z (*MRayls*)	18	29	30	37
k_t	0.44	0.47	0.42	0.55
ε_r	1426	586	327	800*
tanθ (%)	4.5	1.7	0.86	0.5
Thickness (*μm*)	45	73	62	48
Aperture (*mm*)	0.8	1.6	2	0.8
1st matching	**Silver epoxy**			
Velocity (*m/s*)	1343	1343	1343	1343
Z (*MRayls*)	7.3	7.3	7.3	7.3
Thickness (*μm*)	10	11.5	11	10.6
2nd matching	**Parylene**			
Velocity (*m/s*)	1661	1661	1661	1661
Z (*MRayls*)	2.5	2.5	2.5	2.5
Thickness (*μm*)	13	14.7	14	13
Backing	**E-Solder 3022**			
Velocity (*m/s*)	1308	1308	1308	1308
Z (*MRayls*)	5.9	5.9	5.9	5.9
Thickness (*mm*)	>3	>3	>3	>3

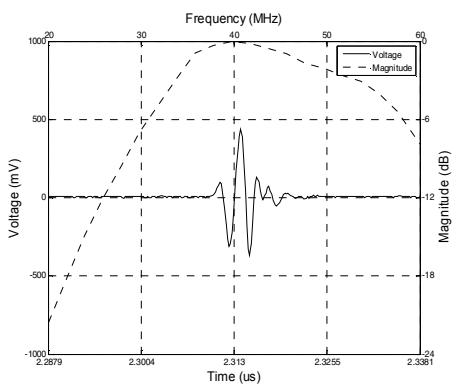
*clamped dielectric constant

Single element transducers were carefully fabricated following the simulation results. To experimentally evaluate and compare the performance of the transducers, a set of measurements were performed. Agilent 4294A electric impedance analyzer (Agilent Technologies, Englewood, CO) was used to measure the electric impedance of the transducers. The center frequency, bandwidth and insertion loss were tested using a pulse-echo test setup. In this setup, a piece of quartz was immersed in a water bath as the target. Panametrics 5900PR (Panametrics Inc, Waltham, MA) and Tektronix AFG2020 function generator were used as the signal source for pulse-echo test and insertion loss test respectively. In the both tests, the quartz target was located at the natural focal distances of the transducers. And, in the insertion loss test, losses due to diffraction and attenuation in the water bath were compensated. The echo signals were acquired and displayed using LeCroy LC534 1*GHz* digital oscilloscope. Figure.1 shows the acquired pulse-echo signals and their spectrum. The measurement results are summarized in Table 3. As presented in Table 3, lead based PMN-PT transducer has better sensitivity than lead-free based transducers, because PMN-PT possess of excellent electromechanical coupling and high

piezoelectric constant; while lead-free material based transducers show their advantage in a wider bandwidth, mainly due to their relatively lower acoustic impedance compared to lead based PMN-PT material.



(a)



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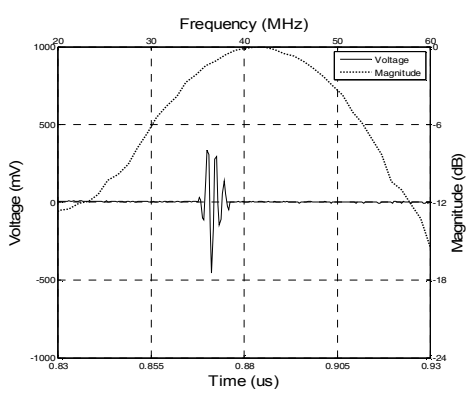

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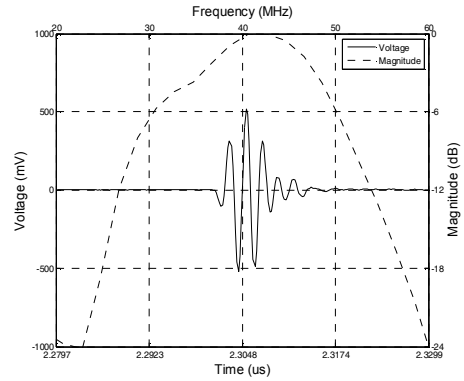

(d)

Figure1. Measured pulse-echo and its spectrum of the transducer fabricated from (a) $NaKNbNO_3$-$LiTaO_3$, (b) Alkali metal Niobate (AAT), (c) Alkali metal Lithrum (AAI), and (d) PMN-PT.

Table 3: Summary of the transducers measurement results

Materials	**F_c (*MHz*)**	**Electric Impedance (*Ω*)**	**Bandwidth (*-6dB*)**	**Two-way insertion loss (*dB*)**
1	40	50	65%	22 (at 40*MHz*)
AAT	40	46	70%	14 (at 40*MHz*)
AAI	41	48	60%	15 (at 41*MHz*)
PMN-PT	42	45	50%	12 (at 42*MHz*)

CONCLUSTIONS

Three types of lead-free piezoelectric ceramics with the excellent piezoelectric and dielectric properties were successfully synthesized and characterized. High-frequency single element transducers based on those ceramics were fabricated, evaluated, and compared to the lead-based PMN-PT transducer. The results are summarized as follows:

1. Lead-free ceramics have relatively low acoustic impedance, suitable for wide bandwidth transducer application.
2. The dielectric constant values of some of ceramics make them candidates for small aperture size application such as needle transducers.
3. All of the three lead-free ceramics exhibit excellent electromechanical coupling coefficients,

(k_t > 0.4). With those materials, it is possible to build high sensitivity, wide bandwidth ultrasound transducers.

In summary, lead-free piezoelectric ceramics are promising piezoelectric materials and may serve as an alterative to lead-based piezoelectric materials in some high-frequency ultrasonic transducer applications in future.

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