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Microscale 1–3-Type (Na,K)NbO₃-Based Pb-Free Piezocomposites for High-Frequency Ultrasonic Transducer Applications

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Abstract

Fine-grained Pb-free (Na_{0.535}K_{0.485})_{0.95}Li_{0.05}(Nb_{0.8}Ta_{0.2})O₃ (NKLNT) piezoceramics prepared by spark plasma sintering (SPS) technique was used to fabricate NKLNT/epoxy 1–3 composites with a modified dice–fill method. Because of its good machinability, SPSed NKLNT ceramic rods could be miniaturized to a lateral width of 50 μm. After lapping down to 56 μm in thickness, the composite was used to fabricate an ultrasonic transducer as the active piezoelectric element. This composite transducer showed a bandwidth at –6 dB nearly 90% at a center frequency of 29 MHz, demonstrating that this Pb-free composite thick film is very promising for the fabrication of high-frequency ultrasonic transducers in medical imaging applications.

I. Introduction

Piezoelectric composites with 1–3 connectivity, which consist of a parallel array of piezoceramic rods embedded in a passive polymer matrix, have received much attention in ultrasonic transducer applications.^{1,2} Such a composite combines the advantages of the ceramic and polymer phases. For example, it enhances high piezoelectric characteristics of the ceramics and exhibits low acoustic impedance because of the incorporation of a passive polymer phase. Most importantly, the 1–3 connectivity effectively enhances the electromechanical coupling coefficient in the thickness mode. Recently, high-frequency ultrasonic transducers have been intensively studied to meet the need for imaging with improved resolution.^{3–8} It is well-known that in the thickness mode, the resonance frequency f_r of a piezoelectric layer is inversely proportional to its thickness t . As a result, in the case of the 1–3 piezocomposites for high-frequency transducer applications, the piezoelectric layer must be lapped to a thickness thin enough to yield high-frequency resonances; in addition, better control and reduction of the spatial scale of piezoceramic rods in the composite is required to minimize lateral resonances.

In recent years, widely used piezoelectric active components in the 1–3 composites were Pb-based ceramics because of their excellent piezoelectric properties.^{4,6,9,10} However, the development of Pb-free alternatives has become urgent and imperative because of environmental concerns.¹¹ Among the Pb-free candidates, (Na,K)NbO₃ (KNN)-based ceramics has been considered the most promising.¹² Particularly, our recent study revealed that Li/Ta-modified KNN ceramics may be a viable alternative as the piezoelectric active component to prepare 1–3 composite for ultrasonic transducers because of its lower dielectric constant and acoustic impedance than those of Pb-based counterparts. However, it has a major shortcoming in that the minimal width of rods fabricated from normally sintered KNN-based ceramics is only limited to 150 μm due to its inferior mechanical strength.¹³ In this study, spark plasma sintered (SPSed) compositionally optimized Li/Ta-modified KNN ceramics were used to fabricate 1–3 composites by the modified dice–fill method. A single element ultrasonic transducer was fabricated and tested from these 1–3 composites and tested. Promising results were obtained.

II. Experimental Procedure

Li/Ta-modified KNN ceramics with optimized nominal composition of $(\text{Na}_{0.535}\text{K}_{0.485})_{0.95}\text{Li}_{0.05}(\text{Nb}_{0.8}\text{Ta}_{0.2})\text{O}_3$ (NKLNT) was prepared by SPS. The relative density of SPSed NKLNT ceramics reached 98.3%. More importantly, as described in our recent work,¹⁴ SPSed NKLNT ceramics showed a fine-grain structure ($\text{GS} < 1 \mu\text{m}$) and higher fracture strength ($\sigma_f = 102.84 \text{ MPa}$) than normally sintered ceramics ($\text{GS} \sim 10 \mu\text{m}$, $\sigma_f = 67.9 \text{ MPa}$). NKLNT/epoxy 1–3 composites were fabricated using a modified dice–fill method as mentioned elsewhere in detail.¹³ Here, the SPSed ceramic rods could be miniaturized to a lateral width of 50 μm because of its improved mechanical strength.

For piezoelectric and dielectric property measurements, both sides of the composite were polished to the end of NKLNT rods and painted with a low-temperature silver paste (drying at 70°C) as the surface electrode, and then poled at room temperature for 10 min under an electric field of 3 kV/mm in silicone oil. The morphology of the NKLNT arrays and the fabricated composite was observed by optical microscopy and scanning electron microscopy (SEM, JSM6460, Tokyo, Japan). The NKLNT volume content in the 1–3 composite was calculated from the size and spacing of ceramic rods array. The piezoelectric constant d_{33} was measured by a quasi-static piezoelectric constant testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Science); an average value of 30 measurements was calculated. The piezoelectric and dielectric properties of the 1–3 composite were measured using an impedance/gain phase analyzer (Agilent 4294A, Hewlett-Packard Co., Palo Alto, CA).

After the poled 1–3 NKLNT/epoxy composite was lapped down to 56 μm in thickness, a single element transducer was fabricated by the same method as described by Zhou *et al.*¹⁵ Electrical impedance measurements were taken using an HP4291 impedance analyzer equipped with the HP16194B impedance probe adapter. The pulse-echo analysis consisted of measuring the received echo pulse reflected from a quartz target in a deionized water bath. A pulser/receiver (Panametrics 5900PR, Olympus Co., Waltham, MA) was used to excite the transducer and receive the echo waveform, which was recorded on a Lecroy LC534 oscilloscope (50 Ω coupling). Insertion loss (IL) was measured using a burst consisting of several cycles of sinusoidal waveforms produced by a Sony/Tetronix (Beaverton, OR) model AFG2020 arbitrary function generator; the signal loss from the attenuation in water ($2.2 \times 10^{-4} \text{ dB} \cdot (\text{mm} \cdot \text{MHz}^2)^{-1}$) and transmission into the quartz target (1.9 dB) was compensated in the final IL calculation.

III. Results and Discussion

Figure 1(a) shows the optical image of the end surface of NKLNT rods after dicing, which shows that a defect-free rod array with good dicing quality and uniform periodically ordered structure. The lateral width of ceramic rods was miniaturized to 50 μm with a rod-to-rod spacing of 50 μm . In contrast, a lateral width of 150 μm could only be achieved by the same dicing method using normally sintered KNN-based ceramics. This is because SPSeD ceramics has finer grain sizes and better densification resulting in higher fracture strength than when normally sintered, making SPSeD ceramics more amenable to mechanical dicing.¹⁴ As seen from Fig. 1(b), which shows the cross-section SEM image of the composite, the epoxy is well backfilled into the kerf spaces, even though the width of spaces is only 50 μm and the depth of the cuts exceeds 500 μm . In addition, as seen from the magnified SEM image of the cross section of the composite shown in Fig. 1(c), no visible gap between the interfaces of the epoxy and ceramic rods can be found, which further illustrates that the epoxy is well backfilled into the rod-to-rod spaces.

Table I compares the experimental results of electrical properties between the monolithic NKLNT ceramics and 1–3 composite thick film. Meanwhile, the theoretical properties of the 1–3 composite are also estimated and listed in Table I according to the modified series and parallel model presented by Chan and Unsworth.¹⁶ The d_{33} , $\epsilon_r (= \epsilon_{33}^T / \epsilon_0)$, g_{33} , and Z of the 1–3 composite are determined by the following equations.:

$$d_{33} = \nu s_{11, \text{epoxy}}^P d_{33, \text{NKLNT}} / s(\nu) \quad (1)$$

$$\epsilon_{33}^T = \nu \epsilon_{33, \text{NKLNT}}^T - \nu(1 - \nu)(d_{33, \text{NKLNT}})^2 / s(\nu) + (1 - \nu) \epsilon_{11, \text{epoxy}}^P \quad (2)$$

$$g_{33} = d_{33} / \epsilon_{33}^T \quad (3)$$

$$Z = \sqrt{\rho \cdot C_{33}^D} \quad (4)$$

where $s(\nu) = \nu s_{11, \text{epoxy}}^P + (1 - \nu) s_{33, \text{NKLNT}}^E$, s is the elastic compliance, c is the elastic stiffness, and ϵ_0 is the permittivity in free space ($= 8.85 \times 10^{-12}$ F/m). In Eqs. (1) and (2), ν refers to the volume fraction of piezoceramics and $(1 - \nu)$ is the volume fraction of polymer in the composite, here $\nu = 25\%$. The k_t of the NKLNT ceramics and the composite thick film are calculated from Eq. (5). The longitudinal electromechanical coupling factor k_{33} of the NKLNT ceramics determined from Eq. (6) is also listed in Table I.

$$k_t^2 = \frac{\pi f_r}{2 f_a} \tan \left[\frac{\pi(f_a - f_r)}{2 f_a} \right] \quad (5)$$

$$k_{33}^2 = (1 - k_p^2)(1 - k_t^2) \quad (6)$$

where f_r is the resonance frequency and f_a is the antiresonance frequency in thickness resonance mode.

As seen from Table I, d_{33} of the composite is 140 pC/N, lower than the calculated value of 198 pC/N. The difference between the experimental and theoretical d_{33} values may be due to the poling temperature of the composite (room temperature), which is much lower than that of NKLNT ceramics (130°C),¹⁴ hence the composite did not achieve the optimum poling state of the NKLNT ceramics. The ϵ_r of the 1–3 composite decreases from 1240 to 302. The lowered ϵ_r enhances another important parameter, i.e., g_{33} increases from 22.1×10^{-3} to 52.4×10^{-3} m²/C, effectively improving the sensitivity in the receiving mode for ultrasonic transducer applications. Although the $\tan \delta$ of the composite (0.048) was found to be a little higher than that of the NKLNT ceramics (0.023), it was still lower than 0.05 and suitable for practical use.

An ultrasound transducer is a device that converts electrical energy into acoustic energy and vice versa via piezoelectricity or electrostriction.¹⁷ In many ultrasonic instruments, a transducer element not only emits an acoustic wave into a given medium, but also senses the weak echoes reflected back, in the so-called pulse-echo mode. Echoes are produced when a sound wave strikes a boundary between two substances possessing different characteristic acoustic impedances, and the strength of the echo is proportional to the acoustic impedance mismatch between the two materials. Therefore, for a transducer designed for ultrasonic imaging and hydrophone applications in biomedicine, its acoustic impedance should be closely matched to that of human tissue ($Z \sim 1.54$ Mrayls) and water ($Z \sim 1.48$ Mrayls) for better acoustic coupling and minimization of the reflection from the transducer/medium interface.¹⁸ In this study, as seen from Table I, the acoustic impedance is reduced from 15 Mrayls for monolithic NKLNT ceramics to 6.6 Mrayls for 1–3 composite, due to the contribution of low acoustic impedance of epoxy ($Z \sim 3.0$ Mrayls). Another important parameter of critical importance for a transducer is the Q_m , which denotes the amount of mechanical loss due to internal friction within a transducer material. In other words, the lower the losses, the higher the Q_m . As usual, piezoceramics/epoxy 1–3 composites have a low Q_m because of the polymer damping.¹⁹ The measured Q_m of developed NKLNT/epoxy 1–3 composite in this study is 18, as listed in Table I, which shows a remarkable reduction as compared with bulk NKLNT ceramics ($Q_m = 85$). Although a high Q_m is desirable to keep the dissipation of acoustic energy at a minimum, a low Q_m is needed to limit ringing to enable the generation of shorter acoustic pulse lengths, required for good axial resolution in imaging.²⁰

A single element transducer was fabricated to evaluate the performance of this 1–3 NKLNT/epoxy composite for ultrasound transducer applications. Two matching layers with a light backing strategy were used in this design for wider bandwidth and higher sensitivity. Before fabrication, the measured piezoelectric and dielectric properties were used in KLM modeling software (PiezoCAD, Sonic Concepts, Woodinville, WA) to determine the aperture size, the thicknesses of piezoelectric material, first matching layer and second matching layer and predict performance of the transducers. First, the 1–3 composite was lapped to 56 μm , and then a matching layer and 2–3 μm silver particles was cured over the 1–3 composite and lapped to 12 μm . A conductive backing material was cured over the opposite side of the 1–3 composite and lapped to 2 mm. A representative finished 1–3 NKLNT/epoxy high-frequency single element transducer is shown in Fig. 2. Figure 3 shows the measured electrical impedance magnitude and phase plots for a 1–3 composite ultrasonic transducer resonating in air. The developed 1–3 composite transducer shows a clear single thickness mode resonance. Its resonance and antiresonance frequencies are 32.2 and 40.9 MHz, respectively. As expected, the calculated k_t value approaches a value as high as

0.655, which is significantly higher than that of bulk NKLNT ceramics ($k_t = 0.34$) and comparable with its k_{33} value (0.671) as seen in Table I.

Figure 4 shows the time domain pulse-echo response and normalized spectrum of the 1–3 composite ultrasonic transducer. It can be seen that the transducer has a center frequency of 29 MHz and –6 dB bandwidth of 89.7%. Meanwhile, the two-way IL of the transducer at 29 MHz is 25.1 dB. These results demonstrate that this 1–3 composite thick film is a promising alternative for high-frequency ultrasonic transducer applications.

IV. Conclusions

Using SPSe Pb-free NKLNT piezoceramics, 1–3 NKLNT/epoxy composite was fabricated by the modified dice–fill method. It was possible to minimize SPSe NKLNT ceramic rods to a lateral width of 50 μm . The composite thick film developed showed good electrical properties as follows: relatively high piezoelectric constant ($d_{33} = 140 \text{ pC/N}$), low acoustic impedance ($Z = 6.6 \text{ Mrayls}$), high electromechanical coupling coefficient ($k_t = 0.655$), reduced dielectric constant ($\epsilon_r = 302$), enhanced piezoelectric voltage coefficient ($g_{33} = 52.4 \times 10^{-3} \text{ m}^2/\text{C}$) and relatively low mechanical quality factor ($Q_m = 18$). Using this 1–3 NKLNT/epoxy composite thick film, a high-frequency single element transducer (29 MHz) with very broad bandwidth 89.7% at –6 dB was fabricated, indicating that it might serve as an alternative to Pb-based piezoelectric materials in a number of high-frequency ultrasonic transducer applications in the future.

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Fig. 1.

(a) Optical image of the end surface of $(\text{Na}_{0.535}\text{K}_{0.485})_{0.95}\text{Li}_{0.05}(\text{Nb}_{0.8}\text{Ta}_{0.2})\text{O}_3$ (NKLNT) rods array after dicing; (b and c) the cross section scanning electron microscopic image of as-developed composite sample.

Fig. 2.
A photograph of 1–3-type $(\text{Na}_{0.535}\text{K}_{0.485})_{0.95}\text{Li}_{0.05}(\text{Nb}_{0.8}\text{Ta}_{0.2})\text{O}_3$ (NKLNT)/epoxy composite transducer.

Fig. 3. Electrical impedance magnitude and phase plots for an air resonating of 1–3-type $(\text{Na}_{0.535}\text{K}_{0.485})_{0.95}\text{Li}_{0.05}(\text{Nb}_{0.8}\text{Ta}_{0.2})\text{O}_3$ (NKLNT)/epoxy composite ultrasonic transducer.

Fig. 4. Pulse-echo response and spectrum of the 1-3-type $(\text{Na}_{0.535}\text{K}_{0.485})_{0.95}\text{Li}_{0.05}(\text{Nb}_{0.8}\text{Ta}_{0.2})\text{O}_3$ (NKLNT)/epoxy composite ultrasonic transducer.

Table I

Electrical Properties of Monolithic NKLNT and Developed 1–3 Composite Thick Film

Parameters	NKLNT	1–3 composite (experimental results)	1–3 composite (theoretical results)
NKLNT content (vol%)	100	25	
d_{33} (pC/N)	243	140	198
ϵ_r (at 1 kHz)	1240	302	313
g_{33} ($\times 10^{-3}$ m ² /C)	22.1	52.4	71.5
Tan δ (at 1 kHz)	0.023	0.048	
Q_m	85	18	
k_t	0.34	0.655	0.671(k_{33})
Z (Mrayls)	15	6.6	6.3

NKLNT, (Na_{0.535}K_{0.485})_{0.95}Li_{0.05}(Nb_{0.8}Ta_{0.2})O₃.