(100)-Textured KNN-based thick film with enhanced piezoelectric property for intravascular ultrasound imaging

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Using tape-casting technology, 35 μm free-standing (100)-textured Li doped KNN (KNLN) thick film was prepared by employing NaNbO_3 (NN) as template. It exhibited similar piezoelectric behavior to lead containing materials: a longitudinal piezoelectric coefficient (d_{33}) of $\sim 150 \text{ pm/V}$ and an electromechanical coupling coefficient (k_t) of 0.44. Based on this thick film, a 52 MHz side-looking miniature transducer with a bandwidth of 61.5% at -6 dB was built for Intravascular ultrasound (IVUS) imaging. In comparison with 40 MHz PMN-PT single crystal transducer, the rabbit aorta image had better resolution and higher noise-to-signal ratio, indicating that lead-free (100)-textured KNLN thick film may be suitable for IVUS ($>50 \text{ MHz}$) imaging. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4919387>]

As a well-known medical imaging technology, catheter-based intravascular ultrasound (IVUS) plays a critical role in diagnosing coronary artery disease which is one of the major causes of human morbidity and fatality.¹ By virtue of the capability of directly imaging the vessel wall, IVUS can provide an accurate evaluation of lumen size, plaque characteristics, and calcium content.^{2,3} Commonly, in a diagnostic process, a tiny single-element transducer with the central frequency between 20 MHz and 45 MHz is placed at an appropriate position inside the blood vessel and driven by a rotational shaft to achieve cross-sectional images of the coronary artery.^{4,5} In order to enhance the imaging resolution, increasing IVUS central frequency to higher than 50 MHz is thought to be an effective way, sacrificing to a certain extent the penetration depth.

Up to now, only limited IVUS studies have been carried out at such high frequencies,^{6–8} because it is a great challenge to fabricate highly sensitive miniaturized transducers. As is well known, a piezoelectric layer is the core part of an IVUS transducer. Most importantly, its thickness is required to be on order of several tens of micrometers to achieve the operational frequency higher than 50 MHz and its property determines the imaging performance. Due to its excellent piezoelectric behaviors, lead-based piezoelectric layer has been most popular for IVUS ($>50 \text{ MHz}$) applications. However, the toxicity of lead is a severe issue in view of the environmental protection and human body safety. Therefore, the development of lead-free piezoelectric layer to replace lead-containing one for IVUS ($>50 \text{ MHz}$) imaging is of urgent importance. Given that lapping down bulk material to the desired thickness is also a time-consuming and difficult task, lead-free piezoelectric thick films apparently are a

promising alternative. Although much effort has been devoted to the exploration of lead-free thick films in recent years,^{9–14} no one has been reported to be competent for IVUS ($>50 \text{ MHz}$) transducer application yet. With this in mind, it would be interesting and worthy to investigate the possibility of IVUS imaging utilizing lead-free piezoelectric thick films at higher frequency ($>50 \text{ MHz}$).

The biggest obstacle to be overcome is to enhance the piezoelectric property of the lead-free piezoelectric thick films. To address this issue, the formation of a preferential oriented structure and the elimination of substrate clamping influence are believed to be two effective approaches. In this letter, tape-casting technology and reactive template grain growth (RTGG) method were employed. A freestanding (100)-textured Li doped KNN thick film with a thickness of 35 μm was prepared and its dielectric, ferroelectric, and piezoelectric properties were characterized. Furthermore, based on this film, a sensitive miniaturized ultrasound transducer with an operational frequency greater than 50 MHz was built and *in vitro* IVUS imaging of a healthy rabbit aorta was carried out to demonstrate the feasibility and the characteristics of these devices.

Matrix particles with a composition of $(\text{K}_{0.504}\text{Na}_{0.496})_{0.933}\text{Li}_{0.067}\text{NbO}_3$ (KNLN) were prepared using Na_2CO_3 (99.8%), K_2CO_3 (99%), Li_2CO_3 (98%), and Nb_2O_5 (99.5%) as raw materials. After calcined at 850°C for 5 h, the ceramic powders were milled in a high energy ball mill machine for 1 h in ethanol to obtain the fine matrix particles of about 0.34 μm average size. The NaNbO_3 template particles synthesized by the top chemical microcrystal conversion method¹⁵ are (100) faceted and have rectangular plate-like shape with high aspect ratio. As shown in inset (a) of Fig. 1, the particle size varies in the range of 10–20 μm in length and 1–2 μm in thickness. Then plate-like NN particles (10 mol. %) and the dried fine

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FIG. 1. XRD pattern of textured KNLN thick film. Insets: (a) SEM morphology of plate-like NN template particle; (b) SEM surface image of textured KNLN thick film.

matrix particles (90 mol. %) were mixed with solvent, dispersant, binder, and plasticizer by ball milling for 3 days to obtain tape casting slurry, and the green sheets were formed by tape casting. Dried green sheet was cut, stacked, and laminated at 70 °C and 50 MPa for 15 min to fabricate green compact with a dimension of 10 mm × 10 mm and a thickness of around 35 μm. After the removal of organic substances from the green compact by heating to 600 °C for 2 h in air, the specimens were sintered at 1120 °C for 2 h.

Figure 1 shows the XRD pattern of the KNLN thick film. It is obvious that the thick film obtained has a typical perovskite structure with (100)-preferred orientation and no impurity phase can be detected. The (200) and (002) peaks that appear at around 46° indicate that KNLN thick film is located in the Morphotropic Phase Boundary (MPB) region where both orthorhombic and tetragonal phases coexist. The degree of grain orientation defined as Lotgering's factor (F) can be given by the following formula:¹⁶

$$F = (P - P_0) / (1 - P_0), \quad (1)$$

where P is the sum $I_{(h\ 0\ 0)} / \text{sum } I_{(h\ k\ l)}$, and P_0 is the sum $I_{0\ (h\ 0\ 0)} / I_{0\ (h\ k\ l)}$. Sum I is the summation of the peak intensities of the XRD pattern of the obtained sample and Sum I_0 is the summation of the peak intensities of equiaxed reference powder, respectively. The value of F is calculated to be 90%, which is much higher than that of textured KNN thick film reported in Ref. 12. The inset (b) of Figure 1 describes SEM surface morphology of textured KNLN thick film. It can be seen that the KNLN thick film is very dense and has no crack. The relative density of the obtained film can reach ~90% according to the measurement using Archimedes method.

The temperature dependences of dielectric constant and loss of the textured KNLN thick film measured at 100 kHz are presented in Fig. 2(a). The T_C is observed to be 443 °C and orthorhombic-tetragonal phase transition temperature (T_{O-T}) is located at around room temperature. Below T_C , the dielectric loss is less than 0.04, guaranteeing that KNLN thick film based transducer can be operated in a broad temperature range. Fig. 2(b) depicts the polarization hysteresis loop of the textured KNLN thick film. It can be found that the remnant polarization (P_r) and coercive field (E_c) are 14 μC/cm² and 22.7 kV/cm, respectively. As illustrated in Fig. 2(c), under the electric field of 50 kV/cm, the induced strain of textured KNLN film can attain 0.075%. This value is much larger than those results for other KNN thick films at the same electric field,^{11,13,14} which is attributed to its high orientation structure and no substrate clamping effect. In a bid to get the longitudinal piezoelectric coefficient of d_{33} of the textured KNLN thick film, a dual-beam laser interferometer was utilized and the applied ac electric field was 5 kHz with the amplitude of 0.1 kV/cm. Its piezoelectric coefficient d_{33} exhibits a clear switching behavior, as shown in Fig. 2(d). The measured d_{33} of ~150 pm/V is superior to other KNN thick films⁹⁻¹⁴ and is comparable to lead-based films,^{17,18}

FIG. 2. (a) Temperature dependence of dielectric constant and loss, (b) polarization-electric field hysteresis loop, (c) field induced strain-electric field curve, and (d) longitudinal piezoelectric coefficient as a function of dc electric field of textured KNLN thick film.

indicating that the obtained KNLN thick film possess the capability for ultrasound transducer applications.

Krimholtz, Leedom, and Mettæi (KLM) model-based simulation software PiezoCAD (Sonic Concepts, Woodinville, WA) was used for side-looking miniature transducer design. First, Cr/Au (500 Å/1000 Å) layers were sputtered onto both sides of the textured KNLN thick film as top and bottom electrodes. Then silver epoxy (7.3 MRays) made from Insulcast 501 (American Safety Technologies, Roseland, NJ) and 2–3 μm of silver particles (Sigma-Aldrich, Inc., St. Louis, MO) was cured on top electrode and acted as the first matching layer. A conductive backing layer, E-solder 3022 (Von Roll Isola, New Haven, CT) with an acoustic impedance of 5.9 MRays, was employed as the backing layer. The active stack, the SEM cross-sectional image of which is shown in Figure 3(a), was diced into small posts with the aperture of 0.4×0.4 mm. The post was inserted into a polyimide tube (MedSource Technologies, Trenton, GA) in which a 0.1-mm-diameter lead wire was connected to the backing layer using conductive epoxy. A stainless steel needle was utilized as the housing, which has a window on the side allowing the acoustic wave to go through. The gap between the piezoelectric post and needle housing was filled with 5-min Epoxy (Henkel Corporation, Irvine, CA) to insulate the inner electrode. Finally, the parylene was evaporated onto the front side of the transducer as the second matching layer after a Cr/Au (500 Å/1000 Å) layer had been sputtered across the silver epoxy and the needle housing to form a ground electrode. The photo of obtained side-looking miniature transducer was illustrated in Fig. 3(b)

As described in Fig. 3(c), it can be seen that resonant and anti-resonant peaks are located at 49.1 MHz and 53.8 MHz, respectively. According to the IEEE standard,¹⁹ the thickness mode electromechanical coupling coefficient (k_t) can be given by

$$k_t = \sqrt{\frac{\pi f_r}{2 f_a} \tan\left(\frac{\pi f_a - f_r}{2 f_a}\right)}. \quad (2)$$

Substituting the appropriate values into Eq. (2), k_t is calculated to be 0.44. It is worthy to be noticed that no previous work has reported such high k_t value for lead-free piezoelectric thick films. Additionally, a peak in the phase curve is observed at 51.7 MHz, which suggests that the central frequency of the KNLN thick film transducer is nearby. The transducer pulse-echo response was tested in deionized water bath at room temperature by reflecting the transmitted signal off a polished x-cut quartz target. A pulser receiver (5900PR, Panametrics, Inc., Waltham, MA) was used to activate the transducer and receive the echo, whose waveform was recorded using a 1-GHz oscilloscope (LC534, LeCroy Corp., Chestnut Ridge, NY). In Fig. 3(d), it is easy to observe that the central frequency of the transducer is 52 MHz, which is in good agreement with the result for the electrical impedance. The bandwidth at −6 dB is measured to be 61.5% and the sensitivity of the pulse-echo signal is 410 mV. These promising results are beneficial for IVUS imaging.

To evaluate the KNLN thick film transducer for IVUS imaging, *in vitro* imaging of a normal rabbit aorta was performed. During the experiment, the miniature transducer was positioned inside the lumen of the sample immersed in water and driven by a rotational motor. A pulser receiver (5900PR, Panametrics, Inc., Waltham, MA) was used to activate the transducer and receive the echo signals, and a 12-bit data acquisition board (Gage Applied Technologies, Lockport, IL) with a sampling rate of 400 MHz was utilized for digitizing RF data. The scanning procedure was controlled a commercial LabVIEW (National Instruments, Austin, TX) program. For the purpose of comparison, a 40 MHz PMN-PT single crystal transducer²⁰ with aperture size of 0.4×0.4 mm was employed to image the same sample. All images were displayed with a 45 dB dynamic range. The rabbit aorta images from 52 MHz KNLN thick film transducer and 40 MHz PMN-PT single crystal transducer are shown in Figs. 4(a) and 4(b), respectively. For both images, the anatomy of the

FIG. 3. (a) SEM cross-sectional imaging of active stack; (b) photograph of side-looking miniature transducer; (c) electrical impedance magnitude and phase of the transducer as a function of frequency; (d) measured pulse-echo waveform and frequency spectrum of the transducer.

FIG. 4. IVUS imaging of healthy rabbit aorta from (a) 52 MHz KNLN thick film transducer and (b) 40 MHz PMN-PT single crystal transducer.

aorta including the vascular wall and the surrounding fatty tissue can be clearly visualized. Due to the greater operational frequency, 52 MHz image shows better resolution (finer speckles). Furthermore, its noise-to-signal ratio (SNR) is also higher than that of image acquired from PMN-PT single crystal transducer. The possible reason is that a slightly electrical impedance mismatch for 40 MHz PMN-PT single crystal transducer with the same aperture size might lead to the lower pulse-echo amplitude. The results indicate that free standing (100)-textured KNLN thick film is at least comparable with PMN-PT single crystal on the IVUS image applications.

In summary, (100)-textured KNLN thick film with a thickness of 35 μm was prepared by tape-casting technology using NN as template. It exhibited higher longitudinal piezoelectric coefficient (d_{33}) and higher electromechanical coupling coefficient (k_t) than any other KNN thick films. Based on this film, a side-looking miniature transducer for IVUS imaging was built with a central frequency of 52 MHz and a bandwidth of 61.5% at -6 dB. Its rabbit aorta image had better resolution and higher noise-to-signal ratio than those of image acquired from PMN-PT single crystal transducer with lower operational frequency. These results demonstrate that lead-free (100)-textured KNN-based thick film is a promising lead-free piezoelectric material for IVUS (50 MHz) imaging. Moreover, this research opens a path for the application of lead-free piezoelectric thick film.

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