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An ultrasonic therapeutic transducers using lead-free $Na_{0.5}K_{0.5}NbO_3$–$CuNb_2O_6$ ceramics

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ABSTRACT

In this work, we reports on the $CuNb_2O_6$ (CN) modified lead-free $Na_{0.5}K_{0.5}NbO_3$ (NKN) based piezoelectric ceramics were synthesized by solid-state reaction methods and sintered at 1075 °C for 3 h. A secondary phase of $K_4CuNb_8O_{23}$ was found in the XRD pattern of NKN-based ceramics as the CN dopants is 1 mol%. Microstructural analyses of un-doped and CN-doped ceramics were performed in a scanning electron microscope. The influence of CN content on the microstructure, electrical properties, temperature stability, and mechanical properties of the synthesized ceramics was investigated. The results show that the synthesized ceramics with CN-doped not only had improved density but also exhibited superior piezoelectric characteristics, temperature stability of resonance frequency (TCF), and a better elastic stiffness coefficient than those of pure NKN piezoelectric ceramics. The bulk density (4.47 g/cm^3), k_p (40%), k_t (45%), Q_m (1642), C_{33}^D (19.64×10^{10} N/m^2), TCF (−0.011%/°C) and TCC (0.135%/°C) values for NKN-01CN ceramics obtained from experiments show excellent 'hard' piezoelectric properties. Furthermore, a lead-free NKN-01CN ultrasonic therapeutic transducer was successfully driven by a self-tuning circuit.

1. Introduction

Piezoelectric ceramics are used in actuators and sensors [1,2]. Thickness extensional ultrasonic transducers acting as applicators in ultrasonic therapeutic systems are routinely applied in the fields of physiotherapy, cosmetic surgery, skin therapy, transdermal delivery, and hard disk driver actuator arm [3–6]. Modified lead-based piezoelectric ceramics, such as lead titanate (PT) and lead zirconate titanate (PZT) has good potential due to its ability to facilitate a desirable combination of properties, such as high surface phase velocity, electromechanical coupling coefficient (k^2), and low temperature coefficient of frequency (TCF). They have been widely studied and used as transducers, piezoelectric actuators, surface acoustic wave (SAW) devices, and sensors because of their excellent piezoelectric properties [7,8]. However, its high content of toxic elements (Pb > 60 wt%) has triggered some concerns in Europe and Japan mainly due to the utilization, recycling, and disposal of lead-based ferroelectrics. These issues have become a driving force for developing lead-free ferroelectric ceramics with properties comparable to those of its lead-based counterparts.

Candidates for lead-free materials include Bi compounds [9–11] and alkaline niobate compounds [12,13]. Bi compounds have a very high mechanical quality factor ($Q_m \sim 7000$) and high phase transition temperature ($T_c \sim 600$ °C) but its electromechanical coupling coefficient k_p is very low (~22%) [10,11]. Sodium potassium niobate (($Na_{0.5}K_{0.5}$)NbO_3, NKN) ceramic is an attractive material that has been thoroughly investigated due to its high electromechanical coupling coefficient (k^2) and high phase transition temperature ($T_c \sim 420$ °C), especially near the morphotropic phase boundary (MPB) [13–15]. NKN ceramics have been considered as a good candidate for lead-free piezoelectric ceramics because of its strong piezoelectricity and ferroelectricity. However, dense NKN ceramics are difficult to be produced using the conventional sintering process. The main problem due to volatilization of potassium oxide (K_2O) at 800 °C, which makes controlling the stoichiometry difficult [16,17]. Besides, PZT-based ceramics have better piezoelectric properties than those of pure NKN ceramics. To replace PZT-based systems, it is necessary to develop the required piezoelectric properties by modifying NKN ceramics. A high mechanical quality factor (Q_m) is required for actuator and high-power applications. The CuO is an excellent sintering aid and has been to improve the sintering performance of piezoelectric ceramics [18,19]. Small amounts of CuO on NKN ceramics effectively improve the Q_m value without

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reducing the piezoelectric properties. On the other hand, the sintering temperature of NKN system is too high (>1075 °C). In order to inhibit the volatilization of K_2O, CuO is often used to improve the sinterability of NKN-based ceramics because of its low melting point and formation of a liquid phase and lower the sintering temperature [20].

Therefore, in this paper, we continued our previous work and small amounts of Cu compounds $CuNb_2O_6$ (CN) were used as the dopant of NKN ceramics to replace CuO. CN can not only improve the sinterability of NKN, but it also decreases the A/B ratio of NKN compounds. The small additions of CN effectively improved both the sinterability of NKN ceramics as well as the Q_m. Variations of the microstructure and piezoelectric properties due to CN addition were investigated. The temperature coefficient of the change rate of the clamped capacitance (TCC) and temperature coefficient of the change rate of the resonant frequency (TCF) of the piezoceramics material were studied. Further, fabrication of NKN ceramics with 1 mol% CN doping for therapeutic transducers is reported.

2. Experiment procedures

In our previous study, it was found that $Na_{0.5}K_{0.5}NbO_3$ ceramics with 1 mol% $CuNb_2O_6$ doping exhibited excellent piezoelectric properties [21]. In this work, the starting materials for $Na_{0.5}K_{0.5}NbO_3$-$x$$CuNb_2O_6$ (NKN-xCN, for x = 0, and 1 mol%) ceramics synthesized by solid-state reaction were pure reagent Na_2CO_3 (SHOWA, 99.5%), K_2CO_3 (SHOWA, 99.5%), Nb_2O_5 (SHOWA, 99.5%), and CuO (SHOWA, 99.5%) powders. $Na_{0.5}K_{0.5}NbO_3$ (NKN) and $CuNb_2O_6$ (CN) were weighed according to the desired compositions. The starting materials were individually transferred to a 100 mm diameter cylindrical plastic jar that was partially filled with 10 mm diameter ZrO_2 grinding balls. Sufficient ethanol (99.5%) was added to cover the powders. Ball milling was carried out for 24 h, followed by drying at 130 °C. Grinding was then conducted using an alumina mortar and pestle to break up large agglomerates formed during drying. The stoichiometric NKN and CN powders were first synthesized via the solid-state reaction method at 850 and 900 °C for 5 h, respectively. After calcination, NKN and CN powders were weighted according to the formula NKN-xCN and ball milled for 24 h. The powders, milled with 5 wt.% PVA aqueous solution, were then uni-axially pressed into a disk of 18 mm diameter, at pressure of 25 kg/cm^2 and subsequently sintered in air at 1075 °C for 3 h.

Bulk densities were measured using the Archimedes method with distilled water as the medium. The crystallographic study was confirmed by X-ray diffraction (XRD) using Cu K_α (λ = 0.154 nm) radiation with a Seimens D-5000 diffractometer operated at 40 kV and 40 mA. The microstructure was observed using field emission scanning electron microscopy (FESEM) with a Hitachi S-4100 microscope. The dielectric and piezoelectric properties were measured with a HP 4294A precision impedance analyzer. To measure the electrical properties, silver paste was painted on both sides of the ceramics to form electrodes. The samples were then fired at 150 °C for 20 min. The samples were poled under 30 kV/cm DC field at 150 °C in silicone oil for 30 min. The electromechanical coupling factors of thickness (k_t) and planar (k_p) modes were calculated using the resonance–antiresonance method. The piezoelectric coefficient d_{33} was measured using a Wide-Range d_{33} Tester 90-2030 (APC International, Ltd.). In this paper, a NKN-01CN piezoelectric disk, 10 mm diameter and 1 mm thickness, for use as a disk-shaped therapeutic transducer was designed and tested.

3. Results and discussion

The XRD analysis of the NKN and NKN-01CN piezoelectric ceramics sintered at 1075 °C are shown in Fig. 1. NKN and NKN-01CN ceramics possess a perovskite structure with orthorhombic symmetry (the XRD patterns can be indexed by JCPDS card no. 32-0822) and a secondary phase of $K_4CuNb_8O_{23}$ (KCN, JCPDS card no. 21-1250) is found in NKN-01CN ceramics. Also, the diffraction angles do not shift obviously, indicating that the lattice constant had changed very little. The ionic radius of Cu^{2+} (0.87 Å) is smaller than A-site ions (K^+: 1.52 Å and Na^+: 1.16 Å) and larger than B-site ions (Nb^{5+}: 0.64 Å). Cu^{2+} may substitute both A and B sites [18]. As shown in Table 1, all of the lattice parameters (a, b, c) are increasing as introducing the CN dopants in the system. That may be due to some of the Cu^{2+} substitute the B-site ions.

Fig. 2 shows the SEM images of NKN and NKN-01CN ceramics sintered at 1075 °C. Both ceramics have a dense structure, and the grains are generally rectangular in shape. For the NKN ceramic, the grain size is in the range of 1–2 μm and the ceramic became denser and the grains became significantly larger as introducing the CN dopants in the system. The abnormal grain growth usually occurred in the presence of the liquid phase and it may be because of the

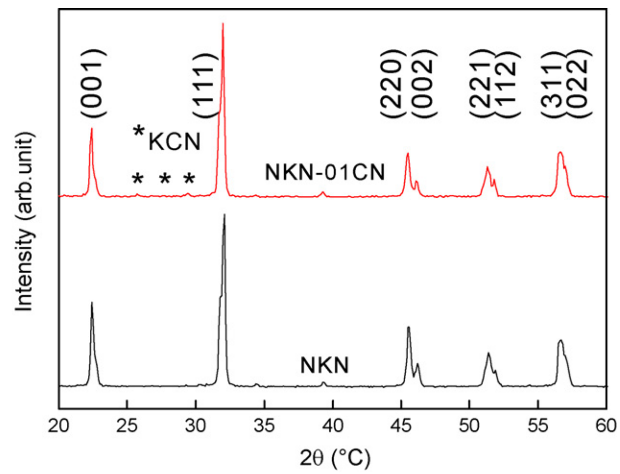

Fig. 1. XRD patterns of the NKN and NKN-01CN ceramics sintered at 1075 °C for 3 h.

Table 1
Comparison of lattice parameters for the NKN-01CN and NKN ceramics.

	a (Å)	b (Å)	c (Å)
NKN-01CN	5.631	5.674	3.937
NKN	5.624	5.649	3.921

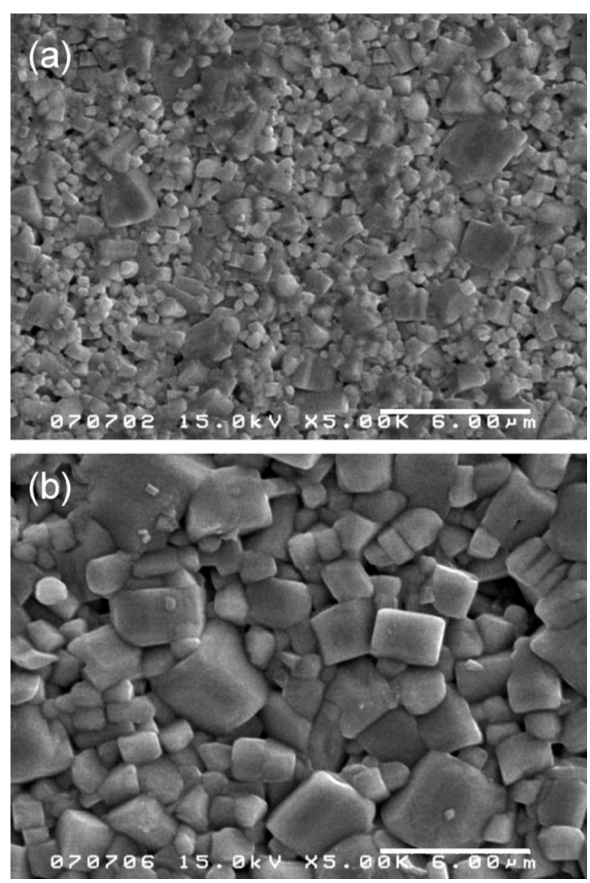

Fig. 2. SEM images of (a) NKN ceramics and (b) NKN-01CN ceramics sintered at 1075 °C for 3 h.

Table 2
Comparison of properties of NKN-01CN, NKN, and PMZT3 ceramics.

	NKN-01CN	NKN	PMZT3
Density, ρ (g/cm^3)	4.47	4.08	7.78
Dielectric constant, ε_r	432	457	1436
Poisson's ratio, σ	0.25	0.26	–
k_p (%)	40	36	60
k_t (%)	45	37	48
k_{33} (%)	57	50	–
d_{33} (pC/N)	93	80	–
Q_m	1642	70	1200
T_c (°C)	410	421	350
TCC (%/°C)	0.135	0.496	0.356
TCF (%/°C)	−0.011	−0.035	0.125
Reference	Our sample	Our sample	[22,23]

$K_4CuNb_8O_{23}$ formed during sintering and the low melting point of $K_4CuNb_8O_{23}$ (1050 °C) [18]. Owing to the formation of a liquid phase, the sintering temperature for NKN ceramics is reduced and the densification is improved.

The material parameters of the NKN and NKN-01CN ceramics are summarized in Table 2. The density of NKN-01CN ceramics (4.47 g/cm^3) is much higher than that of NKN ceramics (4.08 g/cm^3). To achieve high efficiency, it is necessary for the piezoelectric plate to have a high electromechanical coupling factor (k_p and k_t) and mechanical quality factor (Q_m). The planar mode electromechanical coefficient k_p and the thickness mode electromechanical coefficient k_t are calculated using the following equations [24,25]:

$$k_p^2 = \frac{1}{p} \cdot \frac{f_a^2 - {f_r}^2}{{f_a}^2} \quad (1)$$

$$k_t^2 = \frac{\pi}{2} \cdot \frac{f_r}{f_a} \cot\left(\frac{\pi}{2} \cdot \frac{f_r}{f_a}\right) \quad (2)$$

where f_r is the resonance frequency; f_a is the antiresonance frequency; and $p = 2(1+\sigma^E)/\{\eta_1^2 - [1-(\sigma^E)^2]\}$, where σ^E is Poisson's ratio and η_1 is the lowest root of $\eta_1 J_0(\eta_1) - (1-\sigma^E) J_1(\eta_1) = 0$. The longitudinal coupling factor, k_{33}, was estimated from the piezoelectric planar and thickness coupling factor [24]:

$$k_{33}^2 = k_p^2 + k_t^2 - k_p^2 k_t^2 \quad (3)$$

In Table 2, the experimental results show that the k_p, k_t, and k_{33} values of pure NKN ceramics are 36, 37, and 50%, which increase to 40, 45, and 57% after the addition of 1 mol% CN, respectively. However, the values of these ceramics are not as high as those of PMZT3 ceramics [22,23]. The value of the mechanical quality factor (Q_m) was determined using [26]:

$$Q_m = \frac{1}{R} \cdot \sqrt{\frac{L}{C_1}} \quad (4)$$

where R, L, and C_1 calculated using Agilent 4294A with the equivalent electrical circuit shown in Fig. 3. As shown in Table 2, the Q_m value of NKN-01CN ceramic is much higher than those of pure NKN and PMZT3 ceramics. The NKN ceramic exhibits the typical feature of 'soft' piezoelectric ceramics, whereas NKN-01CN ceramics 'hard' features. The strong 'hardening' of the electrical properties can be attributed to the acceptor-doping effect of Cu ions. Therefore, Cu-substitution gives NKN 'hard' piezoelectric characteristics. In the case of PZT, the addition of acceptor ions, such as Mg^{2+}, Sc^{3+} and Fe^{3+}, increases the density of oxygen vacancies, which enhances Q_m. Cu^{2+} is considered to be a substitute for Nb^{5+} and behaves as an acceptor [27]. On the other hand, the Cu^{2+} and Nb^{5+} ions from CN dopant may increase the B-site ions. With decreasing A/B ratio, the numbers of oxygen vacancies change which might reduce the resonance impedance. Therefore, both the addition of Cu ions and the excess B-site ions increase Q_m value. The low A/B ratio and the excess composition of the B-site ions (A/B < 1) effectively improve mechanical quality factor (Q_m), electromechanical coupling factor (k_p), and the sinterability [28]. Moreover, the Q_m value of all NKN ceramics with CN doping is higher than that of pure NKN ceramics.

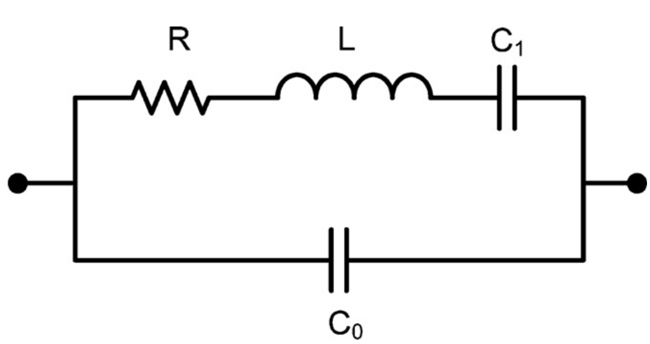

Fig. 3. Equivalent electrical circuit of a piezoelectric vibrator.

Because therapeutic transducers are generally driven near the fundamental thickness mode resonant frequency, low resonant resistance draws considerable current and results in transducer temperature fluctuations. Therapeutic transducers tend to run hot, so the resonant frequency and clamped capacitance temperature stabilities should be carefully considered because the temperature stability properties have a great influence on the design of electrical impedance matching. In piezoceramics-based resonant devices such as transducers, resonators, and oscillators, the change rate of the electromechanical coupling factor, the temperature coefficient of resonant frequency (TCF), and the temperature coefficient of clamped capacitance (TCC) parameters are so important that they are usually used as a key index to evaluate the quality of these devices. To obtain TCF and TCC values, samples were placed in a temperature-controlled furnace to measure the variations from 0 °C (T_1) to 80 °C (T_2). The TCF and TCC values were calculated using [29,30]:

$$\mathrm{TCF} = \frac{f_{rT_2} - f_{rT_1}}{f_{rT_1} \times (T_2 - T_1)} \times 100\% \quad (5)$$

$$\mathrm{TCC} = \frac{C_{T_2} - C_{T_1}}{C_{T_1} \times (T_2 - T_1)} \times 100\% \quad (6)$$

Fig. 4(a) shows the temperature dependence on the change rates of the electromechanical coupling factor (k_t) of pure NKN and NKN-01CN therapeutic transducers. The change rate of this characteristic of NKN-01CN ceramic is positive and lower than that of NKN ceramics. Fig. 4(b) shows the temperature dependence of the change rates of resonant frequency of the two therapeutic transducers. As the temperature increased from 0 to 80 °C, the change rates of resonant frequency of both the NKN and NKN-01CN transducers increased with increasing temperature. The values for the NKN-01CN transducer were lower than those for the NKN transducer. When the temperature was 80 °C, the change rates of resonant frequency were calculated as −0.89% for the NKN-01CN transducer and −2.77% for the NKN transducer. Fig. 4(c) shows the temperature dependence of the change rate of clamped capacitance of these two therapeutic transducers. Again, the NKN-01CN transducer had superior performance. Specifically, it can be seen that the change rate of clamped capacitance of the NKN-01CN transducer is always lower than that for the NKN transducer. When the temperature reached 80 °C, the change rate of the NKN-01CN transducer was 10.8%, whereas that of the NKN transducer was 39.7%. The TCF and TCC values of NKN-01CN and NKN transducers are shown in Table 2. The values of the NKN-01CN transducer are lower than those of NKN and PMZT3 transducers.

To achieve the maximum acoustic power transmission, it is necessary to know the elastic stiffness coefficient (C_{33}^D) and the lon-

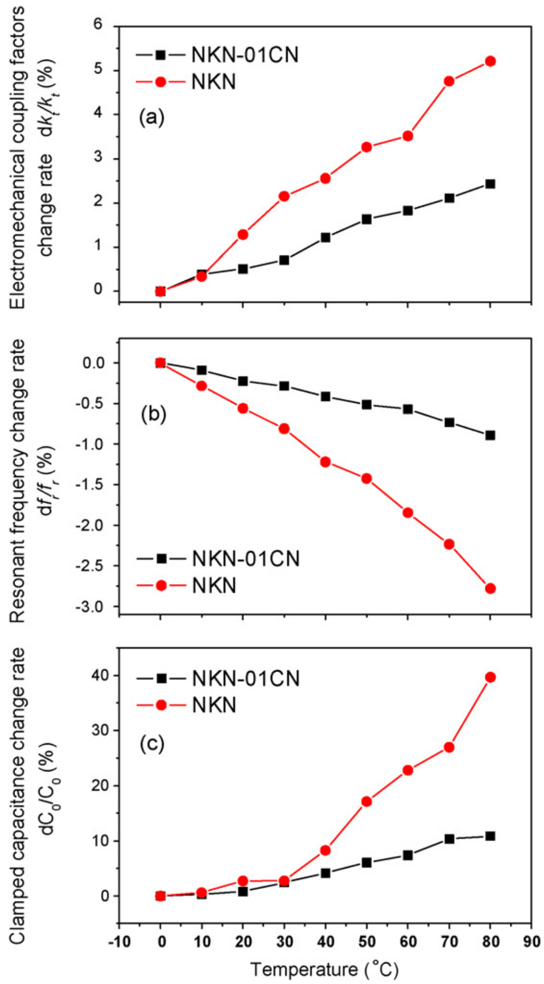

Fig. 4. Change rates of transducer (a) thickness mode electromechanical coefficient k_t, (b) resonant frequency, and (c) clamped capacitance versus temperature.

gitudinal phase velocity (v_t) to calculate the acoustic impedance (Z_{ac}) of the piezoelectric disc to estimate the ratio of transmission energy to incident energy of the ultrasonic therapeutic transducer. Here, only the one-dimensional wave equation, i.e., the thickness direction, is considered. Thus, the above parameters can be obtained according to the following equations [24]:

$$C_{33}^D = 4\rho(tf_a)^2 \quad (7)$$

$$v_t = \sqrt{\frac{C_{33}^D}{\rho}} \quad (8)$$

$$Z_{ac} = \rho \times v_t \quad (9)$$

$$N_t = f_r \times t \quad (10)$$

where ρ is the bulk density of the piezoelectric disc, t is the thickness of piezoelectric disk, f_a is the antiresonance frequency, f_r is resonance frequency, C_{33}^D is the elastic stiffness coefficient, v_t is the longitudinal wave velocity, Z_{ac} is the acoustic impedance, and N_t is the thickness frequency constant. The values of C_{33}^D, v_t, Z_{ac}, and N_t of NKN-01CN and NKN transducers are shown in Table 3. For NKN-01CN transducers, the C_{33}^D, v_t, Z_{ac}, and N_t values are higher than those of NKN transducers. The CN content changes the characterization of the composition of NKN from 'soft' to 'hard', leading to elastic stiffness coefficient, bulk density, wave velocity, and resonance frequency increases [31].

The plots of impedance and phase for both the NKN disk and the NKN-01CN disk are shown in Fig. 5. The resonance frequen-

Table 3
Elastic stiffness coefficient (C_{33}^D), longitudinal wave velocity (v_t), acoustic impedance (Z_{ac}), and thickness frequency constant (N_t) of NKN-01CN and NKN ceramics.

	C_{33}^D ($\times10^{10}$ N/m^2)	v_t (m/s)	Z_{ac} ($\times10^6$ kg/m^2 s)	N_t (kHz mm)
NKN-01CN	19.64	6622	29.6	3069
NKN	15.58	6180	25.2	2884

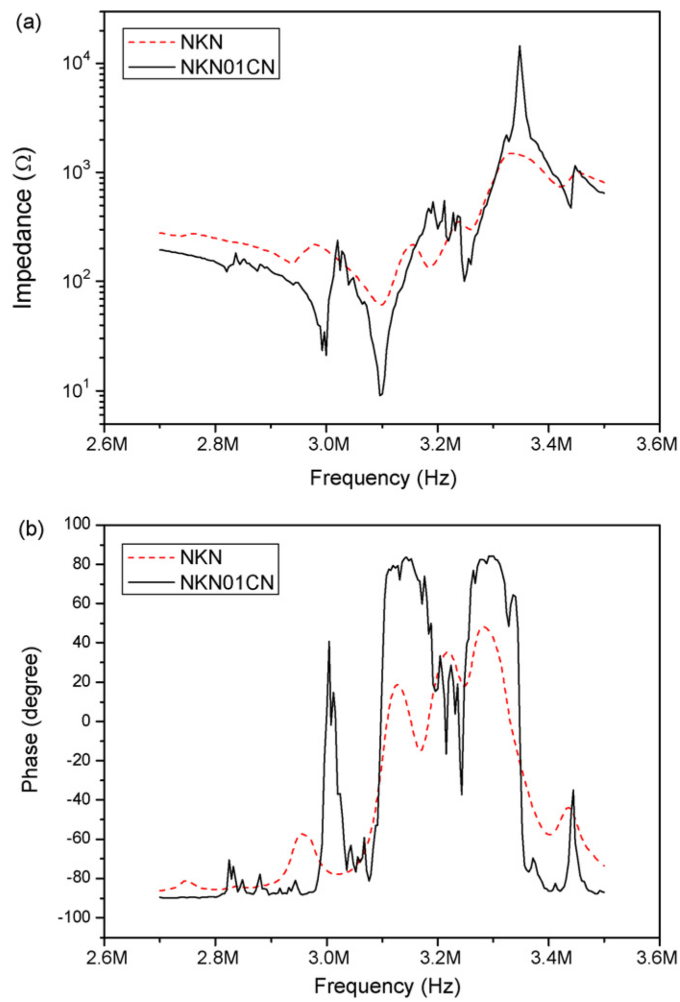

Fig. 5. Plots of (a) the impedance and (b) phase angle of the NKN-01CN and NKN piezoelectric disks versus frequency.

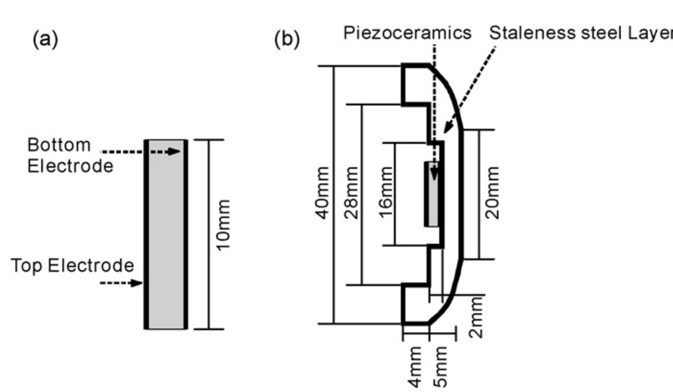

Fig. 6. (a) NKN-01CN disk. (b) Architecture of the implemented ultrasonic therapeutic transducer.

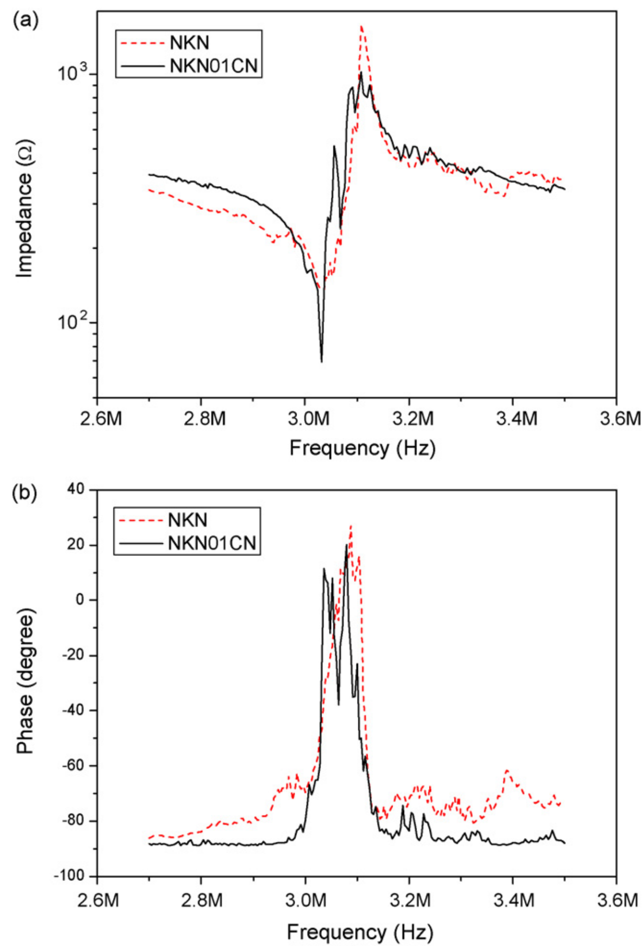

Fig. 7. Plots of (a) the impedance and (b) phase angle of the NKN-01CN and NKN piezoelectric transducers versus frequency.

cies of the NKN disk and the NKN-01CN disk are both 3.096 MHz; the resonance resistance of the NKN disk (61.5 Ω) is higher than that of the NKN-01CN disk (9 Ω). The NKN and NKN-01CN piezoelectric disks were pasted to an aluminum metal plate. A typical ultrasonic therapeutic transducer design uses a piezoceramic disc plated with thin layers of silver as electrical contacts. Then, using a suitable adhesive, the piezoceramic disc is glued to an aluminum metal plate, which functions as an acoustic-impedance matching layer for the front side of the transducer. Air is used as a backing layer. The overall design is intended to maximize the transducer acoustic transmittance to the load (water or skin), generally over a limited frequency range and is electrically driven at a specific power level. The NKN-01CN disks were assembled into

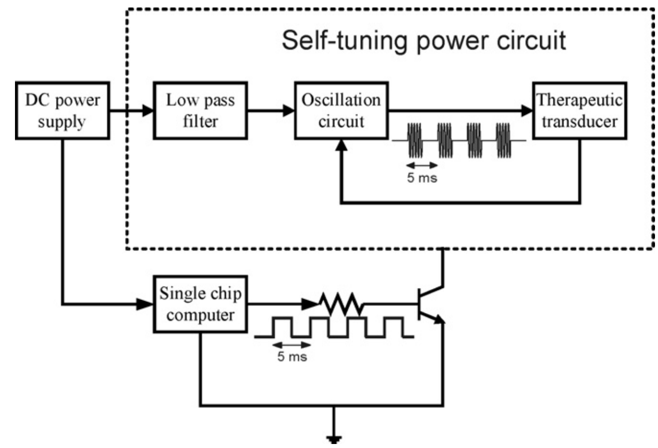

Fig. 8. Block diagram of self-tuning power circuit on ultrasonic therapeutic transducers.

3 MHz ultrasonic therapeutic transducers according to the design in Fig. 6. The diameter of NKN-01CN disk was about 10 mm and the thickness was 0.99 mm. Epoxy was used to glue the disks to the aluminum layer. The architecture is shown in Fig. 6(b). Fig. 7 shows the plots of impedance and phase for both the NKN transducer and the NKN-01CN transducer. A comparison of properties of the two types of transducer is shown in Table 4. The results show that the effective coupling factor of the NKN transducer (0.052) is superior to that of the NKN-01CN transducer (0.048), but the resonance resistance of the NKN transducer (134 Ω) is much greater than that of the NKN-01CN transducer (69.4 Ω). In other words, the ultrasonic wave entering the NKN piezoceramics causes more energy that entering NKN-01CN piezoceramics and the energy decay of the ultrasonic wave due to the greater damping factor (i.e. greater resonance resistance), which leads to decrease acoustic power.

As shown in Fig. 8, the setup of ultrasonic therapeutic transducer includes a self-exciting oscillation circuit, a DC power supply, a single chip computer, and a therapeutic transducer. To

Table 4
Properties of the therapeutic transducers fabricated using the developed NKN-01CN ceramic as compared to those of NKN therapeutic transducer.

	f_r (MHz)	f_r' (MHz)	R (Ω)	R' (Ω)	k^2
NKN-01CN	3.096	3.032	9	69.4	0.048
NKN	3.096	3.036	61.5	134	0.052

f_r and R are the resonance frequencies and resistance of the two types of disk, respectively.
f'_r and R' are the resonance frequencies and resistance of these two types of transducer, respectively.
k^2 is the effective coupling factor.

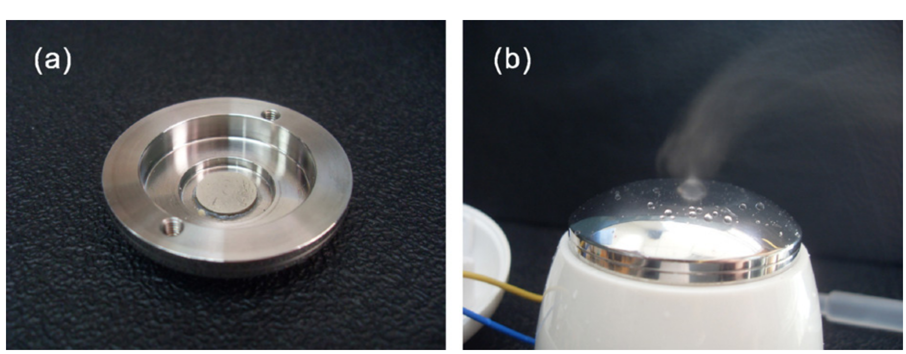

Fig. 9. Photograph of (a) NKN-01CN ultrasonic therapeutic transducers and (b) transducers being driven by self-exciting oscillation circuit.

avoid overheating, the therapeutic transducer is driven by a self-exciting oscillation circuit that produces a 3 MHz sinusoidal and modulated pulse train with a frequency of 20 Hz such that the therapeutic transducer is operated in the on–off condition under self-tuning circuit driving. The 3 MHz ultrasonic therapeutic transducer was fabricated with an NKN-01CN ceramic, as shown in Fig. 9(a). As shown in Fig. 9(b), the mist above the NKN-01CN transducer is steam. The voltage output of the DC voltage supply is 40 V, which is higher than that of commercial transducers (24 V). Thus, the resonance resistance of the transducer needs to be lowered. The development of lead-free compositions that meet the transducer requirements will be continued in future works.

4. Conclusions

In this paper, CN was added to NKN ceramics to decrease the sintering temperature and to improve the density and piezoelectric characteristics. The $K_4CuNb_8O_{23}$ formed during sintering and a secondary phase of $K_4CuNb_8O_{23}$ was found in the XRD pattern of NKN-01CN ceramics. When a small amount of CN was added, the density of the samples had a high value of about 4.47 g/cm^3. NKN-01CN ceramics sintered at 1075 °C for 3 h show excellent properties of k_p = 40%, k_t = 45%, k_{33} = 57%, and Q_m = 1642. The NKN-01CN ceramics, with very low TCF and TCC values (−0.011%/°C and 0.135%/°C), show a great temperature stability, making them promising lead-free ceramics for electromechanical transducers. The values of C_{33}^D (19.64×10^{10} N/m^2), v_t (6622 m/s), Z_{ac} (29.6×10^6 kg/m^{2}s), and N_t (3069 kHz mm) of the NKN-01CN ceramic exhibited a 'hard' characterization. An ultrasonic therapeutic transducer fabricated using the lead-free NKN-01CN ceramics could be driven in thickness mode.

Acknowledgements

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