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Doping effects of Nb additives on the piezoelectric and dielectric properties of PZT ceramics and its application on SAW device

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Abstract

The PZT-based ceramics with a composition of $Pb_{1-0.5x}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO_3$; $x = 0.02$–0.06 were prepared by conventional mixed-oxide method, with sintering temperature at 1250 °C for 2 h. Microstructural and compositional analyses of the PZT-based ceramics have been carried out using XRD and SEM. The dielectric constant measured at 1 kHz is about 1500 and the loss factor is small than 2%. The maximum planar electromechanical coupling coefficient, k_p, is 0.591. It showed that the Nb additives were helpful improve both of the dielectric and piezoelectric properties. Surface acoustic wave (SAW) filters were fabricated and the property, phase velocity, were measured.

Keywords: PZT; Dielectric properties; Piezoelectricity; Surface acoustic wave (SAW)

1. Introduction

Piezoelectric lead zirconate titanate (PZT) has the perovskite structure (general formula, $A^{II}B^{IV}O_3$) with the A-site (Pb^{2+}) occupying the cubo-octahedral interstices described by the BO_6-site octahedral. Many aliovalent compositional alterations to PZT have been studied either with higher valence substitutions (donors), either with lower valence ions (acceptors) [1–6]. La^{3+} is a common substitution on Pb^{2+} site, leading to the well-known high-performance PLZT materials. Therefore, some of the critical properties of PZT were optimized by the addition of donor dopant ions. Nb^{5+} can be considered as a donor dopant for PZT materials, since it substitutes Zr^{4+}/Ti^{4+} ions. Using donor dopant such as Nb^{5+} on the B-site is one of mechanisms thought to promote domain wall motion in PZTs [7,8]. Modified PZT compositions find many applications in piezoelectric sensors [9], actuators [10,11] and electromechanical transducers [12,13]. High values of piezoelectric coefficient d_{33} (>300 pC/N) and electromechanical coupling coefficient k_p (>0.5) in poled PZT ceramics are believed to arise from the motion of domain walls under the action of applied field or stress.

Since 1970s, the applications of piezoelectric ceramics for SAW devices have been investigated [14–20]. The modified lead zirconate titanate piezoelectric ceramics have potential for SAW device applications due to the ability to modify the composition to achieve a desirable combination of properties, such as high-surface phase velocity and high-electromechanical coupling coefficient. However, the use of piezoelectric ceramics in SAW devices has been limited by the high-propagation loss at high-frequency compared to single crystal materials.

Pereira et al. [21] reported that the Nb oxide is a good sintering aid for PZT (65/35)-based materials (high density, small grain size) and the solubility limit of Nb in PZT materials (perovskite structure) is about 7%. Above this concentration, a secondary phase is formed, containing also Pb and Ti. In this paper, we prepare $Pb_{1-0.5x}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO_3$ ($x = 0.02$–0.06) system with additional dopants of Nb to investigate the piezoelectric and dielectric properties. Then, we fabricate the SAW device using the Nb-doped PZT material as the substrate, and measure the surface acoustic wave responses.

2. Experimental

2.1. Sample preparation

A conventional ceramics preparation procedure was used to prepare the sample. Raw materials were mixed by pure

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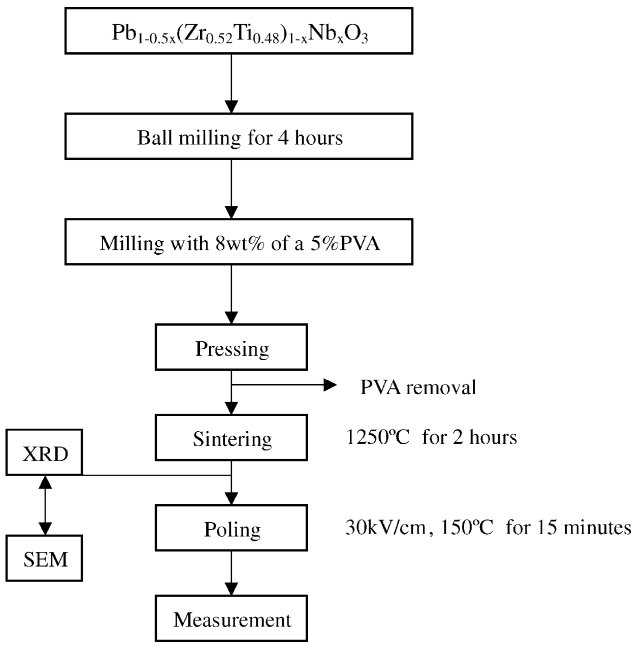

Fig. 1. Flow diagram of the sample preparation procedure.

reagent PbO, ZrO_2, TiO_2 and Nb_2O_5 powders (>99.0% purity). After 4 h ball milling with ZrO_2 balls, the materials $Pb_{1-0.5x}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO_3$; $x = 0.02$–0.06 were calcined at 900 °C for 3 h. About 2 wt.% excess PbO was added to counteract the volatilization of PbO during firing, then followed by pulverization. After that, the powders were dried and milled with 8 wt.% of a 5% PVA solution. Then, the powders were pressed into plates with dimensions; 20 mm × 20 mm × 1 mm, for SAW measurements, and discs of 12 mm diameter and 1 mm thickness, for bulk measurements, using a pressure of 25 kg/cm^2. Specimens were sintered isothermally at a heating rate of 10 °C/min at 1250 °C for 2 h. A PbO rich atmosphere was maintained with PZT powder to minimize the lead loss during sintering. The flow diagram of the sample preparation procedure is shown in Fig. 1.

2.2. Measurements

The bulk densities of sintered bodies were measured by the Archimedes method. The compositional analyses for the sintered bodies were determined using an X-ray diffraction (XRD) and microstructures were observed using a scanning electron microscope (SEM). The mean grain size was obtained from the observation of the SEM by the line intercept method. In order to measure the electrical properties, silver paste was coated to form electrodes on both sides of the sample with thickness of 0.8 mm, then subsequently fired at 750 °C for 30 min. The dielectric (measured at 1 kHz) and piezoelectric properties were measured using an impedance analyzer (HP4294A) after poling under 30 kV/cm bias at 150 °C in a silicone oil bath for 15 min. Piezoelectric properties were calculated from the resonance measurement method [22]. The piezoelectric d_{33} coefficient was measured with a Berlincourt d_{33}-meter.

Table 1
Interdigital transducer (IDT) parameters of the SAW device

Electrode finger pairs	15.5
Electrode width (μm)	20
Wavelength (μm)	80
Electrode overlap (μm)	4
Delay-line distance (mm)	1.6

In order to measure the SAW properties, the plates were polished to a mirror finish on one side with surface roughness below 0.1 μm. Then, aluminum electrode patterns, 0.3 μm thick in the form of interdigital transducers (IDTs), were applied onto the polished surface using the lift-off photolithographic process. The IDT pattern parameters are shown in Table 1. The IDT pattern of 20 μm width leads to a wavelength of 80 μm. The frequency response of SAW device was measured by using a network analyzer (HP8714ES). The experimental phase velocity was obtained from the equation $V_p = f_0\lambda$, where f_0 is center frequency and λ is the wavelength.

3. Results and discussion

Fig. 2 shows the bulk density as a function of the amount of Nb dopants. The density increases at first with the increasing Nb substitutions; it reaches the maximum value as $x = 0.055$, and then dropped. In other words, doping Nb^{5+} is helpful increase the density of PZT ceramics as the concentrate of Nb dopant is smaller than 5.5 mol%. The X-ray diffraction patterns of $Pb_{1-0.5x}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO_3$ ceramics are shown in Fig. 3. The X-ray analyses indicate that the Nb-doped PZT ceramics have mainly a set of peaks with major peak at (1 0 1), and all of them belong to tetragonal phase of perovskite-type structure. It is confirmed that a change in the adding conditions does not change the phase relations of the sintered bodies. In addition, it is worthy to note that, from 2 to 6 mol% Nb, all spectra show no evidence of pyrochlore phase.

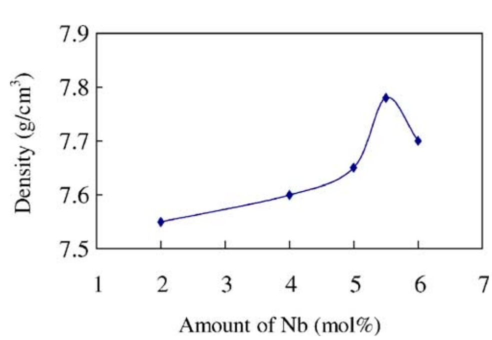

Fig. 2. Dependence of the bulk density of $Pb_{1-0.5x}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO_3$ ceramics on the amount of Nb additives.

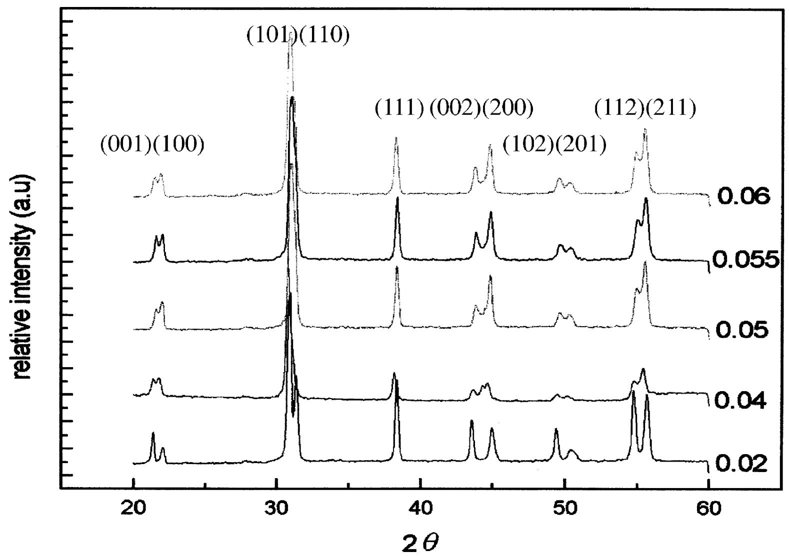

Fig. 3. The XRD patterns of $Pb_{1-0.5x}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO_3$ samples.

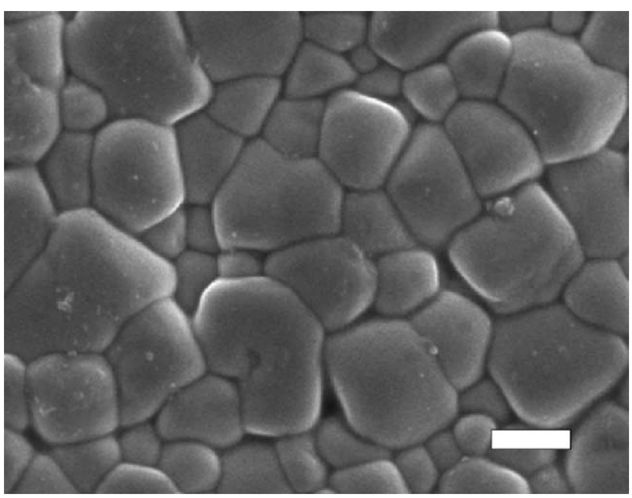

Fig. 4. The SEM photographs of $Pb_{0.9725}(Zr_{0.52}Ti_{0.48})_{0.945}Nb_{0.055}O_3$ (bar = 1 μm).

The SEM pattern of the $Pb_{0.9725}(Zr_{0.52}Ti_{0.48})_{0.945}Nb_{0.055}O_3$ sample is shown in Fig. 4, and it shows that the microstructure of our sample is very dense. Fig. 5 shows the grain size as a function of the amount of Nb. It shows

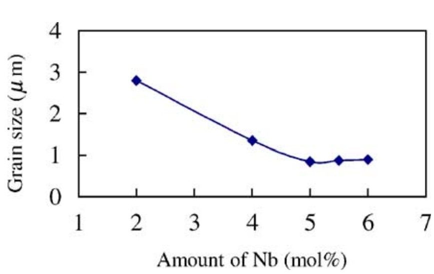

Fig. 5. Dependence of the grain size of $Pb_{1-0.5x}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO_3$ ceramics on the amount of Nb additives.

that a decrease in grain size as the Nb additives increasing (<5 mol%), and then changes little about 0.9 μm. Atkin et al. [23] reported that sintering kinetics of the undoped PZT ceramics can be described by lattice diffusion of vacancies from pores to grain boundaries (Coble's model), and the Nb doping reduces the diffusion coefficient: the vacancies as created by this doping are supposed to be bound to the impurity (Nb), so that they inhibit the mass transport. Considering the grain growth, doping with Nb keeps the grain size small, i.e. Nb is an effective grain growth inhibitor. Rahaman [24] reported that pores, second phase inclusions, or solid solution impurities inhibited the grain growth. So that, the doping ions (Nb) can concentrate near the grain boundaries and reduce their mobility. In addition, a reduced grain size, i.e. remaining reactive, these powders based on Nb-doped PZT are more effective in accelerating sintering.

The results of the thickness (k_t) and planar (k_p) coupling factors as a function of Nb dopants are shown in Fig. 6. As Nb additives increase, k_t value increases at first and reaches its maximum value of 0.51 as Nb = 5.5 mol%. It is worthy that k_t values for $x = 0.05$ and 0.055 compositions are larger than 0.5. The k_p values of all Nb-doped samples are larger than 0.5; the maximum value, $k_p = 0.591$, occurs as Nb = 5.5 mol%, which is higher than the previously reported data for PZT-based systems in Table 2. According to the results of Fig. 6, it shows that the increasing Nb dopant is helpful to improve the electromechanical coupling factors of both modes as Nb < 5.5 mol%. Fig. 7 shows frequency constant versus the amount of Nb additives. The thickness frequency constant (N_t) and planar frequency constant (N_p) of the studied samples changed little as Nb dopants increasing and their values are about 2000 and 2100 Hz m, respectively. The piezoelectric coefficient d_{33} as a function of the amount of Nb additives is shown in Fig. 8. It shows that

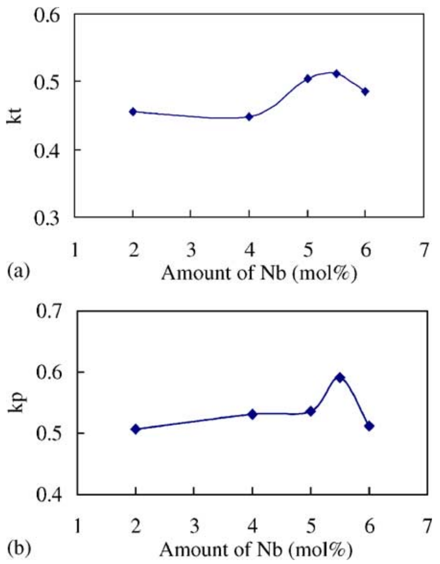

Fig. 6. Dependence of (a) k_t and (b) k_p of $Pb_{1-0.5x}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO_3$ ceramics on the amount of Nb additives.

d_{33} increases with the increase of the amount of Nb dopants till Nb = 0.055. The values of all samples are larger than 330 pC/N, and the maximum value, 386 pC/N, occurs as Nb = 5.5 mol%.

Fig. 9a and b shows the dielectric constant and loss factor of samples versus the amount of Nb, respectively. It shows that dielectric constant increases with the increasing Nb dopant and the maximum value 1529 occurs as $x = 0.055$, then dropped. The loss factors change little as Nb dopant increasing, and loss factors are about 2% of all components. Fig. 10 shows the dielectric constant as a function of temperature measured at 1 kHz for $x = 0.055$. The Curie–Weiss behavior in the curves is well observed. It shows that the Curie point (T_c) of sample is about 443 °C.

Fig. 11 shows the frequency response of the SAW device as Nb = 0.055 with impedance matching. The center fre-

Table 2
The study of k_p and ε_r in different PZT-based system

Compositions	k_p	ε_r	Reference
Pure PZT (52/48)	0.47	707	[3]
PZT:Sr	0.44	973	[3]
PZT:Sr	0.52	1300	[1]
PZT:Ca	0.49	729	[3]
PZT:Y	0.34	841	[4]
PZT:La	0.53	1483	[4]
PZT:Nd	0.49	1395	[4]
PZT:(Nd+Sr)	0.49	1776	[4]
PZT:Nb	0.54	1242	[4]
PZT:(La+Nb)	0.57	1377	[4]
PZT:Ta	0.5	1230	[4]
PZT:Fe	0.59	820	[5]
PZT:Al	0.2	1078	[6]
PZT:Mg	0.381	983	[6]
PZT:Zr	0.446	1396	[6]
$Pb_{0.9725}(Zr_{0.52}Ti_{0.48})_{0.945}Nb_{0.055}O_3$	0.591	1529	Our sample

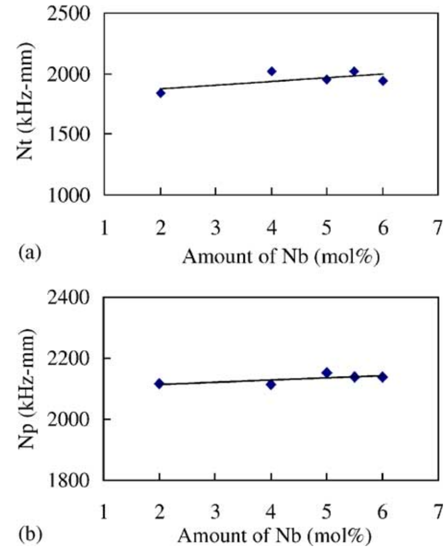

Fig. 7. Dependence of frequency constant (a) N_t and (b) N_p of $Pb_{1-0.5x}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO_3$ ceramics on the amount of Nb additives.

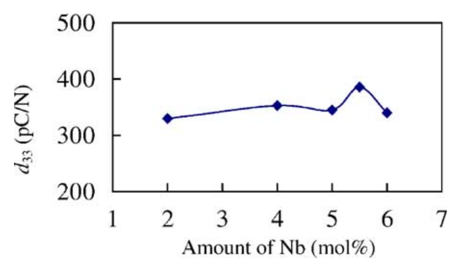

Fig. 8. Dependence of piezoelectric coefficient d_{33} of $Pb_{1-0.5x}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO_3$ ceramics on the amount of Nb additives.

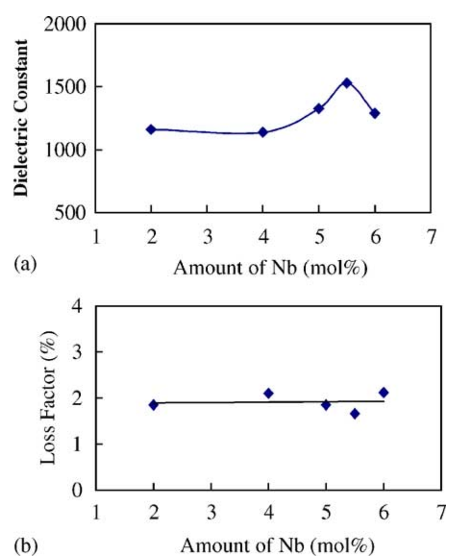

Fig. 9. Dependence of (a) dielectric constant and (b) loss factor of $Pb_{1-0.5x}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO_3$ ceramics on the amount of Nb additives.

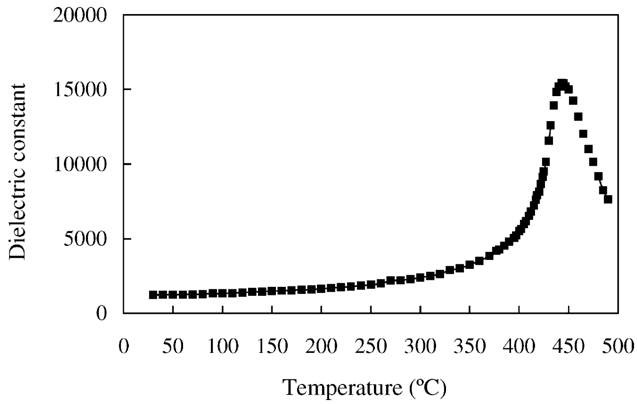

Fig. 10. Dielectric constant of $Pb_{1-0.5x}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO_3$ ceramics as a function of temperature at 1 kHz for $x = 0.02$, 0.04 and 0.06. Inset shows effect of Nb dopants on the Curie point.

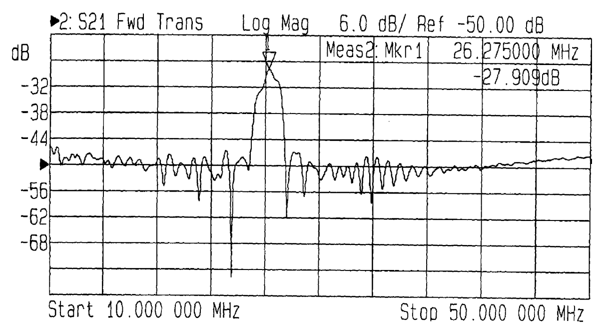

Fig. 11. Frequency response of the SAW device for $x = 0.055$ with impedance matching.

quency is 26.275 MHz and it leads to a phase velocity of 2102 m/s; the insertion loss is about 27.9 dB.

4. Conclusions

Nb oxide not only is a good aid for PZT-based ceramics (high density, small grain size), but also effectively improves the dielectric and piezoelectric properties of the PZT ceramics. According to the experimental results, Nb dopant is helpful increasing the dielectric constant, planar electromechanical coupling coefficient and thickness electromechanical coupling coefficient of PZT ceramics.

The density and electromechanical coupling coefficient reach the maximum value as $x = 0.055$, and loss factor keeps smaller than 0.02. For Nb = 5.5 mol% doped sample gave the following data: $\rho = 7.8\,g/cm^3$, $\varepsilon_r = 1529$, loss factor = 0.016, $k_t = 0.51$, $k_p = 0.591$, $T_c = 443\,°C$ and $V_p = 2102\,m/s$. The Nb-doped modified lead zirconate titanate ceramics have high-electromechanical coupling coefficients that make them suitable for piezoelectric transformers, actuators, transducers, and broad-band SAW devices applications.

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Te-Yi Chen was born in Tainan on January 1, 1977. He is a candidate for PhD in electrical engineering at National Cheng Kung University (Taiwan) since September 2001. He is a lecturer in the Nan Jeon Institute of Technology (Taiwan) teaching microelectronics and microsensors courses. His research interests include microstructural, piezoelectric and dielectric properties of modified lead titanate ceramics, surface acoustic wave (SAW) properties of lead-based ceramic substrates, and properties of SAW sensing for gas detection and chemical analysis.