Fabricating Piezoelectric Tape of PZT-SKN

O. Hemadhulin1, J. Kongphimai2, W. Photankham3, P. Srinuanlue4 and H. Wattanasarn5*

1 Faculty of Science and Technology, Sakon Nakhon Rajabhat University, Sakon Nakhon 47000, Thailand
2 Piezoelectric Research Laboratory, Center of Excellence on Alternative Energy, Research and Development Institution, Sakon Nakhon Rajabhat University, Sakon Nakhon 47000, Thailand

*Corresponding author. Email: w_wattanasarn@hotmail.com

Abstract. Tape ceramics are widely used in the sensor and electronic industries. In this work, we studied the ferroelectric properties of the 0.975Pb(Zr0.52Ti0.48)O3-0.025Sr(K0.25Nb0.75)O3 tape ceramic; (PZT-SKN). We fabricated the PZT-SKN using doctor blade technique with the slurry, obtained from the calcined of PZT-SKN mixing with organic solution. The crystalline structure was investigated by using X-ray diffraction, relative density, and Vickers Hardness technique. We also determined the dielectric properties and polarization electric field loops. The results of crystalline structure show that the percentage of perovskite is 97.57%, the relative density is 98.4%, and Vickers Hardness is 107 MPa. At the thickness 0.89 mm, the dielectric constant temperature is 1499 at 532 °C, the remnant polarization is 17 μC cm⁻², Currie temperature is 552 °C, and piezoelectric coefficient is 235 pC N⁻¹. The PZT-SKN tape ceramic has the ferroelectric properties better than tablet ceramic.

Keywords: PZT-SKN; Piezoelectric tape; Tape ceramic; Fabricated; Ferroelectric

1. Introduction

Piezoelectric devices on lead zirconate titanate ceramic (PZT) base are widely used in the medical, sensor and electronic industries for exceptional piezoelectric properties. The PZT is the most widely for transducer and actuator due to its flexibility in doping materials and property design, and low cost [1,2]. The ceramic plate forming process can be assembled into electronic devices. There are many ways to use in the screen printing, calendaring and tape casting. Tape casting is another interesting which first introduced in the 1940s [2–4]. In tape casting, the slurry is spread over a surface using the doctor-blade process. The doctor-blade process can be controlled a thickness film from 1 μm up to 3000 μm [4–10]. In addition, the ceramic materials are favor application in the electrical equipment. The Sr⁺², K⁺¹, and Nb⁵⁺ doped PZT (PZT-SKN) has been studied for multilayer actuators and transducers [11]. The ratio of Zr/Ti in the PZT-SKN ceramics with formula 0.98PZT-0.02SKN has been studied in morphotropic phase transition. Rhombohedral and tetragonal crystal structure show coexist at 300 °C in the Zr/Ti range of 55/45 to 52/48 [12]. In addition, the PZT-SKN ceramics show high piezoelectric coefficient and permittivity values with a high Curie temperature, which is good thermal stability.

In this work, 0.975Pb(Zr0.52Ti0.48)O3-0.025Sr(K0.25Nb0.75)O3; (PZT-SKN) was fabricated using tape casting technique with doctor blade contorted tape ceramic thickness. The crystal structure was studied by X-ray diffraction technique (XRD). The physical properties were determined by relative density and Vickers Hardness technique. Ferroelectric properties were investigated by dielectric properties, polarization electric field loop, and the piezoelectric coefficient (d₃₃).
2. Materials and Methods

The PZT-SKN powder was prepared by solid state route. Reagent grade of powder lead oxide (PbO, 99.00%) titanium dioxide (TiO₂, 99.00%) strontium carbonate oxide (SrCO₃, 99.00%) potassium carbonate (K₂CO₃, 99.00%) and niobium oxide (Nb₂O₅, 99.00%) were used as the precursor materials. A stoichiometric amount of powders was mixed by a ball for 24 h with zirconia ball using deionized water as media. The mixture was dried at 100 °C overnight in an oven. The mixture was placed in a crucible, which was subsequently inserted into the furnace in the calcine burnt at a temperature of 850 °C for 4h.

Typical PZT-SKN slurry was made as per the composition given in Table 1. The preparation of slurry for tape casting was carried out in two stages. In the first phase, mixture of methyl ethyl ketone (MEK), ethanol and phosphate ester were ball milled for 24 h in polyethylene jar using ZrO2 balls as grinding media. and in the second stage binding system consisted of binder (polyvinyl butyral, PVB) and plasticizers (polyethylene glycol, PEG). In both the cases, they were ball milled for 6 h in polyethylene jar using ZrO2 balls as grinding media. After mixing by ball milling, wire mesh filter slurry, then vacuum the pump out with a vacuum pump (Ax–2000 Vacuum Mixer). Then the slurry was cast in a laboratory tape caster with the stationary reservoir. A casting speed of 1.20 mms/s was maintained in all cases and left for drying. Square dimensional sample (2×2 cm²) were cut from the green tapes. Then bake at a temperature of 100–200 °C for 1 h., leave to room temperature. Then burn binder with a temperature of 350–750 °C. leave it for 2 hours and leave to room temperature. The final sintering using the sintering temperature of 1100 °C, the temperature dropped to room temperature for 2 h. and then leave. After examining the dielectric properties of 1–100 kHz and temperature range 30–600 °C, examination of Ferroelectric Properties by study of hysteresis loop, the polling at room temperature for 10 min using a voltage of 2.5 kV mm⁻¹ and measurement of piezoelectric coefficient.

![Figure 1. The experimental schematic.](image-url)
Table 1 Composition of the PZT-SKN tape casting slurry.

| Ingredient                        | Function   | Weight (%) |
|----------------------------------|------------|------------|
| Powder                           | Ceramic    | 65         |
| Phosphate Ester                  | Dispersant | 1          |
| Methyl Ethyl Ketone + Ethanol    | Solvent    | 26         |
| Polyvinyl Butyral                | Binder     | 4          |
| Polyethylene Glycol              | Plasticizer| 3          |

3. Results and Discussion

The XRD patterns of the (1–x)PZT-xSKN sintered at 1100 °C are illustrated in Figure 2. Our result revealed that the Zr/Ti ratio is 52/48 in a tetragonal structure with lattice parameters a = b = 4.036 Å, c = 4.146 Å. The crystalline structure of the tape PZT ceramic had a tendency to change from tetragonal to rhombohedral structure [4–7] when added SKN. It is noticeable that the (002) and (200) peaks split into two peaks [4]. Therefore, it is confirmed that the crystal structure of the PZT tape ceramic has changed by SKN. The density with value of 6.0353 g cm⁻³ combined with the theoretical density with value of 6.13 g cm⁻³ yielded the relative density value of 98.4 %. The measured Vickers hardness is 107 MPa.

![Figure 2](image_url)  
**Figure 2.** The illustrated of XRD pattern of tape PZT-SKN ceramic.

The Figure 3 shows dielectric constant and dielectric loss of the tape PZT-SKN ceramic at temperature range 30–600°C and frequency range 1–100kHz, respectively. The results showed that the dielectric constant maximum ε_r is 1499 at 532 °C and 1 kHz. Similarly, dielectric losses became reduced at 32 °C and 1 kHz with tanδ value of 0.154. It is contributed to high dielectric properties. The temperature at which this spike occurs is the Curie point, T_c. Above this temperature, the permittivity decreases according to the Curie-Weiss Law the inverse of permittivity versus temperature should provide a linear relationship past the Curie point if the Curie-Weiss Law is followed. The slope of this line will equal the inverse of the Curie constant and the y-intercept will equal T_c, the Curie temperature, divided by the Curie constant. An example plot, fitting, and calculated values are shown in Figure...
From checking the polarization of the PZT-SKN showed the characteristics of piezoelectric the soft type is a characteristic of a hard piezoelectric. Because the squareness loop, indicating that it uses more energy [20–25]. Figure 5 the results measured the polarization and hysteresis loop of the tape PZT-SKN ceramic at thickness 0.89 mm, the coercive field at 3 kV mm⁻¹ and 4 kV mm⁻¹. It was found that the 3 kV mm⁻¹ coercive field had \( P_r \approx 17 \mu \text{C cm}^{-2} \) and \( E_c \approx 20 \text{ kV cm}^{-1} \), the coercive field is 4 kV mm⁻¹ with \( P_r \approx 20 \mu \text{C cm}^{-2} \) and \( E_c \approx 25 \text{ kV cm}^{-1} \). This shows that when there is an increase in coercive field passed on to the polarization hysteresis loops of tape PZT-SKN ceramics is increased. When the tape PZT-SKN ceramic electrodes to induce an electric field under a voltage 2.5 kV mm⁻¹ and a temperature of 150 °C at 15–30 minutes. When the workpiece through the inductor electrodes to measure the piezoelectric coefficient found that piezoelectric coefficient is 235 pC mm⁻².
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Figure 5. Room temperature P–E hysteresis loops of the tape PZT-SKN ceramic.

4. Conclusion

The tape PZT-SKN ceramic were synthesized by tape casting method sintering at 1100 °C at 2 h. The XRD patterns of the PZT-SKN show the trend of crystal structure change from tetragonal to the rhombohedral. It is noticeable that the plane (002) and (200) [1, 5]. The measurement density and Vickers hardness, density 6.0353 g cm$^{-3}$, theoretical density was 6.13 g cm$^{-3}$, it has a relative density of 98.4% and a Vickers hardness of 107 N mm$^{-2}$. The dielectric constant and dielectric loss, $\varepsilon_r = 1499$ of temperature 532 °C at a frequency of 1 kHz, $\tan\delta = 0.154$ at 32 °C with a frequency of 1 kHz. The P–E hysteresis loops at 4 kV mm$^{-1}$ with $P_r \approx 20 \mu$C cm$^{-2}$ and $E_c \approx 25$ kV cm$^{-1}$ and piezoelectric coefficient 235 pC mm$^{-2}$. The study properties of ceramic tape PZT-SKN found that such material is applied to a capacitor in a small electronic circuit.

Reference

[1] Cross L E and Newnham R E. Hight-Technology Ceramics: Past, Present, and Future – The Nature of Innovation and Change in Ceramic Technology. (1986) 289–305
[2] Howatt G N, Breckenridge R G, Brownlow J M, Fabrication of thin ceramic sheets for capactions. Journal of the American Ceramic Society, 30 (1947) 237–142
[3] Hotza D, Greil P, Review: aqueous tape casting of ceramic powders. Mater. Sci Eng. A 202 (1995) 206–217
[4] Fuli Zhu, Jinhao Qiu, et al, Comparative investigations on dielectric properties and humidity resistance of PZT–SKN and PZT–SNN ceramics. Journal of Materials Science: Materials in Electronics, 26(5), 2897–2904 (2015).
[5] G Helke, S Seifert, and S.J. Cho, Phenomenological and Structural Properties of Piezoelectric Ceramics Based on X Pb)(Zr, Ti)(0.5−x)(Sr, K)0.25, Nb0.75O3 (Solid Solutions. Journal of the European Ceramic Society, 19, 1265–1268) 1999.
[6] Niall J. Donnelly, Thomas R. Shrou, and Clive A. Randall, Addition of a Sr, K, Nb)SKN (Combination to PZT) 53/47 (for High Strain Applications. Journal of the American Ceramic Society, 90(2). 490–495 2007.
[7] Wenli Zhang, and Eitel E. Richard, Low-temprature sintering and properties of 0.98PZT-0.02SKN ceramics with LiBiO2 and CuO addition. Journal of the American Ceramic Society, 94(10), 3386–3390 (2011).
[8] Jukkrit Kongphimai, Wattana Photankham, et al, Effect of Sb2O3 Doping Pb)Zr0.5Ti0.47(O3 Ceramics. *Journal of Materials Science and Applied Energy*, **6**(3), 226–229 (2017).

[9] Wattanasarn H, Kongphimai J, et al, Dielectric and ferroelectric properties of Pb)Fe1/2Nb1/2(O3 modification on Pb)Zr0.52Ti0.48(O3 ceramics. *Integrated Ferroelectrics*, **187**(1), 89–99 (2018).

[10] Photankham W, Kongpimai J, et al, Effect of PFN addition on microstructure and piezoelectric properties of PZT58/42 ceramics. *Integrated Ferroelectrics*, **187**(1), 80–88 (2018).

[11] Wattanasarn H, Kongpimai J, et al, Effect of ZnO addition on ferroelectric properties of 0.94PbFe1/2 Nb1/2(O3−0.06PbTiO3 and 0.9Pb)Fe1/2 Nb1/2(O3−0.1PbTiO3 ceramics. *Integrated Ferroelectrics*, **187**(1), 33–44 (2018).

[12] Wenli Zhang and Richard E. Eitel, Sintering Behavior, Properties, and Applications of Co–Fired Piezoelectric/Low Temperature Co–Fired Ceramic (PZT–SKN/LTCC) Multilayer Ceramics. *Journal of Applied Ceramic Technology*, **10**(2), 354–364 (2013).

[13] Xiaolian Chao, Lili Yang, et al, Fabrication, temperature stability and characteristics of Pb(Zr,Ti)O3−Pb(Zn1/2 Nb2/3)O3−Pb(Ni1/2 Nb2/3)O3 piezoelectric ceramics bimorph. *Ceramics International*, **38**, 3377–3382 (2012).

[14] Hong Lian, Rui Nie, et al, Effect of MnO2 doping on piezoelectric, dielectric and ferroelectric properties of PNN–PZT ceramics. *Ceramics International*, **41**, 11359–11364 (2015).

[15] Divya A S, Juairiya P, et al, Influence of A–site Sr2+ substitution on structure, dielectric and ferroelectric characteristics of 0.66[Pb(In0.5 Nb0.5)O3]−0.34[PbTiO3]. *Ceramics International*, **43**, 825–829 (2017).

[16] Alexander V. Petrov, Jan Macutkevic, Synthesis and dielectric properties of ferroelectric–ferromagnetic PZT–SFMO composites. *Modern Electronic Materials*, 26–31 (2017).

[17] Shara Sowmya N, Srinivas A, Studies on magnetoelectric coupling in lead-free [(0.5) BCT−(0.5) BZT]−NiFe2O4 laminated composites at low and EMR frequencies. *Journal of Alloys and Compounds*, **743**, 240–248 (2018).

[18] Chandrakala E, Paul Praveen J, et al, Effect of sintering temperature on structural, dielectric, piezoelectric and ferroelectric properties of sol–gel derived BZT–BCT ceramics. *Ceramics International*, **42**, 4964–4977 (2016).

[19] Divya AS and Kumar V, Influence of Fe3+ substitution on the dielectric and ferroelectric characteristics of Lead Indium Niobate. *Journal of Alloys and Compounds*, **637**, 426–430 (2015).

[20] Corredores a Y, Le Febvrier A, et a, Study of ferroelectric/dielectric multilayers for tunable stub resonator applications at microwaves. *Thin Solid Films*, **553**, 109–113 (2014).

[21] Parveen Kumar, Juneja J K, et al, Effect of Sm on dielectric, ferroelectric and piezoelectric properties of BPTNZ system. *Physica B*, **426**, 112–117 (2013).

[22] Aditya Jain, Anmrish K. Panwar, et al, Improvement in dielectric, ferroelectric and ferromagnetic characteristics of Ba0.6Sr0.1Zr0.1Ti0.8O5−NiFe2O4 composites. *Ceramics International*, **43**, 10253–10262 (2017).

[23] Zhenzhen Song, Yongcheng Zhang, et al, Fabrication and ferroelectric/dielectric properties of La–doped PMN–PT ceramics with high optical transmittance. *Ceramics International*, **43**, 3720–3725 (2017).

[24] Siripong Somwan a, Athipong Ngujamjarojana, et a, Dielectric, ferroelectric and induced strain behavior of PLZT 9/65/35 ceramics modified by Bi2O3 and CuO co–doping. *Ceramics International*, **42**, 10690–10696 (2016).
[25] Abhinay S, Mazumder R, Seal A, Sen A. Tape casting and electrical characterization of 0.5Ba\textsubscript{0.2}Zr\textsubscript{0.8}Ti\textsubscript{0.5}Ba\textsubscript{0.7}Ca\textsubscript{0.3}(TiO\textsubscript{3})BZT–0.5BCT (piezoelectric substrate. *Journal of the European Ceramic Society*, **36**, 3125–3137) 2016.