Influence of ZnO Dopant on Piezoelectric Properties of Potassium Sodium Niobate Thin Films

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ABSTRACT

Lead zirconia titanate (PZT) is widely used due to its ferroelectric and piezoelectric properties. However, toxic lead in PZT is extensively linked to the greenhouse effect. For this constraint, extensive research is being done to find new piezoelectric materials such as potassium sodium niobate ($K_{0.5}Na_{0.5}NbO_3$ or KNN). Due to processing difficulties, KNN has been disregarded for a long time. Volatilization of alkaline elements causes compositional inhomogeneity and lowers piezoelectric activity of ceramics. This research examines how ZnO-doping affects the structural and electrical changes and characteristics of potassium sodium niobate (KNN) ceramics. Potassium Sodium Niobate (KNN) thin films were grown on ITO substrate by using sol-gel spin coating method. The as-deposited thin films were heated 250 ℃ pyrolysis for 5 min and then was annealed at the temperature 650 ℃. Following this, KNN thin films were characterized using X-Ray Diffraction (XRD) and Field Emission Scanning Electron Microscope (FESEM). The electrical properties of KNN thin films were analysed using Atomic Force Microscopy (AFM) and Piezoresponse Force Microscopy (PFM). Based on the findings, it can be inferred that a doping concentration of 0.9 mol ZnO is considered the most appropriate for the production of a homogeneous and cohesive KNN thin film. This film demonstrates favourable electrical properties, making it well-suited for implementation in piezoelectric applications.

1. Introduction

The creation of innovative forms of piezoelectric materials for use in filters, resonators, actuators, sensors, and other devices has drawn substantial attention from all around the world. The utilisation of lead zirconia titanate (PZT) has been extensive owing to its exceptional ferroelectric and piezoelectric characteristics. Nevertheless, it is widely acknowledged that PZT is associated with the greenhouse effect as a result of the inclusion of hazardous lead [1,2]. It is true that despite its

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remarkable electrical properties, PZT has a number of significant drawbacks such as contains over 60 % lead [3]. According to the Comprehensive Environmental Response, Compensation, and Liability Act of 1980, lead is one of the most toxic substances that may cause harm to the nervous system and spermatozoid development.

Extensive research is being done with an emphasis on the search for different piezoelectric materials in order to overcome this limitation. In this regard, potassium sodium niobate ($K_{0.5}Na_{0.5}NbO_3$ or KNN) has been regarded as a potential ceramic material for the development of novel lead-free piezoelectric devices. The material demonstrates a notable Curie temperature of 420 °C, a substantial dielectric constant of approximately ~700, a significant remanent polarisation of 14 $\mu C/cm^2$, a low coercive field of around 140 kV/cm, and a strong piezoelectric constant of approximately 300 pC/N [4-6]. Nevertheless, the historical significance of KNN, which consists of ABO_3 and possesses a perovskite crystal structure, has been largely overlooked throughout time due to the challenges associated with its processing. The occurrence of significant volatilization of alkaline elements contributes to the presence of compositional inhomogeneity, ultimately leading to a ceramic material that exhibits less piezoelectric activity.

Extensive study has been conducted to investigate the increase of the piezoelectric and structural properties of KNN through the production of its bulk ceramics structure. Bulk piezoelectric ceramics are commonly characterised by their greater thickness compared to film structures, hence imposing constraints on their applicability in embedded sensors and micro-sized devices. In this particular scenario, the process of affixing bulk ceramics to specific components of micro-electromechanical systems (MEMS) via a bonding agent is both labour-intensive and financially burdensome. While some researchers have dedicated significant attention to mitigating the impact of volatility on piezoelectric characteristics, there has been limited exploration of enhancing these properties through the incorporation of novel materials into potassium sodium niobate (KNN).

KNN-based compounds are anticipated to exhibit exceptional electrical properties, namely in terms of piezoelectricity, by the incorporation of ZnO into KNN thin films. Hence, the findings of this study may provide valuable guidance to researchers in selecting suitable ZnO materials that can effectively disperse within the KNN matrix. Furthermore, this work will present the theoretical relationship between ZnO donors and the augmentation of KNN piezoelectric characteristics. This paper presents an investigation into the influence of ZnO-doping on the structural and electrical changes observed in ceramics based on potassium sodium niobate (KNN), as well as the resultant properties of these materials. The examination of different concentrations of Zn^{2+} has unveiled a novel approach to the development of materials that are devoid of lead.

2. Methodology

Thin films based on KNN solutions were synthesised utilising a spin coating method. Both potassium and sodium acetate (both from Alfa Aesar, purities of 99 %) were employed as alkaline precursors in the first solution. According to the computed stoichiometry, the initial mol% of precursors is 50 mol%. The precursors solution was spiked with several amounts of ZnO (mol% = 0, 0.1, 0.3, 0.6, and 0.9). With steady stirring at ambient temperature, a solution was dissolved in polar organic solvent 2-methyoxyethanol (Sigma Aldrich, 99.9 %). The solution of KNN precursors was added dropwise to the niobium ethoxide and acetyalcetone mixture, which was then stirred vigorously for 1 hour at room temperature. The solution was then stirred at 80 °C for an hour. Once the mixed resolution was complete, the thin films were spun onto a ITO substrate at 3000 rpm for 60 seconds. The ITO substrate is 2 cm × 1 cm on each side. The wet films were then dried at 250 °C for 1 minute to complete the pyrolysis process. The coating procedures were repeated five times in order

to create a dense and uniform structure for the five-layer films. The films are then annealed for 5 minutes at a rate of 5 °C/s at 650 °C.

X-ray diffraction (XRD) utilising a PANalytical X'Pert Pro at a grazing angle of 0.1° was used to analyse the phase evolution of KNN and ZnO-doped KNN films. Field emission scanning electron microscopy (FESEM) at 15 kV was used to look at the grain morphology and cross section of the generated thin film. Then Atomic Force Microscope NX10 was used to evaluate the films' average surface roughness and to measure the piezoelectric coefficient by the Piezoresponse Force Microscopy.

3. Results and discussions
3.1 Phase Formation of KNN Thin Films

X-ray diffraction (XRD) patterns for a KNN thin film produced on an ITO substrate and annealed at 650 °C are shown in Figure 1. KNN thin films are polycrystalline in nature, as evidenced by the presence of prominent peaks with a single KNN phase at planes (111), (001), (202), (420), (150), and (313) in all films starting at 20° < 2θ < 70° with the obvious preferred orientation at (001). The results were found to be in accordance with KNN orthorhombic structures. There is a stronger attractive force between the ions in the [001] direction than in any of the other orientations. Also, compared to these other orientations, the distance between ions in the [001] direction is less. Therefore, in a KNN structure, the polarisation formed along the [001] because the coulomb force between the ions in this direction is regarded to be stronger than the force between the ions in the other directions [7,8]. Furthermore, minor peaks related to the presence of a secondary phase can be attributed to the modest shifts in the stoichiometric ratio caused by the presence of highly volatile alkaline elements [9,10]. Nevertheless, the peak intensities of the aforementioned thin films exhibited a decline when subjected to dopant concentrations below 0.6 mol. The diminished peak intensities result in the degradation of the crystalline structure of the films [11]. This activity may be correlated with additive inclusion following the KNN-phase development. The diffraction peaks also slightly shifted with increased ZnO content in the samples. Previous study concluded that the addition of Zn^{2+} cations to the perovskite structure was responsible for the observed structural change [9].
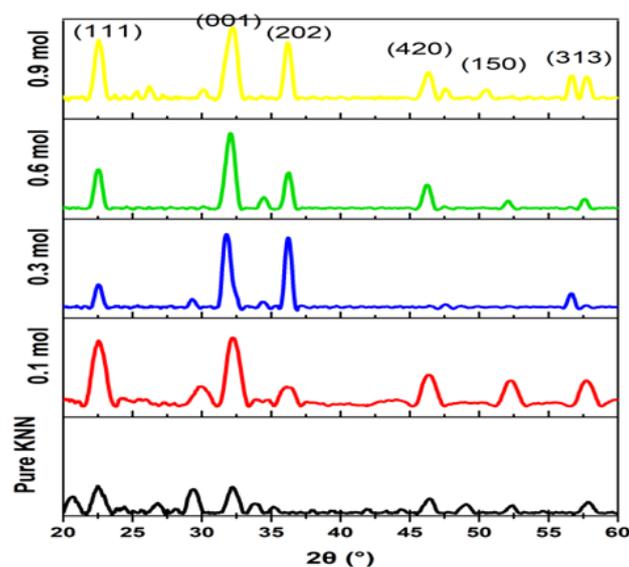

Fig. 1. XRD patterns for ZnO doped KNN thin films

3.2 Surface Morphology of KNN Thin Films

Surface morphology of KNN thin films is shown in Figure 2. Pure KNN in Figure 2 (a) appears to have evaporated an alkaline element, as evidenced by its inhomogeneous shape and open boundary. This suggests that the ITO substrate was exposed as the open grain boundary was developed [10]. Figure 2(b) displays the modified ZnO-KNN thin films, which were composed of extremely small particle clusters at X = 0.1 and 0.3 mol. The fine particles were most likely from the pyrochlore phase, which has a poor crystallinity [10-13].However, after being doped with 0.6 mol of ZnO, the newly produced grains appeared to be denser and more homogenous. At a ZnO = 0.9 % mol concentration, the microstructure became more compact, and the dense boundary was found and further validated by XRD data (Figure 1), indicating that only a single perovskite phase existed in the films. These structural changes are indicative of an easy incorporation of Zn^{2+} into the crystal lattice. Specifically, prior research has indicated that dopant inclusion of ZnO enhances fine-grained, high-density films, likely due to reduced alkaline volatility [9].
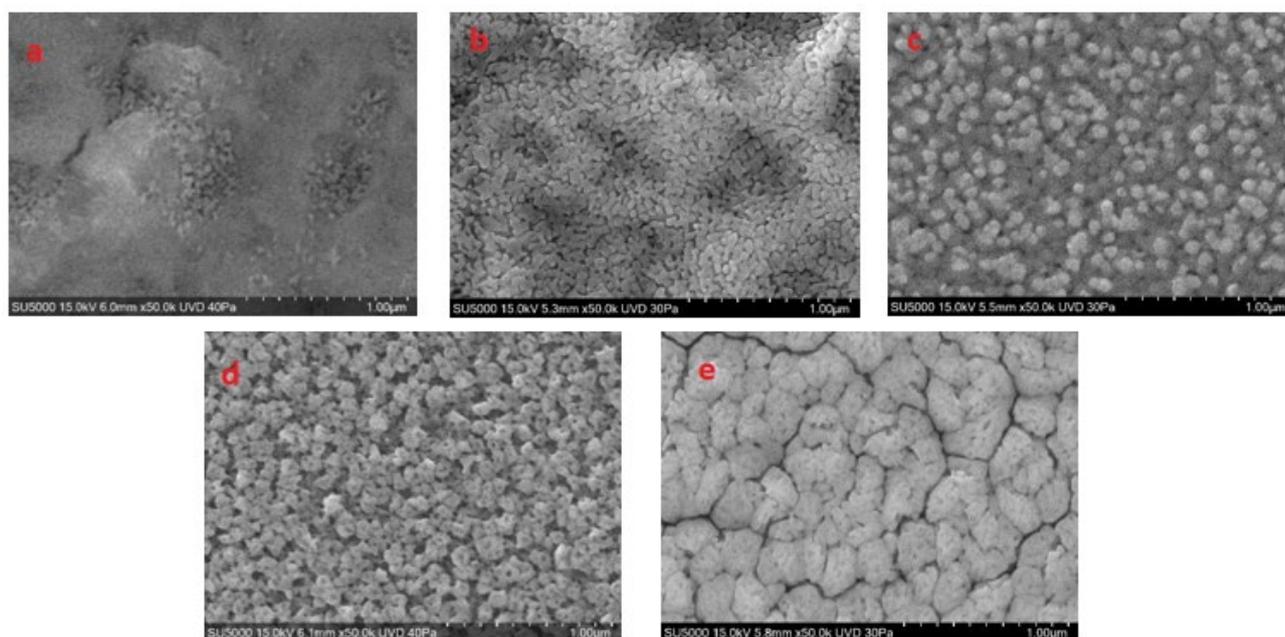
Fig. 2. Morphology structure of KNN thin films doped with ZnO, (a)x = 0 (b) x = 0.1 (c) x = 0.3 (d) x = 0.6 (e) x = 0.9

3.3 Surface Roughness and Topography of Pure and Doped KNN Thin Films

Table 1 depicts the root-means square and average surface roughness of pure KNN and KNN doped with ZnO. In accordance with the graph, the surface roughness of ZnO-doped KNN is higher than that of pure KNN due to the inhomogeneous and porous particle boundaries. The growth properties of thin films have a direct impact on their morphology, microstructure, and surface roughness. The surface roughness of thin films will vary depending on the grain growth of the films. The utilisation of AFM line-scan profiles has been documented in the literature to validate the observed rise in surface roughness and average grain size [14–16]. Data from the AFM post-processing data, including the sample's root mean square (Rq) and average surface roughness (Ra), lend credence to this claim. Figure 3 shows the AFM surface micrograph of KNN thin films doped with

ZnO. It is clear that the surface topography of films varies greatly depending on the amount of ZnO present. Therefore, the surface roughness is significantly affected by the ZnO content.

Table 1
Root-means square and average surface roughness of KNN thin film with different concentration of ZnO

ZnO concentration (mol)	Root means square, Rq (µm)	Average surface roughness, Ra (µm)
0	0.38	0.269
0.1	0.131	0.087
0.3	0.03	0.017
0.6	0.141	0.105
0.9	0.543	0.415

Based on the data, at x = 0.1 mol and x = 0.3 mol has smoother grainy surface compared to pure KNN (0.269 µm). KNN thin films were measured to have an average surface roughness of 0.087 µm and 0.017 µm. Based on this finding, it's reasonable to assume that ZnO doping can reduce the roughness of KNN thin films. However, at a concentration of 0.9 % ZnO, the average roughness of the surface grew to 0.415 µm. The FESEM result demonstrated aberrant grain development, which is thought to be the primary source of the elevated surface roughness of KNN films at high concentrations. This study's surface roughness pattern was consistent with that reported by Deng *et al.,* (2015), who found that doping the film in the outset made it smoother than the pure film. Author also found that as the concentration of dopants was raised, the surface roughness rose [17].
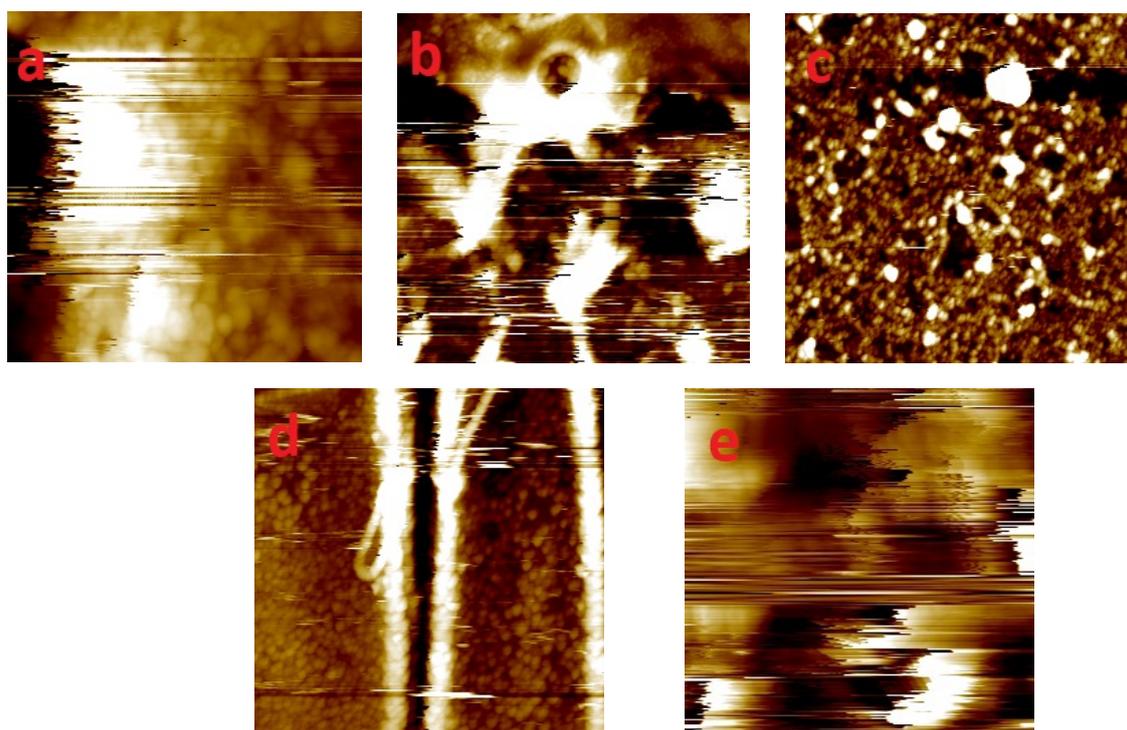
Fig. 3. AFM surface topography of KNN thin films doped with ZnO when (a) x= 0 (b) x= 0.1 (c) x= 0.3 (d) x= 0.6 (d) x= 0.9

The piezoresponse of the sample was studied using imaging of the domain with a scan size area of (10 × 10) µm². The combination of DC and AC voltage that was placed between the tip and the sample allowed for topography analysis as well as piezoresponse analysis to be carried out [18–20]. Out-of-plane PFM measurement was utilised in order to investigate the surface topography and

piezoresponse of the ZnO doped KNN thin film on ITO substrates. According to the findings of a previous study [21-23], it has been noted that various ZnO grains exhibit distinct piezoelectric properties, which may have negative implications for its utilization in device applications. The nature of the sample preparation and the growth method are both connected with the piezoelectric coefficients in KNN films. It is presumable that the substrate will act as a boundary for the deformation that occurs in a piezoelectric KNN when an electric field is applied. The d_{33} values that were estimated for pure and ZnO-doped KNN thin films are presented in Figure 4. It has been discovered that an increase in the concentration of ZnO leads to a decrease in the piezoelectric coefficient. Since the Zn^{2+} is integrated into the A-site due to defects generated by the volatility of the alkaline metal component, the d_{33} decreases with increasing ZnO content for the sample with x ≤ 0.3 mol, as shown in Figure 4. However, the piezoelectric coefficient increased when the ZnO content went from 0.6 mol to 0.9 mol, as expected given the denser and more compact grain boundary at the higher ZnO level. In the meantime, due to the tiny cluster particles of grains, the piezoelectric coefficient drops when ZnO content is less than 0.3 mol. The highest piezoelectric coefficient obtained is at ZnO content 0.9 mol which has the preferred orientation of (001) than those are randomly oriented.
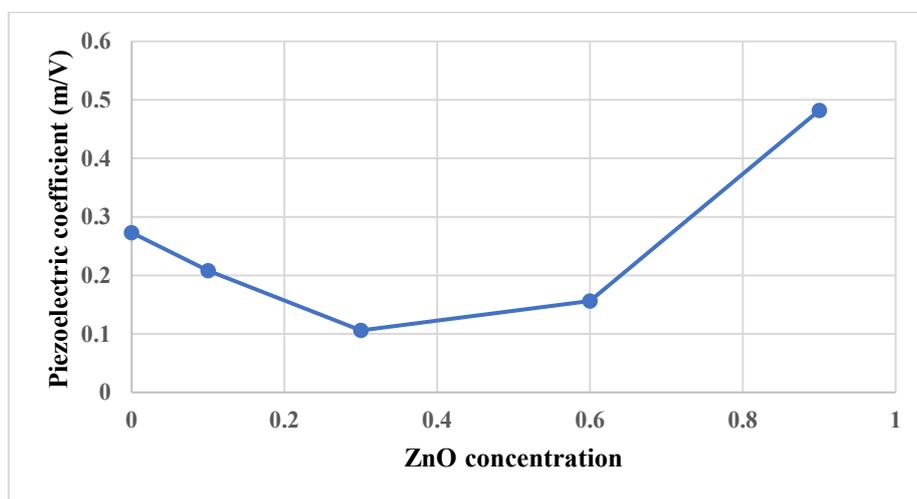

Fig. 4. Piezoelectric coefficient with varied ZnO content of KNN thin films

4. Conclusion

Pure KNN and ZnO-doped KNN were fabricated using the spin-coating technique with varying ZnO concentrations (0.1 mol, 0.3 mol, 0.6 mol, and 0.9 mol) in this study. Either mild doping level or heavy doping level will influence the physical and electrical properties of KNN thin films. According to the obtained results, both pure and doped KNN films exhibited prominent KNN phase peaks. After KNN doping at a concentration of ZnO ≥ 0.6 mol, the morphology of the thin film reveals that the granules are homogeneous and dense. Meanwhile, at a concentration of 0.9 % ZnO, the surface's average roughness increased to 0.415 μm. The results obtained from the FESEM analysis revealed abnormal grain growth, which is believed to be the main cause of the increased surface roughness observed in KNN films with high concentrations. This effect results in an augmentation of the piezoelectric characteristics shown by thin films. In summary, it can be concluded that a doping concentration of 0.9 mol ZnO is deemed as the most suitable for the fabrication of a compact and uniform KNN thin film, exhibiting optimal electrical characteristics for applications in the field of piezoelectricity.

Acknowledgement

References

[1] Matsubara, M., Yamaguchi, T., Kikuta, K. and Hirano., S.I. "Sinterability and Piezoelectric Properties of (K,Na)NbO$_3$ Ceramics with Novel Sintering Aid." *Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers* 43, no. 10 (2004): 7159–7163. https://doi.org/10.1143/JJAP.43.7159

[2] Rani, Rashmi, and Seema Sharma. "Influence of Sintering Temperature on Densification, Structure and Microstructure of Li and Sb Co-Modified (K,Na)NbO$_3$-Based Ceramics." *Materials Sciences and Applications* 02, no. 10 (2011): 1416–1420. https://doi.org/10.4236/msa.2011.210191

[3] Hong, Chang-hyo, Hwang-pill Kim, Byung-yul Choi, Hyoung-su Han, Jae Sung, Chang Won, and Wook Jo. "Lead-Free Piezoceramics e Where to Move On ?" *J Materiomics* 2, no. 1 (2016): 1–24. https://doi.org/10.1016/j.jmat.2015.12.002

[4] Ringgaard, E. and Wurlitzer, T. "Lead-Free Piezoceramics Based on Alkali Niobates." *Journal of the European Ceramic Society* 25, no. 12 SPEC. ISS. (2005): 2701–2706. https://doi.org/10.1016/j.jeurceramsoc.2005.03.126

[5] Mgbemere, H.E., Jellito, H. and Schneider, G.A.. "Investigation of the Fracture Toughness and Electrical Properties of (K, Na, Li) (Nb, Ta, Sb)O3 Ceramics." *Ceramics International* 42, no. 15 (2016): 17711–17716. https://doi.org/10.1016/j.ceramint.2016.08.093

[6] Matsubara, M., Yamaguchi, T., Kikuta, K. and Hirano, S.I.. "Effect of Li Substitution on the Piezoelectric Properties of Potassium Sodium Niobate Ceramics." *Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers* 44, no. 8 (2005): 6136–6142. https://doi.org/10.1143/JJAP.44.6136

[7] Hemra Hamrayev, and Kamyar Shameli. 2023. "Synthesis and Characterization of Ionically Cross-Linked Chitosan Nanoparticles". *Journal of Research in Nanoscience and Nanotechnology* 7 (1):7-13. https://doi.org/10.37934/jrnn.7.1.713.

[8] Wang, Zhong Lin, Xiang Yang Kong, Yong Ding, Puxian Gao, William L. Hughes, Rusen Yang, and Yue Zhang. "Semiconducting and Piezoelectric Oxide Nanostructures Induced by Polar Surfaces." *Advanced Functional Materials* 14, no. 10 (2004): 943–956. https://doi.org/10.1002/adfm.200400180

[9] Le, Anh Thi, Mohsen Ahmadipour, and Swee Yong Pung. "A Review on ZnO-Based Piezoelectric Nanogenerators: Synthesis, Characterization Techniques, Performance Enhancement and Applications." *Journal of Alloys and Compounds* 844 (2020): 156172 https://doi.org/10.1016/j.jallcom.2020.156172

[10] Ramajo, Leandro Alfredo, Jonathan Taub, and Miriam Susana Castro. "Effect of ZnO Addition on the Structure, Microstructure and Dielectric and Piezoelectric Properties of K$_{0.5}$Na$_{0.5}$NbO$_3$ Ceramics." *Materials Research* 17, no. 3 (2014): 728–733 https://doi.org/10.1590/S1516-14392014005000048

[11] Hatta, Maziati Akmal Mohd, Mohd Warikh Abd Rashid, Umar Al-Amani Haji Azlan, Nurul Azuwa Azmi, Mohd Asyadi Azam, and Toshihiro Moriga. "Influence of yttrium dopant on the structure and electrical conductivity of potassium sodium niobate thin films." *Materials Research* 19 (2016): 1417-1422. https://doi.org/10.1590/1980-5373-MR-2016-0076

[12] Yu, Qingjiang, Wuyou Fu, Cuiling Yu, Haibin Yang, Ronghui Wei, Yongming Sui, Shikai Liu, et al. "Structural, Electrical and Optical Properties of Yttrium-Doped ZnO Thin Films Prepared by Sol–Gel Method." *Journal of Physics D: Applied Physics* 40, no. 18 (2007): 5592. https://doi.org/10.1088/0022-3727/40/18/014

[13] Du, Z. H., T. S. Zhang, M. M. Zhu, and J. Ma. "Perovskite crystallization kinetics and dielectric properties of the PMN-PT films prepared by polymer-modified sol-gel processing." *Journal of Materials Research* 24, no. 4 (2009): 1576-1584. https://doi.org/10.1557/jmr.2009.0181

[14] Park, Seung Ho, Cheol Woo Ahn, Sahn Nahm, and Jae Sung Song. "Microstructure and Piezoelectric Properties of ZnO-Added (Na$_{0.5}$K$_{0.5}$)NbO$_3$ Ceramics." *Japanese Journal of Applied Physics, Part 2: Letters* 43, no. 8B (2004): L1072. https://doi.org/10.1143/JJAP.43.L1072

[15] Ding, J. N., Y. B. Liu, C. B. Tan, and N. Y. Yuan. "Investigations into the impact of various substrates and ZnO ultra thin seed layers prepared by atomic layer deposition on growth of ZnO nanowire array." *Nanoscale research letters* 7 (2012): 1-9. https://doi.org/10.1186/1556-276X-7-368

[16] Son, Nguyen Thanh, Jin Seo Noh, and Sungho Park. "Role of ZnO Thin Film in the Vertically Aligned Growth of ZnO Nanorods by Chemical Bath Deposition." *Applied Surface Science* 379 (2016): 440–45. https://doi.org/10.1016/j.apsusc.2016.04.107

[17] Tao, Yinglei, Ming Fu, Ailun Zhao, Dawei He, and Yongsheng Wang. "The Effect of Seed Layer on Morphology of ZnO

Nanorod Arrays Grown by Hydrothermal Method." *Journal of Alloys and Compounds* 489, no. 1 (2010): 99–102. https://doi.org/10.1016/j.jallcom.2009.09.020

[18] Deng, Licheng, Zhiyu Wen, Xingqiang Zhao, Chengwei Yuan, Guoxi Luo, and Jike Mo. "High Voltage Output MEMS Vibration Energy Harvester in D31 Mode with PZT Thin Film." *Journal of Microelectromechanical Systems* 23, no. 4 (2014): 855–61. https://doi.org/10.1109/JMEMS.2013.2296034

[19] Gruverman, A., and Kalinin, S.V. "Piezoresponse Force Microscopy and Recent Advances in Nanoscale Studies of Ferroelectrics." *Journal of Materials Science* 41, no. 1 (2006): 107–16. https://doi.org/10.1007/s10853-005-5946-0

[20] Soergel, Elisabeth. "Piezoresponse Force Microscopy (PFM)." *Journal of Physics D: Applied Physics* 44, no. 46 (2011). https://doi.org/10.1088/0022-3727/44/46/464003

[21] Kalinin, Sergei V, and Dawn A Bonnell. "Imaging Mechanism of Piezoresponse Force Microscopy of Ferroelectric Surfaces." *Physical Review B* 65, no. 12 (March 11, 2002): 125408. https://doi.org/10.1103/PhysRevB.65.125408

[22] Maziati Akmal, MH, Warikh ARM, Azlan UAA, Azam MA, Ismail S. "Effect of Amphoteric dopant on the dielectric and structural properties of yttrium doped potassium sodium Niobate Thin Film." *Materials Letters* 170 (2016): 10-14: https://doi.org/10.1016/j.matlet.2016.01.135

[23] Bdikin, I.K., Gracio, J., Ayouchi, R., Schwarz, R. and Kholkin, A.L. "Local Piezoelectric Properties of ZnO Thin Films Prepared by RF-Plasma-Assisted Pulsed-Laser Deposition Method." *Nanotechnology* 21, no. 23 (2010): 235703. https://doi.org/10.1088/0957-4484/21/23/235703