SYNTHESIS AND CHARACTERIZATION OF Mn-DOPED SODIUM POTASSIUM NIOBATE (KNN) THIN FILM

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ABSTRACT: The objective of this study is to produce and analyse thin films of Mn-doped potassium sodium niobate (KNN) using the sol-gel process. The purpose is to investigate and find a solution for the issue of high leakage current density that occurs at high electric fields in KNN films. The aim is to improve dielectric and ferroelectric properties by introducing manganese (Mn) dopants at different concentrations ranging from 0.0% to 0.9%, while ensuring that insulation resistance remains satisfactory. X-ray diffraction (XRD) research was utilized to look into the Mn-doped KNN thin films crystalline structure. The production of Mn-doped KNN thin films displays an orthorhombic crystal structure, according to the results of the XRD investigation. The occupancy of KNN thin films is demonstrated by XRD peaks, indicating a successful synthesis. The thin films microstructure and surface morphology were investigated by using field-emission scanning electron microscopy (FESEM). The greatest results for dense grain development and consistent grain size were seen in 0.3% Mn-doped KNN thin films. According to the results of the FESEM and AFM, the cracks were densely coated with thin films of consistent thickness, and they were not supported by the surface data of the KNN thin films. AFM and PFM analysis shows that 0.3% of Mn-doped KNN thin films significant increase on the surface morphology and the value of piezoelectric coefficient.

KEYWORDS: *KNN; Manganese; thin film; doped; structural*

1.0 INTRODUCTION

This work aims to examine the influence of manganese (Mn) doping on the properties of potassium sodium niobate (KNN) thin film. Our objective is to investigate the impact of Mn dopants on the structural and electrical characteristics of KNN films. By investigating the alterations in crystal structure, electrical insulation properties, and ability to exhibit ferroelectric behaviour caused by the addition of manganese, we may customise potassium sodium niobate (KNN) thin films for a range of uses, such as sensors, energy harvesting devices, and non-volatile memory components. In addition, we will examine the impact of Mn doping on the resistivity and leakage current density, which are essential for optimising KNN thin films in advanced technology. The work aims to gain useful insights into improving the performance of KNN thin films by carefully incorporating Mn, hence boosting their practical applications.

Manganese (Mn) is one such dopant of great importance. Mn doping can lower the leakage current density of KNN-based piezoelectric ceramics [1]. It has been shown that adding Mn to KNN thin films can affect the films structural and electrical characteristics. Mn dopants can drastically alter the KNN crystal structure, producing material properties that are tailored to the demands of certain applications. Mn doping can alter the films resistivity, dielectric qualities, and other electrical properties all at once.

Atomic and crystallographic changes brought about by Mn doping have an impact on the structural characteristics of KNN thin films. It might lead to variations in the crystal symmetry, modifications to the unit cell, and adjustments to the lattice constants. These structural changes, which are made visible by techniques like X-ray diffraction (XRD), are essential for understanding how the film behaves. Understanding how Mn dopants affect the structure is essential for tailoring KNN thin films to meet the needs of different applications [2]. Both the A and B sites might be replaced by Mn ions doping KNN piezoelectric ceramics, which would further reduce oxygen vacancies and leakage. For the Mn-doped KNN thin films synthesis, variety preparation methods have been applied such as dip coating, spin coating, chemical solution deposition and pulsed laser deposition. Among these techniques, sol-gel spin coating is one of the simple, cost effective, fast, good homogeneity methods suitable for thin film deposition on different concentrations [3].

The addition of Mn dopants modifies the electrical properties of KNN thin films. These alterations could manifest as enhanced piezoelectric responses, altered dielectric constants, or better ferroelectricity. Furthermore, the resistivity of the films may be impacted by Mn doping, which could have an impact on how well the films perform in electromechanical and electrical devices. Mn doping of KNN thin films can greatly enhance their ferroelectric characteristics and lower their leakage current. In the perspective view of FESEM analysis showed that there were significant changes on the microstructure, surface morphology and distributions of dopants inside the thin film with the varying amount of manganese dopant that showed the enhancement performance of piezoelectric properties of KNN thin film.

The study addresses the impact of manganese (Mn) doping on potassium sodium niobate (KNN) thin films. While KNN thin films have garnered attention for their ferroelectric and piezoelectric properties, the specific role of Mn dopants remains an area of interest. The research aims to elucidate the intricate relationship between Mn incorporation and KNN film properties, including nucleation, growth, and perovskite phase transformation activation energies. By comprehensively investigating these effects, the study contributes to our understanding of how Mn modifies both the structural and electrical characteristics of KNN thin films. This deeper insight can guide the development of materials that surpass existing limitations, paving the way for novel applications in electrical and electromechanical devices.

2.0 METHODOLOGY

Figure 1 shows how the sol-gel method is used to fabricate Mn-doped KNN thin films (0.0 %, 0.1%, 0.3%, 0.5%, 0.7%, and 0.9%) on Si substrate. KNN thin film fabrication is a popular use of the sol-gel chemical solution deposition (CSD) technique. Starting solutions consisted of two alkaline precursors: CH_3COOK, potassium acetate, and CH_3COONa, sodium acetate. Different amounts of manganese (mol% = 0.1%, 0.3%, 0.5%, 0.7%, and 0.9%) were added to the precursor solutions to make up for the loss of the alkaline element. At room temperature, these substances were continuously stirred while dissolving in 2-methoxyethanol, a polar organic solvent. Niobium precursor solution was later created by dissolving $Nb_2(OC_2H_5)_{10}$, niobium ethoxide, 2-methoxyethanol, and acetylacetone in combination. Acetylacetone strengthens the solution's stability against water attack by acting as a chelating agent. The produced KNN precursors were subsequently combined with the niobium solution. After 1 h, the resulting solutions were maintained at 80°C. The Si substrate was cut with an incision of 1 cm by 1 cm. Following that, the substrate spent 20 min submerged in acetone in an ultrasonic bath. Then, the substrates were washed with deionized water. After soaking the substrates in ethanol for 20 min, they were rinsed with deionized water. Nitrogen gas was furthermore utilized to clean the substrate one more time in order to eliminate a small quantity of impurities. The Mn-doped KNN sol solution was applied to the Si substrate by using a spin coater, and it was spun for 60 s at 3,000 rpm. After spin coating, the substrate was treated at 250°C for 1 min of heat transfer in the hot plate. The spin coating process was repeated five more times to produce the multi-layered thin film The annealing process should next be started by setting the furnace's temperature to 650°C for 5 min. The five samples were made by depositing and growing crystals after adding 0.1%, 0.3%, 0.5%, 0.7%, and 0.9% of Mn, respectively.

The originality of this part is the production technique of Mn-doped KNN thin films utilising the sol-gel method. The primary procedure entails the amalgamation of alkaline precursors (CH_3COOK and CH_3COONa) with manganese (Mn) to generate KNN precursors. Subsequently, these preliminary substances are combined with a solution containing niobium. The solution obtained is then deposited onto a silicon (Si) substrate using a spin coater, and subsequently subjected to heat treatment. The multi-layered thin film effect is obtained by iteratively applying the spin coating process. In addition, subjecting the thin films to the annealing process at a temperature of 650°C for a duration of 5 minutes enhances their crystallinity. The range of Mn concentrations (0.0%, 0.1%, 0.3%, 0.5%, 0.7%, and 0.9%) enables the examination of its influence on the characteristics of the film.

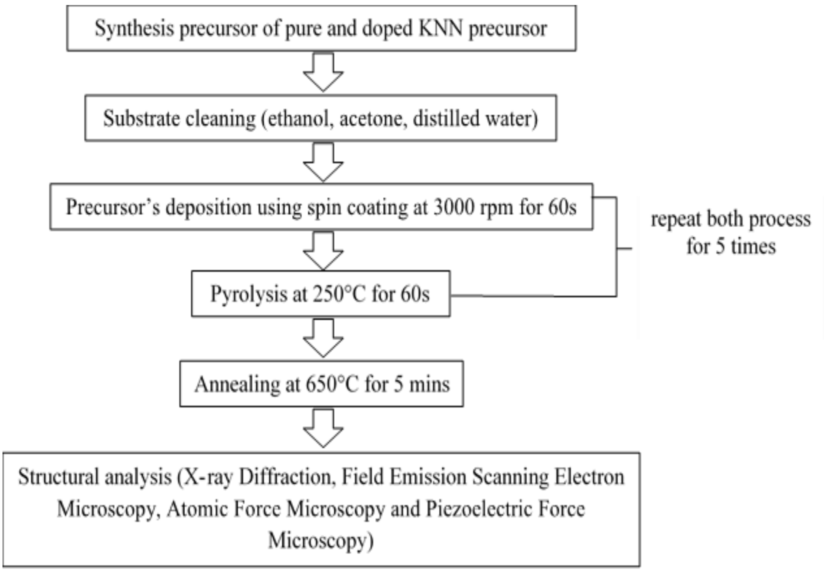

Figure 1. Flowchart of the process for manufacturing Mn-doped KNN thin film

X-ray diffraction (XRD) was employed to determine the crystalline nature of the Mn-doped KNN thin film. A CuKα wavelength of 1.54Å was employed to determine the diffraction angle within the range of 20° to 60° (2θ). In addition, Field emission scanning electron microscopy (FESEM) was employed to analyse the surface of the sample in order to investigate the specimen's surface shape and determine the chemical composition of the generated thin layer. The electrical properties was obtained by using AFM and PFM analysis in the scan range of 5μm x 5μm thin film with a tip bias of 5V to obtain the surface roughness and piezoelectric coefficient respectively.

3.0 RESULTS AND DISCUSSION

3.1 X-ray Diffraction (XRD) Analysis

Ferroelectric KNN ceramics were generated by the crystallization of a densely packed perovskite structure, according to the XRD analysis conducted in the previous study describes the application of XRD to validate the monoclinic MC structure of sol-gel-prepared Mn-doped KNN epitaxial thin films [5]. To examine the crystal structure and surface morphology, Mn-doped KNN thin films were deposited by replacing Mn in KNN thin films at concentrations ranging from 0.1% to 0.9%.

The stability of the sol-gel solution produced by the sol-gel process was verified. The chemical characteristics of group 5 transition metals, Nb, and alkali metals, including K and Na, differ greatly, it is generally very difficult to synthesize these elements into KNN thin films [6]. Consequently, it is possible to produce the ferroelectric thin layer on the stable single perovskite. Determining the chemical composition of the perovskite Mn-doped KNN thin layer on Si substrate heat treatment is a challenging task. On the other hand, stoichiometric sol-gel was steadily created during the raw material manufacturing process in order to deposit Mn-doped KNN thin films, with concentrations ranging from 0.1% to 0.9%.

Regardless of the amount of Mn supplied, Figure 2 demonstrates that the half-width of the diffraction peak on the thin film surface did not change appreciably. Pure perovskite thin films were produced from Mn-doped KNN thin films (0.1%–0.9%) that were stabilized and crystallized. This is because, by decreasing the crystallization temperature and increasing the crystallization density, KNN can be slightly replaced with Mn to produce rather stable thin films. The paper details how processing parameters, like annealing temperature and duration, affect the final films crystal structure and texture.

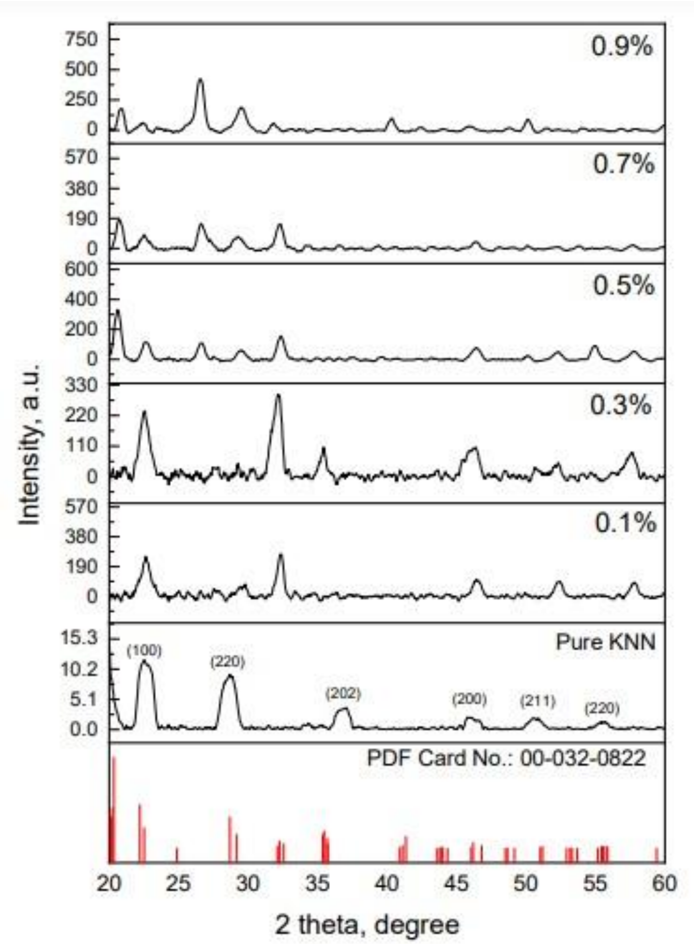

Figure 2. XRD patterns of Mn-doped KNN thin films fabricated with different concentrations of manganese dopant

The XRD patterns of the Mn-doped KNN thin films with varying manganese concentration percentages are displayed in Figure 2. Consistent with previously published findings in the literature, the existence of prominent peaks at 2θ= 23°, 32°, 46°, 52°, and 57° diffracted at distinct planes clearly indicated that the produced films are polycrystalline in nature. The Mn-doped KNN thin film showed a pristine perovskite orthorhombic crystal structure (PDF Card No.: 00-032-0822) with no secondary phase observed, as confirmed by the XRD investigation. In this work, Mn-doped KNN thin films were fabricated by using the sol-gel process, and the XRD results showed good agreement with the study's findings that KNN single crystals and thin films grow to have orthorhombic symmetry [7]. Resulted that the crystalline structure of KNN films was unaffected by the addition of 2.0 mol% Mn and Co ions. The perovskite ABO3 single phase's challenging KNN thin film growth can enhance ferroelectricity and piezoelectricity by substituting manganese in the A and B sites of the ABO3 crystalline structure.

3.2 Field Emission Scanning Electron Microscopy Analysis

Field-emission scanning electron microscopy (FESEM) is a useful analytical technique for analysing the surface morphological and structural characteristics of materials at the micro- and nanoscale. When examining the effects of manganese (Mn) dopants on the structure and electrical properties of potassium sodium niobate (KNN) thin films, FESEM research provides significant insights into the microstructure, surface morphology, and distribution of dopants inside the film. With the use of this technique, it will be possible to understand how Mn influences electrical properties and how the film's structure is impacted. FESEM was used to study the microstructure of KNN films which discussed the relationship between the microstructure of KNN films and their leakage properties [8].

FESEM was used to explain the demonstration of how to obtain dense and homogeneous microstructure of KNN thin films with five coating layers [9]. Figure 3 displays the annealed thin film FESEM images at x30.0k magnification. The 0.3% concentration of Mn-doped KNN was seen to have a less dense surface microstructure than the 0.5% concentration of Mn-doped KNN. It is evident that the sample's surface microstructure developed cracks and grew less thick when the manganese dopant concentration rose above 0.5%. As compared to concentrations of 0.3% and 0.5% manganese doped, the grain boundaries appeared nearly featureless. An increase in the manganese dopant concentration from 0.1% to 0.9% resulted in an increased number of visible grains with irregular surface shape. Larger grains were observed in the KNN thin film with higher manganese dopant concentration, suggesting that the grains were continuously developing in step with the rise in manganese dopant concentration. According to [10], there was a noticeable increase in the average grain size of KNMN thin films as a result of the Mn substitution. Conversely, the XRD results indicated that the rapid volatilization of alkali ions in Mn-doped KNN thin films resulted in the development of pyrochlore phases in a limited unit area, which analysed the creation of grains mixed with spherical and columnar structure.

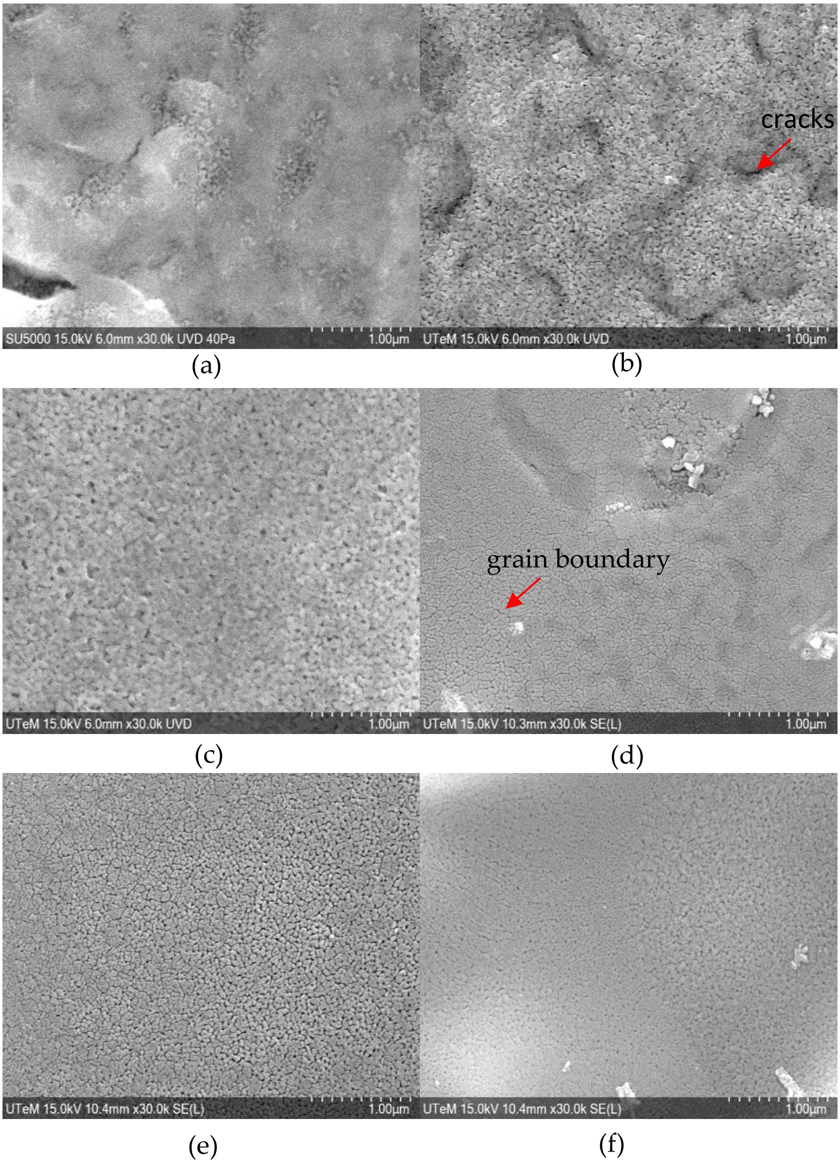

Figure 3. FESEM images showed surface morphology and microstructure of Mn-doped KNN thin films at x30.0k magnification with different concentrations of (a) Pure KNN, (b) 0.1%, (c) 0.3%, (d) 0.5%, (e) 0.7%, (f) 0.9%

The partial cracks depicted in Figure 3 resulted from residual strain on the thin film's surface, which changes the crystal structure per unit volume of the thin films as a result of the Si substrate's thermal expansion and up to five repetitions of pyrolysis of the deposition layer during the spin coating process [11]. One possible explanation is the doping influence on the temperature of crystallization. All of the samples showed the same homogeneous film surface, indicating the absence of a secondary phase. It is interesting that for thin films with 0.1% concentration, irregular grains and an uneven surface were visible. Thin film densification was made possible by the growth of the grains with increasing concentrations, as was seen, which improved the coalescence between the grains.

3.3 Atomic Force Microscopy (AFM) Analysis

Figure 4 displays the Ra (surface roughness) of KNN thin films that have been doped with different concentrations of Mn (0.1%, 0.3%, 0.5%, 0.7%, and 0.9%). The surface roughness values were determined by conducting AFM analysis of the films using a scan range of 5μm x 5μm. The findings demonstrate an initial rise in surface roughness as the Mn concentration increases from 0.1% to 0.3%, followed by a subsequent decline at 0.5%. As the Mn concentration reaches 0.9%, there is another increase in surface roughness.

The observed trend can be ascribed to the impact of Mn doping on the initiation and expansion mechanisms of KNN thin films. When Mn is added at lower concentrations (0.1% to 0.3%), it can improve the formation of nucleation sites, resulting in the growth of larger and more irregular grain structures. As a consequence, this leads to an increase in surface roughness. The reduction in roughness observed at a concentration of 0.5% indicates a more even dispersion of Mn ions, perhaps leading to a film that is more uniform in nature and possesses smaller grain sizes. After beyond the threshold of 0.5%, the roughness experiences a subsequent increase, maybe attributed to the emergence of larger grain sizes and more prominent surface imperfections resulting from elevated Mn concentrations.

The measured root mean square (RMS) roughness values (0.023μm at 0.1%, 0.092μm at 0.3%, 0.047μm at 0.5%, 0.056μm at 0.7%, and 0.112μm at 0.9%) confirm this pattern, indicating changes in surface roughness corresponding to varying degrees of Mn doping. The observed pattern aligns with the findings of the FESEM investigation, which also demonstrates variations in grain size and surface morphology that are associated with the concentration of Mn.

These findings are consistent with previous observations in the literature that indicate that Mn doping has a considerable impact on the surface morphology and roughness of KNN thin films. Nevertheless, this work suggests that the influence of crystallisation temperature, as shown by other studies, is quite minor. However, the level of Mn dopants is essential in influencing the surface properties of the films.

Overall, the findings depicted in Figure 4 offer valuable insights into the impact of Mn doping concentrations on the surface roughness and morphology of KNN thin films. The results emphasise the importance of accurately managing doping levels and synthesis circumstances in order to enhance the structural and electrical characteristics of Mn-doped KNN thin films for more advanced uses. These discoveries are consistent with prior research, while also providing fresh insights into the intricate relationships between dopants and the characteristics of thin films.

Furthermore, it was analysed that the addition of Mn had a significant influence on the nucleation and crystal growth process of the Mn-doped KNN thin films. This result is generally due to active volatilization of alkali ions and excessive oxygen deficiency during the pyrolysis of KNN thin films. Thus, the introduction of Mn^{2+} can absorb this h* (hole) by increasing the valence of Mn^{2+}, which is represented by $Mn^{2+} + h^* \rightarrow Mn^{3+}$, $Mn^{3+} + h^* \rightarrow Mn^{4+}$. Therefore, the chemical composition of KNN deposition solution should be controlled precisely, unlike pure KNN thin films, since the ferroelectric properties can be improved by significantly reducing oxygen deficiency and hole of KNN thin films substituted with Mn on KNN thin films.

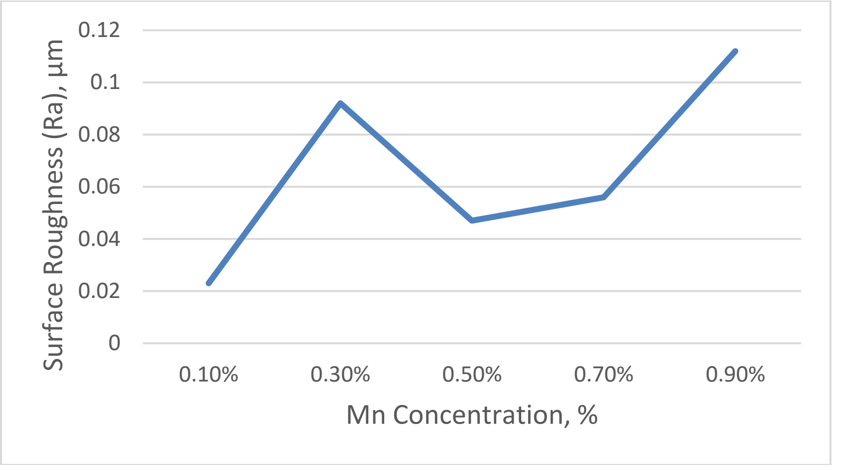

Figure 4. Surface roughness of KNN thin films correspond to the different Mn concentrations

3.4 Piezoresponse Force Microscopy (PFM) Analysis

Figure 5 depicts the relationship between the piezoelectric coefficient (m/V) of KNN thin films and the concentration of Mn, which ranges from 0% to 0.9%. The piezoelectric coefficient exhibits a gradual rise from 0% to around 0.2% manganese content, reaching its maximum at around 0.3%. After reaching its highest point, the coefficient remains generally consistent with little variations until it reaches 0.7%. Subsequently, there is another significant rise observed at 0.9%.

The observed pattern suggests that the addition of Mn has a substantial influence on the piezoelectric characteristics of KNN thin films. The first increase in the piezoelectric coefficient can be attributed to the heightened polarisation and greater alignment of dipoles inside the crystal structure as a result of the inclusion of Mn. At concentrations below 0.3%, manganese ions can occupy certain lattice positions that improve the piezoelectric response. The little variations and subsequent stabilisation within the moderate concentration range (0.3% to 0.7%) indicate that the material attains an equilibrium state where additional manganese (Mn) does not noticeably affect the piezoelectric characteristics. The subsequent 0.9% rise may be attributed to either further lattice distortions or enhanced domain alignment as a result of higher amounts of Mn doping.

When comparing these findings to previous research, it has been seen that the addition of a moderate amount of manganese (Mn) can improve the piezoelectric capabilities of KNN thin films. This improvement is achieved by decreasing the number of oxygen vacancies and enhancing the alignment of dipoles. Nevertheless, an overabundance of doping can result in a saturation effect or even a decrease in piezoelectric performance due to the formation of defects or secondary phases. The findings depicted in Figure 5 align with previous observations, indicating a range of doping concentrations that yield the highest value of the piezoelectric coefficient. This is followed by a period of stabilisation, and then another rise at higher levels of doping.

Overall, the information displayed in Figure 5 is consistent with previous studies, providing further evidence that Mn doping can improve the piezoelectric characteristics of KNN thin films. The observed trends underscore the need of optimising the concentration of Mn in order to attain the optimal piezoelectric performance. These findings align with previous research that emphasise the need to strike a balance between the level of doping and the features of the material.

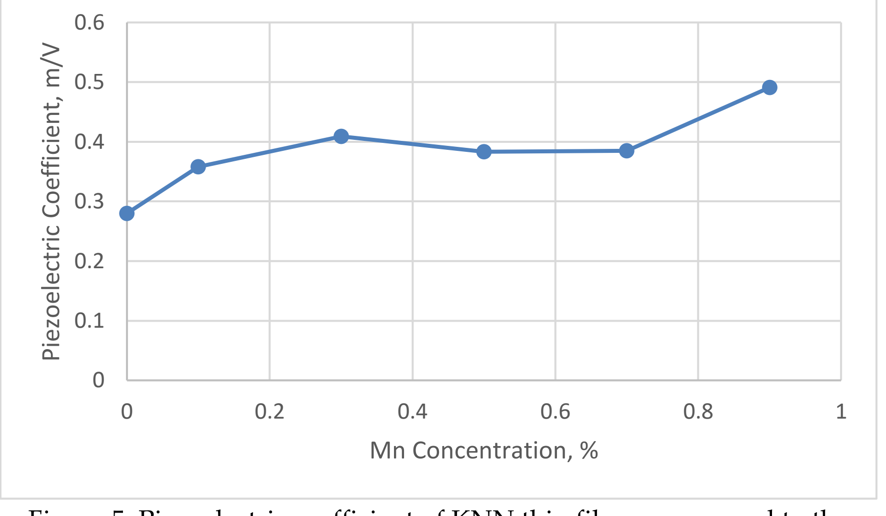

Figure 5. Piezoelectric coefficient of KNN thin films correspond to the different of Mn concentrations

4.0 CONCLUSION

The aim of this study was to use a sol-gel approach to create and enhance the ferroelectric and piezoelectric capabilities of Mn-doped KNN thin films, while examining their surface shape and crystal structure. The study effectively produced nanocrystalline KNN thin films with different Mn concentrations (0.1%, 0.3%, 0.5%, 0.7%, and 0.9%) despite the difficulties presented by the chemical characteristics of group 5 transition metals and alkali metals. The XRD examination verified the existence of orthorhombic crystal structure phases that are crucial for piezoelectric applications, while the FESEM investigation offered vital information about the morphological alterations caused by Mn doping. The thin films of KNN doped with 0.5% Mn displayed the most compact surface microstructure, whilst the samples doped with 0.3% and 0.5% Mn showed a uniform surface morphology. This is important for improving the structural and electrical characteristics. The AFM research emphasises the substantial influence of Mn doping on the surface properties of KNN thin films, underscoring the importance of precise regulation of doping levels and synthesis circumstances to enhance their structural and electrical attributes for advanced applications. The PFM study emphasises the importance of optimising the concentration of Mn for achieving the best piezoelectric performance. This aligns with previous research that have highlighted the need to find a balance between doping levels and material features. Therefore, the research successfully accomplished its goal by showing that the addition of Mn can efficiently enhance the structural and electrical characteristics of KNN thin films for eco-friendly, non-toxic ferroelectric applications.

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AUTHOR CONTRIBUTIONS

H.A.M. Afiq: Methodology, Experimental Set-up, Original Draft

Preparation; A.R.M. Warikh: Methodology and Supervision; U.A.A. Azlan: Data Collection and Data Analysis; M.H. Maziati Akmal: Experimental Set-up and Data Collection; T. Moriga: Writing-Reviewing.

CONFLICTS OF INTEREST

The article has not been published elsewhere and is not under consideration by other journals. All authors have approved the review, agreed with its submission, and declared no conflict of interest on the article.

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