# EFFECT OF MANGANESE DOPANT ON THE STRUCTURE AND ELECTRICAL PROPERTIES OF POTASSIUM SODIUM NIOBATE THIN FILM

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**Abstract**. This research paper presents a comprehensive investigation into the synthesis and characterization of manganese (Mn)-doped potassium sodium niobite (KNN) thin films with different concentration of manganese starting from 0.1%, 0.3%, 0.5%, 0.7% and 0.9% prepared via the sol-gel method. The introduction of Mn dopants with different concentrations into KNN thin films offers a pathway to further enhance their performance. The Mn-doped KNN thin films were synthesized using the chemical solution deposition method, a versatile technique known for its ability to produce uniform, high quality films. X-ray diffraction (XRD) analysis was employed to investigate the crystalline structure of the Mn-doped KNN thin films. The XRD analysis results show that the fabrication of Mn-doped KNN thin films exhibit an orthorhombic crystal structure. XRD peaks show that the occupancy of KNN thin films which indicate the synthesis was successfully done. Field-emission scanning electron microscopy (FESEM) was employed to examine the surface morphology and microstructure of the thin films. 0.5% Mn-doped KNN thin films show the best result of a uniform grain size and dense grain growth. The electrical properties of the Mn-doped KNN thin films were evaluated through resistivity measurements. Resistivity analysis showed that 0.3% Mn-doped KNN thin films have the lowest resistivity among the other concentrations.

**Keywords:** KNN; manganese; thin film; doped; structural

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## 1. INTRODUCTION

Potassium sodium niobate (KNN) thin films have emerged as a focal point in the realm of advanced materials due to their exceptional ferroelectric and piezoelectric properties. Because of these characteristics, KNN is a desirable option for a number of electrical and mechanical applications, such as energy harvesting devices, transducers, sensors, and non-volatile memory components. Due to its inherent appeal, scientists have tried to increase KNN thin film performance by adding dopants; this approach could open up new possibilities for material development and application flexibility.

One such dopant of significant interest is manganese (Mn). Gao et al reported that [1] Mn doping can reduce the leakage current density of KNN-based piezoelectric ceramics. Mn inclusion into KNN thin films has demonstrated potential in influenced both the electrical and structural properties of the films. Mn dopants have the ability on significant changes of the KNN crystal structure, resulting in material qualities that are specifically suited to meet the needs of particular applications. Mn doping can simultaneously change resistivity and dielectric characteristics, as well as other electrical properties of the films.

Mn doping introduces atomic and crystallographic alterations that affect the structural properties of KNN thin films. It could result in changes to the unit cell, variances in the crystal symmetry, and adjustments to the lattice constants. These structural alterations, as revealed by methods like as X-ray diffraction (XRD), are crucial in defining the behaviour of the film. Comprehending the structural influence of Mn dopants is crucial for customizing KNN thin films to fulfil the demands of various applications. The doping of Mn ions in KNN piezoelectric ceramics could replace both the A and B sites, further reducing the oxygen vacancies and leakage [1-2].

The electrical characteristics of KNN thin films are altered when Mn dopants are added. These modifications may show up as improved ferroelectricity, changed dielectric constants, or increased piezoelectric responses. Moreover, Mn doping may affect the films' resistivity, which may affect how well they function in electromechanical and electrical devices. Mn doping can significantly improve the ferroelectric properties and reduce the leakage current of KNN thin films [2-3]. A thorough investigation into the electrical impact of Mn doping is essential to realizing KNN thin film's full potential in cutting-edge technology.

The function of dopants such as manganese in altering the characteristics of KNN thin films becomes more significant as the search for high-performance materials grows in response to changing technological demands. The activation energies for nucleation, growth, and perovskite phase transformation of manganese-doped KNN thin films have been reported [3]. This study explores the complicated interaction between Mn dopants and KNN thin films, providing insight into the subtle interplay between electrical improvements and structural modifications. Researchers can create materials that surpass present constraints and open up new avenues for electrical and electromechanical applications by better understanding the impact of manganese dopants on KNN thin films [4].

## 2. MATERIALS AND METHODS

Figure 1 illustrates the fabrication of Mn-doped KNN thin films (0.1%, 0.3%, 0.5%, 0.7%, and 0.9%) on Si substrate using the sol-gel process. The sol-gel chemical solution deposition (CSD) method is commonly used to fabricate KNN thin films. Two alkaline precursors which are $CH_3COOK$, potassium acetate and $CH_3COONa$, sodium acetate are used as starting solutions. In order to compensate the loss of alkaline element, different content of manganese (mol% = 0.1%, 0.3%, 0.5%, 0.7% and 0.9%) was added to the precursor solutions. These chemicals were dissolved in a polar organic solvent, 2-methoxyethanol with constant stirring at room temperature. Later, niobium ethoxide, 2-methoxyethanol and acetylacetone were dissolved together to produce niobium precursor solution. Acetylacetone functions as a chelating agent and makes the solution more stable against attack by water. Then, the niobium solution was mixed with the prepared KNN precursors. The resultant solutions were kept standing at 80 °C for 1 hour.

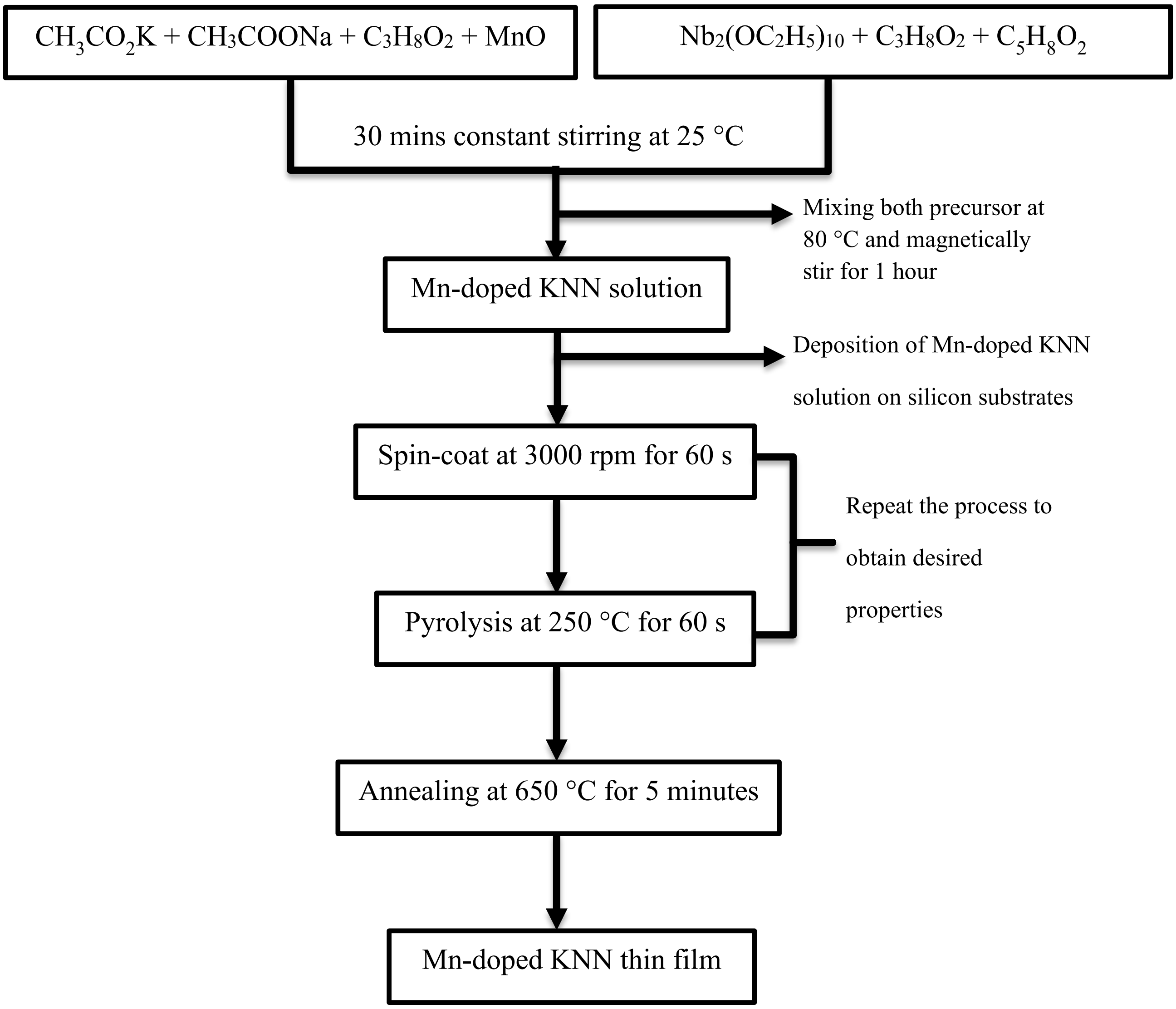



**Figure 1:** Flowchart of fabrication on Manganese-doped Potassium Sodium Niobate thin film via sol-gel method

A 1 cm by 1 cm incision was made in the Si substrate. After that, the substrate was immersed in acetone in an ultrasonic bath for 20 minutes. Deionized water was used to wash and rinse the substrates after soaking them in ethanol for 20 mins. Finally, clean the substrates once more using nitrogen gas to remove any remaining contaminants.

Using a spin coater, the Mn-doped KNN sol solution was placed onto the Si substrate and spun at 3000 rpm for 60 seconds. The substrate was treated at 250 °C for one minute of heat transfer in the hot plate following spin coating. The reason behind the selected value for pyrolysis temperature due to better degree of crystallinity has been produced. To attain the desired multi-layered thin film effect, the spin coating procedure was repeated five additional times, to enhance homogeneity and uniformity. Next, set the furnace's temperature to 650 °C for five minutes to begin the annealing process. The five samples were created by adding 0.1%, 0.3%, 0.5%, 0.7%, and 0.9% of Mn, respectively, and then depositing and developing crystals.

X-ray diffraction (XRD) was used to establish the Mn-doped KNN thin film's crystallinity. CuK α of λ = 1.54 Å was used to measure the diffraction angle between 20° and 60° (2θ). Additionally, Field emission scanning electron microscopy (FESEM) was used to analyze the surface of the sample that was prepared to examine the specimen's surface morphology and measure chemical composition of grown thin film. In addition, an LCR meter operating at room temperature with the testing frequency of 1 kHz was used to analyze the resistivity measurement.

## 3. RESULTS AND DISCUSSION

### *3.1 X-ray Diffraction (XRD)*

XRD can be used to confirm the crystal structure of the resulting films [4]. In the previous study, the XRD analysis of ferroelectric KNN ceramics showed that it was grown by the crystallization of perovskite structure with a dense and uniform structure. The use of XRD to confirm the monoclinic crystal structure of Mn-doped KNN epitaxial thin films prepared by the sol-gel method [5-6].

Figure 2 shows the XRD patterns of the Mn-doped KNN thin films with different percentage of manganese concentration. The presence of pronounced peaks at 2θ= 23°, 32°, 46°, 52° and 57° diffracted at different planes clearly indicate that the grown films are polycrystalline in nature which is in line with the previously reported studies in literature. As it was confirmed by the XRD analysis, the Mn-doped KNN thin film exhibited pure perovskite orthorhombic crystal structure (PDF Card No.: 00-032-0822) with no secondary phase was detected. The fabrication of Mn-doped KNN thin films by sol-gel technique in this experiment was stable in the perovskite crystal, and the XRD results are well consistent with the results of the study that KNN single crystals and thin films grows to have orthorhombic symmetry. The introduction of 2.0 mol% Mn and Co ions did not affect the crystalline structure of KNN films [7-8]. The difficulty of growing KNN thin film of the perovskite *ABO3* single phase can improve ferroelectricity and piezoelectricity by replacing manganese in A and B site of the *ABO3* crystalline structure.

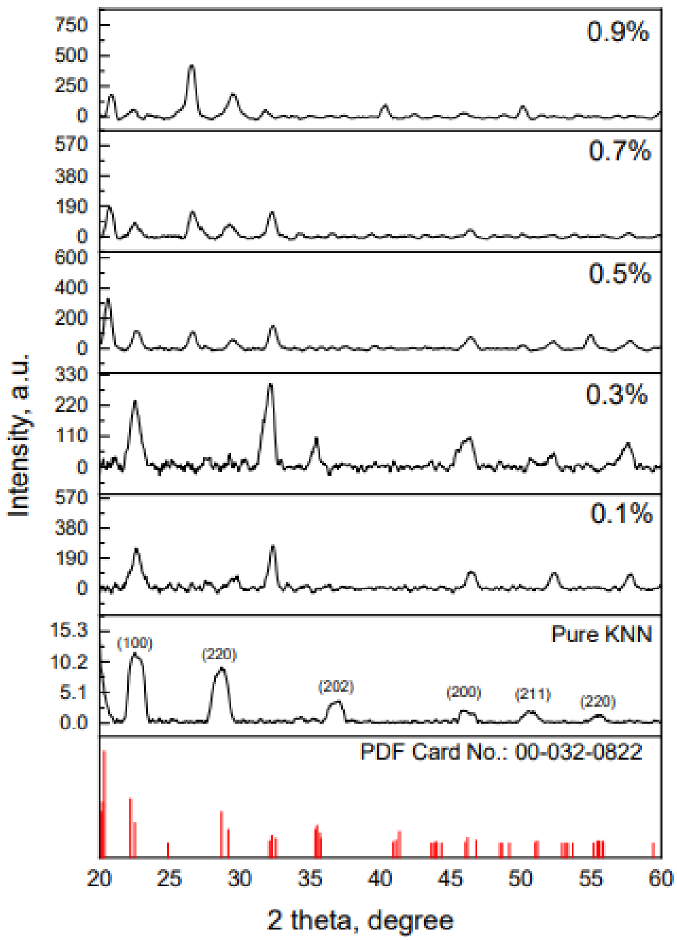



**Figure 2:** XRD patterns of Mn-doped KNN thin films fabricated with different concentration of manganese dopant

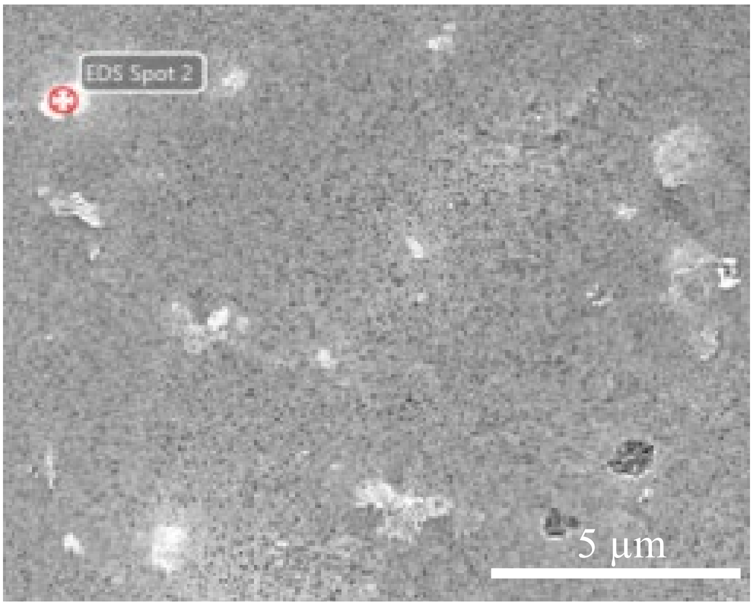
Figure 2 have shown that the diffraction peak on the thin film surface did not change significantly regardless of the amount of Mn added. Mn-doped KNN thin films (pure KNN - 0.9%) substituted were stably crystalized, and as a result, they were grown into pure perovskite thin films. This is because small amounts of Mn can be substituted for KNN to grow relatively stable thin films due to drop in crystallization temperature and an increase in crystallization density. The use of XRD to investigate the phase purity and texture of KNN thin films deposited by aqueous chemical solution deposition [9]. The study reports the effect of processing conditions, such as annealing temperature and time, on the crystal structure and texture of the resulting films.

By substituting Mn into KNN thin films with concentrations ranges from pure KNN ,0.1%, 0.3%, 0.5%, 0.7% and 0.9%, Mn-doped KNN thin films were deposited to analyze the crystal structure and surface morphology. It was confirmed that the sol-gel solution via sol-gel method was stably synthesized. Generally, it is very difficult to synthesize group 5 transition metals Nb and alkali metals such as K and Na into KNN thin film due to the difference in chemical properties of these elements. As a result, the ferroelectric thin film on the stable single perovskite can be fabricated. It is not an easy to determine the chemical composition of perovskite Mn-doped KNN thin film on Si substrate heat treatment. However, when the raw materials were fabricated, the stoichiometric sol-gel was stably prepared to deposit Mn-doped KNN thin films with concentration varies from 0.1% to 0.9% [10].

Because of their remarkable ferroelectric and piezoelectric qualities, potassium sodium niobate (KNN) thin films have attracted a lot of interest and are considered to be excellent choices for a range of electrical and electromechanical applications. Researchers have investigated the integration of dopants, with manganese (Mn) being of particular interest, to further improve their performance and customize them for certain needs. An effective technique for examining the structural alterations brought about by Mn doping and comprehending the effects of these alterations on the electrical characteristics of KNN thin films made using the sol-gel process is X-ray diffraction (XRD) analysis [10].

### *3.2 Energy-dispersive X-ray analysis (EDX)*

The chemical composition of the films was confirmed by using EDX method. The EDX analyses of Mn-doped KNN thin films deposited on Si substrate derived at 650 °C are shown in Figure 3. EDX analyses showed the presence of Mn, K, Na and Nb elements in the Mn-doped KNN thin film and Si from substrates. The alkaline ions of KNN-based films consist of potassium and sodium were deposited by sol-gel method were easily volatilized during the thermal process. Thermal process can reduce the volatilization of K and Na by adding dopant which is manganese. The effect of solution conditions on the properties of sol-gel derived KNN thin films on platinized sapphire substrates [11-12].




**eZAF Quant Result - Analysis Uncertainty: 12.84 %**

| Element | Weight % | Atomic % |
|---|---|---|
| Na | 15.7 | 28.2 |
| Mg | 1.2 | 2.1 |
| Al | 0.7 | 1.0 |
| Si | 22.0 | 32.3 |
| K | 1.6 | 1.7 |
| Ca | 4.0 | 4.2 |
| Mn | 20.5 | 15.4 |
| Nb | 34.2 | 15.2 |

**Figure 3:** EDAX analysis of 0.5 mol% Mn-doped KNN thin film deposited on Si substrate after sintering at 650 °C (scale not clear)

The Mn, Nb and alkali chemical homogeneity of Mn-doped KNN thin film were investigated using EDAX analysis. This technique has previously been used to quantify Mn, Na, K and Nb amounts in Mn-doped KNN thin films for all different of concentrations. Based on the table of on Figure 3, Nb exhibit the largest atomic and weight percentage followed by Na, Si, Mn, K and Al respectively. Since Nb concentration is homogeneous in all films, it is presumed that the effects of microstructural features on the EDAX mapping are not dominant. It is worth noting that films with alkali chemical inhomogeneity also exhibit larger variations in grain size. Homogeneous grain size seems to be one of the signs of chemical homogeneity of films [12].

### *3.3 Field Emission Scanning Emission Microscopy (FESEM) analysis*

The use of FESEM to show that KNN thin films with five coating layers have a dense and uniform microstructure. The FESEM images with x 50.0 k magnification of annealed thin films was presented in Figure 4. As it can be clearly seen, the 0.5% Mn-doped KNN thin film displayed a dense surface microstructure followed by Mn-doped KNN with 0.3% concentration. As the concentration of the Mn dopant increased above 0.5%, it can be seen that the surface microstructure of the sample contained cracks and became undensed. The grain boundaries seemed almost featureless compare to 0.3% and 0.5% of manganese doped concentration. As the Mn dopant was increased from 0.1% to 0.9%, more visible grains with inhomogeneous surface morphology were observed. In the event of the KNN thin film with increased manganese dopant, the grains were found to be larger, indicating that the grains were continually developed in line with the increase in the manganese dopant concentration. The Mn substitution had a pronounced effect on the grain size of KNMN thin films, and the average grain size was significantly increased [13-15].

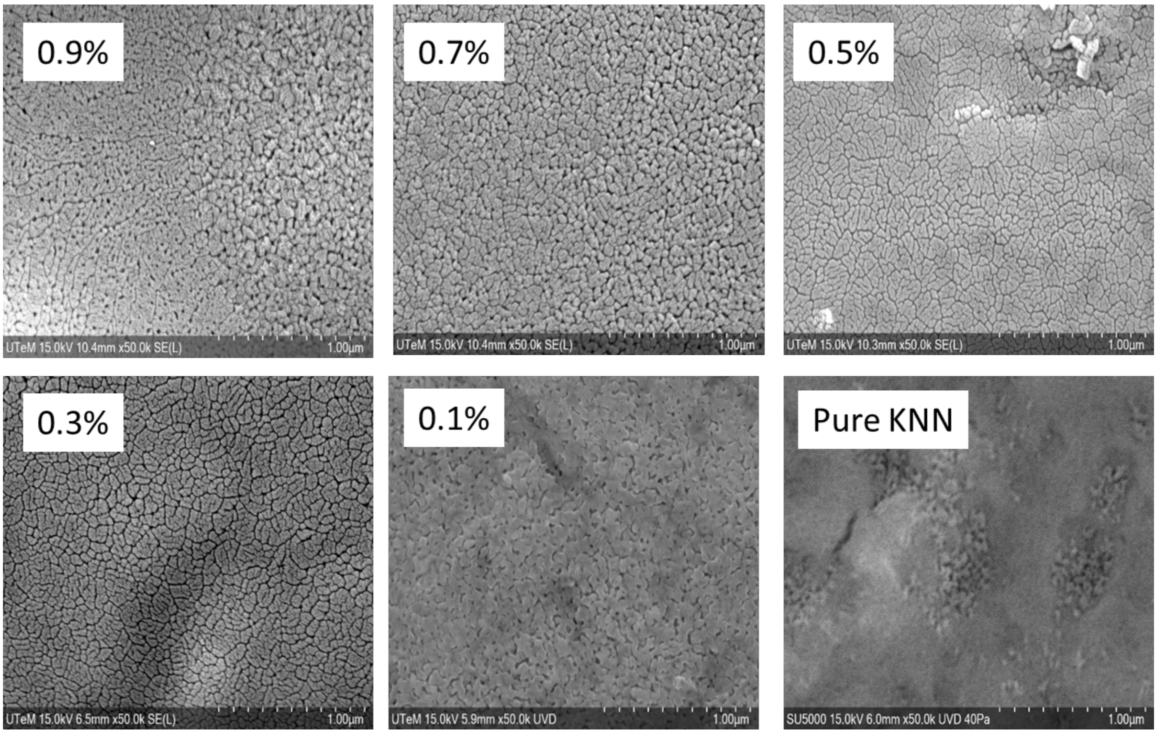



**Figure 4:** FESEM images showed surface morphology and microstructure of Mn-doped KNN thin films at x 50.0k magnification with different concentrations

On the other hand, the formation of grains mixed with spherical and columnar structure in Mn-doped KNN thin films were analyzed by the formation of pyrochlore phases in a small unit area due to rapid volatilization of alkali ions as analyzed by XRD results. The partial cracks shown in Figure 4 were caused by residual strain on the surface of the thin film, which causes a change in the crystal structure per unit volume of the thin films due to the thermal expansion of the Si substrate and repeated pyrolysis of the deposition layer in the spin coating process up to 5 times. The doping effect on crystallization temperature can be the reason [15]. The uniform film surface indicated that there is no secondary phase in all samples. It is noteworthy that uneven grains and inhomogeneous surface are noticeable for thin film with 0.1% concentration. As observed, the growth of the grains with increasing number of Mn dopant concentrations enhanced the coalescence between the grains and hence, allowing thin film densification.

An effective analytical method for examining the surface morphological and structural properties of materials at the micro and nanoscale was field-emission scanning electron microscopy (FESEM). FESEM analysis offers important insights into the microstructure, surface morphology, and distribution of dopants inside the film while investigating the impact of manganese (Mn) dopants on the structure and electrical characteristics of potassium sodium niobate (KNN) thin films. Using this method, one may clarify the effect of Mn on electrical characteristics and see how it affects the structure of the film. Discussion on the relationship between the microstructure of KNN films and their leakage properties [16]. FESEM was used to study the microstructure of KNN films.

### *3.4 Resistivity*

The resistivity of Mn-doped KNN thin films were measured as a function of different Mn concentration as shown in Figure 5. As it can be seen, the resistivity of Mn-doped KNN thin film at (0.1%-0.9%) is 0.1, 0.03, 0.09, 0.23 and 0.28 MOhm respectively. The sudden decreased of resistivity from 0.1% to 0.3%, the grains nucleated and merged, forming grains with bigger grain sizes, resulting in a reduced number of the grains boundaries, which was empirically supported by the FESEM observation. The introductions of Mn dopant in the range of 0.1- 0.3 mol % reduce the resistivity of KNN thin films significantly. The enhanced resistance magnitude in doped KNN thin films is due to the introduction of Mn dopant. Thus, as Mn concentration increases, the number of conduction electron increases, causing an abrupt decrease in resistivity. It is generally attributed to electronic compensation of the incorporated cation as reported by [16].

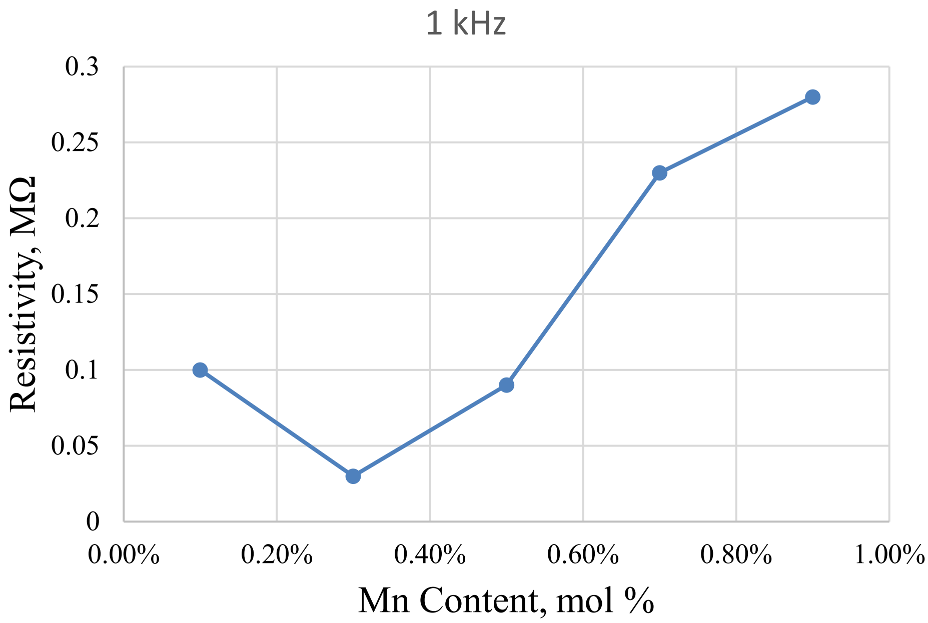



**Figure 5**: Resistivity of Mn-doped KNN thin films correspond to the different Mn concentrations at 1kHz

Because of their remarkable ferroelectric and piezoelectric qualities, potassium sodium niobate (KNN) thin films have shown significant promise in a variety of electrical and electromechanical applications. Researchers have looked into incorporating dopants to improve their performance even further and customize them for particular applications. In particular, manganese (Mn) doping has drawn interest because to its ability to alter the electrical and structural characteristics of KNN thin films. In this regard, resistivity analysis is an essential technique for comprehending how Mn dopants affect these films' electrical behavior. In order to better understand the impact of Mn doping in KNN thin films made using the sol-gel process, this work primarily use resistivity measurements. The films' resistivity was assessed at room temperature using a testing frequency of 1 kHz [16].

## 4. CONCLUSIONS

This study investigated the fabrication of environmentally friendly lead-free ferroelectric Mn-doped KNN thin films using a sol-gel method to enhance their ferroelectric and piezoelectric properties. Different concentrations of Mn (ranging from 0.1% to 0.9%) were incorporated into the KNN thin films. Analysis using XRD, EDS, FESEM, and resistivity measurements revealed significant findings:

XRD analysis demonstrated that Mn doping notably influenced the structural properties of the KNN thin films, confirming the persistence of desired ferroelectric phases crucial for piezoelectric applications. EDS analysis revealed the homogeneous distribution of Mn dopants within the crystal lattice, essential for consistent electrical properties, while also indicating the potential formation of secondary phases due to Mn incorporation. FESEM analysis highlighted variations in grain size and shape induced by Mn doping, with 0.5% Mn-doped KNN thin films exhibiting the densest surface microstructure. Furthermore, the presence of homogeneous surface morphology in films doped with 0.3% and 0.5% Mn could significantly impact both structural and electrical properties. Resistivity measurements indicated variations, suggesting changes in electrical conductivity attributed to Mn doping's impact on charge carrier concentration. Additionally, temperature-dependent resistivity measurements provided insights into the films' behaviour under different thermal conditions.

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### Author Contributions

All authors contributed toward data analysis, drafting, and critically revising the paper and agree to be accountable for all aspects of the work.

### Disclosure of Conflict of Interest

The authors have no disclosures to declare.

## Compliance with Ethical Standards

The work is compliant with ethical standards.

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