A flexible piezoelectric generator using KNN-Li/PVDF/MWCNT for energy harvesting application

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Submitted by:

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JUNE, 2024

CANDIDATE'S DECLARATION

We, Jatin Chauhan (2K22/MSCPHY/15) and Richa (2K22/MSCPHY/33), students M.Sc. (Physics), hereby declare that the project Dissertation titled "A flexible piezoelectric generator using KNN-Li/PVDF/MWCNT for energy harvesting application" which is submitted by us to the Department of Applied Physics, Delhi Technological University , Delhi in partial fulfilment of the requirement for the award of the degree of Master of Science , is original and not copied from any source without proper citation.. This work has not previously formed the basis for the award of any Degree, Diploma Associateship, Fellowship or other similar title or recognition.

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DECLARATION AND SUPERVISOR'S CERTIFICATE

We, **Jatin Chauhan (2K22/MSCPHY/15)** and **Richa (2K22/MSCPHY/33)** hereby certify that the work which is presented in the Dissertation-II entitled in fulfilment of the requirement for the award of the Master in Science in **Physics** and submitted to the Department of **Applied Physics**, Delhi Technological University, Delhi is an authentic record of our own, carried out during a period from January 2024 to May 2024 under the supervision of Dr. **Richa Sharma.**

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I, hereby certify that the Project Dissertation titled " **A flexible piezoelectric generator using KNN- Li/PVDF/MWCNT for energy harvesting application**" which is submitted by JATIN CHAUHAN, Roll No. 2K22/MSCPHY/15 and RICHA, Roll No. 2K22/MSCPHY/33, Department of Applied Physics, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the degree of Master of Science, is a record of the project work carried out by the students under my supervision. To the best of my knowledge this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere

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ABSTRACT

The subject of energy harvesting has advanced significantly within the previous couple of years in response to the growing need for renewable, portable, and sustainable energy sources. The purpose of such devices is to capture ambient energies and convert them into usable electrical energy. In this reported work, piezoelectric generator (PEG) based on Li modified (K,Na)NbO3, and MWCNT as a filler in Poly-vinylidene fluoride (KNN-Li/PVDF/MWCNT) flexible composite films were made by use of different KNN-Li percentage (0%,10%,15% and 20%) on the polymer's weight. The films were characterized using X-Ray diffraction to determine the crystallinity of the films and Fourier- transform infrared spectroscopy (FTIR) to determine the presence of β-phase in the synthesized films. Scanning Electron Microscopy (SEM) is used to analyse the morphology of composite films. Piezoelectric energy harvesting performance of the constructed device was analysed by applying the force on the surface of device with the help of finger tapping method. The maximum open circuit voltage obtained in the present work is 31.1 V for 10 wt.% KNN-Li in the MWCNT and PVDF. The obtained results for PEG can be used to derive self-powered and wearable devices.

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Place: Delhi

Date: 07 June 2024 Jatin Chauhan

Richa

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LIST OF SYMBOLS AND ABBREVIATIONS

1	DMF	N,N-dimethylformamide
2	C_3H_8O	Propanol
3	Na_2CO_3	Sodium carbonate
4	Li_2CO_3	Lithium carbonate
5	Nb_2O_5	Niobium pentaoxide
6	(Na,k)NbO_3(NKN) /KNN	Potassium sodium niobate
7	MWCNT	Multiwall carbon nanotube
8	PVDF	Polyvinylidene fluoride

1. INTRODUCTION

Over the past few years to produce energy, we require unconventional or environmentally friendly resources. One such form of energy which can be utilized is piezoelectric energy [1]. Piezoelectricity refers to stress-induced electricity [2]. Thus piezoelectric materials are those materials which have the functionality of producing an electrical potential in response to an applied force or generating mechanical movement when subjected to an electric field [3]. However, piezoelectric materials have the potential to operate at high voltages. Several piezoelectric and ferroelectric materials like lead zirconate titanate PZT, sodium potassium niobate (KNN), barium titanate ($BaTiO_3$) etc. are being used for changing mechanical stress into electrical energy [4-5].

In this work, we synthesized Lead-free piezoelectric ceramics that are the development goal for the sustainable human development [6]. We synthesis KNN-based ceramics which is a lead free and have piezo characteristics vary from 80 to 160 pC/N and strong electromechanical coupling was seen in suitably doped KNN-based piezoceramics in the intermediate and low-temperature range (25 °C – 200 °C), with d_{33} values ranging between 350 and 700, similar to those of soft commercial PZT piezoceramics in terms of pC/N [6,7]. KNN ceramics are mainly used when we need to made a lightweight, suitable and low-cost generator [8]. Then we added lithium, the main objectives of adding lithium are to enhance the phase structure, thermal steadiness as well as piezoelectric qualities of KNN powder. The compositions containing Li exhibited the highest recorded properties in KNN materials, and this maximum has been linked to the existence of an morphotropic phase boundary (MPB) between an orthorhombic and a tetragonal phase [9].

Polymers are also being used as piezoelectric materials, polymers like PVDF-HFP, PVDF-TrFE etc. show piezoelectric properties instead of nylon-11 etc. we use PVDF (Poly vinylidene fluoride) polymer additionally it was also the first polymer to exhibit piezoelectricity in 1961, reported by Kawai. PVDF is very stable in the environment [10]. It is investigated that PVDF is commercially used because of its good piezo electric properties [11,12]. PVDF is typically produced as a film because of its wide range of uses, including energy harvesters, actuators and sensors. Nanoparticles like carbon nanotubes (CNTs) and other materials such as graphene, clay, and metal-oxides were added to induce additional β-phases [13]. Films of semicrystalline poly (vinylidene fluoride) (PVDF) in the β-phase were studied by Fourier transform infrared (FTIR) spectroscopy [14].

We used MWCNT to enhance mechanical and electrical properties of KNN-Li. MWCNT has the ability to raise impedance over a broad frequency range, which aids in the development of electrically insulated KNN-Li/PVDF films. [15]. A small amount of conductive MWCNT to primary PVDFKNN/Li composites can affect the electrical properties by severely interfering in the charge distribution within the sample [16-17]. Moreover, we added multi-wall carbon nanotubes (MWCNTs) to KNN-Li/PVDF to reduce internal resistance [18].

In this present work, we have reported flexible piezoelectric material based KNN-Li/PVDF/MWCNT films i.e. KNN-Li doped with MWCNT with different weight percentage (0%,10%,15%,20%) of KNN-Li ceramic. Firstly, we have synthesized KNN ceramic doped with Li using simple ball milling method. And then using PVDF as a polymer and adding appropriate amount of MWCNT, we have made films by drop casting method. The synthesis of KNN-Li material is characterized by XRD pattern. The presence of α and β phases is confirmed by Fourier-transform infrared spectroscopy. Piezoelectric generator was made of KNN-Li/PVDF/MWCNT films using aluminium tape acting as electrodes which then connected to output circuit to measure output voltage. The piezoelectric response depends on PVDF, MWCNT and different weight percentage KNN-Li films.

2. EXPERIMENTAL SECTION

2.1 Material used: -

Alfa-Aesar, India was the source of the following materials: propanol (C_3H_8O), sodium carbonate (Na_2CO_3, 98%), potassium carbonate (K_2CO_3, 99%), lithium carbonate (Li_2CO_3, 99%), and niobium pentaoxide (Nb_2O_5, 99.5%). Without any additional purification, all of these compounds were utilized in the manufacture of pure KNN-Li.

2.2 Why we choose KNN-Li Ceramic: -

We choose KNN-Li ceramic because to its excellent piezoelectric qualities, environmental friendliness, and lack of lead. KNN-Li exhibits a high temperature of curie. Among the promising lead-free piezoelectric materials is KNN-Li. A flexible generator with a high voltage output that is based on lead-free KNN nanofibers modified by Li.

2.3 Why we choose POLYVINYLIDENE FLUORIDE(PVDF) Polymer: -

PVDF is used because it is chemically inert beyond potential use and does not react with electrolytes or lithium. PVDF has a higher piezoelectric coefficient than other polymer m materials such as nylon 11, polypropylene and polydimethylsiloxane. PVDF has a density (1.78 g/cm3), is rare, and is used in applications requiring maximum purity and resistance e to solvents, acids, and hydrocarbons. Good value and lightweight. PVDF has excellent dielectric constant ($\varepsilon r \approx 11$), low glass transition temperature, high mechanical strength and electrochemical stability.

2.3 *Synthesis of KNN-Li ceramic powder: -*

Leadfree (KNN-Li) ceramics were produced by ball milling process. Potassium carbonate , sodium carbonate and lithium carbonate added niobium pentoxide are used as raw materials.

BALANCED CHEMICAL REACTION: -

$$\mathbf{0.226\ K_2CO_3 + 0.252\ Nb_2CO_3 + 0.025Li_2CO_3 + 0.496\ Nb_2O_5 \longrightarrow}$$

$$\mathbf{[0.942(K_{0.48}Na_{0.535})NbO_3 + 0.05LiNbO_3] + 0.5\ CO_2} \uparrow$$

individual raw materials in After weighing all weighing machine, mix all in one container. Now mixture is placed in tank roller mills for 24 hours using zirconium balls and some ratio of propanol for finely mixing. By using filter paper, the KNN-Li powder is removed from Propanol. The well-mixed powder combination was then oven-dried for three to four hours at eighty degrees Celsius. Using a mortar and pestle, the dried powder is now broken down into superior powder. Lastly, using the temperature profile for 900º C as a guide, the dried powder is calcined for four hours in the air at 850ºC, 900ºC, and 950ºC.

2.4 *Synthesis of KNN-Li /PVDF/MWCNT films: -*

Flexible composite films of KNN-Li/PVDF/MWCNT were synthesized using drop casting method. PVDF powder and DMF were mixed in a beaker and then dissolved using magnetic stirrer at 300 rpm and 30°C for 2 hours. Simultaneously, prepared KNN-Li powder with 0%, 10%, 15 % and 20 % on the weight of the polymer and appropriate amount of MWCNT were introduced individually to DMF and subjected to a 30 minutes ultrasonication at 25°C. Next, various weight percentages of the resulting KNN-Li solution were combined with the PVDF solution obtained from magnetic stirrer. Then the solution again mixed with the help of magnetic stirrer at 40^0C for 3 hours and at 400rpm. Now, the obtained homogenous solution is casted over a glass substrate by using micropipette. then dried it in vacuum oven at 80 °C for 1 hour to form films. So, a composite flexible KNN-Li/PVDF/MWCNT based films are obtained on glass slide. Finally, peeled off the films from glass. **Figure 1** shows appropriate schematic diagram for fabrication of films.

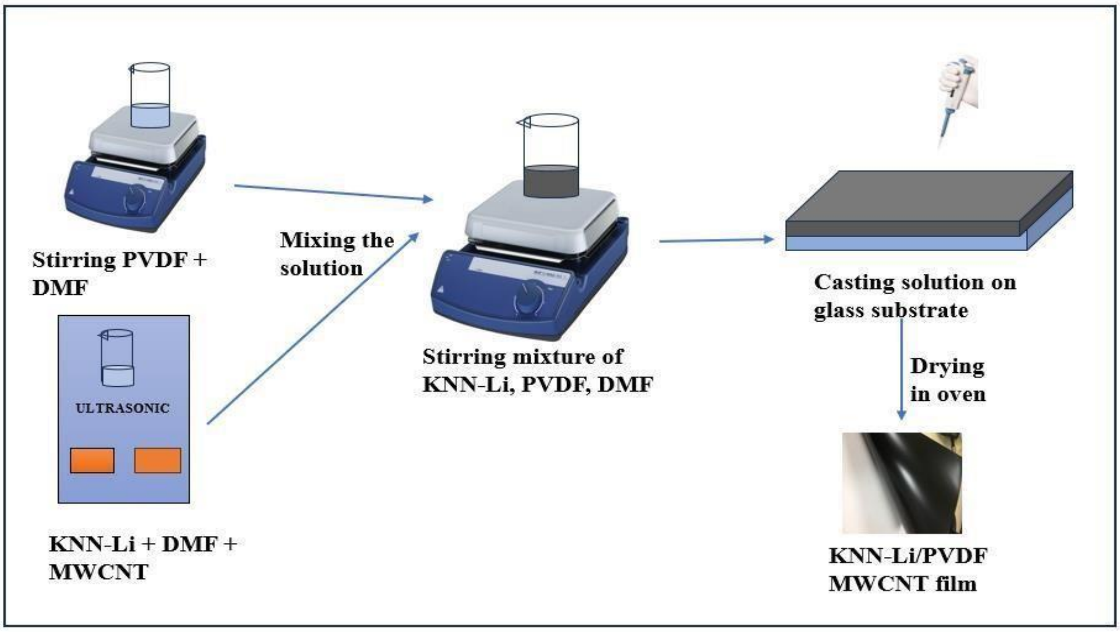

Figure 1: *Diagrammatic illustration of KNN-Li/PVDF/MWCNT flexible composite film fabrication.*

2.5 FABRICATION OF PIEZOELECTRIC ENERGY HARVESTOR BASED ON KNN-Li/PVDF/MWCNT: -

To fabricate piezoelectric generator, we take composite flexible KNN-Li/PVDF/MWCNT film after this, to create the top and bottom electrode, attach aluminium tape on both sides of the films to create upper and lower electrodes. Then using finger tapping method, output voltage is generated. The schematic diagram for production of a Piezoelectric generator is shown in **Figure 2**.

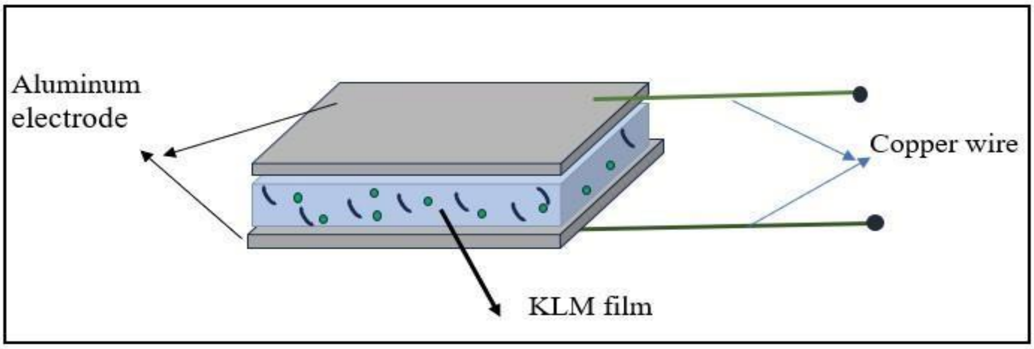

Figure 2: Diagrammatic illustration of a manufactured piezoelectric generator

3. CHARACTERIZATION TECHNIQUE

3.1 XRD

The maximum usually used technique is referred to as X-ray, which matches using crystal structures and mirrored image of monochromatic X-rays. The cathode ray tube produces X-rays; those are then collected for concentration, filtered to provide monochromatic radiation, and then directed into the pattern. whilst Bragg's law is glad, the interplay between the beam and the pattern may be fine. The crystal shape and section purity of KNN ceramic powder calcined and sintered at specific temperatures had been analyzed the use of X-ray powder diffraction (Cu-Ka radiation, k = 1.5406 A^; Chemical manufacturer source: Bruker; version: D8 find out).

3.2 FTIR

The technique for infrared spectroscopy this is most often hired is called Fourier rework infrared spectroscopy, or FTIR. it's miles an analytical technique for figuring out the composition of polymeric, organic, and every now and then inorganic substances. Infrared mild is used within the FTIR evaluation procedure to scan test substances and take a look at chemical characteristics. An infrared absorption spectrum is produced using Fourier rework Infrared Spectroscopy (FTIR), that's used to determine the chemical bonds of a molecule. The profile of the pattern, that is created by way of the spectra, is a unique molecular fingerprint that may be used to display screen and test samples for an expansion of components.

3.3 SEM

Scanning Electron Microscopy (SEM) is a powerful technique used to examine the surface structure and composition of materials at high magnifications. By directing a focused beam of electrons onto a specimen, SEM produces detailed images that reveal the topography, morphology, and compositional information of the sample. The interaction between the electron beam and the atoms in the sample generates signals that are collected and analyzed to form a high-resolution image. SEM is widely used in various fields, including materials science, biology, and nanotechnology, due to its ability to provide intricate details that are not attainable with traditional optical microscopy.

4 RESULT AND ANALYSIS

4.1 XRD Plot of KNN-Li ceramic: -

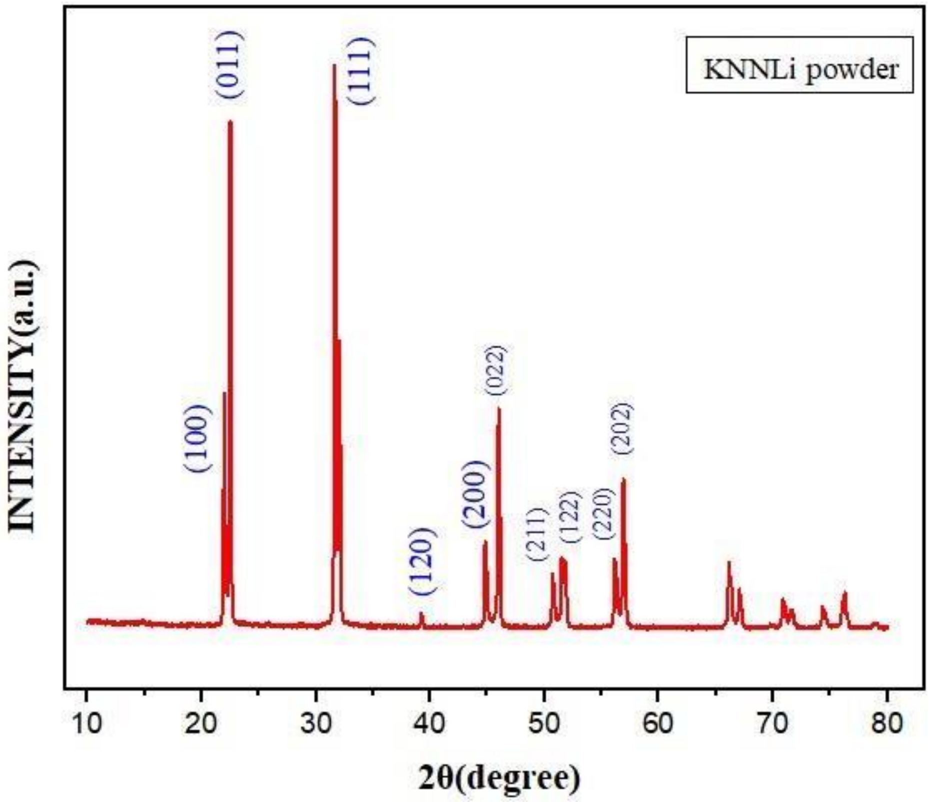

Figure 3: XRD pattern of calcined KNN-Li ceramic powder

4.2 *XRD Analysis: -*

X-ray Diffraction (XRD) examined the crystalline structure of KNN-Li powder that is shown in **Figure 3**. The XRD plot's peaks display a structure devoid of any impurity peaks, indicating that KNN-Li powder was synthesized via the Solid-State process in a successful manner. Bragg peaks were seen in various patterns from the calcined crystallographic faces of the sample (100), (011), (111). One can use the (002) and (200) peaks at about 2˚ = 44.7°–46° to ascertain the phase structure of ceramics based on KNN. The calcined ceramic is in the tetragonal phase, as indicated by the increased intensity of the (200) diffraction peak when compared to the (002) diffraction peak. [19-27].

4.3 XRD PLOT OF KNN-Li FILMS: -

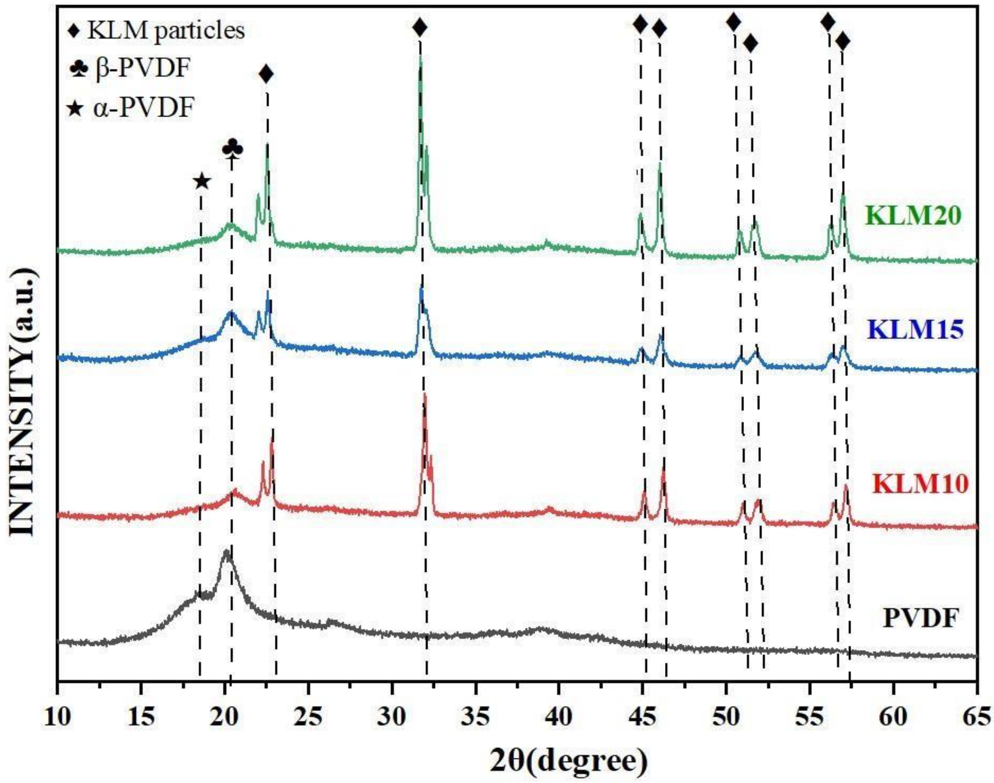

Figure 4: XRD pattern of fabricated films with different weight percentage of KNN-Li in PVDF matrix and MWCNT.

4.4 XRD Analysis:-

The XRD pattern of synthetic polymer composite films in a PVDF-DMF matrix at different weight percentages of KNN-Li MWCNT (0%, 10%, 15%, and 20% wt%) is displayed in the figure. Every film has two distinct peaks: the one at 18.5° is linked to PVDF's nonpolar nature and doesn't improve the material's piezoelectricity, while the one at 20.3° is associated with the polar phase, or β phase, which gives rise to the piezoelectric property. The symbol "♦" designates the peaks of KNN-Li MWCNT. Additionally, "★" denotes the polar or beta phase and "★" denotes the non-polar or alpha phase.

Additionally, the above figure shows that the synthesis of polymer composite films at different concentrations was successful as evidenced by the rise in peak intensity corresponding to an increase in the weightage percentage of KLM (KNN-Li and MWCNT).

4.5 FTIR PLOT OF FILMS OF KNN-Li/PVDF and MWCNT: -

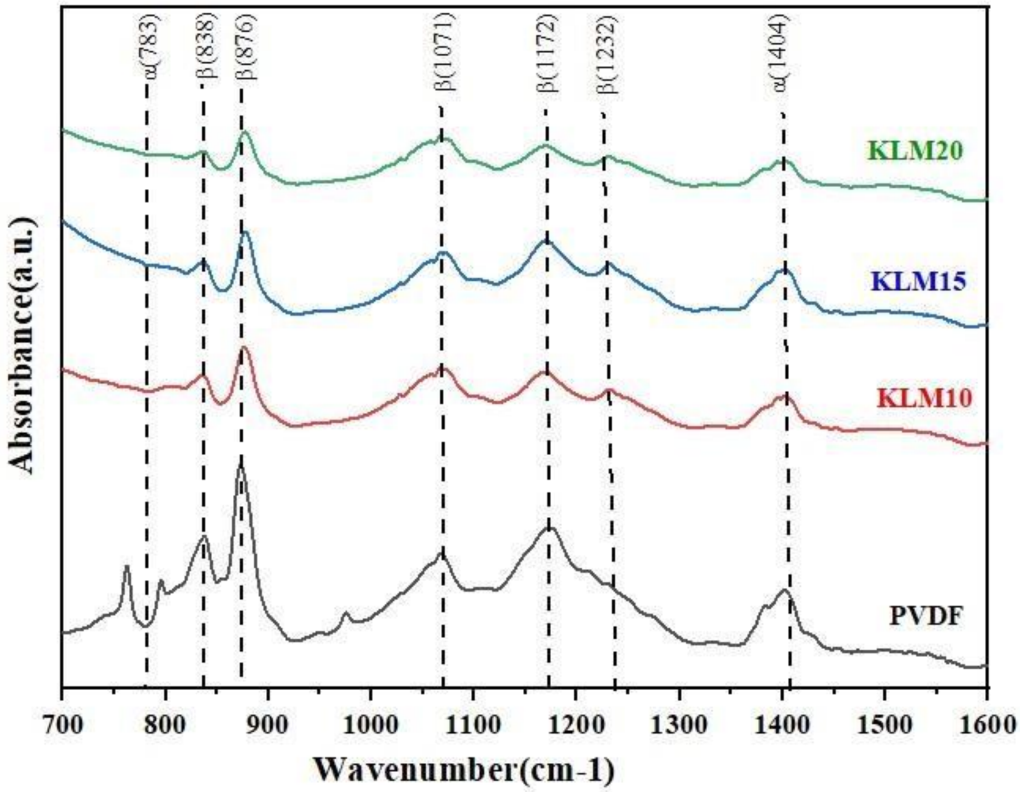

Figure 5: FTIR PLOT OF FILMS OF KNN-Li/PVDF and MWCNT

4.6 FTIR Analysis: -

The following figure displays the (FTIR) of films of produced flexible polymer composite. The figure shows the locations of the α and β phases. Because the β phase contains the biggest dipole moment, it is essential for the piezoelectric capabilities.

The formula determines the β phase's content.

$$F(\beta) = \frac{A_\beta}{\left(\frac{K(\beta)}{K(\alpha)}\right)A_\alpha + A_\beta} * 100\%$$

The absorption coefficients for 840 cm-1 and 762 cm-1, respectively, are K(β) = 7.7 X 104 cm2/mol and K(α) = 6.1 X 104 cm2/mol. To obtain crystallographic information about the pure PVDF film and KNN-Li/PVDF/MWCNT flexible composite films, XRD were done and their corresponding graphs are shown in **Figure 5**. Every film has distinct peaks: the one at 18.5° is linked to PVDF's non-polar nature and doesn't improve the material's piezoelectricity, while the one at 20.3° is associated with the polar phase, or β phase, which gives rise to the piezoelectric property. The diffraction peak corresponding to the β-phase is stronger than the α-phase, indicating the predominance of the β-phase over the α-phase of PVDF in all prepared films. Furthermore, the XRD plots clearly show that as the concentration of KNN-Li particles in the PVDF matrix increases, the intensity of diffraction peaks corresponding to PVDF decreases.

[22-26]. Additionally, it has been shown that following doping, the first β phase increases to 10 weight percent of KLM before decreasing as a result of particle agglomeration.

4.7 SEM graphs of KNN-Li/PVDF and MWCNT films with different weight percentage of KNN-Li: -

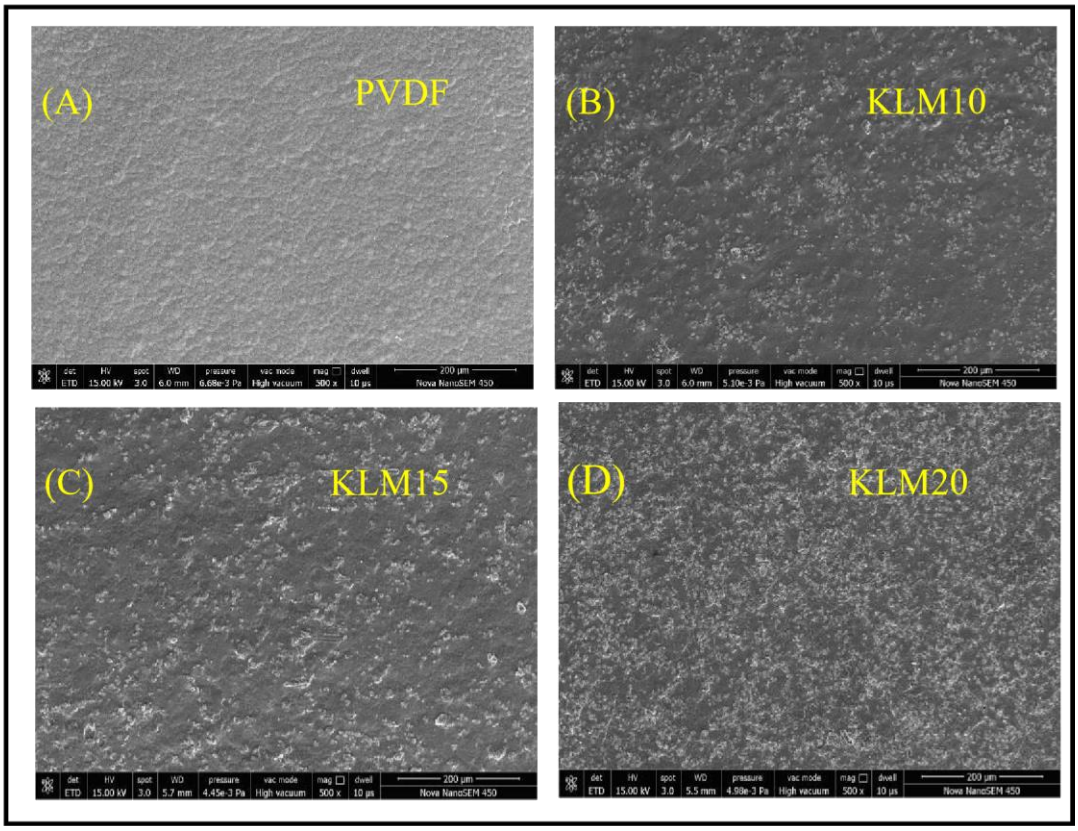

Figure 6: SEM graphs of KNN-Li/PVDF and MWCNT films with different weight percentage of KNN-Li.

4.8 *SEM Analysis: -*

Morphological study is done using Scanning Electron Microscopy (SEM). **Figure 5** makes it evident that the KNN is present throughout the film and is distributed uniformly. The KNN films' homogeneity and lack of cracks are also shown by the pictures. KNN-Li and MWCNT are uniformly distributed across the PVDF matrix and do not appear to be grouped together, indicating that the fillers were evenly distributed throughout the PVDF matrix. [22,25,26].

4.9 PIEZOELECTRIC RESPONSE: -

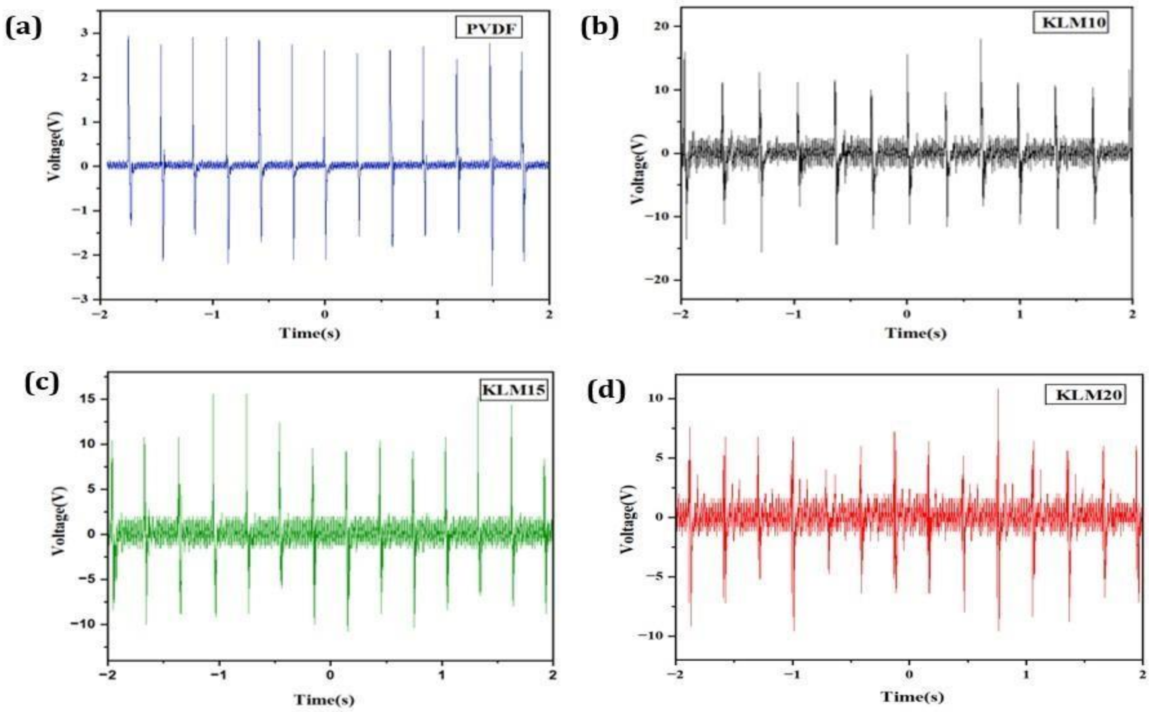

Figure 7: Voltage generation using KNN-Li/PVDF/MWCNT piezoelectric generator device containing different weight percentage of KNN-Li.

The piezo response of fabricated piezoelectric generator and energy harvesting capability was studied by using finger tapping process. By continuously tapping on the prepared piezoelectric generators using hand. So, peak to peak open circuit voltage was observed on the screen generated by the prepared generators as pattern seen in the **Figure 7**. The open circuit peak to peak voltage values for different piezoelectric generator is listed in the table 1.

It can be clearly seen from the plots in the figure which indicates that the voltage first increases with increase in weightage of KNN-Li content in the PVDF matrix up to 10 wt.% and after that it is observed that, it decreases with the further increment in the weightage percentage of KNN-Li.

Hence, KNN-Li/PVDF/MWCNT films have a mainly KNN-Li/MWCNT concentration dependent effect on particle nucleation in PVDF matrix. Table 1 shows that the maximum output voltage recorded is 31.1 V, which is approximately 6 times higher than that of pure PVDF film. Enhanced piezoelectricity in KNN-Li/PVDF/MWCNT composite films is due to the intrinsic piezoelectric properties of KNN-Li/MWCNT and uniform dispersion in PVDF. [34,35]

Table 2: Peak to peak output voltage obtained by applying force on the piezoelectric generator.

S. No.	**Piezoelectric Generators**	**Peak to Peak to output voltage**
1	Pure PVDF	5.5 V
2	KLM10	31.1 V
3	KLM15	24.6 V
4	KLM20	20.3 V

5. CONCLUSIONS: -

In this research, we successfully synthesized an environmental friendly lead-free piezoelectric composite film using lithium-doped (K,Na)NbO3 (abbreviated as KNN), MWCNTs, and PVDF. KNN-Li ceramics were made using the traditional ball milling technique and then sintered at various temperatures between 850 and 950 ºC. After examining how sintering temperature affects microstructure piezoelectric characteristics, densification, and so on, the following conclusions can be taken from the experimental data collected: According to the XRD data, the KNN-Li ceramic powder was effectively made. There was not an impurity phase found in any of the samples. After that, flexible films were fabricated. X-ray diffraction was then used to evaluate these films in order to verify their crystallinity, Fourier transform infrared spectroscopy (FTIR) to detect the presence of β-phase in the synthesized films, and to ascertain the crystalline morphology, scanning electron microscopy (SEM) was used. The prepared piezoelectric device's ability to harvest piezoelectric energy was examined by applying force on the surface of the device using finger tapping method. The voltage stored in the composite film can be used to operate small equipment that requires low voltage. In the Voltage graphs, we observed that 10 wt% films show more output voltage as compared to others i.e. 31.1 V. For better results or making good piezoelectric generator, material chosen play an important role. In this reported work, we have used KNN ceramic doped with Li because Li is lead free which is environment friendly. We improve the mechanical and electrical characteristics of KNN-Li ceramic by using MWCNT. The results demonstrate that material doping significantly enhances the β-phase.

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CONFERENCE PAPER

A flexible piezoelectric generator using KNN-Li/PVDF/MWCNT for energy harvesting application

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ABSTRACT

The subject of energy harvesting has advanced significantly within the previous couple of years in response to the growing need for renewable, portable, and sustainable energy sources. The purpose of such devices is to capture ambient energies and convert them into usable electrical energy. In this reported work, piezoelectric generator (PEG) based on Li modified (K,Na)NbO3, and MWCNT as a filler in Poly-vinylidene fluoride (KNN-Li/PVDF/MWCNT) flexible composite films were made by use of different KNN-Li percentage (0%,10%,15% and 20%) on the polymer's weight. The films were characterized using X-Ray diffraction to determine the crystallinity of the films and Fourier-transform infrared spectroscopy (FTIR) to determine the presence of β-phase in the synthesized films. Scanning Electron Microscopy (SEM) is used to analyse the morphology of composite films. Piezoelectric energy harvesting performance of the constructed device was analysed by applying the force on the surface of device with the help of finger tapping method. The maximum open circuit voltage obtained in the present work is 31.1 V for 10 wt.% KNN-Li in the MWCNT and PVDF. The obtained results for PEG can be used to derive self-powered and wearable devices.

KEYWORD: - Energy Harvesting, Piezoelectric generator, KNN-Li, MWCNT, Flexible composite films.

1. INTRODUCTION

Over the past few years to produce energy, we require unconventional or environmentally friendly resources. One such form of energy which can be utilized is piezoelectric energy [1]. Piezoelectricity refers to stress-induced electricity [2]. Thus piezoelectric materials are those materials which have the functionality of producing an electrical potential in response to an applied force or generating mechanical movement when subjected to an electric field [3]. However, piezoelectric materials have the potential to operate at high voltages. Several piezoelectric and ferroelectric materials like lead zirconate titanate PZT, sodium potassium niobate (KNN), barium titanate ($BaTiO_3$) etc. are being used for changing mechanical stress into electrical energy [4-5].

In this work, we synthesized Lead-free piezoelectric ceramics that are the development goal for the sustainable human development [6]. We synthesis KNN-based ceramics which is a lead free and have piezo characteristics vary from 80 to 160 pC/N and strong electromechanical coupling was seen in suitably doped KNN-based piezoceramics in the intermediate and low-temperature range (25 °C–200 °C), with d_{33} values ranging between 350 and 700, similar to those of soft commercial PZT piezoceramics in terms of pC/N [6,7]. KNN ceramics are mainly used when we need to made a lightweight, suitable and low-cost generator [8]. Then we added lithium, the main objectives of adding lithium are to enhance the phase structure, thermal steadiness as well as piezoelectric qualities of KNN powder. The compositions containing Li exhibited the highest recorded properties in KNN materials, and this maximum has been linked to the existence of an morphotropic phase boundary (MPB) between an orthorhombic and a tetragonal phase [9].

Polymers are also being used as piezoelectric materials, polymers like PVDF-HFP, PVDF-TrFE etc. show piezoelectric properties instead of nylon-11 etc. we use PVDF (Poly vinylidene fluoride) polymer additionally it was also the first polymer to exhibit piezoelectricity in 1961, reported by Kawai. PVDF is very stable in the environment [10]. It is investigated that PVDF is commercially used because of its good piezo electric properties [11,12]. PVDF is typically produced as a film because of its wide range of uses, including energy harvesters, actuators and sensors. Nanoparticles like carbon nanotubes (CNTs) and other materials such as graphene, clay, and metal-oxides were added to induce additional β-phases [13]. Films of semicrystalline poly (vinylidene fluoride) (PVDF) in the β-phase were studied by Fourier transform infrared (FTIR) spectroscopy [14].

We used MWCNT to enhance mechanical and electrical properties of KNN-Li. MWCNT has the ability to raise impedance over a broad frequency range, which aids in the development of electrically insulated KNN-Li/PVDF films. [15]. A small amount of conductive MWCNT to primary PVDFKNN/Li composites can affect the electrical properties by severely interfering in the charge distribution within the sample [16-17]. Moreover, we added multi-wall carbon nanotubes (MWCNTs) to KNN-Li/PVDF to reduce internal resistance [18].

In this present work, we have reported flexible piezoelectric material based KNN-Li/PVDF/MWCNT films i.e. KNN-Li doped with MWCNT with different weight percentage (0%,10%,15%,20%) of KNN-Li ceramic. Firstly, we have synthesized KNN ceramic doped with Li using simple ball milling method. And then using PVDF as a polymer and adding appropriate amount of MWCNT, we have made films by drop casting method. The synthesis of KNN-Li material is characterized by XRD pattern. The presence of α and β phases is confirmed by Fourier-transform infrared spectroscopy. Piezoelectric generator was made of KNN-Li/PVDF/MWCNT films using aluminium tape acting as electrodes which then connected to output circuit to measure output voltage. The piezoelectric response depends on PVDF, MWCNT and different weight percentage KNN-Li films.

2. EXPERIMENTAL SECTION

2.1 MATERIAL

Potassium carbonate (K_2CO_3, 99%), Sodium carbonate (Na_2CO_3, 98%), Lithium carbonate (Li_2CO_3, 99%) and niobium penta-oxide (Nb_2O_5, 99.5%) are purchased from Alfa Aesa as raw materials. Propanol and Polyvinylidene fluoride (PVDF, 99%) are purchased from Thermo Fisher. Multiwall carbon nanotubes (MWCNT, 99.9%) and N,N-Dimethylformamide (DMF, 99.4%) are purchased from Sigma Aldrich.

2.2 MATERIAL SYNTHESIS

To synthesize 10gm KNN ceramic doped with Li, simple ball milling method is used. In this method, appropriate amount raw materials Potassium carbonate (K_2CO_3) 1.85gm, sodium carbonate (Na_2CO_3) 1.58gm, niobium penta-oxide (Nb_2O_5) 7.83gm and lithium carbonate (Li_2CO_3) 0.1098gm are used.

To create homogenous mixture these raw materials were stoichiometrically mixed in propanol for 12 hours using zirconium ball and then this mixture was drying in the oven for 24 hours at 80°C. The dry mixture was calcined at 900ºC in a muffle furnace, and then further grinded for further use in films.

2.3 FILM SYNTHESIS

Flexible composite films of KNN-Li/PVDF/MWCNT were synthesized using drop casting method. PVDF powder and DMF were mixed in a beaker and then dissolved using magnetic stirrer at 300 rpm and 30°C for 2 hours. Simultaneously, prepared KNN-Li powder with 0%, 10%, 15 % and 20 % on the weight of the polymer and appropriate amount of MWCNT were introduced individually to DMF and subjected to a 30 minutes ultrasonication at 25°C. Next, various weight percentages of the resulting KNN-Li solution were combined with the PVDF solution obtained from magnetic stirrer. Then the solution again mixed with the help of magnetic stirrer at 40^{0}C for 3 hours and at 400rpm. Now, the obtained homogenous solution is casted over a glass substrate by using micropipette. then dried it in vacuum oven at 80 °C for 1 hour to form films. So, a composite flexible KNN-Li/PVDF/MWCNT based films are obtained on glass slide. Finally, peeled off the films from glass. **Figure 1** shows appropriate schematic diagram for fabrication of films.

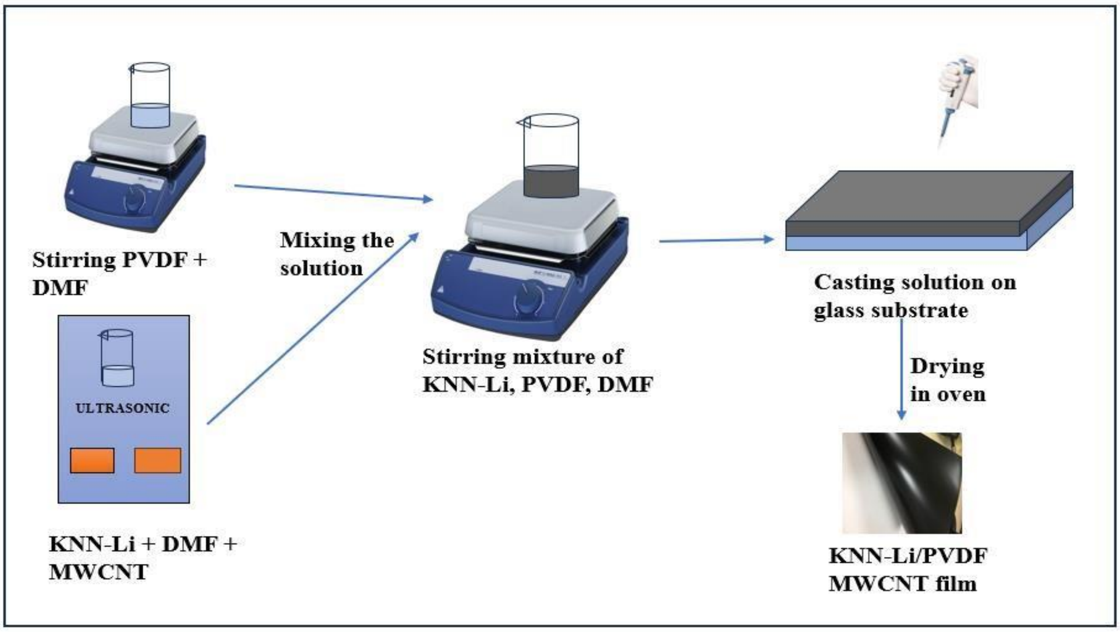

Figure 1: Diagrammatic illustration of KNN-Li/PVDF/MWCNT flexible composite film

fabrication.

2.4 FABRICATION OF PIEZOELECTRIC ENERGY HARVESTOR BASED ON KNN-Li/PVDF WITH MWCNT

To fabricate piezoelectric generator, we take composite flexible KNN-Li/PVDF/MWCNT film after this, to create the top and bottom electrode, attach aluminium tape on both sides of the films to create upper and lower electrodes. Then using finger tapping method, output voltage is generated. The schematic diagram for production of a Piezoelectric generator is shown in **Figure 2**.

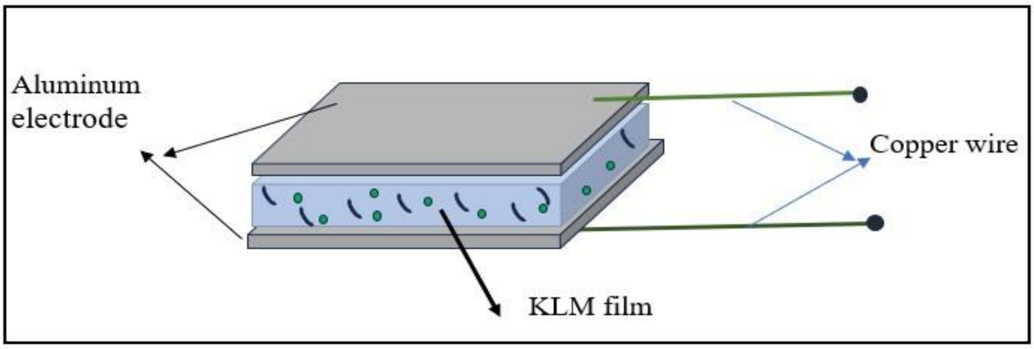

Figure 2: Diagrammatic illustration of a manufactured piezoelectric generator

2.5 CHARACTERIZATIONS

Crystalline structure of the prepared powder KNN-Li and KNN-Li/PVDF/MWCNT composite films was analysed by using X-ray Diffraction pattern. The morphological nature of the flexible KLM films was analysed using Scanning Electron Microscopy (SEM). In order to analyse the β phase information in the KNN-Li/PVDF/MWCNT composite films, Fourier transform infrared (FTIR) spectroscopy was used. Moreover, the piezoelectric generator's output voltage was tested and measured using the finger tapping method.

3. RESULTS AND DISCUSSION

3.1 STRUCTURAL ANALYSIS OF KNN-Li POWDER MATERIAL

X-ray Diffraction (XRD) examined the crystalline structure of KNN-Li powder that is shown in **Figure 3**. The XRD plot's peaks display a structure devoid of any impurity peaks, indicating that KNN-Li powder was synthesized via the Solid-State process in a successful manner. Bragg peaks were seen in various patterns from the calcined crystallographic faces of the sample (100), (011), (111). One can use the (002) and (200) peaks at about 2˚ = 44.7°–46° to ascertain the phase structure of ceramics based on KNN. The calcined ceramic is in the tetragonal phase, as indicated by the increased intensity of the (200) diffraction peak when compared to the (002) diffraction peak. [1927].

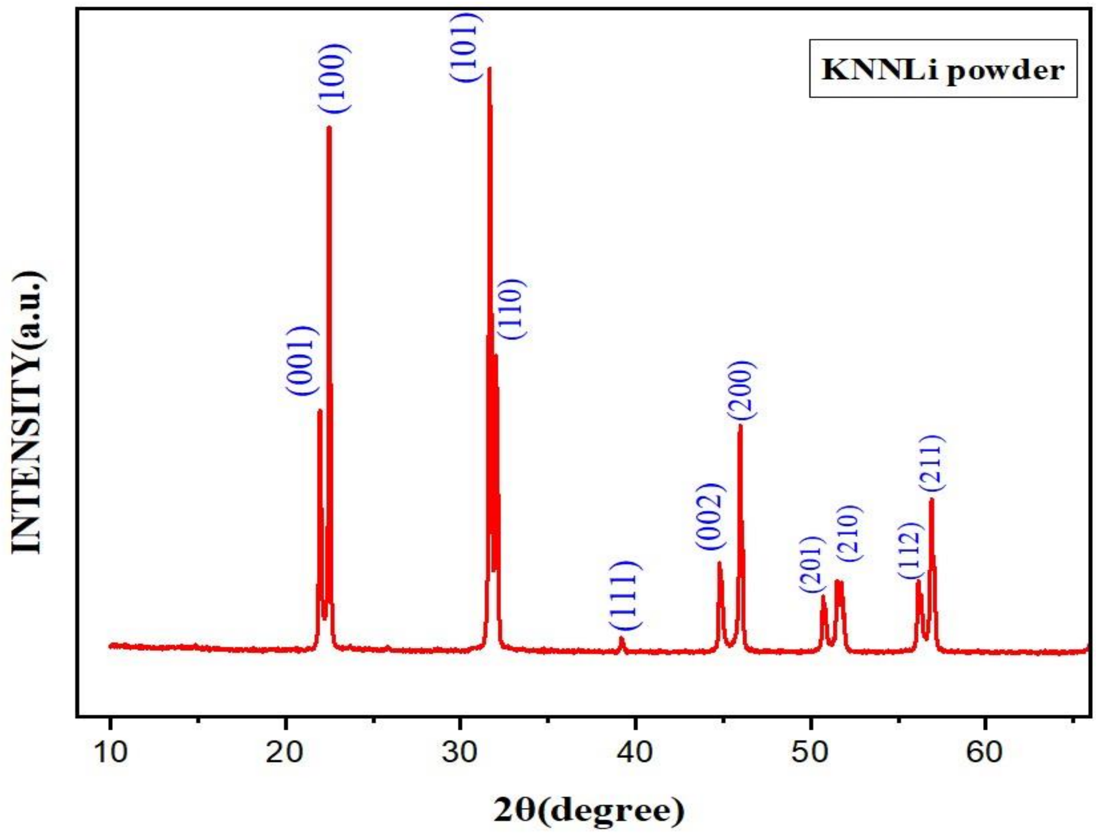

Figure 3: XRD pattern of calcined KNN-Li ceramic powder

3.2 STRUCTURAL ANALYSIS OF PURE PVDF AND KNN-Li/PVDF WITH MWCNT

To obtain crystallographic information about the pure PVDF film and KNN-Li/PVDF/MWCNT flexible composite films, XRD were done and their corresponding graphs are shown in **Figure 4**. Every film has distinct peaks: the one at 18.5° is linked to PVDF's non-polar nature and doesn't improve the material's piezoelectricity, while the one at 20.3° is associated with the polar phase, or β phase, which gives rise to the piezoelectric property. The diffraction peak corresponding to the βphase is stronger than the α-phase, indicating the predominance of the β-phase over the α-phase of PVDF in all prepared films. Furthermore, the XRD plots clearly show that as the concentration of KNN-Li particles in the PVDF matrix increases, the intensity of diffraction peaks corresponding to PVDF decreases. [22-26]

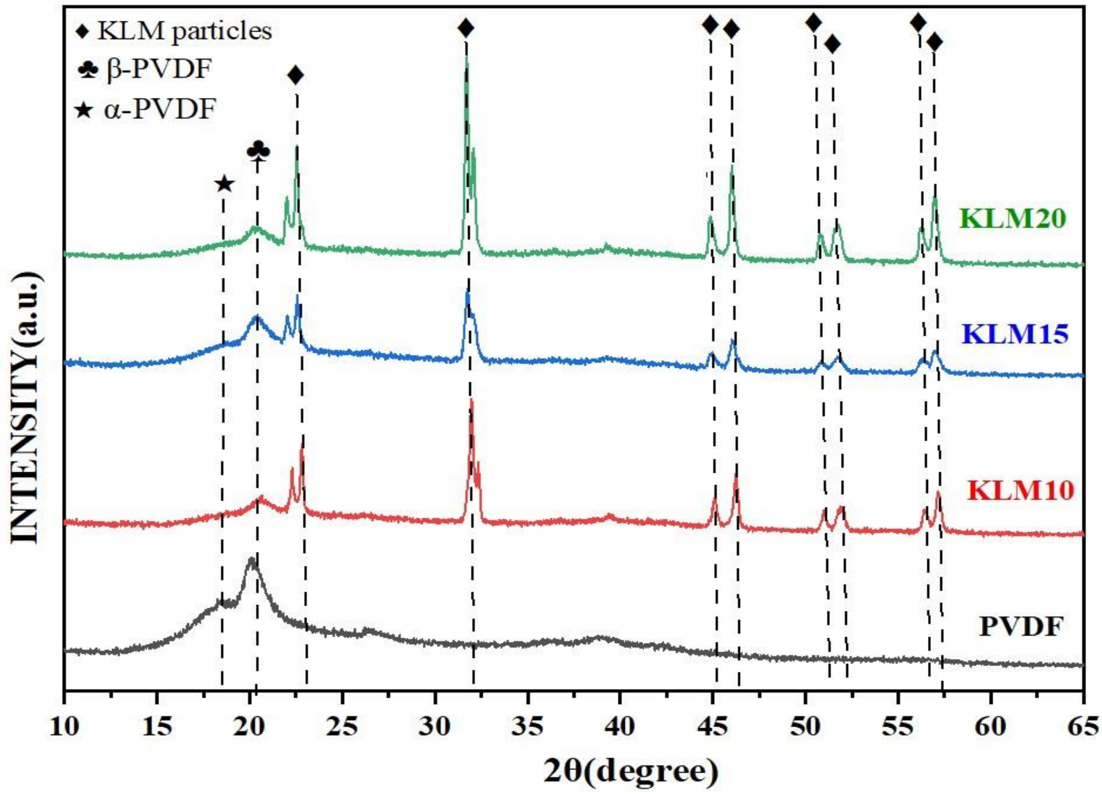

Figure 4: XRD pattern of fabricated films with different weight percentage of KNN-Li in PVDF matrix and MWCNT.

3.3 MORPHOLOGICAL STUDY OF PURE PVDF AND KNN-Li/PVDF/MWCNT

Morphological study is done using Scanning Electron Microscopy (SEM). **Figure 5** makes it evident that the KNN is present throughout the film and is distributed uniformly. The KNN films' homogeneity and lack of cracks are also shown by the pictures. KNN-Li and MWCNT are uniformly distributed across the PVDF matrix and do not appear to be grouped together, indicating that the fillers were evenly distributed throughout the PVDF matrix. [22,25,26]

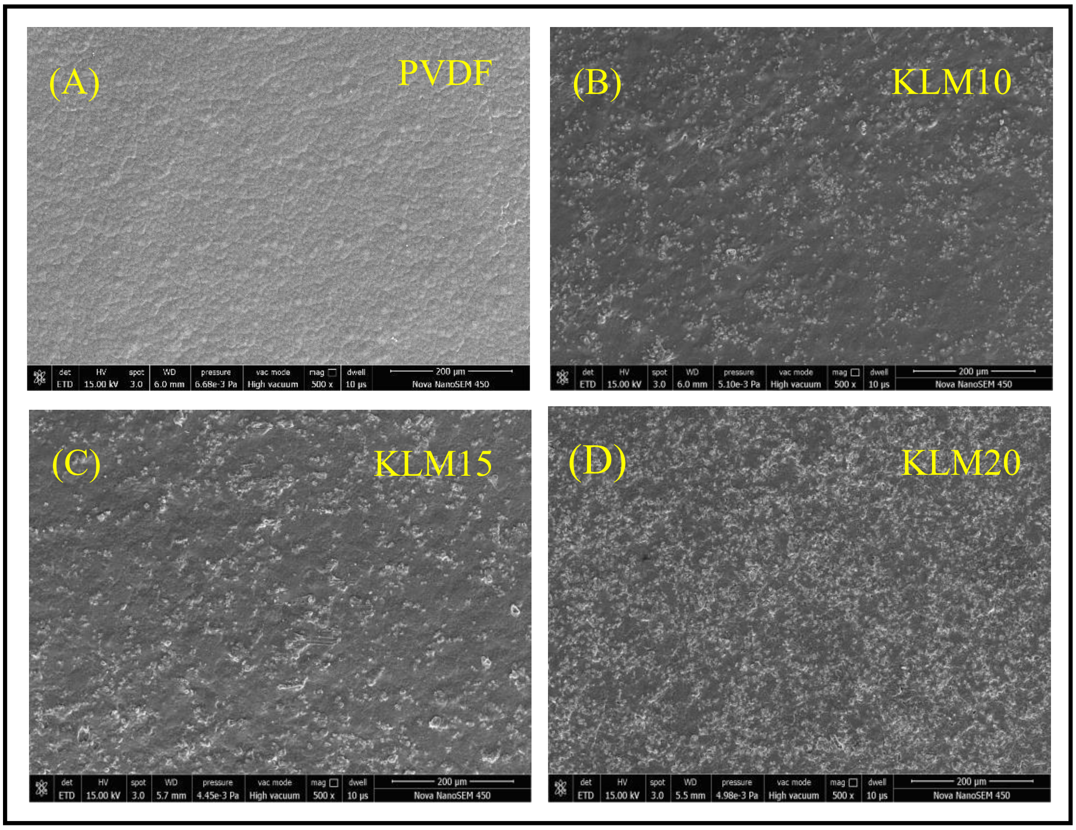

Figure 5: SEM graphs of KNN-Li/PVDF and MWCNT films with different weight percentage of KNN-Li

3.4 STUDY OF FOURIER-INFRARED SECTROSCOPY (FTIR)

The following **Figure 6** displays the (FTIR) of films of produced flexible polymer composite KLM films in the range of 700 – 1600 cm^{-1} at room temperature. The figure shows the locations of the α and β phases. FTIR analysis shows that all prepared films contain α and β phases.

The absorption bands at 783, 1404 cm^{-1} are assigned as the peaks of α phase of PVDF. And, the absorption bands at 838, 876, 1071, 1172 and 1232 cm^{-1} ae assigned as peaks of β phase of the PVDF.

The FTIR of the films were done to demonstrate the result of KNN-Li ceramic on the PVDF. The highest dipole moment in the prepared generator can be observed in the β -phase of the PVDF, which also plays a role in the piezoelectric performance of the device [27-32].

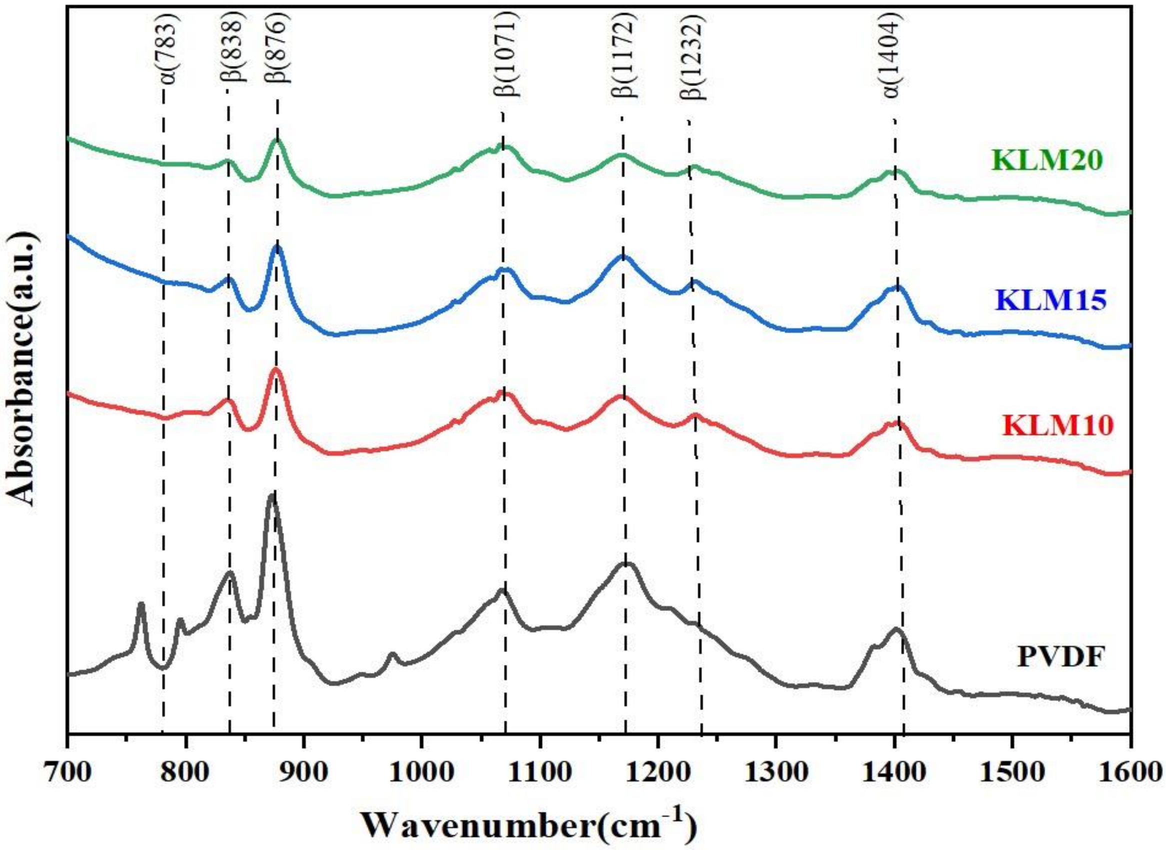

Figure 6: FTIR pattern of fabricated films with different weight percentage of KNN-Li in PVDF matrix and MWCNT.

3.5 PIEZOELECTRIC RESPONSE

The piezo response of fabricated piezoelectric generator and energy harvesting capability was studied by using finger tapping process. By continuously tapping on the prepared piezoelectric generators using hand. So, peak to peak open circuit voltage was observed on the screen generated by the prepared generators as pattern seen in the **Figure 7**. The open circuit peak to peak voltage values for different piezoelectric generator is listed in the table 1.

It can be clearly seen from the plots in the figure which indicates that the voltage first increases with increase in weightage of KNN-Li content in the PVDF matrix up to 10 wt.%

and after that it is observed that, it decreases with the further increment in the weightage percentage of KNNLi.

Hence, KNN-Li/PVDF/MWCNT films have a mainly KNN-Li/MWCNT concentrationdependent effect on particle nucleation in PVDF matrix. Table 1 shows that the maximum output voltage recorded is 31.1 V, which is approximately 6 times higher than that of pure PVDF film. Enhanced piezoelectricity in KNN-Li/PVDF/MWCNT composite films is due to the intrinsic piezoelectric properties of KNN-Li/MWCNT and uniform dispersion in PVDF. [34,35]

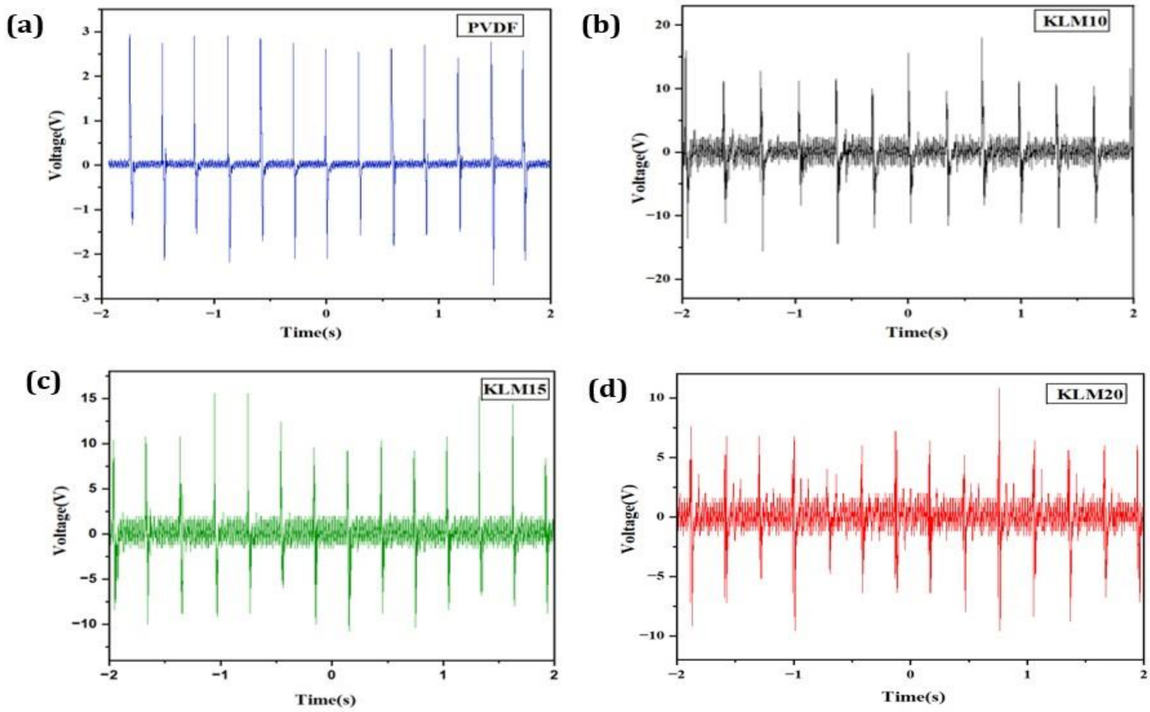

Figure 7: Voltage generation using KNN-Li/PVDF/MWCNT piezoelectric generator device containing different weight percentage of KNN-Li.

Table 1: Peak to peak output voltage obtained by applying force on the piezoelectric generator.

S. No.	Piezoelectric Generators	Peak to Peak to output voltage
1	Pure PVDF	5.5 V
2	KLM10	31.1 V

3	KLM15	24.6 V
4	KLM20	20.3 V

4. CONCLUSION

In this research, we successfully synthesized an environmental friendly lead-free piezoelectric composite film using lithium-doped (K,Na)NbO3 (abbreviated as KNN), MWCNTs, and PVDF. KNN-Li ceramics were made using the traditional ball milling technique and then sintered at various temperatures between 850 and 950 ºC. After examining how sintering temperature affects microstructure piezoelectric characteristics, densification, and so on, the following conclusions can be taken from the experimental data collected: According to the XRD data, the KNN-Li ceramic powder was effectively made. There was not an impurity phase found in any of the samples. After that, flexible films were fabricated. X-ray diffraction was then used to evaluate these films in order to verify their crystallinity, Fourier transform infrared spectroscopy (FTIR) to detect the presence of β-phase in the synthesized films, and to ascertain the crystalline morphology, scanning electron microscopy (SEM) was used. The prepared piezoelectric device's ability to harvest piezoelectric energy was examined by applying force on the surface of the device using finger tapping method. The voltage stored in the composite film can be used to operate small equipment that requires low voltage. In the Voltage graphs, we observed that 10 wt% films show more output voltage as compared to others i.e. 31.1 V. For better results or making good piezoelectric generator, material chosen play an important role. In this reported work, we have used KNN ceramic doped with Li because Li is lead free which is environment friendly. We improve the mechanical and electrical characteristics of KNN-Li ceramic by using MWCNT. The results demonstrate that material doping significantly enhances the β-phase.

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