NIILM University International Journal of Applied and Behavioural Sciences (IJABS)

ISSN:3048-9083 2025, Vol.02, Issue 01

An Approach Towards the Fabrication of Flexible Piezoelectric Composite Film of Ca-Doped ZnO/PVDF for Energy Harvesting Application

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Orchid Id: 0009-0008-6594-1924

DOI: https://doi.org/10.70388/ijabs250104

Received on Sep 20, 2024

Accepted on Nov 20, 2024

Published on Jan 01, 2025

Abstract

In the present time, there is a gradual increase in the demand for energy, especially green energy; therefore, significant advancements have occurred in the field of energy harvesting in recent years to meet the growing demand for portable, sustainable, and renewable energy sources. Corresponding gadgets are specifically engineered to capture and transform the surrounding energies into practical electrical energy. Using piezoelectric material, we are working to increase the energy output voltage from this material using different techniques. In this reported work, we synthesize the ZnO and Ca-doped ZnO (CaZ) powder with the help of the co-precipitation method calcined at 650° C. X-ray diffraction (XRD) confirmed the prepared ceramic powders' phase formation. The calcined ZnO and Ca-doped ZnO (CaZ) particles were mixed with PVDF to prepare flexible composite films of 5 wt. % with a thickness of~60 µm by drop cast method. Structural analysis of the fabricated flexible composite film was performed by XRD and Fourier Transform Infrared (FTIR) spectroscopy, which indicated the formation of the β- β-phase in the composite film. SEM images were used to analyze the composite film's morphology and structure. The fabricated devices' energy harvesting performance was measured with a shaker's help. Then, a voltage output is measured by making electrical connections with the flexible films. The voltage output is 3.76V, 18.9V, and 21.8 V, respectively, for PVDF, 5 wt. % of ZnO and CaZ fillers with PVDF can run various small electrical devices.

Keywords: Piezoelectric, PVDF, Composite films, Microstructure

Introduction

As humans develop in the global society, we need more and more energy to fulfill our requirements. The current energy problem, caused by a scarcity of fossil fuels, has prompted the Explore several renewable energy sources, including hydroelectric, wind, solar, and others. Mechanical vibration is an attractive source of ambient energy due to its convenient accessibility and compatibility with piezoelectric materials; it has the potential to convert mechanical stress energy into electrical energy. Following that, various efforts have been made to create ways to convert mechanical to electrical energy [1-5]. Several inorganic piezoelectric materials, including barium titanate (BaTiO3), zinc oxide (ZnO), and lead zirconia titanate (PZT) and others, have been extensively used in energy scavenging applications [6-10]. The first documented nanogenerator was an array of ZnO nanowires [11]. Later, other nanogenerators employing various additional piezo materials were reported to power small-size electronic devices. Having piezoelectric properties, polymers, such as poly(vinylidene fluoride) (PVDF) and its derivatives, are well-suited for overcoming the drawbacks of ceramic-based piezoelectric materials, particularly their susceptibility to breakage. These polymers are eco-friendly, compatible with living organisms, and easy to produce. The fluorine and hydrogen atoms in PVDF's repeating unit (-CH2-CF2-) form several polar and non-polar configurations, including α, β, γ, and δ phases [12]. Polar in nature, β-phase PVDF with all-trans conformation (TTTT) has superior piezoelectric characteristics, making it ideal for energy harvesting applications [13-16]. Furthermore, the copolymerization approach has resulted in several PVDF copolymers with comparable piezoelectric characteristics. The substitution of a hydrogen atom with an additional fluorine atom results in steric hindrance and modifies the potential energy of the polymer chains, rendering it appropriate for exclusively trans conformation [17-18]. However, as we compared them to ceramic properties, polymers have lesser piezoelectric capabilities, demanding the introduction of specific piezoelectric particles. The significant piezoelectric coupling factor of ZnO nanostructure makes it a highly researched semiconducting material. Furthermore, their lack of toxicity and ability to interact well with living organisms make them extremely valuable in the majority of energy-harvesting systems. The simplicity of changing and adding external features further broadens their uses. Various attempts have been made to improve the piezoelectric efficiency of nanogenerators manufactured from diverse piezoelectric polymer composites [19-25].

Research has demonstrated that utilizing non-ferroelectric ZnO in conjunction with piezoelectric polymers enhances the performance of piezoelectric devices. This combination

produces a flexible nanogenerator with a larger electrical output [26-30]. Research has focused on increasing polymer or filler qualities by chain modifications or dopant ion addition to nanofiller to enhance performance. Various piezoelectric nanofillers have been mixed with PVDF copolymers and terpolymers, while dopant ions and molecules have been used to modify ZnO nanostructures. These modifications aim to enhance the performance of piezoelectric devices [31-34].

A unique piezoelectric energy harvesting device was created using a straightforward technique, mixing PVDF polymer with calcium ion-doped ZnO(CaZ) nanoparticles that had not been described before. Ca-doped ZnO particles synthesized using the co-precipitation technique were used as a ceramic filler in the polymer matrix. Several crystallographic and morphological investigations were conducted to confirm the integration of calcium (Ca) into the crystalline structure of zinc oxide (ZnO) in the generated nanofiller. The CaZ/PVDF composite film was deposited by drop casting a solution and used as a thin active layer in a piezoelectric energy harvesting device.

Prior to manufacturing the ultimate device, an examination was conducted on the crystalline and morphological properties of the synthesized films. The piezoelectric performance of the films was evaluated in comparison to a pure PVDF film, and the underlying mechanism responsible for the enhanced performance of the films was also investigated. Ultimately, the sensing capability of the fabricated devices was assessed in the presence of fluctuating pressures.

2. Materials and Methodology

2.1 Synthesis of CaZ filler:

Zinc chloride and calcium chloride are utilized as precursors to synthesize stoichiometric $Zn_{(1-x)}Ca_{(x)}O$ (x = 0.05) nanoparticles using the co-precipitation approach, which has been previously employed in similar studies [35]**.** Zinc chloride and calcium chloride dissolved separately in de-ionized water at room temperature on a magnetic stirrer. The two solutions were then combined to form a homogeneous solution. After 1 hour of continuous stirring, a 0.1 M NaOH (Sodium Hydroxide) solution was added slowly to the zinc and calcium chloride mixture. The precipitates were collected via centrifugation and then washed repeatedly with de-ionized water and ethanol to remove any residual chemicals. The precipitate was dehydrated

in a hot air oven at a temperature of 70°C for an extended period of time and subsequently subjected to calcination at a temperature of 600°C for a duration of 2 hours in a furnace, resulting in the formation of Ca-doped ZnO particles. Zinc oxide particles were made using the same technique described above, excluding adding the calcium precursor calcium chloride.

2.2 Synthesis of Ca-doped ZnO/PVDF composite film

A precise amount of PVDF was dissolved in N'N'-dimethylformamide (DMF) and agitated using a magnetic stirrer at a temperature of 45 degrees Celsius for a duration of 2 hours in order to obtain a homogeneous and transparent solution. Subsequently, particles of $Zn_{(1-0.05)}Ca_{0,05x)}O$ were incorporated into the solution created earlier, with a concentration of 5wt. % relative to the polymer matrix. The mixture was then agitated for an additional 3 hours. Next, the evenly distributed solution was applied onto a pristine glass petri dish to create a composite film of Ca-doped ZnO/PVDF. The film was dried in a hot air oven at 80°C until the solvent had evaporated.

3. Material Characterisation

The crystal structure of the $Zn_{(1-0.05)}Ca_{(0.05)}O$ particles and composite films were analysed using an X-ray diffractometer (PAN analytical X'pert PRO). The experiment involved exposing the sample to radiation with a wavelength of 1.5406 Å, over a range of 2θ angles from 120° to 80° for powder and 10° to 80° for composite films. The morphology of the CaZ/PVDF composite films was analysed using scanning electron microscopy (SEM) with a Zeiss EVO40 apparatus from JNU, India. The effect of CaZ particles on composite film's phase crystallization was further studied using a Fourier transform infrared spectrometer (FTIR, Thermo Scientific).

4. Results and Discussion.

4.1 Analysing the structure and microscopic properties of CaZ ceramic powder.

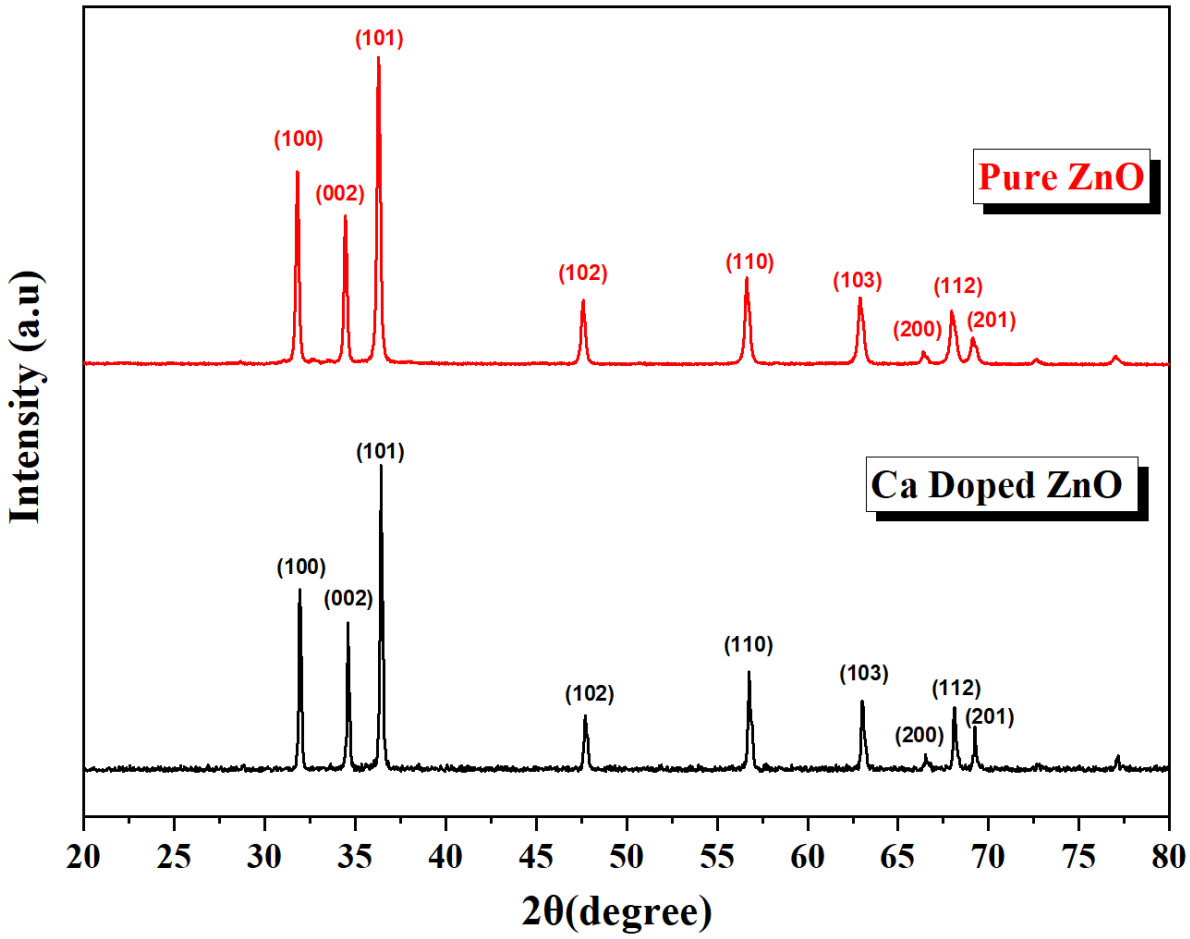


Fig. 1. XRD Analysis of ZnO and CaZ ceramic powder

Fig. 1 shows the powder X-ray diffraction patterns for both unmodified ZnO and Ca-doped ZnO (CaZ) particles. ZnO, a wideband semiconducting inorganic material, can exist in two primary crystalline forms: zinc wurtzite and zinc blende. The Wurtzite structure of ZnO, characterized by its two polar surfaces of Zn and O, generates a dipole moment and spontaneous polarization along the c-axis, which endows ZnO with piezoelectric properties [36]. These peaks align closely with the pure ZnO crystalline structure as referenced in the JCPDS database (card number: 361451), confirming the hexagonal wurtzite phase of ZnO [37]. The inclusion of calcium as a dopant does not significantly alter the diffraction pattern of the ZnO crystal structure. The absence of additional peaks suggests that Ca ions substitute Zn ions in the lattice points without disrupting the hexagonal wurtzite structure. However, the diffraction peak intensity for CaZ nanoparticles is lower than unmodified ZnO, indicating the successful substitution of Zn ions with Ca dopant ions [38].

4.2 Analysis of the structure of a composite film of PVDF and CaZ/PVDF

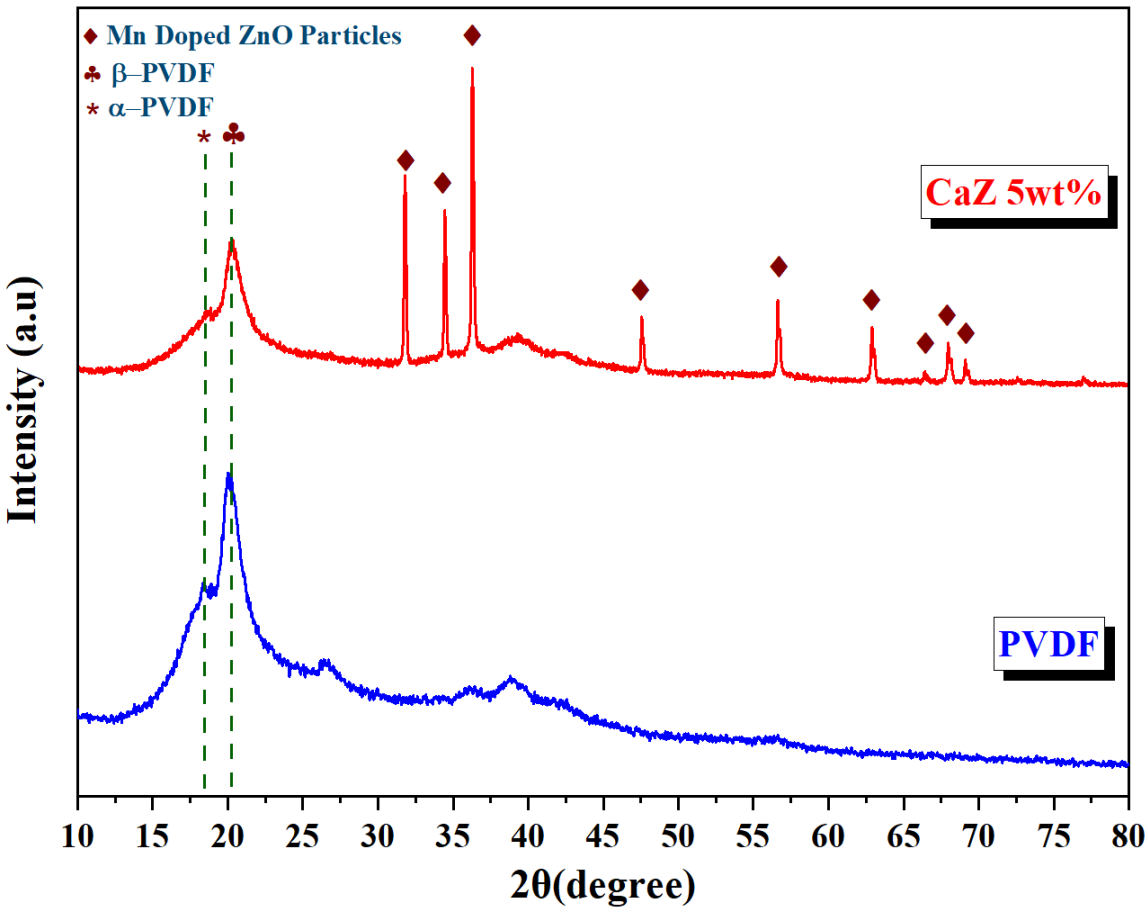


Fig. 2. The X-ray diffraction pattern of both pure PVDF and CaZ/PVDF composite film.

Fig. 2 displays the X-ray diffraction (XRD) patterns for pure PVDF film and a CaZ/PVDF composite film. In the pure PVDF film, both crystalline and amorphous diffraction peaks can be observed, highlighting its polycrystalline nature. A notable diffraction peak at 20.4° is attributed to the (110/200) planes of the electroactive polar β phase of PVDF. Additionally, a broad peak at 18.0° indicates the presence of the non-polar α-phase, specifically reflecting the (020) plane. Peaks at 35° and 41° correspond to the polar β-phase, representing the (001) and (201) planes, respectively [39]. In the composite film, the increased intensity at the 20.0° peak and the decreased intensity at the 18.0° peak suggest a higher content of the polar β-phase. The comparison of the 35° peak between the composite and pure films indicates that the composite film's diffraction pattern combines the polymer and the filler. The significant peaks between 30° and 36° in the CaZ nanofillers suggest that the pattern in this region of the composite film indicates the presence of CaZ within the polymer matrix. The presence of both the β-phase polymer peak and the CaZ filler peak after incorporating CaZ into the PVDF polymer suggests that the CaZ fillers minimally affect the polymer chain' crystallographic alignment [40].

4.3. Morphological characterization of CaZ/PVDF composite films

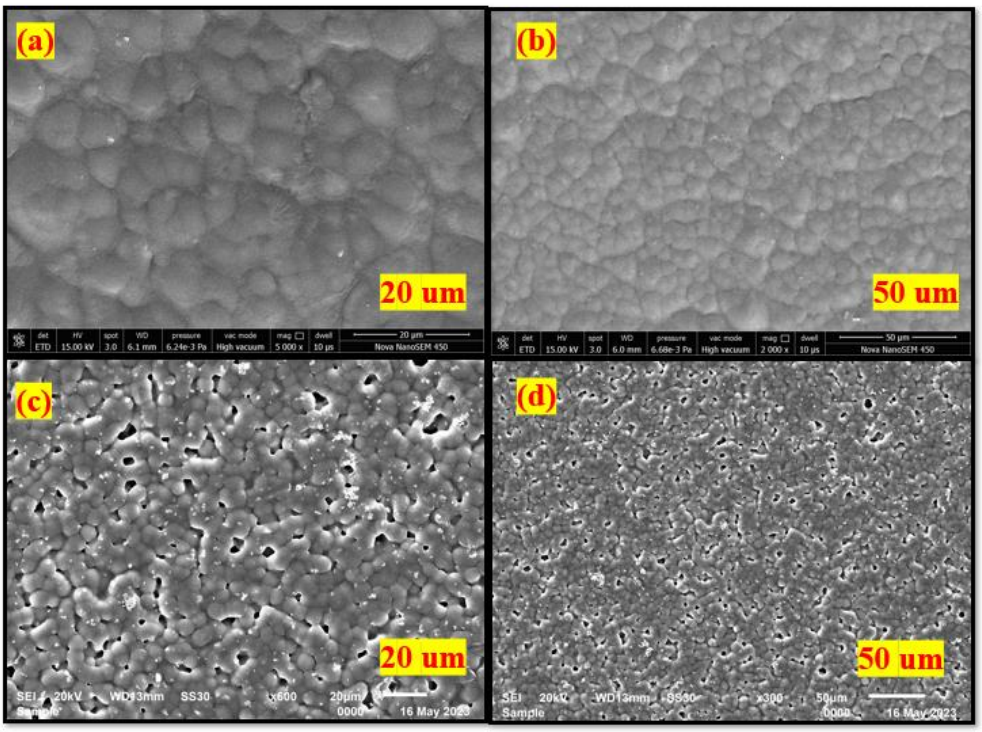


Fig. 3. Sem images at 20 µm and 50µm of Pure PVDF 3(a) and 3(b), 5 wt.% CaZ/PVDF 3(c) and 3(d)

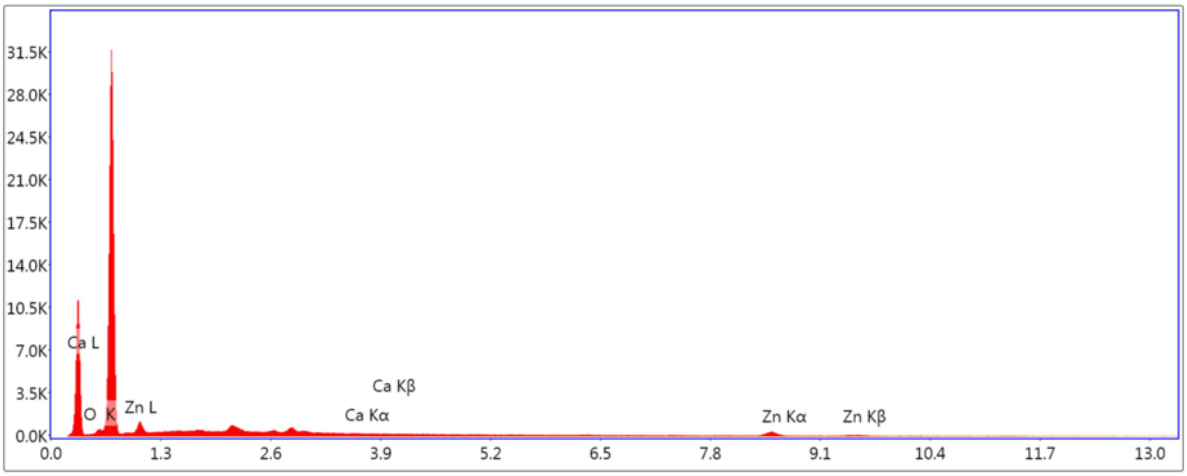


Fig. 4. EDS spectrum of the CaZ/PVDF composite film

Fig. 3 shows SEM images of the top surfaces of pure PVDF and CaZ/PVDF composite films. The pure PVDF film exhibits a smooth and flat surface, whereas the CaZ/PVDF composite film has a distinct surface texture. The air/solution interface of the composite film displays numerous spherical features, likely due to the presence of CaZ fillers [41]. The white regions

in the SEM image of the composite film indicate gaps between these spherical areas, while the small dot-like structures are the evenly distributed CaZ nanofillers on the polymer matrix surface [42]. Fig. 4 presents the Energy-dispersive X-ray spectroscopy (EDS) spectra for the composite film with 5 wt. % CaZ, showing peaks corresponding to Ca and ZnO, confirming their presence within the PVDF film.

4.4 Fourier transform-infrared (FTIR) spectroscopy studies.

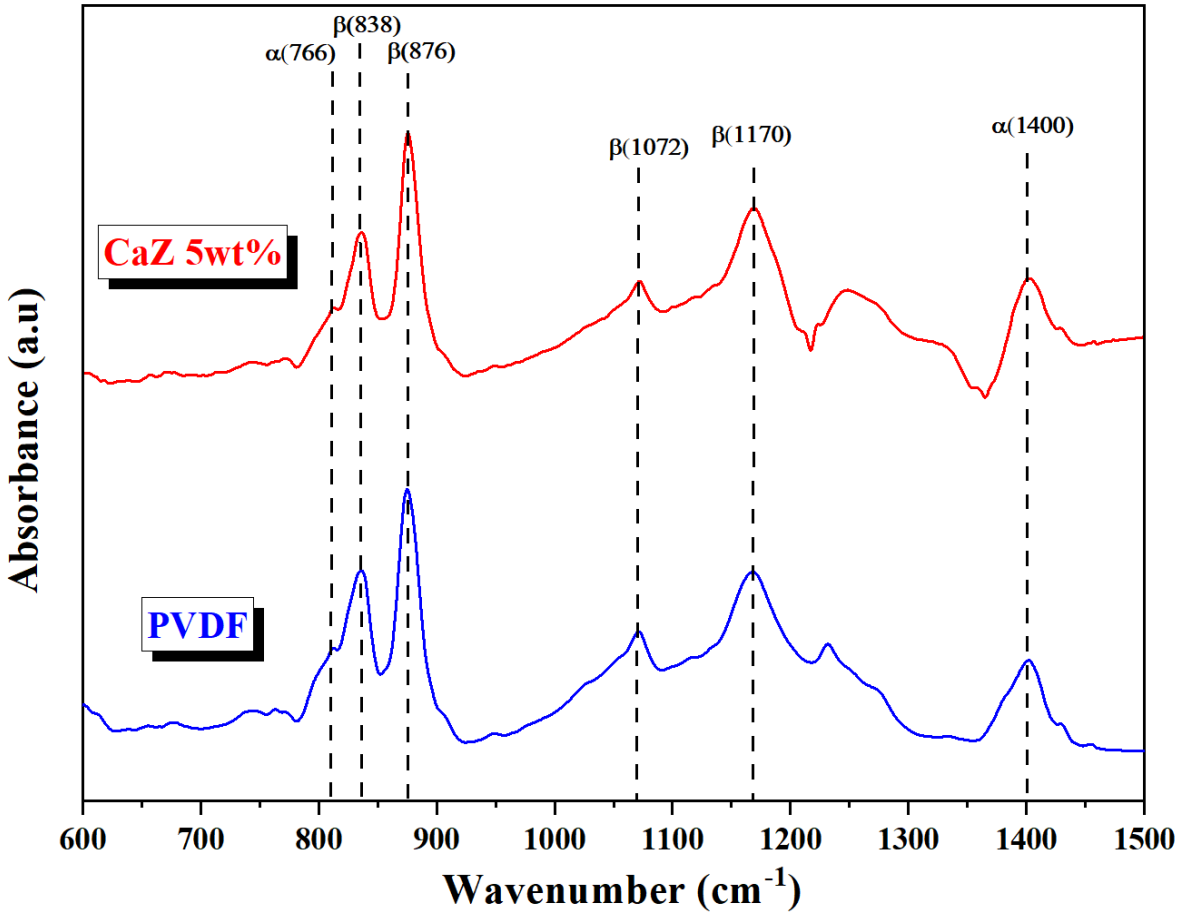
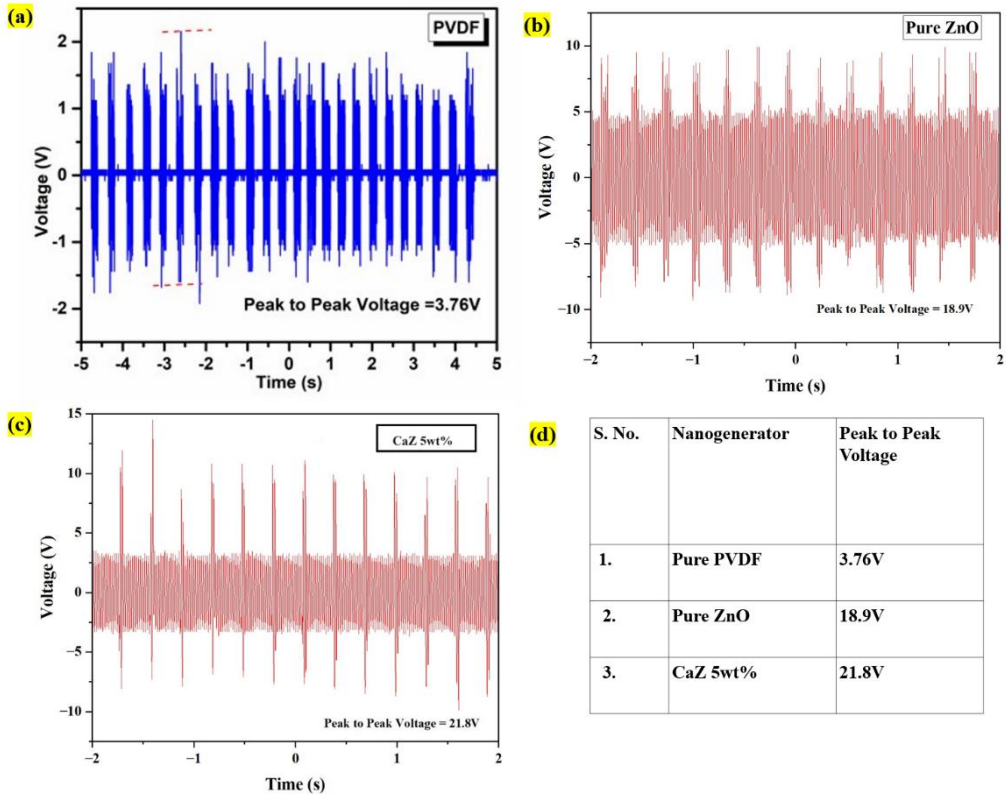


Fig. 5 Shows the FTIR spectra of pure PVDF film and a composite film of 5 wt.% CaZ ceramics in the PVDF matrix.

FTIR research was conducted on both the pure and produced composite films to examine the impact of CaZ ceramic particles on the crystal structure of PVDF. The Fourier Transform Infrared (FTIR) spectra of a pure Polyvinylidene fluoride (PVDF) film and composite films made of CaZ and PVDF were obtained at ambient temperature. The spectra were recorded in the region of 600–1500 cm^{-1} and are shown in Fig. 5. The FTIR spectra indicate the presence of both α and β phases in all produced films. The peaks corresponding to the α and β phases are indicated in Fig 5. The FTIR data obtained was consistent with the XRD data, indicating

the presence of the β phase of PVDF in both the pure PVDF films and the CaZ/PVDF composite films. The absorption bands seen at 766 and 1400 cm^{-1} are identified as the distinctive peaks of the α phase of PVDF [43-46]. Conversely, the absorption bands observed at 838, 876, 1072 and 1170 cm^{-1} are identified as the distinctive peaks of the β phase of PVDF [47]. In addition, compared to the pure PVDF film, the absorption peaks corresponding to the β phase of PVDF were strengthened in all the CaZ/PVDF composite films. This suggests that the incorporation of CaZ ceramic powder in PVDF resulted in an improved crystallization of the β phase of PVDF. The β phase of PVDF plays a crucial role in enhancing the piezoelectric performance of the generator.

5. Piezoelectric properties of fabricated PEG devices.



S. No.	Nanogenerator	Peak to Peak Voltage
1.	Pure PVDF	3.76V
2.	Pure ZnO	18.9V
3.	CaZ 5wt%	21.8V

Fig. 6. Voltage output of the (a) PVDF (b) ZnO/PVDF (c) 5 wt.% CaZ.

Fig. 6(a), (b), and (c) display the voltage responses of three different devices were evaluated: one made of pure PVDF, a second incorporating ZnO/PVDF, and a third consisting of a CaZ/PVDF composite film. Testing was conducted without using a rectifier. The inclusion of CaZ fillers in the composite film significantly increased the voltage potential compared to both the pure PVDF and ZnO/PVDF devices. As shown in Fig. 6(d) and summarized in a table, the peak voltages of the composite film devices are highlighted over a short time span. The

generated voltage reached a maximum of 21.8 V for the CaZ/PVDF, 18.9 V for the ZnO/PVDF and 3.76 V for pure PVDF PEG. This voltage generation is due to the film's crystal structure deformation under applied stress, leading to the alignment of electric dipoles.

6. Conclusion

We successfully synthesized CaZ powder and analysed it using XRD techniques. Additionally, composite films created through the solvent casting technique were examined with XRD and FTIR to investigate their crystalline properties. The results show that incorporating CaZ enhances the polar electroactive phase, leading to increased crystallinity in the fillers. The CaZ content within the PVDF matrix affects various device characteristics and improves piezoelectric performance. The voltage output of the PEG was measured by applying force to the film using a shaker, and the CaZ/PVDF PEG achieved a maximum voltage output of 21.8 V

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