# Electrical Studies of Lead Free Piezoelectric Nanbo$_3$ Ceramic Polymer Composites

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**Abstract**

**The sodium niobate (NN) polymer composites of different compositions were prepared through Solid state route and solution casting method. The prepared film samples were characterized by XRD to study the microstructure of the composites. The SEM studies on composite films revealed a better dispersion of ceramic crystallites in the PVA matrix. The dielectric constant and the ac conductivity of the composites with different concentrations at various frequencies (100 Hz–5MHz) were investigated. The results showed an increment of dielectric constant of ceramic-PVA composites with ceramic concentration and ac conductivity of the sodium niobate composites increased with increasing frequency. The electric modulus and complex impedance of the composites and ferroelectric behaviour were also calculated to understand the dielectric behaviour of the composites.**

## Introduction

The combination of a polymer material with flexible properties and a ceramic material with high dielectric constant to form a tailor made composite is a new approach towards dielectric composite materials [1]. The selection of appropriate polymer ceramic matrix can lead to the development of good composites whose dielectric properties can be varied over a range by changing composite concentrations [2]. These composites can be easily processed and can be used for various electrical and electronic applications [3].

The development of lead free piezoelectric materials can replace the toxic lead zirconate titanate is the base of this work. The barium titanate, alkali niobates based piezoelectric ceramics are promising because of their relatively high dielectric constants among the non-lead piezoelectrics. Alkaline niobate ceramics are considered a good replacement to toxic Pb-containing piezoelectric ceramics [4]. Sodium niobate ($NaNbO_3$ or NN) is an oxide with perovskite-type structure exhibiting antiferroelectric characteristics. Researchers have used NN for various applications due to its significant electrical properties. At room temperature, NN ceramic exhibits antiferroelectric nature [11–13], substituting Na–site with K [15] resulting in phase transition to ferroelectric nature which imparts piezo electric properties thereby finding application in the fabrication of high frequency devices [16]. In this study, Sodium niobate in different weight percentage was combined with PVA polymer to form NN/PVA composite films and its electrical properties were studied.

## Materials and Methods

The NN ceramics was synthesized by conventional solid state reaction technique. AR grade $Na_2CO_3$ and $Nb_2O_5$ were used for the preparation of NN ceramics.. The ingredients were well dried and thoroughly mixed using agate mortar and pestle in acetone medium for1 hour and then it was dried. The obtained powder was calcined at 900 ˚C for 4 hours [5-7]. The PVA mixed with 50 ml of hot distilled water was continuously stirred. The NN of different weight percentage was added to the above cooled PVA suspension and this gel type solution was casted on to a glass substrate and allowed to dry at room temperature. The composite films of NN/PVA of different weight percentage was prepared [8]. The prepared NN/PVA composites were characterised using XRD and SEM.

## Results and Discussion

**XRD Analysis:** The XRD pattern of the NN/PVA composites with different ceramic concentrations 10%, 30% and 50% were analyzed to study the influence of the inclusion of the ceramic particles in polymer matrix which is shown in Figure 1. The phase of the obtained sodium niobate was determined to be orthorhombic [9, 10]. The crystallite size was found to be almost same in all compositions and The ceramic did not undergo any transformation during the composite preparation and the lattice parameters of the composites were found to be almost same. XRD of composites did not exhibit any other additional peak other than that of the parent material[11]. With the changing concentration of NN , the peaks were slightly shifted to the higher side.

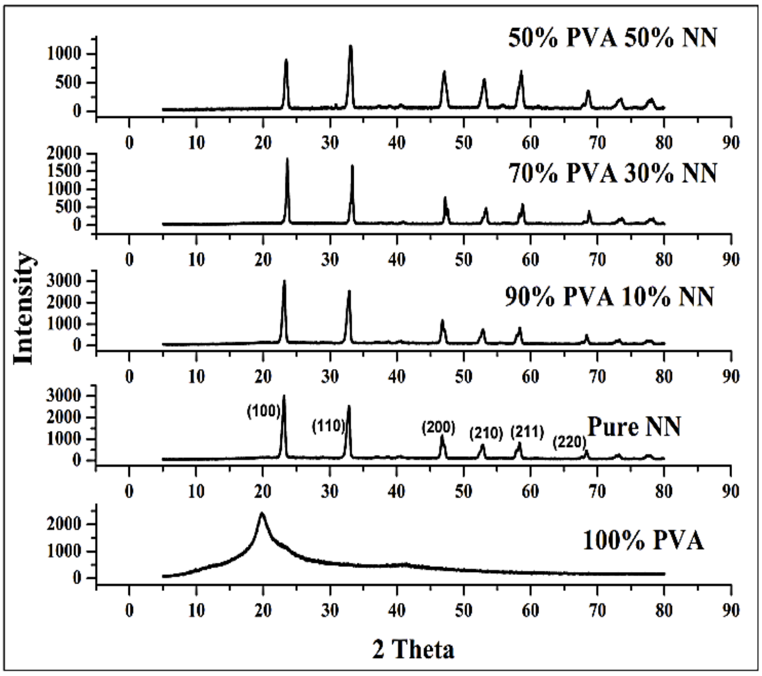



**Figure 1: XRD of NN/PVA in different weight percentage**

**SEM:** The SEM images gives morphological information of NN/PVA which is shown in figure 2**.** From SEM micrographs of the NN/PVA composites with different volume fractions of NN ceramics, the black region refers to PVA matrix and the gray particles to the calcined NN ceramic powders.

In all NN/PVA composites the ceramic particles appeared to be well dispersed in the polymer matrix without any agglomeration. The properties of the composite depends on the phase connectivity, weight percent of ceramic, [11]. The ceramic powder is evenly surrounded by PVA matrix showing a 0-3 type of connectivity.

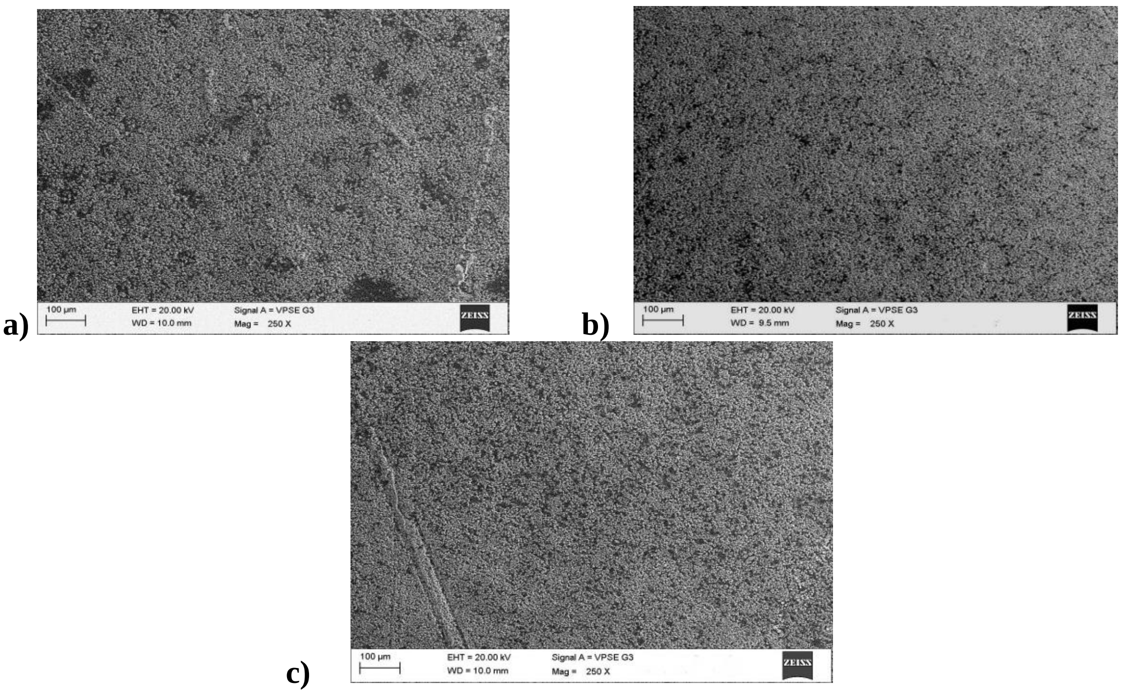
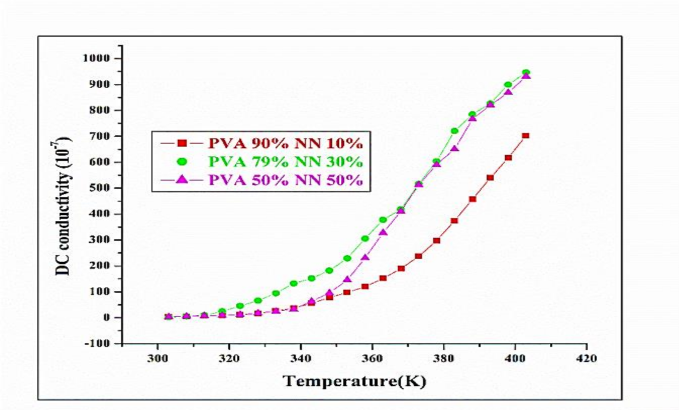



**Figure 2: SEM images of NN in PVA matrix (a) 90:10 b) 70:30 c) 50:50**

**Dc Conductivity Studies:** Figure 3 shows $\sigma_{dc}$ behaviour with inverse of temperature, which gives the value of activation energy for electrical conduction of NN/PVA composites, which was calculated by Arrhenius law. The value of activation energy was calculated from the slope of figure 3. This result indicates the occurrence of conduction mechanism in material due to oxygen vacancies or hopping of electrons [12]. The dc conductivity observed at higher temperature may be due to motion of oxygen vacancies across the grain-boundary. The calculated activation energy was 0.285eV for 10%, 0.263eV for 30% and 0.329eV for 50% inclusion of NN filler**.**



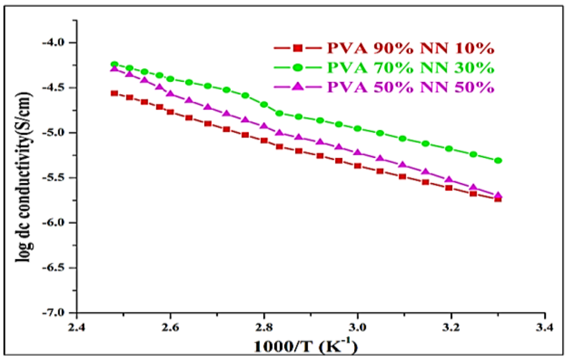
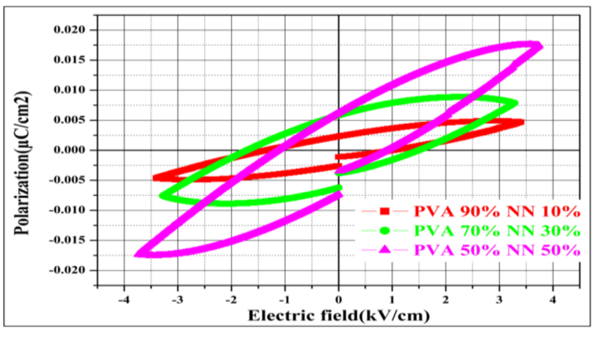



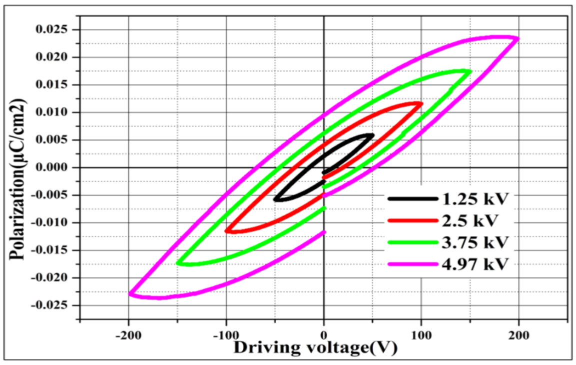

**Figure 3: Variation of dc conductivity with temperature.**

**Ferroelectric and Piezoelectric Studies:**When compared the hysteresis loops of all NN composites (figure 4), 50% NN composite exhibits a better saturation loop comparitively. When the field was increased, the composite breaks down and a fully complete saturated loop could not be acquired . A fully saturated loop shows that the domains are fully switched and aligned with the direction of the applied field in both directions. In ferroelectric ceramics, the crystallite grains are oriented randomly and they contain several ferroelectric domains(12). As the domains in one grain tries to switch under an applied electrical field, they are stopped by differently oriented neighboring grains, and so the coercive field Ec of ceramics is found to be much higher than those of single crystals [13,14].

The hysteresis behaviour of NN composites were investigated. The P-E hysteresis loops shows better saturation on increasing the weight of NN in the composite matrix. The measured parameters are listed in table 4.




a)




b)

**Figure 4: a) P-E hysteresis loop for NN/PVA composites (b) P E loop of 50% NN inclusion at different field**

**Table 1: Ferroelectric parameters of NN composites**

| Composites | $P_{sat}$ (μC/cm2) | $P_r$ (μC/cm2) | $E_c$ (kV) | Loop area (μC/cm2·volts) |
|---|---|---|---|---|
| 10% NN | $4.71\times10^{-3}$ | $2.31\times10^{-3}$ | 0.92 | 0.92 |
| 30% NN | $7.85\times10^{-3}$ | $5.82\times10^{-3}$ | 1.52 | 2.26 |
| 50% NN | $1.74\times10^{-2}$ | $6.21\times10^{-3}$ | 0.75 | 2.54 |

The hysteresis loops of all composites at an applied voltage at around 4 kV/cm were not saturated due to the non-piezoelectric polymer NN particles. The piezoelectric constant ($d_{33}$) values of NN/PVA composite samples were noted. The piezoelectric studies shows $d_{33}$ of composites vary from 2 pC/N to 8pC/N. On comparison the maximum value of $d_{33}$ was found for 50% of filler content in the composites.

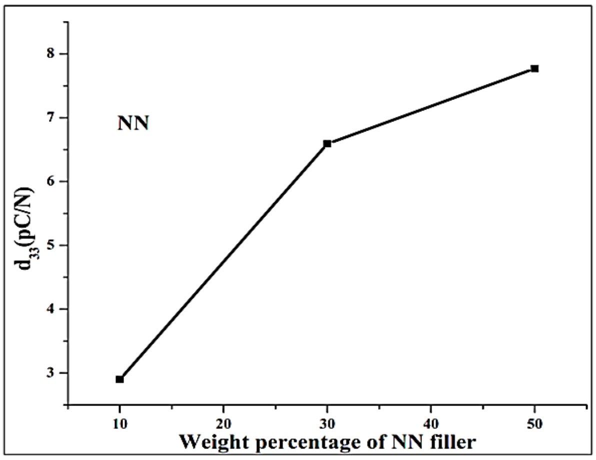



**Figure 5: Variation of d33 values with weight percentage of NN ceramic in NN/PVA composites.**

**Conclusions**

The XRD patterns of the PVA/NN composites showed a orthorhombic phase. NN/PVA was synthesized through Solid State Reaction technique. XRD pattern of NN/PVA shows unchanged peak positions in composites of all concentrations. No additional peaks were observed other than that in parent material. The crystallite size is observed to be less than 100 nm. The morphological studies confirmed 0-3 connectivity pattern of the composites with the homogeneous distribution of the NN ceramic particles in the PVA polymer. The composite with 50% ceramic exhibited values of the dielectric constant 137 at 1kHz at RT and $d_{33} \sim 8$ pC/N. The obtained results suggests that PVA/NN composite with 50% ceramic is suitable for embedded capacitor and piezoelectric applications.

## References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