

Ferroelectric Properties of Potassium Nitrate-Polymer Composite Films

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ABSTRACT

The Ferroelectric, Dielectric, and Raman studies of Potassium Nitrate (KNO₃): Polyvinylidene fluoride (PVDF) composite films have been studied. The composite film shows the largest value of remanent polarization (P_r) in 50 wt. % composition. The ferroelectric phase (phase-III) of potassium nitrate in the composite films shows the nature of ferroelectricity up to room temperature using dielectric measurements. Raman spectroscopy of potassium nitrate (KNO₃) composite films indicates the coexistence of ferroelectric phase (phase-III) with paraelectric phase (phase-II). Results of Raman spectroscopy can be attributed to the predominant presence of ferroelectric phase (phase III) in the composite films at room temperature. The current-voltage (I-V) characteristic shows the polarization current, which is the nature of ferroelectricity in the composite films.

Keywords: Ferroelectricity, Potassium Nitrate, Dielectric Properties, Ferroelectric Polymers, Composite Films.

INTRODUCTION

In the recent past, remarkable progress has been made in the field of ferroelectric materials, especially in the area of memory devices¹. The current progress of ferroelectric thin-film material and its micro- and nanocomposites in thin films/layers form²⁻⁶ have attracted the attention of the research area

all over the world, because of the advance properties of ferroelectric materials such as nonvolatile random access memories (NV-RAMs), ferroelectric random access memories (Fe-RAMs) and dynamic random access memories (DRAMs)^{1,5-8}. Now a days the main focus of current research is towards the developments of ferroelectric nanocomposites, nanotubes, nanowires and nanodots^{1,9-14}.

GENERAL BACKGROUND

Many ferroelectric materials, such as, barium titanate (BaTiO_3), barium strontium titanate (BST), lithium niobate (LiNbO_3), lead zirconate titanate (PZT), strontium bismuth tantalate (SBT), strontium barium niobate (SBN) and tri-glycine sulphate (TGS) etc, have been studied in a variety of forms like, single crystal, thick and thin film for the use of these materials in memory devices for low voltage operation¹⁰⁻¹². Generally the ferroelectric materials have very high coercive field (~few kV/cm). Therefore, it is necessary to fabricate these materials in thin film/layer form. These ferroelectric materials are usually fragile and show difficulties for fabrication in thin layer form for low voltage operation^{13,14}.

PROPERTIES OF POLYMER-FERROELECTRIC COMPOSITE FILMS

The ferroelectric- polymer composite materials are emerging as a new class of electronic and dielectric materials¹⁻⁴. The ceramic-polymer composite with ferroelectric properties combines many useful properties of the polymer and ceramic such as flexibility of the polymer and electro activity of the ceramic to produce large area devices with reasonable mechanical strength. Furthermore, the composites made of electro active ceramics and polymers are suitable for many applications since they can be easily prepared in a variety of shapes. The composite materials have been processed using mixtures of ceramic as filler in a matrix of polymer, where the fillers are included in the matrix in order to modify its physical properties over a large range. The ceramic fillers such as PZT, BaTiO_3 , and PbTiO_3 in PVDF with different doping have been produced in the past^{15,19}.

Figure 1 shows the lay out of ferroelectric-polymer composite films.

The composites in the form of films/layers are becoming important due to application in large area devices operated at low voltages^{1,6,7,10-13}. Among the composite studies, the simplest type is the 0-3 connectivity, which consists a three-dimensionally connected polymer matrix loaded with ferroelectrically active ceramic particles. One of the most attractive features of the 0-3 design is its versatility in fabricating a variety of geometric forms including thin films/layers and certain molded shapes.

PURPOSE OF THIS STUDY

This paper reports investigations carried out on a potassium nitrate/polyvinylidene fluoride composite having 0-3 connectivity in which the KNO_3 particles are not self connected but the polymer phase play a crucial role in three dimensions in this composites. It has been confirmed by dielectric, and (P-E) loop characteristics of the composite layers. The present research work is based on the experimental study of the ferroelectric composite films/layers. We have prepared composite layers of KNO_3 and polyvinylidene fluoride to obtain ferroelectric phase (phase-III) of KNO_3 at room temperature. In the present study, the presence of the ferroelectric phase (phase-III) of KNO_3 in the composite layers has been investigated using dielectric measurements and ferroelectric hysteresis loop behaviour. The electrical conductivity behaviour with temperature (heating/cooling modes) shows the existence of phase transformations in the composite. The dielectric constant variations with temperature were also investigated and correlated with the ferroelectric hysteresis curve. An attempt is made to establish relationship amongst results of various experiments.

FERROELECTRIC MATERIAL

Potassium Nitrate (KNO₃): Before going into the experimental details, we should know about the background and structure of KNO₃. It has been known that KNO₃ exists in one of several crystallographic phases depending on external state variables¹⁶⁻¹⁹ as shown in *Figure 2*.

Only one phase, called phase-III, this is ferroelectric and has many applications in the area of ferroelectric memory devices. The creation of phase-III of KNO₃ is due to a small shift of 0.55 Å of the nitrate groups along the c-axis from the centre of the unit cell, which creates a dipole moment as shown in *Figure 3*.

This ferroelectric phase (phase- III) of KNO₃ is twisted upon cooling. This ferroelectric phase (phase-III) exists- for pure bulk materials- only between about 124°C and 110°C, upon cooling from another rhombohedral phase-I at atmospheric pressure²⁰. Ferroelectric Phase III in KNO₃ would be of technological interest if it is stable at room temperature²¹⁻²⁷. Thus we have prepared the thin composite layers of potassium nitrate to obtain the ferroelectricity at room temperature.

POLYMER

The nature of the polymer in the fabrication the composite can play key role in the modification of the ferroelectric properties^{3,4, 19}. Broadly speaking, polymers can be divided in two categories viz., polar and nonpolar. The polar polymers can further be subdivided into two categories viz., ferroelectric and nonferroelectric. *Figure 4* shows the classification of the polymer phases.

Poly (vinylidene fluoride): PVDF is well-known semi crystalline ferroelectric polymer and has been studied by many workers¹⁻⁴. The amorphous phase occupies about 50% of the

polymer volume. It is clear that the amorphous part itself does not contribute to the residual polarization, but nevertheless, plays an important role in the ferroelectric polarization build-up in the ferroelectric crystallite³. Poly (vinylidene fluoride) (PVDF) has been intensively investigated because of its interesting ferroelectric properties and technological applications. PVDF can exist in several crystalline phases^{3,4,19}. Of the five known phases, the α - and β -phases are most common. The α - form, is stable and arises usually from the melt when PVDF crystallizes in quiescent conditions. The form II is monoclinic and the unit cell of form II structure has no net dipole moment. Thus PVDF of form II structure may not be expected to be ferroelectric and piezoelectric⁴.

(a) Form I (β -phase): The β -phase is all-trans planar zigzag conformation with the dipole moments perpendicular to the chain axis. Form I has an orthorhombic structure and belongs to the space group Cm2m (C2v14) with lattice constants, $a=8.58\text{\AA}$, $b=4.91\text{\AA}$ and $c=2.56\text{\AA}$ (chain axis). The dipoles of the monomer units in the polymer chain backbone are aligned in such a way that self-cancellation among them does not occur and therefore spontaneous polarization occurs. The β -phase PVDF is a polar phase associated with the highest piezo-, pyro and ferroelectric properties^{3,4,19}.

The magnitude of the dipole moment for each monomer unit is $7 \times 10^{-30}\text{ C m}$ (2.1D). Assuming a rigid dipolar model, the spontaneous polarization of a single crystal of the form I type PVDF will be $13\text{ }\mu\text{C}/\text{cm}^2$. The typical values of polarization and coercive field are $2.5\text{ }\mu\text{C}/\text{cm}^2$ at 200 MV/m have been obtained from the ferroelectric hysteresis loop measurements⁴.

PROCESS

Experimental Details and Fabrication

Process of the Composite Films: Purified and vacuum dried potassium nitrate powder of Merck India and polyvinylidene fluoride (PVDF) powder of Aldrich U.S.A were used for preparation of the composite layers. The fine powder of KNO_3 crystals was filtered through standard sieves [mesh No.240 (particle size $\approx 60 \mu\text{m}$)]. The purified powder of KNO_3 (50% by weight ratio) was mixed in PVDF powder. The powder mixture was kept in a stainless steel die in the melt press/hot press machine. The mixture was heated up to temperature 218°C (heating rate $2^\circ\text{C}/\text{min}$) and then a stress of $250 \text{ Kg}/\text{cm}^2$ was applied for 30 second. The temperature of die was brought down slowly to room temperature and then the pressure was released. *Figure 5* shows the fabrication process of the ferroelectric-polymer composite films.

The same method of preparation was adopted for other compositions of the composite layers. The thickness of composite layer measured was to be about 30-50 μm . The circular indium electrodes having an area of $125.6 \times 10^{-3} \text{ cm}^2$ were vacuum ($\approx 10^{-5} \text{ mbar}$) deposited on both the surfaces of the sample. This sample was poled at temperature 125°C and applied input is 5V of frequency 50 Hz. The dielectric measurements were carried out using Keithley 590 C-V analyzer at frequency 100 KHz.

RESULTS AND DISCUSSIONS

Temperature Dependence of Remanent Polarization (P_r): The ferroelectric hysteresis loop characteristics of the composite films were recorded using a standard and modified Sawyer-Tower circuit along with a digital storage oscilloscope connected to a computer

as shown in *figure 6*. The temperature dependence ferroelectric hysteresis loop characteristics were investigated for 50 wt.% KNO_3 : PVDF composite layers in the temperature range 25°C to 140°C . *Figure 6* shows three typical P-E hysteresis loops taken at three different temperatures 25°C , 103°C , and 120°C . The reduction in the area of the hysteresis loop, remanent polarization and coercive field with temperature can be clearly seen in this figure.

The temperature dependence of the remanent polarization in 50wt.% KNO_3 : PVDF composite layer was studied in the temperature range from 25°C to 140°C . *Figure 7 (a) & 7 (b)* shows the trend of polarization dependence and area of the hysteresis curve as a function of temperature in the composite layer. It is clear from these characteristics that the ferroelectric behaviour of the composite layers has disappears about 128°C and very near to the curie transition temperature of the potassium nitrate²¹⁻²⁵.

It is further seen that with the increase in temperature, the value of P_r reduces. However, P_r shows slight decrease from room temperature up to 80°C , and registers a sharp decrease in the temperature range 80°C to 128°C . *Figure 7 (b)* shows the beaviour of declination of area of the hysteresis loop with temperature. This curve also supports the nature of ferroelectricity in the composite layer. It has been observed in many ferroelectric materials that the ferroelectricity usually disappears above a certain temperature called the Curie transition temperature T_c . Above T_c the material is known to be in paraelectric state. This is also observed in the KNO_3 : PVDF composite layers. This seems to be related to the ferroelectricity of phase-III of KNO_3 ²⁵.

ROLE OF FERROELECTRIC POLYMER IN THE COMPOSITE

One important reason to choose the ferroelectric polymer PVDF in the composite layers is that the presence of PVDF can also reduce the fragile nature and enhance cohesion to the composite layers because both the materials have almost same physical properties. A good dispersion of potassium nitrate particles in to the PVDF is responsible for the polarization in the field direction of each individual KNO₃ particle to obtained the ferroelectricity at room temperature. Another reason could be that PVDF is a ferroelectric polymer with polarized phase. It may be speculated that there is some sort of the beneficial coupling by the individual polarized particles of both the materials after the application of electric field to improve the ferroelectric properties at room temperature. The polarization of PVDF matrix can provide electric field to the neighboring KNO₃ particles and probably enhance the transition of phase –I to phase –III on cooling. These observations are in accordance with the model suggested by Westphal²², whereas KNO₃ particles of ferroelectric phase-III enhance conversion by electric polarization interaction. In case of pure PVDF the ferroelectricity is not possible in this field range as measured in the present composite layers.

THERMAL CONDUCTIVITY MEASUREMENTS

Temperature Dependence of Conductivity:

The value of electrical conductivity of the composite layer was obtained by using the relation:

$$\sigma = [Id.(AV)^{-1}] \quad (1)$$

where d is the sample thickness, A is the area of the electrode on the composite layer and I is the current flowing at applied voltage of 10V. It was evaluated as a function of temperature for 50wt.% KNO₃ composite layer for the heating and cooling modes ($\approx 5^\circ\text{C}/\text{min}$). The dc conductivity variation with temperature has been found to provide knowledge of the phase transition in KNO₃²³.

Figure 8 shows the behaviour of the conductivity as a function of temperature. Initially, the composite is assumed to contain mixed phases namely phase -II and phase -III as revealed by the X-ray diffraction (XRD) studies²²⁻²⁶. The phases -II and phase-III seem to coexist up to about 77°C. During the cooling process the ferroelectric phase remains upto room temperature. The Raman studies on KNO₃, in the past²³, also observed the phase transformation temperature ranges and coexistence of phases-II and phase-III. The thermal expansion studies on KNO₃ films showed a transition peak for phase -III to phase -II²²⁻²⁶. The composite may contain crystallites of different sizes and in all probability some of the phase -III small crystallites may convert to phase -II. Therefore possibly the phases -II and phase-III coexist in the lower temperature range.

The early study of X-ray diffraction experiments also supports the existence of crystallite distribution in the composite²⁴. The Differential Scanning Calorimetry (DSC) experiments for endothermic reaction also show transition peak of phase- II to phase I at 130°C during heating²². On the other hand, the DSC experiments show peak of phase I to phase -III in the temperature interval 118 to 105°C²². This temperature range of the exothermic DSC experiment is almost the same as from that observed from polarization

experiment shown in figure 7. This may be due to different nature and sensitivity of the experiments; however, both the experiments do show the existence of phase transitions in the composite sample. The conductivity activation energy E_A was evaluated using the relation:

$$\sigma = \sigma_0 e^{-\left(\frac{E_A}{kT}\right)} \quad (2)$$

The activation energies calculated for different phases during heating and cooling modes are shown in Table I. These are lower than observed by other workers²³ in pure KNO_3 .

DIELECTRIC PROPERTIES

Figure 9 and Figure 10 shows the variation of the dielectric constant and dielectric loss ($\tan \delta$) with temperature in the composite layers at frequency of 100 KHz. From this we can find out the phase transition. The behaviour of dielectric constant in a single crystal of KNO_3 was reported by Man Singh & Smith²³ at the same frequency, the value of dielectric constant is strongly dependent upon the transition of paraelectric to ferroelectric phase (I \rightarrow III) during cooling process. The value of dielectric constant in the composite layers showing such type of transition and ferroelectric phase –III exist up to room temperature. The value of dielectric constant increased ~2 to 4 times from that at room temperature in the composite layer; this is comparable with KNO_3 ^{16,17,14}. The dielectric constant shows two times increase in the temperature range 130°C-165°C. This corresponds to the transition from phase (II \rightarrow I) with transition temperature 130°C during heating cycle and support the nature of figures 6 & 7. The DSC curve of KNO_3 : PVDF composite also show a peak in this temperature range during heating cycle. This shows that temperature dependence of dielectric constant

has a correlation with the DSC transition peak²².

During the cooling cycle, the dielectric constant shows a sharp drop in the temperature range 128°C \rightarrow 102°C. On the other hand the exothermic DSC curve shows a peak at 115°C, which was attributed to the transition from phase-I \rightarrow phase-III of KNO_3 in the composite. Therefore, in all probability the dielectric constant variation in the temperature range 128°C \rightarrow 102°C in the cooling mode can be related to the phase change I \rightarrow III and its stable up to room temperature as shown in figure 9.

RAMAN SPECTROSCOPY

In order to understand the nature, stability, and existence temperature width of phase I, phase II, and phase III (ferroelectric phase), in KNO_3 a detailed Raman investigation was carried out²⁶⁻²⁸ with various heating/ cooling rates, repeated thermal cycles, and different preheating temperatures. The increase in the existence temperature width of the phase III of KNO_3 was observed with the increase of heating/ cooling rate but the repeated thermal cycling reduced it. The ferroelectric phase III to phase II transformation extended to a lower temperature in the cooling process when the sample was subjected to a higher preheating temperature²⁶⁻²⁸.

Raman Spectroscopy in the composite films of KNO_3 : PVDF Composite Films

Figure 11 shows the Raman spectra of 50 wt. % KNO_3 : PVDF composite films at room temperature. Both phases were observed at different Raman shift in the composite films. PVDF –II form was also observed at Raman shift 59 cm^{-1} . The Raman spectroscopy in

KNO₃ at room temperature was also observed by Scott *et al.*²⁶⁻²⁸. The existence of phase-III, and phase-II in the composite films by Raman spectroscopy as shown in Table 2.

and for y-axis 0.5V/cm respectively. The existence of the current – voltage (I-V) characteristics in the composite films was shown in *figure 12*.

Current-Voltage (I-V) characteristics

The current – voltage (I-V) characteristics was observed in the 50wt. % KNO₃: PVDF composite films with the help of OMNIGRAPHIC 2000 X-Y recorder. The voltages were scans in the x – axis 2.5 V/cm

The maximum current was found where the voltage >3.5V. The current increases up to 3.5 V and then decreases above this voltage. This could be due to the saturation of the polarization beyond peak voltage hence the current falls down. Therefore, the polarization current is predominant in these films.

Table: I

Activation energies for different phases during heating and cooling modes are shown in Table I.

Modes (Heating / Cooling)	Temperature Range (°C)	Phases	Activation Energy (eV)
Heating	84~128°C	II	0.725 eV
Heating	53~77°C	II+III	0.460 eV
Cooling	130~104°C	I	0.250 eV
Cooling	77~55°C	III	0.785 eV

Table: II

Table 2- Raman shift at different phases of KNO₃ in the composite films

Temperature (°C)	KNO ₃ Phases	Thickness	Wave No. Shift (cm ⁻¹)
22°C (Room temperature)	KNO ₃ – (II)	35 μm	50,55,137
	KNO ₃ – (III)		95, 114,119,
	PVDF (Form-II) α- phase	35 μm	59

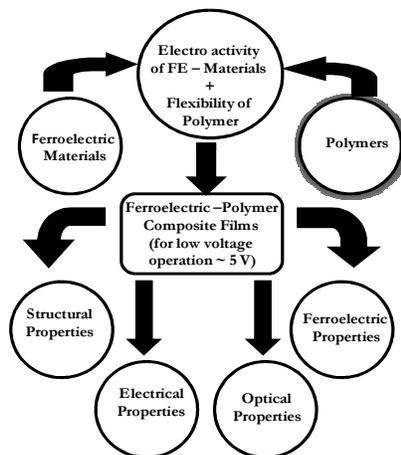


Figure 1: Block diagram of ferroelectric-polymer composite films

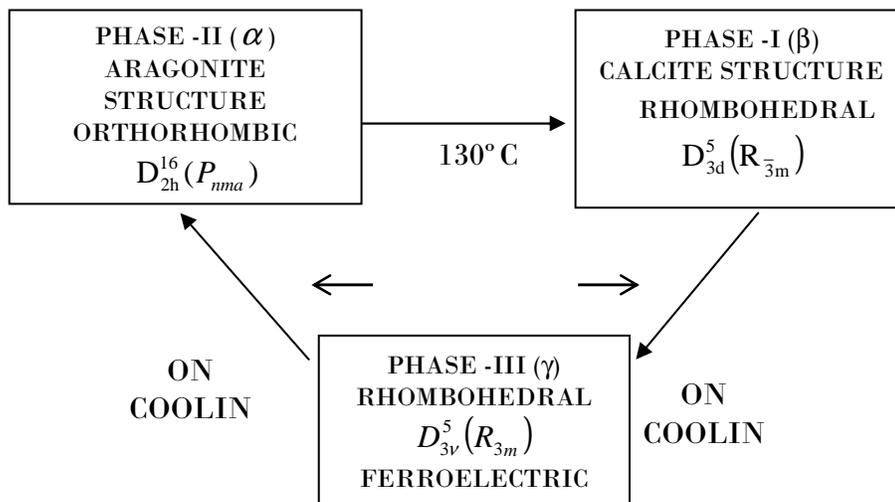
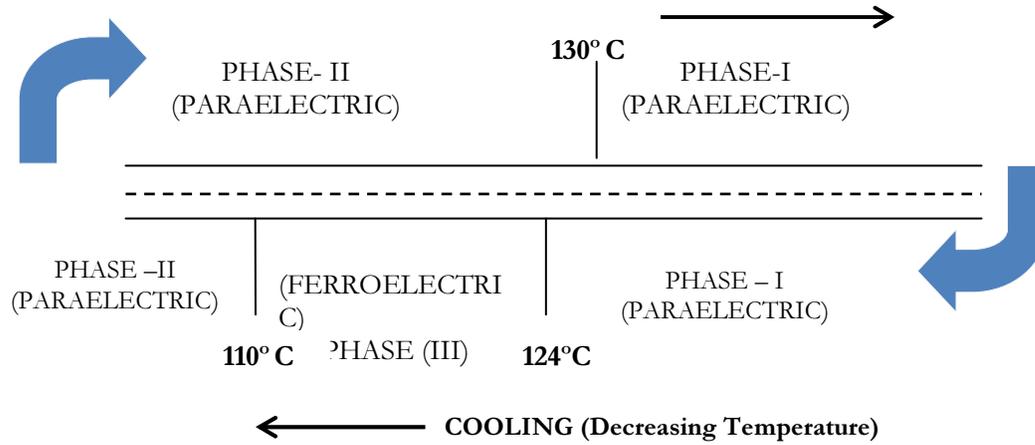


Figure 2 (a & b): Different Phases and the crystal structure changes observed when KNO_3 passes through the heating and cooling cycles.

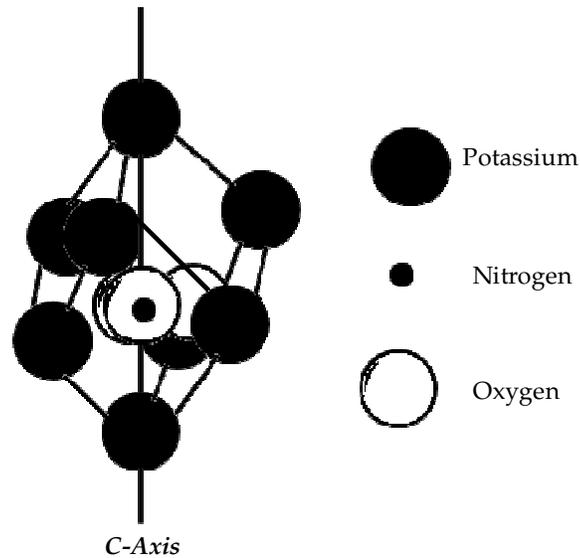


Figure 3: Rhombohedral unit cell in the ferroelectric phase - III of KNO_3 [27-30].

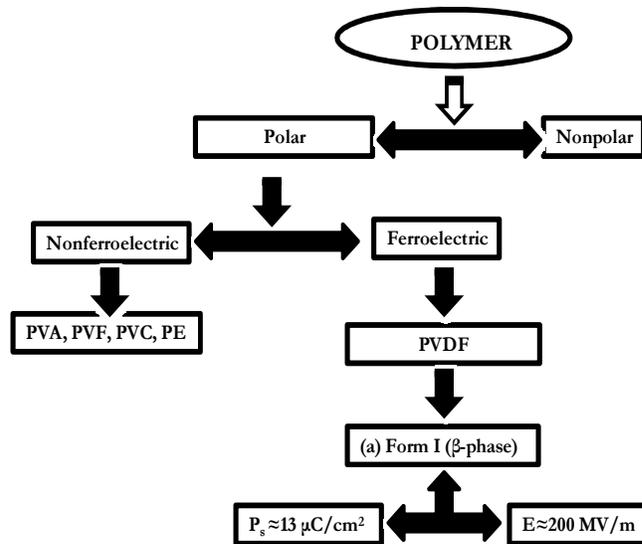


Figure 4: Classification of the polymer phases

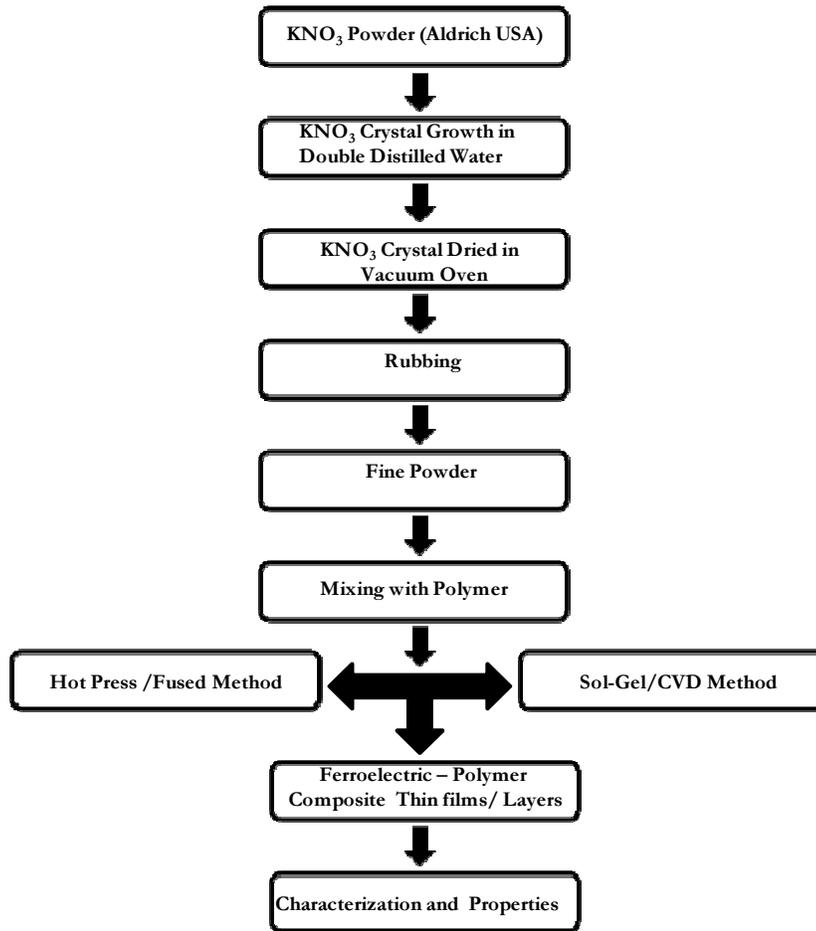


Figure 5: Fabrication process of the ferroelectric-polymer composite films.

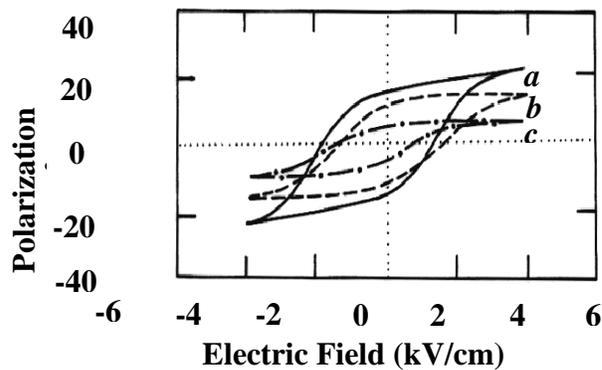


Figure 6: P-E hysteresis loops of 50wt.% KNO_3 : PVDF composites for different temperatures [a= 25°C; b= 103 °C, and c=120°C].

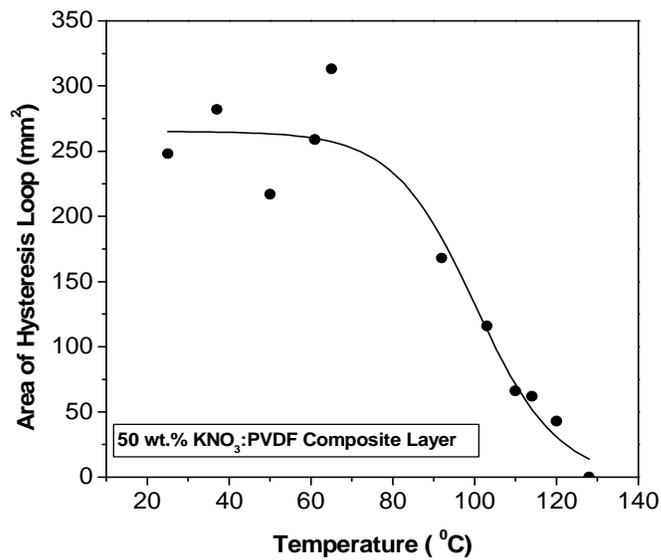
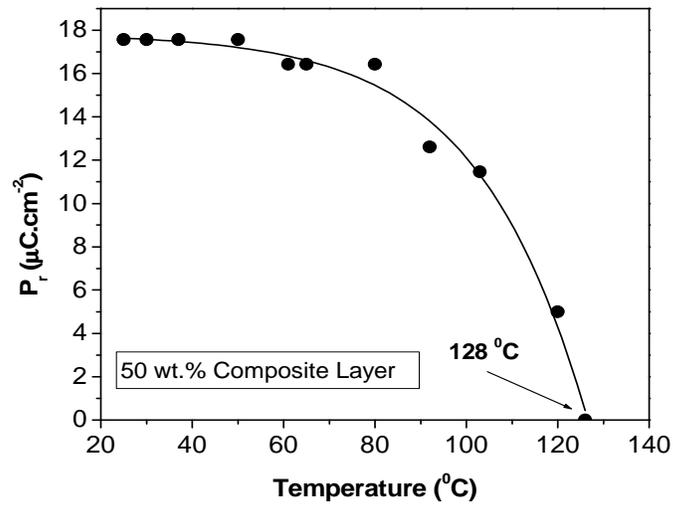


Figure 7 (a) & 7 (b): Polarization and area of hysteresis loop versus temperature of the composite layer.

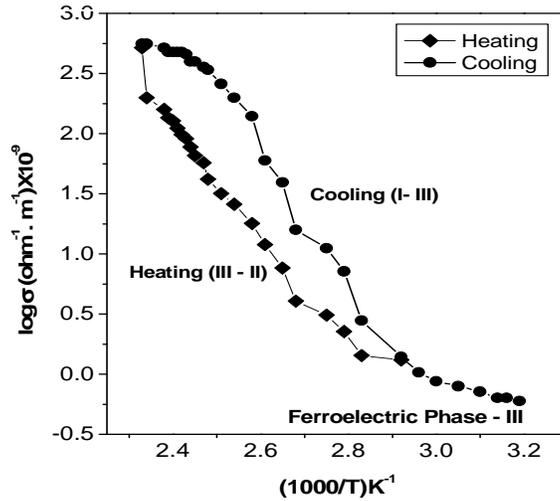


Figure 8 : Behaviour of the conductivity as a function of temperature

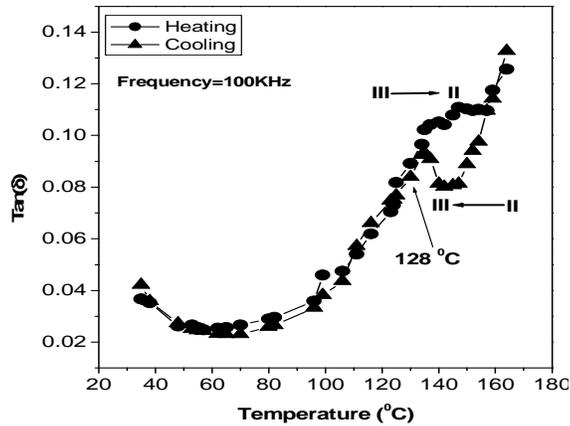
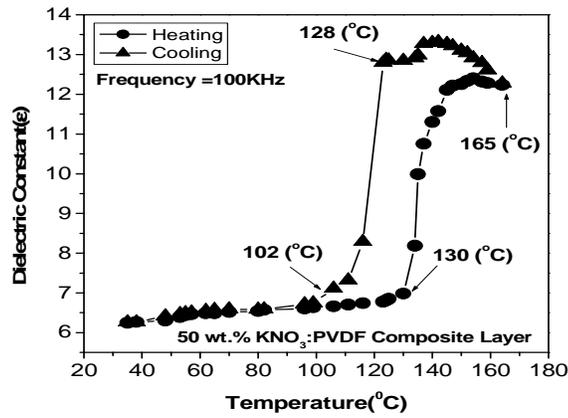


Figure (9) & (10) : Temperature dependence of the dielectric constant and dielectric loss.

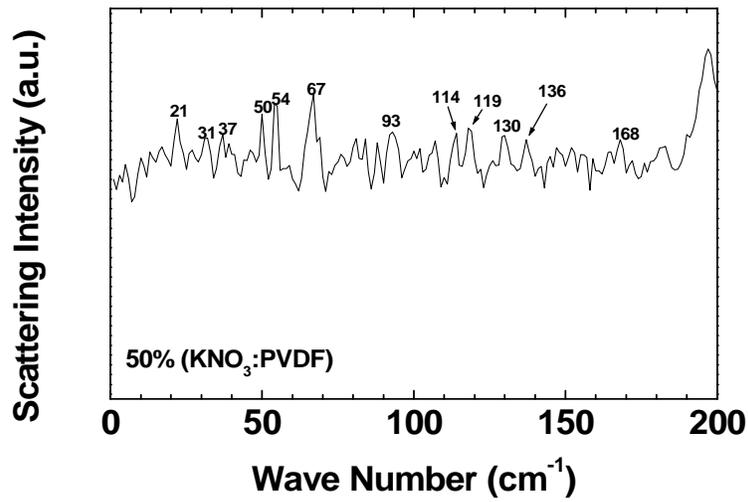


Figure 11: Raman spectra of 50 wt.% KNO₃ : PVDF composite films at room temperature

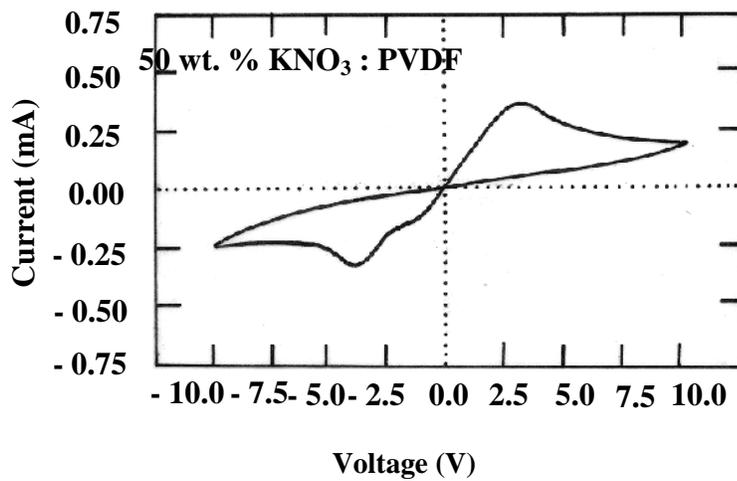


Fig. 12- The existence of the current – voltage characteristics in the composite films

CONCLUSIONS

The present study on composite films show improved ferroelectric properties and stability of ferroelectric phase –III of potassium nitrate at room temperature. This may be attributed to the favorable dipolar field interaction of PVDF base with KNO_3 , which enhances the phase III conversion in this composite. The temperature dependence of the remanent polarization characteristics revealed that the presence of ferroelectric to paraelectric transition near 128°C , at this temperature the hysteresis loop collapses. The results of the electrical conductivity also exhibit the temperature ranges of the phase transformations and the coexistence of phases-II and phase III. The value of dielectric constant increased two folds in the temperature range $130\text{-}165^\circ\text{C}$ when heated from room temperature. This abrupt change can be attributed to the transition of phase II to phase I. Raman spectroscopy confirms the presence of ferroelectric phase –III at room temperature in the composite films. The current-voltage (I-V) characteristics in the 50wt. % KNO_3 : PVDF composite films showed current maxima, which may be attributed to the polarization switching. If there were no ferroelectricity in the film the I-V characteristics should usually results in straight line.

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