J. Mater. Environ. Sci. 2 (4) (2011) 379-386
ISSN : 2528-2028

Evidence of Ferroelectric Polarization Switching in Potassium Nitrate Composite Thick Films

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Received in 16 Aug 2011, Revised 7 Sept 2011, Accepted 7 Sept 2011.

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Abstract

The aim of the present study is to investigate and analyze the ferroelectric polarization switching (FPS) in potassium nitrate (KNO_3) composite films at room temperature. Ferroelectric Polyvinylidene Fluoride (PVDF) polymer and non-ferroelectric Polyvinyl Fluoride (PVF) polymer have been used to prepare composite films using simple melt /hot pressed method in 50-50 wt. % compositions. The polarization switching current is observed using square wave bipolar signals across a resistance of 100Ω in series with the samples. Ishibashi and Takagi theory have been employed to the switching current transient. The existence of switching current pulse supports ferroelectric nature and indicates the stability of ferroelectric phase –III of KNO_3 at room temperature in the composite.

Key words: Ferroelectric KNO_3, PVF, PVDF, Ferroelectric Composite Films, Polarization Switching.

1. Introduction

Ferroelectric materials and its composites in thin film form have attracted an immense interest due to their vital role in advanced electronic technology with their wide variety of applications as ferroelectric devices. Many ferroelectric materials, such as, Barium Titanate ($BaTiO_3$), Barium Strontium Titanate (BST), Potassium-Di Hydrogen Phosphate (KDP), Potassium Nitrate (KNO_3), Cesium Nitrate ($CsNO_3$), 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, pellet and thin film for the use of these materials in memory devices operated at low voltage [1].

Normally the ferroelectric materials in the forms of bulk, crystal and pallet, have very high coercive field (kV/cm) for operation. Further these ferroelectric materials are usually brittle and are fairly difficult to fabricate in thin film form. Therefore, it is necessary to fabricate these materials in thin film form for low voltage operation.

The composite materials have been processed using mixtures of ceramic as filler in a matrix of polymer; the fillers are included in the matrix in order to modify its physical properties over a large range. The ceramic fillers such as PZT, $BaTiO_3$, $PbTiO_3$ in PVDF with different doping concentration have been produced in the past [2-8]. The composites in the film form are becoming important from the application point of view in large area devices operated at low voltages. In the present study we have chosen potassium nitrate as ferroelectric material discovered in 1958 by Sawada et. al. [9]. arises because of the attractive large signal switching properties of its thin films [1]. The square hysteresis loop, low switching potential (5V), and fast switching times (20ns) make KNO_3 thin films promising material as a permanent storage medium in large scale integrated random access memories (RAMs)[1]. KNO_3 has been found to exist in variety of phases as described in Figure 1. On heating, the crystal structure changes from orthorhombic (phase-II) to rhombohedral (phase-I) and on cooling, the phase-I changes first to phase-III at about 124ºC which is ferroelectric and then to phase-III to phase-II at about 110ºC [9-12]. Our main motivation is to investigate the ferroelectric polarization switching properties of potassium nitrate together with PVDF and PVF composite films, which retain the ferroelectric phase (III) of potassium nitrate at room temperature for low voltage operation. To reduce the brittleness and remove the excessive moisture from KNO_3, it is necessary to fabricate this material in the form of composite film under suitable experimental condition. In order to obtain and analyze the ferroelectric phase-III of KNO_3 at room temperature, we have prepared the composite film of ferroelectric polymer and non ferroelectric polymer.

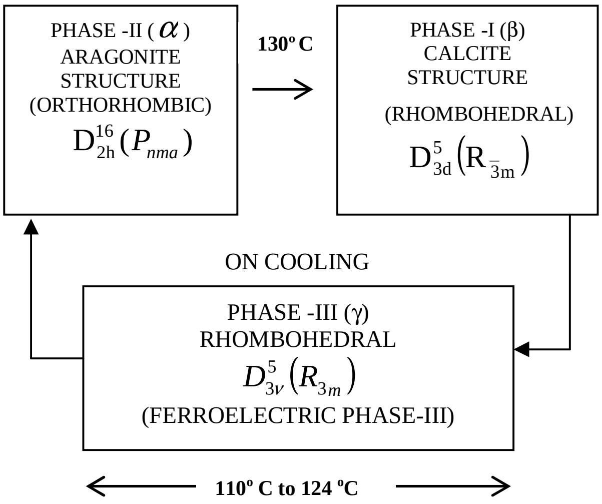

Fig 1: Phase diagram and the crystal structure of KNO_3 during the heating and cooling cycles.

Table 1: Shows the physical properties of ferroelectric materials (KNO_3), ferroelectric and non-ferroelectric polymer.

Material	Melt. point (°C)	Thermal cond. (W/m.K)	Linear coeff. of thermal exp.	Density (g/cm^3)	Dielectric constant	Dipole Moment (C.cm)
KNO_3	334	0.39	10×10^{-5} °C	2.10	12	4.4×10^{-28}
PVDF	171	0.13	4.2×10^{-5} °C	1.76	12	6.9×10^{-28}
PVF	220	0.17	2.8×10^{-5} °C	1.38	5	3.3×10^{-28}

2. Experimental details

2.1 Materials and Sample preparation

In this study, we prepared the ferroelectric composite films of 50wt. % KNO_3 with PVDF and PVF using melt press (hot-press) machine in the following way. 50wt. % of purified and vacuum dried potassium nitrate crystalline powder filtered through standard brass sieves, mesh no. 240 (particle size ~ 60 µm) was added to 50 wt. % of PVDF and 50 wt.% of PVF powder (supplied by Aldrich USA) and thoroughly mixed for both the materials. The mixture of both materials was spread on a thin aluminum foil and then kept in a fine stainless-steel die in the melt press machine. The mixture was heated up to a temperature of 218ºC ±2 ºC and subjected to a pressure of 250 Kg/cm^2. After the procedure, the temperature of stainless steel die was brought down slowly to room temperature at the rate of 30ºC/hr and then the pressure was released. The composite films were normally 30-40 µm thick. The circular indium [13] electrodes of diameter 5 mm were deposited by thermal evaporation under the vacuum ≈ 2×10^{-5} mbar on top and bottom surfaces of the composite films [(In/x/In) where; x= (KNO_3: PVDF) and x= (KNO_3: PVF) for electrically contact]. Figure 2 shows the flow chart of the fabrication steps involved in making of the composite films.

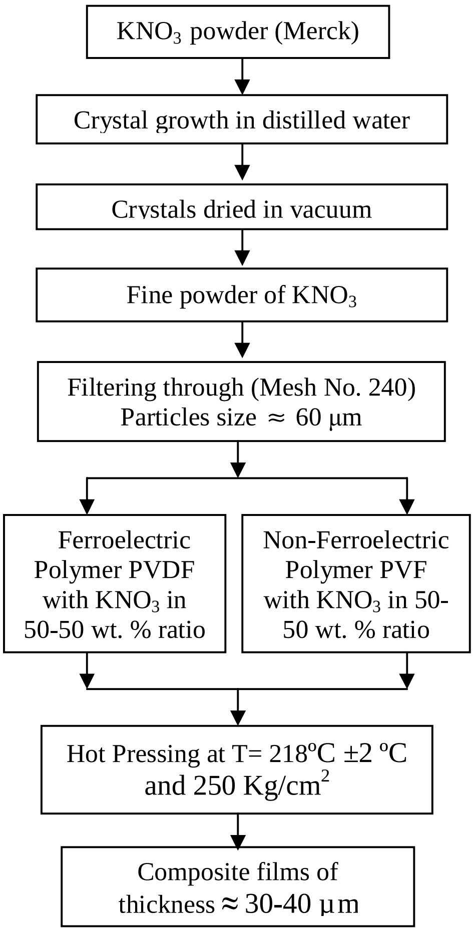

Fig 2: Flow chart of the fabrication steps involved in making of the composite films.

2.2 Ferroelectric polarization switching measurements

The ferroelectric polarization switching measurements have been studied by applying the bipolar square pulses from Scientific make function generator to the composite films. The resultant switching current transients characteristics were observed across a resistance of 100 Ω connected in series with the sample. The switching pulses of the composite films were recorded with the help of digital storage oscilloscope (HM 407-2, Germeny) connected with computer by the standard software RS-232. The surface morphology of the composite films was studied by using the Scanning Electron Microscopy (SEM).

3. Results and Discussions

3.1 Switching response in 50 wt.% (KNO_3:PVDF) composite films

The polarization switching or polarization – reversal effect is the change of the direction of the spontaneous polarization by an applied electric field, is the most important property of ferroelectric materials. Switching time t_s, is defined as the time from the onset pulse to a point 90% decrease from the maximum value of polarized switching pulse curve. Switching phenomenon in ferroelectric films depends strongly upon the thickness of the sample [14-16]. The polarization switching in 35 µm thick 50 wt.% (KNO_3 : PVDF) composite film was studied using square wave bipolar signal in the voltage range of 24 to 30V. The output current was observed across a resistance of 100 Ω in series with the sample. The following equation for switching transient [17] gives the current variation with time as:

$$i(t)=\left(\frac{2P_sAn}{t_0}\right)\left(\frac{t}{t_0}\right)^{n-1}\exp\left[-\left(\frac{t}{t_0}\right)^{n}\right] \qquad ….(1)$$

where P_s is the spontaneous polarization, n is the dimensionality of the domain growth, A is the area of the sample and t_0 is the characteristic switching time. Theoretical fit to the 28V output switching transient pulse is shown in Figure 3. The fitting parameters are: n=2.1, and t_0=270 µs. The high value of 'n' indicate nonhomogeneous nucleation in these films [1,14-16]. The effective dimensionality n= 2.1, the ratio $u=t_0/t_m$=1.37 are obtained here in the 35µm 50 wt.% (KNO$_3$: PVDF) composite films at room temperature.

From Table 2, we find $i_m t_m/Q_s$=0.813, which is in reasonable agreement with the continuous nucleation model [14-16]. On the basis of this model, $D=n-1$, which gives $D=1.1$, for 50 wt.% (KNO$_3$: PVDF). Table 2 shows the effect of pulse amplitude on switching parameters of 50 wt.% (KNO$_3$: PVDF) composite film.

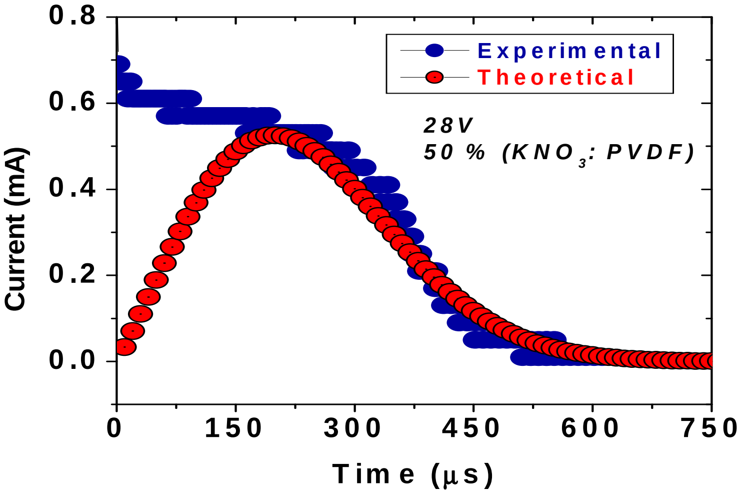

Fig 3: Theoretical fit (eq.1) to the experimental switching response for 50 wt.% (KNO$_3$: PVDF) composite films at 28V; fitting parameters: n=2.1, t$_0$=270 µs.

Table 2: The effect of pulse amplitude on switching parameters of 50 wt.% (KNO$_3$: PVDF) composite film.

Amplitude (V)	t_m (µs)	t_s (µs)	i_m (mA)	$i_m t_m$(nC)	Q_s (nC).cm^{-2}	$i_m t_m/Q_s$
24	85	515	0.18	15.30	58.27	0.26
25	100	453	0.20	20.00	51.56	0.39
26	127	437	0.23	29.21	66.60	0.44
27	142	421	0.53	75.26	145.68	0.52
28	230	437	0.50	115.00	141.50	0.81
29	242	437	0.46	111.32	139.44	0.80
30	287	437	0.50	143.50	158.17	0.91

3.2 Activation field

The polarization switching proceeds by two successive mechanisms that is nucleation and domain growth. If the nucleation rate is small switching behaviour is limited by nucleation rate and switching time obeys the exponential law given by the relation [1] as: $t_s = Ae^{\frac{\alpha d}{V}}$; where A is constant, V is the applied voltage, α is the activation field and d is the sample thickness. The switching time in the composite sample has been found to decrease with the increase in applied voltage (table 2). The semilog plot of t_s versus electric field is shown in figure 4 for 50wt.% (KNO$_3$: PVDF) doped sample.

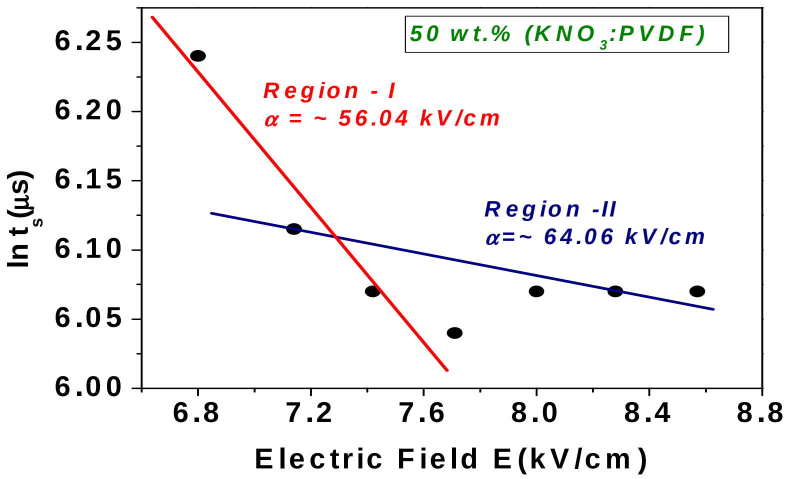

Fig 4: The semilog plot of t_s versus electric field for 50wt.% (KNO_3 : PVDF) composite film.

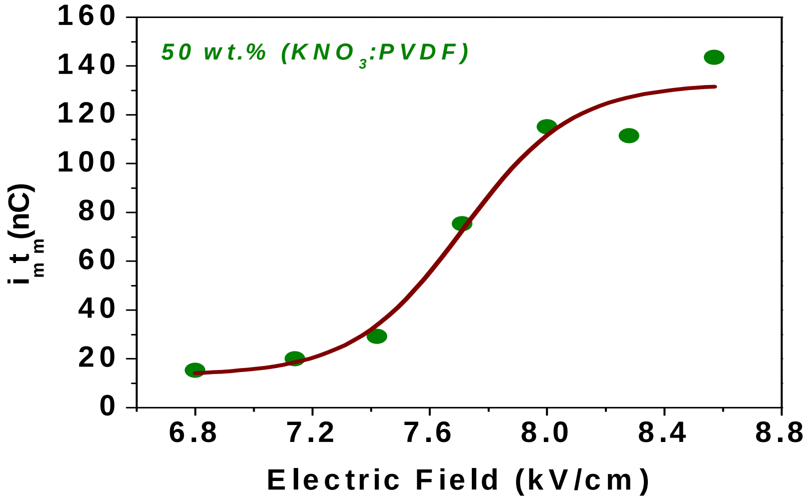

Fig 5: Shows the $i_m t_m$ versus electric field in 50% KNO_3: PVDF composite film.

The value of α in low voltage region is 56.04 kV/cm and in high voltage region is 64.06 kV/cm. It seems that in the low voltage region, the nucleation rate is the limiting process. However, in the high voltage region the domain growth mechanism is becoming limiting process. In the composite films, the nucleation rate may be a controlling process in the low field region because of the presence of PVDF in the composite [13-16, 18-20]. The variation of $i_m t_m$ products with electric field plotted in Figure 5, which shows saturation behaviour with voltage. This type of trend has earlier been reported by other worker in many ferroelectric materials [1, 15, 16].

3.3 Switching response in 50 wt.% (KNO_3 :PVF) composite films

The polarization switching in 35 - μm thick 50 wt.% KNO_3 : PVF composite film was studied using square wave bipolar signal. The switching current peak (t_s) occurs at time (t_m). The switching time (t_s) taken as the time required for the switching pulse current to fall down by 0.9 (90%) of the current peak value (i_m).The area under the switching current pulse gives the charge released (Q_s) per unit area. The output current was observed across a load resistance of 100 Ω in series with the sample. The theoretical fit to the 28V output switching transient pulse is shown in Figure 6.

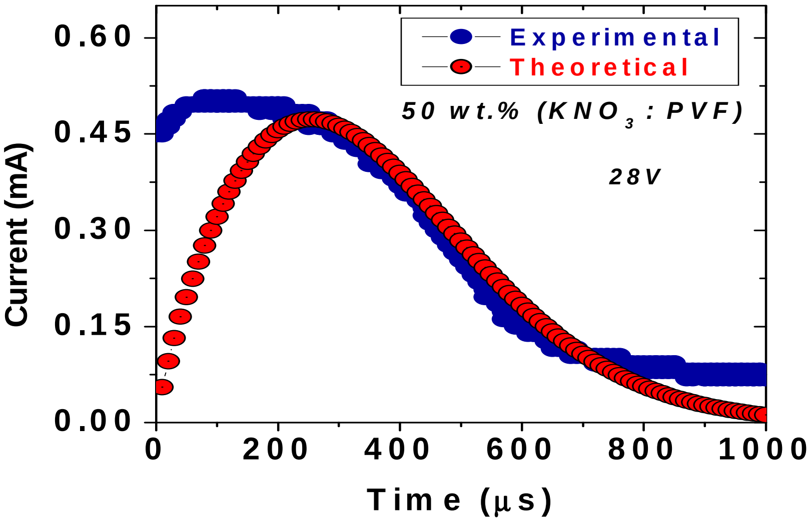

Fig 6: Theoretical fit (eq.1) to the experimental switching response for 50 wt.% (KNO_3 : PVF) composite films; fitting parameters: n=1.8, t_0=400 µs.

The fitting parameters are: n=1.8, and t_0=400 µs. The effective dimensionality of domain growth n= 1.8, the ratio $u=t_0 / t_m$=1.65 are obtained here in the 35 µm 50% wt.% (KNO_3:PVF) composite films at room temperature. We find $i_m t_m /Q_s$=0.425, for 50 wt.% (KNO_3 : PVF) films which is a small value and can be attributed to polarization reversals. This value of similar magnitude has been obtained in $NaNO_2$ by other workers [16-27]. Table 3 shows the effect of pulse amplitude on switching parameters for 50 wt.% (KNO_3 : PVF) films. The fitting parameters are: n=1.8, and t_0=400 µs. The effective dimensionality of domain growth n= 1.8, the ratio $u=t_0 / t_m$=1.65 are obtained here in the 35 µm 50% wt.% (KNO_3:PVF) composite films at room temperature. We find $i_m t_m /Q_s$=0.425, for 50 wt.% (KNO_3 : PVF) films which is a small value and can be attributed to polarization reversals. This value of similar magnitude has been obtained in $NaNO_2$ by other workers [16-27]. Table 3 shows the effect of pulse amplitude on switching parameters for 50. wt.% (KNO_3 : PVF) films.

Table 3: The effect of pulse amplitude (28 V) on switching parameters for 50 wt.% (KNO_3 : PVDF) and 50 wt.% (KNO_3 : PVF) films.

Samples	Amplitude. (V)	Max. (t_m) (µs)	(t_s) (µs)	Max. (i_m) (mA)	$i_m t_m$ (nC)	Q_s (nC).cm^{-2}	$i_m t_m / Q_s$
(KNO_3 :PVF)	28 V	165	440	0.53	87.50	205.00	0.425
(KNO_3:PVDF)	28 V	230	437	0.50	115.0	141.50	0.810

3.4 SEM images of composite films

From the Scanning Electron Micrograph (SEM), the images of 50 wt.% (KNO_3 :PVDF) composite films at different magnification illustrated in Figure 7. It is clear from these images that ferroelectric domains need not always be rectilinear. They can be spaghetti-like, often called labyrinthine, particularly at surfaces [1, 20-27].

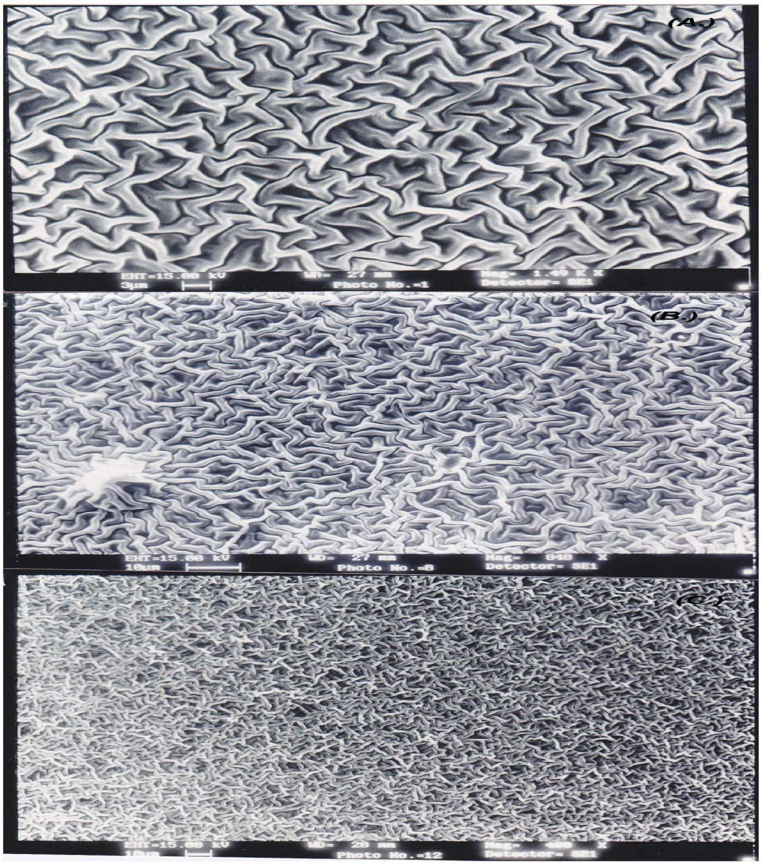

Figure 7: SEM images of 50 wt.% (KNO_3 :PVDF) composite films.

Conclusion

Finally, the effects of pulse amplitude on the switching characteristics of KNO_3 composite films have been studied and the switching current exhibits the exponential dependence on field. Ishibashi and Takagi theory gives the value of dimensionality of domain growth D=0.8 [D= (n-1); n=1.8] for PVF composites. This value of D (=0.8) indicates one dimensional growth and implies needle-like domains with walls moving in one direction perpendicular to the ferroelectric axis [14-16, 27]. For PVDF composites Ishibashi and Takagi theory gives the value of dimensionality of domain growth D=1.1 [D= (n-1); n=2.1]. This value of D (=1.1) may be depicted the two-dimensional growth, because the dimensionality of domain growth (D is >1).

Acknowledgement

One of the authors Dr. Neeraj Kumar thankfully acknowledges to his research supervisor ***Prof. R. Nath*** and ***Prof. R. S. Sirohi (Padmashree),*** Ex-Director IIT Delhi, to enlighten this work as a manuscript.

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