The studies presented in the thesis mainly deal with the ferroelectric and switching properties of KNO₃ and its mixed system with PVA. The structural and morphological studies have also been carried out. The analysis of switching kinetics of these composite films with application of nucleation limited switching models has been presented. The main aim of this chapter is to provide an overall summary, correlations, and conclusions of various studies undertaken such as structural, morphological, ferroelectric, current density - electric field (J-E), switching kinetics, differential dielectric, capacitance - voltage (C-V), and conductance - voltage (G-V) on the composite films of KNO₃: PVA and (NH₄)₀.₃⁹K₀.₆₁NO₃: PVA. The composite films of KNO₃: PVA and NKN: PVA were prepared by spray deposition methods.

### 7.1. Structural Studies

The structural and morphological studies of the composite films of KNO₃: PVA and NKN: PVA have been investigated using the x-ray diffraction (XRD), atomic force microscopy (AFM), field emission scanning electron microscopy (FE-SEM). The XRD scans of KNO₃/NKN: PVA composite films containing different proportions of KNO₃ and NKN have been analyzed. In all these XRD’s the peak corresponding to phase III of KNO₃ was developed in addition to the polymer peaks (Figs. 3.5 and 3.9, Chapter III,). The particle size of KNO₃ and NKN in the composite films of KNO₃/NKN: PVA was estimated from the XRD scans of these composite films having different compositions of KNO₃ and NKN.
The x-rays diffraction scans of pure KNO₃ and NH₄NO₃ (Figs. 3.1 and 3.2, chapter III) in powder form were also recorded. The x-ray diffraction peak corresponding to phase III was not seen in the x-ray scans of pure KNO₃ and NKN. The values of the lattice parameters (a, b and c) were calculated from these scans and which were found to be in good agreement with reported values in literature.

7.1.1. Composite films of KNO₃: PVA

In the spray deposited composite films of KNO₃: PVA containing different weight percentages of KNO₃ (deposited at 200°C), the diffraction peak of phase III was found to lie within 2θ = 29.72°±0.01° for plane (003) and that of phase II occurred within 2θ = 29.52° of reflection (002) (Fig.3.5, Page no. 61). The relative intensity ratio of phase-III to phase-II (I_III/I_II) was estimated for all compositions from expanded x-ray diffraction scans (Fig.3.6, Chapter III). The composite film containing 50wt.% KNO₃: PVA showed the maximum peak intensity ratio 2.67 (Chapter III, Page no. 64). The average crystallite size was calculated using Eq. 3.2 (Table 3.4, Chapter III), the crystallite size was found to increase from 63.4 to 79.2 nm as the wt.% of KNO₃ in the composite films increases from 20 to 50%. Thereafter, decrease in the values of crystallite size was observed with further increase of the KNO₃ percentage in these composite films. Hence, the composite films of KNO₃: PVA (50 wt.% of KNO₃) deposited at 200°C showed maximum crystallite size of 79.2 nm (Table 3.4, Chapter II). This large crystallite size might have facilitated the alignment of domains. This enhances P_r in the composite films in the similar fashion as reported in literature in case of KNO₃: PVDF [176] and NaNO₂: PVA [179] composite films.

The surface morphology of the spray deposited composite films of KNO₃: PVA containing different weight percentages of KNO₃ was studied using field emission scanning electron microscopy (FE-SEM) (Fig. 3.21, Chapter III). These images of composite films exhibit spherical grains of KNO₃ with an average size in the range of 195–310 nm. The KNO₃ composition in these composite films vary from 20-80 wt.%
The image of the composite film containing 50 wt.% of KNO₃ show the uniform distribution of KNO₃ in PVA matrix and grain size of ~225 nm. These images reveal that the KNO₃ particles were homogeneously dispersed in PVA up to 50 wt.% composition. However, the clustering of the KNO₃ particles was observed in the composite film containing above 50 wt.% KNO₃ composition. The clustering creates porosity between the KNO₃ particles in the interstitial regions [178] and has been thought to be responsible for the decrease of remanent polarization, Pᵣ in the composite films containing more than 50 wt.% KNO₃ composition.

In the spray deposited composite films of KNO₃: PVA (1:1) prepared at different deposition temperatures. It was observed that the composite films of 50wt.% KNO₃: PVA prepared at 150, 200 and 250°C exhibit the peaks corresponding to phase II and ferroelectric phase III of KNO₃ in the range 2θ = 29.51°±0.01° and 29.72°±0.01° respectively (Fig. 3.10, Chapter III). The relative intensity ratio of phase-III to phase-II (I₃/I₂) was maximum for the composite film deposited at 200°C. It is inferred that the composite film deposited at 200°C have more stable ferroelectric phase, hence cause larger remanent polarization, Pᵣ.

The crystallite size of KNO₃ particle in the composite films of KNO₃: PVA (1:1) was calculated using Eq. 3.2 (Page no. 62, Chapter III) and found to be 76.8, 79.2, and 84.5 nm for the composite films prepared at temperatures 150, 200, and 250°C respectively. The crystallite size was found to increase with the deposition temperature. The crystallite size seems to play an important role in the existence of ferroelectric phase III in the composite films at room temperature. The large crystallite size of ferroelectric phase III in 50wt. % composite films deposited at 200°C may be responsible for producing stable ferroelectric phase at room temperature. Moreover, the distance-dependent repulsive force between neighboring domains was observed to play a crucial role in domain orientation in ferroelectric thin films [178]. The repulsive force between neighboring domains becomes weak in the composite film deposited at 200°C due to large crystallite size (Fig. 3.19, Chapter III). This may faciliate more domains to orient in the field direction causing large Pᵣ.
small coercive voltage, $V_c$. However, the composite film deposited at 250°C gave small $P_r$ even the crystallite size (~84.5 nm) is slightly greater than the film deposited at 200 °C (~240nm). This can be correlated with the larger porosity between grains in composite film deposited at 250 °C as revealed by the AFM images. The orthorhombic distortion $c/a$ ratio is found to be maximum in the composite film deposited at 200°C (Table 3.3, Chapter III). The larger $c/a$ ratio could result in high non-centrosymmetricity of KNO$_3$. This may in turn lead to enhanced polarization in KNO$_3$ composite films deposited at 200°C.

The AFM images of the composite films prepared at 150 and 200°C clearly show well-grown spherical KNO$_3$ particles homogenously dispersed in PVA matrix. The average grain size was estimated to be 186 and 230 nm respectively in these films. The root mean square (rms) roughness in these composite films deposited at 150 and 200°C was found to be 74 and 61 nm, respectively. However, the interconnected clusters of KNO$_3$ grains were seen in the AFM image of the composite film deposited at 250°C. The average grain size was found to be 290 nm with very large rms roughness of 170 nm. This might be due to melted PVA, which created the clustering of KNO$_3$ particles in the composite films.

The XRD scans of the composite films (containing equal proportions of KNO$_3$ and PVA) deposited at 150, 200, and 250°C, reveal lesser peak intensity ratio for the composite films deposited at 250°C which could be attributed to the porosity, clustering, line imperfections and large roughness in these composite films.

Therefore, the presence of ferroelectric phase III, high peak intensity ratio, larger orthorhombic distortion, larger crystallite size, uniform dispersion of KNO$_3$ in PVA matrix and least roughness in the composite films of KNO$_3$: PVA (1:1) prepared at optimized conditions seems to have lead to the enhanced polarization in these composite films.
7.1.2. Composite films of NKN: PVA

Similarly, the scans of the spray deposited composite films of NKN: PVA containing different weight percentages of NKN were studied. The relative intensity ratio of phase-III to phase-II ($I_{III}/I_{II}$) was estimated for all compositions from expanded x-ray diffraction scans (Fig. 3.11, Chapter III). The composite film containing 50wt.% NKN: PVA showed the maximum peak intensity ratio and crystallite size (Table 3.5, Chapter III). This large crystallite size and maximum peak intensity ratio reveals better domain alignment resulting in enhanced $P_r$, as explained earlier.

The surface morphology of the spray deposited composite films of NKN: PVA containing different weight percentages of NKN prepared at optimized temperature (170°C) was studied using FE-SEM (Fig. 3.30, Chapter III). These images of composite films exhibit spherical particles of NKN with an average grain size lying in the range of 229 – 371 nm. The grain size increases with increasing composition of NKN in these films. The image of the composite film containing 50 wt.% of NKN show the uniform distribution of NKN particles in PVA matrix. The grain size of ~312 nm was observed. These images reveal that the NKN particles have homogeneous dispersion in PVA up to 50 wt.% composition. However, the some defects and clustering of the NKN particles was observed in the composite film above 50 wt.% composition. The clustering creates porosity between the NKN particles in the interstitial regions and that could result in the decrease in remanent polarization, $P_r$ for the composite films containing NKN composition above the 50 wt.%.

For the spray deposited composite films of 50wt.% NKN: PVA, prepared at different deposition temperatures, peak intensity ratio was maximum 2.81 for the composite films deposited at 170°C (Table 3.6, Chapter III). Thus, it is inferred that the composite film deposited at 170°C have more stable ferroelectric phase, hence cause larger remanent polarization, $P_r$. The crystallite size seems to play an important role in the existence of ferroelectric phase III in the composite at room temperature. The larger crystallite size of ferroelectric phase III in 50wt. % composite films deposited
at 170°C could be responsible for producing stable ferroelectric phase at room temperature. This may facilitate more domains to orient in the field direction causing large \( P_r \) and lesser coercive field, \( E_c \). However, the composite film deposited above 170°C gave smaller \( P_r \) even if their crystallite size is slightly greater [178, 179]. This can be correlated with the porosity between grains in composite film deposited above 170°C as revealed by the AFM images.

The AFM images of the composite films prepared at 130, 150 and 170°C clearly show well-grown spherical NKN particles homogenously dispersed in PVA matrix and the average grain size was estimated to be 230, 278 and 321 nm respectively. The AFM images of composite films clearly show the homogeneous dispersion of \( (NH_4)_{0.39}K_{0.61}NO_3 \) particles in PVA up to 170°C temperature. However, the clustering of the NKN particles was observed in the composite film prepared above 170°C temperature. The root mean square (rms) roughness of the composite films deposited at 130, 150 and 170°C was found to be 45, 53 and 43nm, respectively. However, the interconnected clusters of NKN grains were seen in the AFM images of the composite films deposited at 200 and 250°C. The average grain size was found to be 375 and 430 nm with very large rms roughness of 158 and 185 nm respectively.

The lesser peak intensity ratio as revealed from XRD scans for the composite films deposited above 170°C might be correlated with the porosity, clustering and large roughness of the composite films deposited at 200 and 250°C.

### 7.2. Ferroelectric Studies

The ferroelectric properties such as P-E loop, current density-electric field (J-E), differential dielectric constant, back switching percentage, capacitance –voltage (C-V) and fatigue characteristics were investigated in the spray deposited composite films of KNO\(_3\): PVA and NKN: PVA. The comparative studies show that spray deposited composite films of 50wt.% KNO\(_3\): PVA (deposited at 200°C) and 50wt.% NKN: PVA (deposited at 170°C) have larger \( P_r \) value with high stability than in pure fused KNO\(_3\)
and NKN films. This shows that the nature of polymer matrix plays important role in the ferroelectric properties of the composite films.

7.2.1. Composite films of KNO₃: PVA

The investigation on hysteresis loop (P-E), current density - electric field (J-E), back switching percentage characteristics, differential dielectric constant, capacitance – voltage (C-V) and conductance – voltage (G-V) characteristics in spray deposited KNO₃: PVA composite films were carried out. The effect of fabrication temperatures and composition of KNO₃ on these characteristics was studied.

The value of \( P_r \) increases from 3.95 to 20.10 \( \mu \text{C/cm}^2 \) as the weight percentage composition of KNO₃ increases from 10 to 50 wt.% in the composite films. It becomes maximum for 50wt.% KNO₃: PVA films. With further increase in the KNO₃ composition \( P_r \) follows a decreasing trend. Hence, the composite film containing 50wt.% KNO₃:PVA showed the maximum \( P_r \sim 20.10 \ \mu \text{C/cm}^2 \) at 50 Hz. The coercive field, \( E_c \) decreases with the increase of the weight percentage of the KNO₃ in the composite films of KNO₃: PVA (Table 7.1). The values \( P_r \) were found to be optimum \( \sim 20.10 \ \mu \text{C/cm}^2 \) at 50 Hz in the 50wt.% KNO₃: PVA composite films deposited at 200°C (Table 7.1). The composite films containing greater than 50wt.% of KNO₃ were found to be more brittle and porous as was observed in the FE-SEM images of these samples (Fig. 3.21, Chapter III). The porosity have caused smaller \( P_r \). The smaller value of \( P_r \) in the composite films with KNO₃ composition less than 50wt.% can be correlated with the lesser connectivity between the KNO₃ particles and PVA (polymer) matrix.

In the composite films of KNO₃: PVA containing equal proportions of KNO₃ and PVA, the value of \( P_r \) was found to be maximum in the composite films deposited at 200°C (Table 7.2). The distance dependent repulsive forces become weak with larger crystallite and grain sizes with increase in deposition temperature. This facilitates
domain growth resulting in large domain size which in turn causes larger $P_r$. The $P_r$ increases with rise in the deposition temperature. The composite films deposited at 250°C gave lower $P_r$ though the average crystallite and grain sizes (discussed in chapter III) are slightly larger than those in the composite films deposited at 200°C. The decrease in $P_r$ could be due to melting of PVA which create the porosity between the KNO$_3$ clusters (Fig. 3.20, Chapter III). Thus, the value of $P_r \sim 20.10 \, \mu\text{C/cm}^2$ is maximum in the 50 wt.% KNO$_3$: PVA composite films deposited at temperature 200°C. However, the substrate temperature does not appear to affect much the coercive field, $E_c$.

### TABLE 7.1 Composition Dependence of Various Ferroelectric Parameters in KNO$_3$: PVA Composite Films.

<table>
<thead>
<tr>
<th>Wt. % of KNO$_3$ in the composite films of KNO$_3$: PVA</th>
<th>$P_r$ ($\mu\text{C/cm}^2$)</th>
<th>$E_c$ (kV/cm)</th>
<th>Percentage of Back Switching</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>3.95</td>
<td>4.25</td>
<td>31.18</td>
</tr>
<tr>
<td>30</td>
<td>7.02</td>
<td>4.02</td>
<td>29.20</td>
</tr>
<tr>
<td>40</td>
<td>12.06</td>
<td>3.60</td>
<td>26.02</td>
</tr>
<tr>
<td>50</td>
<td>20.10</td>
<td>3.42</td>
<td>25.85</td>
</tr>
<tr>
<td>60</td>
<td>15.4</td>
<td>3.33</td>
<td>31.12</td>
</tr>
<tr>
<td>70</td>
<td>8.76</td>
<td>3.29</td>
<td>42.28</td>
</tr>
<tr>
<td>80</td>
<td>4.25</td>
<td>3.25</td>
<td>45.17</td>
</tr>
</tbody>
</table>
The value of $P_r$ was found to be optimum ~ 17.0 $\mu$C/cm$^2$ at 1kHz in the 50wt.% KNO$_3$: PVA composite films deposited at 200°C. The space charge contribution to $P_r$ was eliminated at higher frequencies of applied field.

**TABLE 7.2 Temperature dependence of $P_r$ and $E_c$ in Ferroelectric 50 wt.% KNO$_3$: PVA Composite Films.**

<table>
<thead>
<tr>
<th>Substrate Temperature (°C)</th>
<th>$P_r$ (μC/cm$^2$)</th>
<th>$E_c$ (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>13.70</td>
<td>3.55</td>
</tr>
<tr>
<td>200</td>
<td>20.10</td>
<td>3.30</td>
</tr>
<tr>
<td>250</td>
<td>9.80</td>
<td>3.65</td>
</tr>
</tbody>
</table>

The back switching percentage and differential dielectric constant, $\epsilon_d \cong \frac{1}{\epsilon_0} \left( \frac{dP}{dE} \right)$ have been derived from hysteresis loop characteristics of each composite film. The value of back switching percentage was found least ~25.85% in the optimized KNO$_3$: PVA composite films. The least back switching percentage suggests that the 180° domain switching is relatively more predominant and is responsible for larger $P_r$ in the optimized composite films of KNO$_3$: PVA. In all films, differential dielectric constant, $\epsilon_d$ exhibits nonlinear behavior with applied field which is typical nature of a ferroelectric material. It arises from the domain switching in these ferroelectric films.

The current density-electric field (J-E) characteristics of all the composite film exhibited butterfly behavior. The maximum current density, $J_{max}$ was found to be 37.04 mA/cm$^2$ in the optimized KNO$_3$: PVA films. The peak current density occurs at the vicinity of coercive field. The butterfly behavior was also reported in many ferroelectric materials in past in which the current density peaks were observed in the vicinity of coercive field.

The C-V characteristics of the composite films of KNO$_3$: PVA with varying composition of KNO$_3$ (20-80 wt.%) prepared at 200°C exhibit butterfly features and
strong bias dependence. The initial increase in the capacitance with bias voltage may be due to orientation of domains in the field direction. Moreover, the maxima in C-V curves occur in the vicinity of coercive voltage, $V_c$. Thus, the contribution from the domain wall motion to the dielectric properties is maximum, which results in the sharp peaks around $V_c$ in C-V characteristics. The decrease in the capacitance in the forward and reverse cycles could be due to the reduction in domain movement/growth. The two sharp peaks were observed at the voltages -4V and +5V in each positive and negative cycles respectively. These sharp peaks may be attributed to the polarization switching phenomena. The peaks observed at -4V and +5V may be related with the orientation of the 180° domains, where as the minor peak shoulders arose due to 90° domain orientation. The highest value of $C_{max} \approx 0.21$ nf and its strong bias dependence could be correlated with larger value of $P_r \approx 20.10 \mu$C/cm$^2$ in the composite films of KNO$_3$: PVA containing equal proportions of KNO$_3$ and PVA. The conductance-voltage (G-V) characteristics of these composite films also exhibit non-linear butterfly behavior. The current density-voltage (J-V) curves were obtained from G-V curves and exhibit non-linear behaviour. The butterfly features in C-V, G-V and J-V curves of the NKN: PVA composite films strongly corroborate the presence of the ferroelectric nature of the composite films at room temperature.

The dependence of normalized remanent polarization on the number of reversal cycles was tested in the 50wt.% KNO$_3$: PVA composite film prepared under the optimized conditions. The value of the $P_r$ drops to 0.65 of the initial value after $2 \times 10^6$ cycles in the 50wt.% KNO$_3$: PVA composite film. Thus, the composite films show better fatigue life span than quenched KNO$_3$.

The larger value of $P_r$, lesser $E_c$, least back switching percentage, maximum current density ($J_{max}$), non linear behavior and strong bias dependence, prominence of 180°C domains and larger stability of the composite films of KNO$_3$: PVA prepared under the optimized conditions, strongly corroborate the presence of the ferroelectric phase in the composite films at room temperature.
7.2.2. Composite films of NKN: PVA

The investigation on hysteresis loop (P-E), current density - electric field (J-E), back switching percentage characteristics, differential dielectric constant, capacitance – voltage (C-V) and conductance – voltage (G-V) characteristics in spray deposited NKN: PVA composite films were carried out. The effect of fabrication temperatures and composition of NKN on these characteristics was studied.

In the composite films of NKN: PVA with varying compositions of NKN prepared at 170°C, initially, the value of \( P_r \) was found to increase from 5.93 to 27.15 μC/cm\(^2\) as the wt.% of NKN in the composite films increases from 20 to 50%. Thereafter, decrease in the values of \( P_r \) was observed with further increase in NKN percentage in these composite films. Hence, the composite films of NKN: PVA prepared at 170°C containing equal proportions of NKN and PVA showed maximum \( P_r \approx 27.15 \) μC/cm\(^2\) (Table 7.3). The composite films containing more than 50 wt.% of NKN composition also possess porosity due to the clustering of NKN grains which could be responsible for decrease of \( P_r \) in the films containing higher wt.% of NKN in the composite films. The smaller value of \( P_r \) in the composite films with composition less than 50wt.% can be correlated with the lesser connectivity between the NKN particles and PVA (polymer) matrix.

In the composite films of NKN: PVA containing equal proportions of NKN and PVA prepared at different substrate temperatures. The value of \( P_r \) was found to be maximum in the composite films deposited at 170°C. The relevant reasons are explained earlier. Thus, the value of \( P_r \) is maximum in the 50 wt.% NKN: PVA composite films deposited at temperature 170°C.
TABLE 7.3 Composition Dependence of Various Ferroelectric Parameters in NKN: PVA Composite Films.

<table>
<thead>
<tr>
<th>Wt. % of NKN in the Composite Films</th>
<th>P_r (μC/cm^2)</th>
<th>E_c (kV/cm)</th>
<th>J_{max} (mA/cm^2)</th>
<th>Back switching Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>5.93</td>
<td>4.84</td>
<td>8.26</td>
<td>38.12</td>
</tr>
<tr>
<td>30</td>
<td>9.24</td>
<td>4.24</td>
<td>13.82</td>
<td>34.70</td>
</tr>
<tr>
<td>40</td>
<td>15.47</td>
<td>4.09</td>
<td>28.59</td>
<td>23.19</td>
</tr>
<tr>
<td>50</td>
<td>27.15</td>
<td>3.91</td>
<td>48.23</td>
<td>14.78</td>
</tr>
<tr>
<td>60</td>
<td>18.14</td>
<td>3.72</td>
<td>33.82</td>
<td>27.79</td>
</tr>
<tr>
<td>70</td>
<td>11.75</td>
<td>3.78</td>
<td>16.25</td>
<td>30.83</td>
</tr>
<tr>
<td>80</td>
<td>9.95</td>
<td>3.83</td>
<td>14.01</td>
<td>34.53</td>
</tr>
<tr>
<td>100</td>
<td>5.81</td>
<td>4.05</td>
<td>9.23</td>
<td>29.70</td>
</tr>
</tbody>
</table>

The percentage of back switching and differential dielectric constant, $\varepsilon_d \equiv \frac{1}{\varepsilon_o} \left(\frac{dP}{dE}\right)$, have been derived from hysteresis loops characteristics of each composite film. The value of back switching percentage was found to be least ~14.78% in the optimized NKN: PVA composite film. This suggests that the 180° domain switching is relatively more predominant and is responsible for large P_r in the optimized composite films of NKN: PVA. In all these composite films differential dielectric constant, $\varepsilon_d$ exhibits nonlinear behavior with applied field which is a typical behavior of a ferroelectric material and arises from the domain switching.

The current density-electric field (J-E) characteristics of all the composite film exhibited butterfly behavior. The maximum current density, $J_{max}$ was found to be
48.23 mAcm$^{-2}$ in the optimized NKN: PVA films. The peak current density occurs at the vicinity of coercive field. The butterfly behavior of the many ferroelectric materials was reported in past in which the current density peaks were also observed in the vicinity of coercive field.

The C-V characteristics of the composite films of NKN: PVA with varying composition of NKN (20-80 wt.%) prepared at 170°C exhibit butterfly features and strong bias dependence. Two sharp peaks at ±4V and ±6V corresponding to 180° and 90° domains switching were observed in all the composite films of NKN: PVA. The composite films of NKN: PVA prepared under optimized conditions showed the maximum capacitance ~ 0.37 nf and highest peak intensity ratio ~1.75 of the 180°/90° domains. The C-V studies gave direct evidence of the role of both 180° and 90° domains in the composite films. The conductance-voltage (G-V) characteristics of these composite films also exhibit non-linear butterfly behavior. The current density-voltage (J-V) curves were obtained from G-V curves and exhibit non-linear behaviour. The butterfly features in C-V, G-V and J-V curves of the NKN: PVA composite films strongly corroborate the presence of the ferroelectricity in these composite films at room temperature.

The dependence of normalized remanent polarization on the number of reversal cycles was tested in the 50wt.% NKN: PVA composite film prepared under the optimized conditions. The value of the $P_r$ drops to 0.84 of the initial value after $2 \times 10^6$ cycles in this composite film. Thus, the composite films show better fatigue life span than pure spray deposited NKN films, in which $P_r$ drops to almost half of the initial value after $2 \times 10^5$ cycles. Thus, high stability of $P_r$ in the composite films may be attributed to small back switching and absence of porosity. Thus, the composite films show better fatigue life span than pure NKN, quenched KNO$_3$ and KNO$_3$: PVA composite films.

The larger value of $P_r$, lesser $E_c$, least back switching percentage, maximum current density ($J_{\text{max}}$), non linear behavior and strong bias dependence, prominence of 180°C
domains and larger stability of the composite films of NKN: PVA (1:1) prepared under the optimized conditions, strongly corroborate the presence of the ferroelectricity in these composite films at room temperature.

7.3. Switching Kinetics

The switching kinetics of spray deposited 50wt.% KNO₃: PVA, pure NKN and 50wt.% NKN: PVA have been studied and analyzed by applying nucleation limited switching (NLS) model.

7.3.1. Composite films of KNO₃: PVA

The switching kinetics of the spray deposited KNO₃: PVA (1:1) composite films prepared at different deposition temperatures have been studied. The switching current transients have been analyzed by considering domain growth limited process with the Lorentzian distribution function of characteristic domain growth times based on nucleation limited switching (NLS) model. This model gives excellent agreement with the experimental polarization reversal transients throughout the whole time range. The excellent fit means that the composite film as a whole can be treated as an ensemble of regions where the switching process takes place independently. The existence of independent switched regions can be understood from the saturation of $P_s$ with applied pulse amplitude. This is because each region will contribute to the reversal of polarization only if the applied voltage is above the coercive voltage of individual region. The values of $P_s$ estimated from switching transients are in good agreement with the values estimated from the P-E loops (Subsection 4.2.1.2, Chapter IV). The peak value of polarization current $i_{max}$ at time $t_{max}$ was found maximum, and $\log t_1$ and $w$ was minimum for the composite film deposited at 200°C at pulse amplitude 15V. The broadening of $F(\log t_0)$ indicates the increase in local field variation. It was observed that the composite film deposited at 200°C gave least
broadening, hence least variation in the local field. The variation in the local field might be related to the dipole defects and porosity inside the films (Fig. 3.20, Chapter III).

The local field variation in the composite film deposited at 200 °C is minimum and thus the polarization reversal is more efficient. The switching time is found to be relatively faster in the spray deposited KNO₃: PVA films deposited at 200°C at pulse amplitude 15V (Table 5.1, Chapter V) due to high nucleation rate and presence of more 180° domains.

Hence, the spray deposited KNO₃: PVA composite films (50 wt.% each) deposited at 200°C gave maximum value of the peak current and excellent fit with the theoretical NLS model.

7.3.2. Pure NKN films

In the polarization switching curves of the spray deposited NKN films. The current peaks were found to become sharp and shift to lower time with increase in the applied pulse amplitude. The iₘₐₓ starts to increase from 90 to 717 µA and tₘₐₓ decreases from 94 to 51 µs as the applied voltage increases from 15 to 10 V. This might be due to the creation of more stabilized domains in addition to the existing domain switching. The iₘₐₓ values showed exponential dependence on the reciprocal of electric field.

The value of log t₁ and w is minimum for the film at pulse amplitude 15V. The Lorentzian distribution functions were obtained and the broadening of F(log t₀) indicates the increase in local field variation. The variation in the local field might be related to the dipole defects and porosity inside the films. This causes the variation in the value of t₀ for local switching of different regions in the composite films. The distribution of local field due to defects is given by Eq. 5.5, the local field, E and half-width at half maximum, Γ of the local field distribution F(logE) is the related to the concentration of the pinning sites. The activation field, αₑₑ value estimated from switching parameter curve is found to be 17.80 kV/cm. This value is close to
activation field, $\alpha_i$, calculated from section 5.5.2, Chapter V. This activation field may be due to the interaction between structural defects, porosity and ferroelectric domains (Fig. 3.23 and 3.30, Chapter III.). The activation field, $\alpha_i$, is found to be lower than the activation field of pure quenched KNO$_3$ films. The value of log $t_1$ and $w$ is minimum at pulse amplitude 15V.

7.3.3. Composite films of NKN: PVA

The switching current transients of the spray deposited 50wt.% NKN: PVA composite films prepared at different substrate temperatures show the excellent agreement between experimental switching data that obtained using NLS model. As discussed earlier the values of parameters $t_1$ and $w$ are obtained from these fitting curves. The values of $P_s$ estimated form the switching transients are in good agreement with the values estimated from the P-E loops (Subsection 4.2.1.4, Chapter IV). The peak value of polarization current $i_{max}$ occurs at time $t_{max}$ and was found to be maximum for the composite film deposited at 170°C. The Lorentzian distribution functions were obtained using the fitting values of $t_1$ and $w$ for the composite films. The variation in the local field might be related to the dipole defects and porosity inside the films as explained earlier. The value of log $t_1$ and $w$ is minimum for the film deposited at 170°C.

Hence, the least variation of the local field, larger polarization current, excellent fits to the experimental data, and minimum value of the log $t_1$ and $w$ in the spray deposited composite films of KNO$_3$: PVA and NKN: PVA prepared at optimized conditions revealed that these films can be represented as an ensemble of elementary regions which could be switched independently. The switching is limited by the nucleation of reversed domains rather than by the sidewise motion of domain walls. The local field variation is minimum in the composite films of KNO$_3$: PVA and NKN: PVA deposited at 200°C and 170°C respectively, thus the polarization reversal is more efficient.
7.4. Main Conclusions

The following are the main conclusions drawn from the structural, ferroelectric and switching studies of KNO$_3$: PVA and NKN: PVA composite films.

1. (a) The spray deposited composite films of KNO$_3$: PVA prepared under optimized conditions have shown more than twice $P_r$ and $J_{\text{max}}$, better stability and faster switching time as compared to pure quenched KNO$_3$ films. The enhanced value of $P_r \sim 17.0$ μC/cm$^2$ is measured at 1kHz, measurement at higher frequencies to eliminate the space charge contribution.

(b) The spray deposited composite films of NKN: PVA prepared under optimum conditions have shown four times $P_r$ and $J_{\text{max}}$, better stability and faster switching time as compared to spray deposited pure NKN films. The enhanced value of $P_r \sim 23.89$ μC/cm$^2$ is measured at 1kHz to eliminate the space charge effect.

Hence, the composite films of NKN: PVA better ferroelectric properties than KNO$_3$: PVA films.

2. The XRD, AFM and FE-SEM studies have revealed that the formation of ferroelectric phase III peak, large peak intensity ratio, strain relaxation, more orthorhombic distortion, least roughness and uniform distribution of KNO$_3$/NKN grains in PVA matrix prepared under optimized conditions lead to larger $P_r$ with high stability and faster switching time.

3. The back switching calculations provided information of the relative contributions of 180° and 90° domains to the polarization. The differential dielectric and C–V studies gave direct evidence of the existence of more 180° domains in spray deposited composite films of KNO$_3$: PVA and NKN: PVA.

4. The NLS theory fitted well to the experimental switching transients of composite films of KNO$_3$: PVA and NKN: PVA and pure NKN films. The nucleation mechanism is found to be responsible for the switching processes. The switching taking place in different regions of the sample independently
and these switched regions in the composite films are justified from the observation of saturation of switchable polarization with applied pulse amplitude.