CHAPTER-II

EXPERIMENTAL: DESIGN, FABRICATION, MATERIALS AND MEASUREMENTS

2.1 INTRODUCTION

This chapter contains the detailed description of the materials used, fabrication process of the composite films, design of the circuits, and measuring cell. The procedures adopted for sample preparation, electrode deposition, ferroelectric hysteresis loop (P-E), switching transients, capacitance - voltage (C-V) and conductance - voltage (G-V) studies is also presented. The brief descriptions of the specifications of the instruments used for x-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) are also included.

2.2 MATERIALS USED AND THEIR SPECIFICATIONS

(i) **Potassium Nitrate (KNO₃)**
Source: E-Merck, INDIA
Form: Powder
Solubility: Water-soluble
Atomic weight: 101.11 g/mol

(ii) **Ammonium Nitrate (NH₄NO₃)**
Source: E-Merck, INDIA
Form: Powder
Solubility: Water-soluble
Atomic weight: 80.043 g/mol

(iii) **Polyvinyl Alcohol (PVA)**
Structure: [-CH₂CH (OH)-]ₙ
2.3. CHARTERIZATION TECHNIQUES

2.3.1. X-Ray diffraction (XRD)

The x-ray diffraction scans for ferroelectric samples were taken using X’ Pert-Pro X-ray diffractometer (PANalytical, B.V Lelyweng, the Netherlands) with Ni-filtered CuKα radiation of wavelength 0.154 nm. The goniometer speed was kept as 2°/min. and the ferroelectric samples were scanned in the range of 10-80°.

X-ray diffraction is a tool for the investigation of the fine structure of matter. The X-ray diffraction pattern of a substance is like a fingerprint of the substance. Experimentally, the Bragg law is utilized that is by using x-rays of known wavelength \( \lambda \) and measuring \( \theta \), we can determine the spacing \( d \) of various planes in a crystal. According to Bragg’s law of diffraction,

\[
2d \sin \theta = n\lambda
\]

where, \( \lambda \) is the wavelength of x-rays, \( \theta \) is diffraction angle, \( n \) is order of diffraction and \( d \) is inter-planar spacing in a crystal.

The essential features of an x-ray spectrometer are shown in Fig. 2.1. X-rays from the tube T are incident on a crystal C which may be set at any desired angle to the incident. The x-ray spectrometer beam by rotation about an axis through O, the center of the spectrometer circle. D is an ionization chamber or some form of counter which measures the intensity of the diffracted x-rays; it can also be rotated about and set at any desired angular position. The crystal is so positioned that its reflecting planes make some particular angle \( \theta \) with the incident beam, and D is set at the
corresponding angle $2\theta$ [159]. The intensity of the diffracted beam is then measured and its wavelength calculated from the Bragg law, this procedure is repeated for various angles $\theta$.

![X-ray spectrometer](image)

**FIGURE 2.1** X-ray spectrometer.

### 2.3.2. Differential scanning calorimetry (DSC)

In the differential scanning calorimetry (DSC), heat is supplied by using the electrical energy to the reference material or the sample to maintain both the substances at the same temperature. The rate of heat flow is measured as a function of temperature. In DSC, the measuring principle is to compare the rate of heat flow to the sample and to the reference material which are heated or cooled at the same rate [160]. The phase transitions in the sample which are associated with absorption or evolution of heat cause a change in the differential heat flow which is then recorded as a peak. The area under the peak is directly proportional to the enthalpic change and its direction indicates whether the thermal event is endothermic or exothermic. The schematic diagram of the DSC setup is shown in **Fig. 2.2**.

The DSC measurements of the films were carried out at $10^\circ$C/min and 10 mg of the samples were used. A Perkin-Elmer, Pyris Diamond model for employed for
measuring the phase transition temperatures and the corresponding transition enthalpies. The DSC measurements were carried out in the temperature range of 30 to 300°C in the presence of air. The result of the DSC scans of the different composite films and the pure components are discussed in chapter III.

FIGURE 2.2 Schematic diagram of DSC setup.

2.3.3. Field emission scanning electron microscopy (FE-SEM)

A field emission scanning electron microscope (FE-SEM) is used for imaging the topography of tiny structures as small as 1 nanometer in size. Under high vacuum, the electrons are generated by a field emission source and are accelerated under the influence of a strong electrical field gradient. Within the high vacuum column, these so called primary electrons are passed through electromagnetic lenses, to produce a narrow beam of electrons which focuses onto the specimens. The interaction of primary electrons with the atoms at the surface of the sample produces secondary electrons. These electrons contain valuable information which relates to the surface structure of the sample. A detector catches the secondary electrons and produces an electronic signal (Fig. 2.3). This signal is amplified and used to reconstruct a very detailed image of the topography of the surface of the specimen [161]. The schematic diagram of FE-SEM is shown in Fig. 2.4.
FIGURE 2.3 The emission of secondary electrons form the specimen

FIGURE 2.4 The block diagram of Field Effect Scanning Electron Microscopy

The sample surface must be electrically conducting, otherwise the electron beam would charge up the surface [162]. The surface morphology of the composite films was scanned using field emission scanning electron microscopy (FE-SEM) by coating gold layer on the upper surface of the composite films. The detailed specifications of the FE-SEM microscope are given below.

Model & Make: Quanta 200 FEG & FEI Netherlands

Source: Schottky emitter based field emission gun

Voltage in electron gun: 200 V to 30 kV

Resolution: $\leq 2$ nm
Detector for secondary electrons: Conventional Everhart–Thornley detector

Detector for back scattered electrons: Solid-state back scattered electron detector

Vacuum in chamber: \(10^{-8}\) Torr

Distance between detector and sample: 10 mm

2.3.4. **Atomic force microscopy (AFM)**

The atomic force microscopy has been employed to examine the morphology and roughness of the spray deposited films. The AFM is one of the foremost tools for imaging, measuring, and manipulating matter at the nanoscale level. Piezoelectric elements that facilitate tiny but accurate and precise movements on electronic command enable very precise scanning. AFM can capture almost all the type of surfaces, which includes including polymers, ceramics, composites, glass, and biological samples [163-165].

The two- and three dimensional AFM images of the composite films were taken using NT-MDT & Ntegra model. In present studies, tapping mode is chosen to scan the composite films. The results are discussed in the chapter III.

2.4. **DETAILS OF THE OTHER INSTRUMENTS USED**

(i) **Vacuum coating unit:**

Vacuum coating unit was used to deposit the Indium electrodes of various areas onto the composite films.

Model & Make: 12 A 4D & Hind High Vacuum Co., India

Vacuum (maximum): \(10^{-6}\) mbar

Pirani gauge (range): \(10^{-2} - 10^{-3}\) mbar
Penning gauge (range): $10^{-3} – 10^{-6}$ mbar

Deposition process: Physical vaporization method (PVD)

(ii) Digital storage oscilloscope:

The digital storage oscilloscope was connected to the computer to record the hysteresis loop, current density-voltage and the switching characteristics of the composite films.

Model: HM 407-2

Source: Hameg Instruments, Germany

Software: SP107e

(iii) Function generator:

Model & source: SM 5060 & Scientific Instruments, India

Voltage range: 0 – 30V (peak to peak)

Frequency range: 0.1 Hz – 1 MHz

Waveform: Sinusoidal, square, and triangular.

(iv) C–V analyzer:

The C–V analyzer is used to measure the dc voltage dependence of capacitance, conductance and current density.

Model & Make: 590 & Keithely Instruments

DC bias range: -15 V to +15 V

Bias step: 1 V

Sweep time: 30 sec
Trigger: Pulse

Frequency: 100 kHz and 1 MHz

(v) **Capacitance bridge**

Model: LCRQ Bridge 6018

Source: Scientific Instruments, Roorkee, India

Frequency: 100 Hz and 1 kHz

DC bias: 2 V

(vi) **Electronic micro balance:**

Model & Source: HM 202 & Hameg Instruments, Germany

Range: 42 g

Least count: 0.1 mg

(vii) **Digital temperature controller:**

Make: Digitech, Roorkee, India

Temperature range: 30 – 350°C

Sensor: Cr – Al thermocouple

### 2.5. SAMPLE PREPARATION

The following procedure was adopted for the fabrication of the KNO₃: PVA composite films. The films were obtained by dissolving the different weight percentages of KNO₃ and Polyvinyl alcohol (PVA) in double distilled water. The step wise out line of fabrication process of the composite films is described with the help of a flow chart (Fig. 2.5).
2.5.1. Purification of Potassium Nitrate (KNO₃)

The KNO₃ was purified by recrystallization from aqueous solution. For this purpose, the crystal growth method was adopted in which KNO₃ was dissolved in double distilled water until saturation. The crystals were grown by keeping the solution at a constant temperature for about 100 hrs in closed environment. Good and larger size crystals of KNO₃ were obtained and excessive water was removed by using the whatmann 1 filter paper. These crystals were kept in vacuum oven at pressure $10^{-3}$ mbar at 100°C for 2 days. Pure crystals of KNO₃ thus obtained were ground in a mortar and pestle to obtain the powder.

![Flow chart for the fabrication of the composite films.](image)

Similarly, the $(\text{NH}_4)_{0.39}K_{0.61}\text{NO}_3$ was also prepared by dissolving a definite molar ratio of KNO₃ and NH₄NO₃ in double distilled water and purified using the same
method as explained above. The powders of KNO$_3$ and (NH$_4$)$_{0.39}$K$_{0.61}$NO$_3$ were used to prepare the composite films with the polyvinyl alcohol (PVA).

2.5.2. Spray deposition setup

The purified KNO$_3$ and PVA were dissolved in different proportions by weight in 50 ml of double distilled water at 40°C and stirred well. PVA has good solubility at this temperature without precipitation. The composite films of KNO$_3$ with polyvinyl alcohol (KNO$_3$: PVA) comprising of varying weight percentages of KNO$_3$ were prepared at different substrate temperatures using spray deposition setup assembled in the laboratory. Fig. 2.6 shows the schematic diagram of spray deposition setup used for the deposition of the composite films of KNO$_3$ and PVA. The deposition system consists of a nozzle of diameter 0.8 mm and length 7 cm encapsulated in a teflon cylinder with a provision for carrier gas and the solution to meet at the bottom of the cylinder. The compressed air was used as a carrier gas. The air flow line is fitted with air filter, controller and pressure gauges as shown in Fig. 2.2. The hot plate was attached to the programmable temperature controller to keep the substrate at desired elevated temperature. The films were deposited onto a polished circular brass disc of diameter 1.5 cm. The flow rate of the solution was 0.2 ml/min and gas pressure 2 kg/cm$^2$. The solution was sprayed for five minutes onto the hot substrate at a distance of 15 cm from the bottom of teflon cylinder. The composite films were deposited at the different elevated temperatures such as 100, 150, 200 and 250°C. These were annealed at the deposition temperatures for 24 hours. The thickness of the composite films were maintained as ~ 16 μm.

Similarly, the spray deposited films of pure (NH$_4$)$_{0.39}$K$_{0.61}$NO$_3$ (NKN) and composite films of NKN: PVA consisting of varying composition of NKN at different temperatures such as 100, 130, 150, 170, 200 and 250°C have been prepared.
2.5.3. Electrode deposition

Fig. 2.7 shows the layout of vacuum coating unit used for electrode deposition on the upper surface of the composite films under the vacuum $\approx 2 \times 10^{-5}$ mbar. Electrodes of various cross-sectional areas $1.867$, $3.253$ and $5.726 \times 10^{-2}$ cm$^2$ were deposited onto the films. The experimental studies of other workers have shown that indium electrodes gave ohmic contact and have good adhesion with ferroelectric materials [3, 105, 166-168]. Therefore, indium electrodes were chosen for the KNO$_3$: PVA and NKN: PVA films for carrying out all the electrical characterization on composite films.
FIGURE 2.7 The layout of vacuum coating unit

2.6. INSTRUMENTATION AND MEASUREMENT TECHNIQUES

The present experimental research work involves various types of measurements viz., polarization-electric field (P-E), current density-electric field (J-E), polarization switching, fatigue, differential dielectric, capacitance-voltage (C-V), and conductance-voltage (G-V) measurements. A brief description of the measurement techniques with the experimental setups and the equipment involved is outlined below.
2.6.1. Measurement cell

The measurement cell used to investigate the ferroelectric properties such as polarization-electric field (P-E), current density-electric field (J-E), polarization switching, fatigue, differential dielectric, capacitance-voltage (C-V), and conductance-voltage (G-V) of the composite films is shown in Fig. 2.8. The cell consists of metallic cylindrical box of diameter 6 cm over which the BNC connections were made. The cylinder was kept onto a metallic base fitted with heater and shielding. The heating can be done in the temperature range 20 – 250°C with the help of a temperature controller. The sample was held in a sandwich configuration in the sample holder consisting of pressure contact probe for proper electrical contact to the upper surface of the sample. Proper electrical shielding is also done by grounding the measurement cell to prevent the extra noise created by the external circuit disturbances. The electrical connections were made by shielded wires through BNC connectors with teflon insulations.

2.6.2. Ferroelectric hysteresis loop measurements

The measurements of P-E hysteresis loop are important because the existence of the loop together with the reversal of spontaneous polarization on application of electric
field is commonly accepted as a proof of ferroelectricity. **Fig. 2.9** shows the modified Sawyer-Tower circuit [62, 169] designed and fabricated for the investigations on ferroelectric hysteresis (P-E) and J-E loops in the composite films.

**FIGURE 2.9 Block diagram of modified Sawyer-Tower circuit.**

The a.c. signal in a frequency range, 10 Hz-1kHz from the function generator (Scientific SM 5060) was used to obtain the hysteresis loops for a ferroelectric material. The voltage lying across the ferroelectric sample is put on the horizontal plates of the digital storage oscilloscope, thus plotting, a quantity which is proportional to the field across the sample on the horizontal axis. The parallel RC circuit is connected in series with the sample, which allows compensation for any phase shift due to conductivity or dielectric loss in the sample [169]. The value of capacitance, C is chosen to be large enough so that most of voltage drop in the circuit occurs across the ferroelectric material.
FIGURE 2.10 Typical ferroelectric hysteresis loop of the composite films of KNO$_3$: PVA.

FIGURE 2.11 Typical butter-fly loop for J-V characteristics of the composite films of KNO$_3$: PVA.

The voltage, V developed across C is proportional to the charge flowing through the polar materials [169, 170]. Thus, the polarization P = $q/A = CV/A$ (where A is area...
of sample) is plotted on vertical axis [3]. The Sawyer-Tower circuit not only displays the hysteresis loop on the oscilloscope screen but also measures the important quantities such as \( P \) and \( E_c \). In the present studies, the sinusoidal signal of peak to peak amplitude 30 V was applied to obtain the P-E loop characteristics of the composite films of KNO\(_3\): PVA prepared under variety of conditions. The loops were recorded using a digital storage oscilloscope connected to the computer with standard software (SP 107e). A variable resistance potentiometer was connected in parallel to the capacitor for adjusting the hysteresis loop. The typical hysteresis loop obtained on storage oscilloscope is shown in **Fig. 2.10**. The corresponding J-V characteristics were also recorded in the composite films as shown in **Fig. 2.11**.

Similarly, the P-E loops of the pure NKN and composite films of NKN: PVA with varying preparation and deposition conditions were also traced.

The percentage of back switching and differential dielectric behaviour of the composite films have been derived from P-E characteristics. The detailed analysis of the P-E, J-E, back switching and differential dielectric measurements are presented in the chapter IV of the thesis.

### 2.6.3. Ferroelectric polarization switching transient measurements

The schematic circuit diagram for measuring the switching characteristics of ferroelectric films is shown in **Fig. 2.12** [9, 171]. The polarization current was observed across a resistance in series with the ferroelectric capacitor [68]. The resistor was chosen to be small enough (10 – 1000 \( \Omega \)) so that most of voltage drops across the ferroelectric material. The voltage developed across the resistor is proportional to the current flowing in the circuit [3]. Therefore, polarization switching current in the composite films were measured across a 100 \( \Omega \) resistor, connected in series with the composite films. The storage oscilloscope kept in X-t mode was used for these measurements. Generally sinusoidal, triangular, bi-polar square pulses, double bi-polar pulse train and synthesized wave forms are used to study the switching
transients. In the present studies bipolar square pulse (Function generator, Scientific make, SM 5060) are used to study the switching kinetics of composite films. The experimental switching current curves were fitted using MATLAB programming with the Nucleation Limited Switching model (NLS) assumptions. The MATLAB programme used to fit the experimental switching current transients is given below.

![Schematic Circuit Diagram](image)

**FIGURE 2.12** The schematic circuit diagram for measuring the switching characteristics

### 2.6.3.1 MATLAB Program used to fit the experimental switching curves

```matlab
clear all;
format long;
t1=.000052
w =0.16
fid=fopen('the','w')
syms t;
t=linspace(0,5.1125*10^-4,200);
for i = 1:length(t)
    f=@(x)(1-exp(-t(i)./10.^x).^2).*w./((x-log10(t1)).^2+w.^2)/pi;
    q(i) = ((2*3.14*w)^0.5).*quadl(f,-6,1.0);
end
```
w = diff(t);
for j =1:length(w);
    m = diff(q);
    r=2*1.99*10^-6.*3.8*10^-2.*(m./w(j))
end
fprintf(fid,' %0.5fn',r)
fclose(fid)
t2=linspace(2.5691E^-6*10^-6,5.1125*10^-4,199);
plot(t2,r);
hold on
i2=[input current data];
t3=[input time]
plot(t3,i2);

2.6.3.2 MATLAB Program used for Lorentzian distribution function

clear all;
format short e;

w=input('enter w value: ');
t1=input('peak value: ');
t=linspace(-6,-1,200);
lornf=w./(w.^2+(t-log10(t1)).^2);
y=((2*pi*w).^0.5).*lornf./pi;
data=[t' y']
plot(t,y)
save -ascii lorndata.dat data

2.6.4. Capacitance–Voltage (C–V) and Conductance-Voltage (G-V) measurements

The C-V measurements on ferroelectric film were performed on composite films at 100 kHz using a Keithley 590 CV analyzer in parallel mode. The voltage was swept from -15 V to +15 V in 30 second in the forward cycle and +15 V to -15 V in reverse
cycle with the same rate. The conductance voltage measurements (G–V) were also taken along with the C–V measurements. The current density voltage characteristics were derived from the G-V data using the relation \( J=GV/A \), where \( G \) is the conductance, \( V \) is the bias voltage and \( A \) is the area of the electrode deposited. The C–V, G–V and J-V characteristics of the composite films exhibit butterfly features of a ferroelectric material. These have been discussed in detail in chapter VI.