This chapter presents the improvement in electric field-induced pyroelectric properties of Polyurethane (PU) elastomer, brought about by the incorporation of Strontium Barium Niobate, Sr$_{0.3}$Ba$_{0.7}$Nb$_2$O$_6$ (SBN30) nanopowders. Attempts have been made to develop highly sensitive and flexible thermal/IR detector materials with SBN30/PU nanocomposites prepared in the form of cast films with varying the volume fraction of SBN30. Pyroelectric coefficients of poled samples were determined by Byer and Roundy method. The dielectric properties and thermal properties are measured following photopyroelectric (PPE) technique. The figures of merit for the material to act as a thermal/infrared detector are calculated. In order to understand the corresponding change of flexibility, Shore hardness for each composite has been measured.

5.1 Introduction

Thermal/IR detectors based on pyroelectric effect have potential advantages such as room temperature operation and wide spectral response. In the past decades major thrust in this area has been on development of
materials for infrared detection and thermal imaging for military night vision, target acquisition and missile guidance. In recent years the thrust has shifted more towards biomedical applications, waste energy harvesting, human movement detection etc [1-5]. Crystalline pyroelectric materials such as Triglycine Sulphate (TGS) and deuterated TGS have extensively been used as thermal/IR detectors for many years owing to their high pyroelectric coefficient [6, 7]. However, they suffer from serious disadvantages such as susceptibility to humidity and other environmental conditions. Ceramic/polymer based pyroelectric composite materials have the potential to be used as commercial thermal/IR detectors mainly due to the possibility to fabricate large area light weight detectors with enhanced strength and immunity to humidity and environment, eventually useful for thermal/infrared detection applications without use of substrates [8, 9].

Electro-active polymers (EAPs) have been widely studied for the past few years for various sensor applications, owing to their high field-induced polarization [10-12]. In this chapter, commercially available Polyurethane (PU), an electro-active polymer, is selected as the host polymer matrix. PU was invented during 1930s, as a result of research efforts to develop polymeric fibre materials similar to but different from nylon fibres. It was discovered even earlier but was protected by US patents [13]. Polyurethanes are one of the most versatile classes of materials today. Their industrial demand continues to grow, as they are unique materials that offer elasticity of rubber combined with the toughness and durability of hard plastics. Because urethane is available in a very broad hardness range, it allows engineers to replace rubber or plastics with the ultimate material in abrasion resistance as well as other desirable physical properties [13].
Ferroelectric materials with tetragonal tungsten bronze (TTB) structures are important due to their superior pyroelectric, piezoelectric and excellent electro-optic properties with very fast response times [14-17]. Strontium Barium Niobate ($\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$, $0.25 \leq x \leq 0.75$) or SBN, is one such interesting ferroelectric material with TTB crystal structure, which finds applications in thermal/infrared detection and diverse device applications including memory devices, surface acoustic wave (SAW) devices and so on. Moreover, SBN possesses excellent pyroelectric properties with very fast response times [18]. At low annealing temperatures, say below 950°C, SBN crystallizes into a mixture of orthorhombic and TTB phase and transforms completely into TTB phase at higher temperatures, say above 1000°C, and longer annealing times ($\approx 5$ hours) [19]. The structure of tetragonal tungsten bronze is shown in Fig. 5.1. The characteristic feature of the TTB crystal structure is interconnected...
corner sharing oxygen octahedral with three types of pseudo symmetric open channels i.e., three fold, four fold and fivefold as shown in the Fig. 5.1. All ferroelectric materials show good performance below their Curie temperatures. In the case of SBN the temperature of transition ($T_C$) from ferroelectric tetragonal to paraelectric phase depends on the concentration of strontium. As the strontium content in SBN increases the Curie temperature decreases [20]. SBN with 30 wt. percent Sr, $\text{Sr}_{0.30}\text{Ba}_{0.70}\text{Nb}_2\text{O}_6$ (or SBN30), has a high transition temperature, compared to other SBNs with higher percentages of strontium content. It is suitable for applications below 230°C, which is the Curie temperature for SBN30. Below $T_C$, SBN exhibits TTB crystal structure. Even though the pyroelectric coefficient increases with strontium content in SBN series, it is also known that SBN compositions with lower strontium content presents lower relative dielectric constants at room temperature [21]. Even for a slight increase in strontium content, there is drastic increase in dielectric constant. So, in SBN series, SBN30 composition possesses good pyroelectric coefficient, at the same time low permittivity, which are the most important factors to improve the figures of merit for a material to act as a pyroelectric infrared/thermal detector.

Though different combinations of polymers (mostly PVDF and its co-polymers) and pyroelectric ceramics (mostly titanates, niobates and TGS) have been tried to develop sensitive thermal/IR sensor materials [22], no efforts have been made so far to develop SBN/PU based polymer-ceramic nanocomposites for this application. This work is a part of an effort to develop more sensitive, polarisable and flexible composites, than already reported in literature. Different compositions of SBN30/PU have been
prepared and relevant properties measured to estimate their pyroelectric performance and compare with results reported on similar materials.

5.2 Experimental techniques

The various experimental techniques used to study the properties of the prepared SBN30/PU nanocomposite samples, including the synthesis of SBN30 and its polymer composite preparation are outlined below.

5.2.1 Sample preparation

Sample preparation includes the synthesis of nanoparticles of SBN30, the polyurethane polymer matrix preparation and fabrication of SBN30/PU nanocomposites with varying volume fractions of SBN30 ceramic inclusion in PU polymer matrix.

5.2.1.1 Synthesis of SBN30 nanopowders

Analytically pure Barium nitrate (Ba(NO$_3$)$_2$, Aldrich), Strontium nitrate (Sr(NO$_3$)$_2$, Aldrich), Niobium pentoxide (Nb$_2$O$_5$, Aldrich), Ethylene Diamine Tetra Acetic acid (EDTA, Merck), ammonia solution (Merck) and citric acid (Merck) were used as raw materials for synthesis of SBN30 nanoparticles. Nanopowder was prepared by a known aqueous organic gel route [23]. Here the citric acid and EDTA are used as the chelating agents. First the Ba-EDTA and Sr-EDTA complex solutions have to be prepared. For this, Ba(NO$_3$)$_2$ and Sr(NO$_3$)$_2$ powders are separately dissolved in deionised water and mixed with aqueous EDTA. Then in order to get transparent complex solutions, pH of both the solutions were adjusted to greater than 7 using ammonia solution. Then the pH of each of the solutions was adjusted to 7 by the addition of nitric acid.
Next step is the preparation of the Nb-citrate solution. For this Nb$_2$O$_5$ was dissolved in hydrofluoric acid by heating for 48 hours. Then aqueous solution of ammonium oxalate was added into the solution, followed by ammonia solution with continuous stirring to form precipitate of Nb$_2$O$_5$.nH$_2$O. This precipitate was filtered and washed with water to make it fluoride free. After this the precipitate was aged at 80$^\circ$C for 12 hours. The powder thus obtained was then dissolved in aqueous solution of citric acid by continuous stirring and heating at 60$^\circ$C to form a transparent pale yellow Nb-citrate complex.

Then for the preparation of SBN30 ceramic nanopowders, stoichiometric amounts of Ba-EDTA, Sr-EDTA and Nb-citrate solutions were mixed together followed by the addition of citric acid in the molar ratio of citric acid:Nb = 3:1. Then the pH was adjusted to 8 by the addition of ammonia solution. A clear transparent Sr-Ba-Nb precursor solution had high stability and no precipitation was obtained with continuous stirring. This precursor solution was then heated at 80$^\circ$C for 24 hours to produce a gelatinous precursor which was then calcined at 800$^\circ$C for 2 hours in air to form the SBN30 nanopowders.

5.2.1.2 Preparation of PU polymer solution

The polymer matrix used was commercially available PU granules (Otto Chemie Pvt. Ltd.). 15 (weight/volume)% polymer solution was prepared by dissolving required amount of PU granules in N,N-Dimethyl formamide (DMF) of S. D. Fine Chem. Ltd., solvent under continuous stirring at a constant temperature of about 75$^\circ$C for one hour. (The glass transition temperature of PU elastomer obtained from DSC analysis was
76.43°C). Thus prepared solution was kept undisturbed for some time to get bubble free polymer solution.

### 5.2.1.3 Synthesis of SBN/PU nanocomposite films

In order to measure properties of SBN30/PU nanocomposites, the samples were prepared in the form of free standing films. Ceramic-polymer nanocomposite films with different volume fractions SBN30 (0, 0.001, 0.01, 0.05, 0.09, 0.15 and 0.25) were fabricated by solvent cast technique [24]. The same 15(w/v)% PU matrix was used for fabricating each composites. Required quantities of the SBN30 nanopowder was added to it and dispersed well by sonication to avoid agglomeration of nanoparticles. The as prepared composite solution was then poured into an open glass container for the solvent to evaporate completely. Finally, free-standing films of SBN30/PU nanocomposites of thickness in the range 35-50 µm were peeled off from the container. We restricted our composite films preparation with up to the volume fraction 0.25 of SBN30 due to problem of excess particle agglomeration.

### 5.2.2 Sample characterization

Synthesized SBN30 nanopowders were characterized by powder XRD and elemental analysis was done by EDS. All the composite film samples were subjected to SEM and TEM analyses to estimate dispersion of nanoparticles in polymer matrix and to understand their exact range of particle size.

#### 5.2.2.1 Dielectric measurements

Circular pieces (diameter ≈10 mm) of dry composite film samples were coated with silver paste on both sides which acted as electrical...
contacts for the specimen. Electrode coated samples were mounted between two spring loaded copper discs (diameter ≈10 mm) for dielectric and pyroelectric measurements. The relative dielectric constant and dielectric loss were measured by capacitance method with an Impedance analyzer. Capacitance and $\tan\delta$ values were measured in the frequency range 100 Hz-5 MHz in room temperature. Values of dielectric constant and loss were calculated using these parameters. The necessary expressions are given in section 2.7 of chapter 2.

5.2.2.2 Pyroelectric measurements

The pyroelectric coefficients of the samples were determined by Byer and Roundy method [25]. For this the sample was placed in a homemade cell and the heating rate was maintained uniform at 2°C/min with the help of a temperature controller and the pyroelectric current developed was monitored with an auto-ranging picoammeter. The expression used to determine pyroelectric coefficient $p(T)$ is given in section 1.5.1 of chapter 1.

Before measuring the pyroelectric coefficient of the samples, they were electrically poled in a very high DC field. The poling technique adopted was corona poling, generally used for poling thin polymer films [26]. Corona discharge is a partial breakdown of air, usually at atmospheric pressure, and is initiated by a discharge in an inhomogeneous electric field. Usually corona poling is done at elevated temperatures. Raising the temperature in a polymer guest-host system close to or just above its glass transition temperature before poling increases the mobility of the guest molecules and allows rotation to occur during poling. In this work circular
film samples of diameter 40 mm got uniformly poled into ferroelectric domains by a single point corona by heating them up to 78°C and applying an electric field of 16 MV/m for 1 hour, and then slowly cooling the samples back to room temperature before removing the electric field.

5.2.2.3 Thermal studies

Thermal properties such as thermal conductivity and specific heat capacity are important parameters for a thermal/IR detector. These properties for the prepared samples were measured following the photopyroelectric (PPE) technique mentioned in chapter 2. Here the measurements are carried out with a commercially available pyroelectric detector used as thermal detector [27]. Sample was attached to the pyroelectric detector with a thermally thin layer of a heat sink compound whose contribution to the signal was negligible. The output signal was measured with a dual-phase lock-in amplifier in the form of amplitude and phase. From these parameters the thermal conductivity and specific heat capacity of the samples could be obtained. All measurements were carried out at room temperature.

5.2.2.4 Hardness measurements

Measurement of Shore hardness is used to understand the flexibility and hardness of polymers. Generally Shore A scale is used for 'softer' rubbers/plastics and Shore D for 'harder' ones. In the case of polyurethane selected for the study, we measured the Shore A hardness. The Shore A values for all samples were measured following indentation method.
5.3 Results and discussions

The results of the studies undertaken on SBN30/PU nanocomposite film samples are given and discussed in this section. Besides the experimental measurements, the theoretical values of thermal conductivity ($k$), specific heat capacity ($C$) and dielectric constant ($\varepsilon$) were calculated using effective medium theory [28-30]. The effective medium theory expressions used for the calculations are given in section 3.3 of chapter 3. Here the values used for the calculations of $k$, $C$ and $\varepsilon$ of the composites are 0.22 $\text{Wm}^{-1}\text{K}^{-1}$, 1662 $\text{Jkg}^{-1}\text{K}^{-1}$ and 7.13 respectively for PU matrix and the corresponding values for SBN30 ceramic filler are 1.17 $\text{Wm}^{-1}\text{K}^{-1}$, 210 $\text{Jkg}^{-1}\text{K}^{-1}$ and 930 respectively.

5.3.1 Material identification, structure and morphology

![Powder XRD pattern of the SBN30 nanopowder](image)

Fig. 5.2 Powder XRD pattern of the SBN30 nanopowder (step size: 0.020°, step time: 31.2 s)
The tetragonal tungsten bronze structure and concentrations of strontium and barium are confirmed from powder XRD and EDS analyses. The powder X-ray Diffraction pattern reproduced in Fig. 5.2 has been indexed according to JCPDS File No.73-126, and the tetragonal tungsten bronze structure for SBN30 powder is confirmed. The particle size calculated using Debye - Scherer formula is in the range 40–90 nm. The diffraction peaks at 2 theta values 27.459°, 29.367°, 31.859°, 45.684° and 51.599° were used to determine particle size. The diffraction peak at 31.859° was used to make correction for instrumental line broadening. The atomic percentages of strontium and barium present in the nanopowder obtained from EDS analysis are 23% (Sr) and 77% (Ba), which correspond to the stoichiometric composition of SBN30.

![SEM image of composite film with volume fraction 0.09 of SBN30 and TEM image of SBN30 nanoparticles](image)

**Fig. 5.3** (a) SEM image of a composite film with volume fraction 0.09 of SBN30 and (b) TEM image of SBN30 nanoparticles

The SEM image of composite film with volume fraction 0.09 of SBN30 and TEM image of the prepared SBN30 nanoparticles are shown in Fig. 5.3. From the SEM image it is evident that SBN30 nanoparticles are
dispersed nearly uniformly in the polymer matrix. Since the particles are in nanometer size, it is difficult to prevent particle agglomeration completely. However, at most care was taken to minimize agglomeration by ultrasonicating all composites before casting into films. The SEM images of other compositions also show similar results. From the TEM image it is clear that the particle size is below 100 nm. This is in tune with the average particle size calculated from the XRD pattern.

5.3.2 Sample density

![Graph](image.png)

**Fig. 5.4 Variations of theoretical and experimental densities of SBN30/PU nanocomposites**

The densities of the samples were measured by direct weighing and theoretical densities calculated by the rule of mixtures following the expression given in section 3.3.2 of chapter 3. A comparison of theoretical and measured densities is shown in Fig. 5.4.
As the volume fraction of SBN30 increases, density increases. At higher filler concentrations the measured densities are smaller than corresponding theoretical ones, indicating that lower density is due to possible particle agglomeration and presence of voids as volume fraction of SBN30 increases. But all the samples attained 94–87% theoretical density as the volume fraction of SBN30 nanoparticles increases from 0 to 25%.

### 5.3.3 Dielectric properties

![Fig. 5.5 Variations of dielectric constant with frequency for different SBN30/PU nanocomposites](image)

Dielectric properties are key parameters for thermal/IR sensor materials. The variation of the dielectric constant with frequency for pure PU and samples with different concentrations of SBN30 nanoparticles are shown in Fig. 5.5. The dielectric constant of the composite increases as the SBN30 content in PU matrix increases due to the increase in the internal
polarization of the sample. As the frequency increases the dielectric constant decreases. The dielectric loss also show slight increase with increase in SBN30 content, but decrease with frequency for all samples, as shown in Fig. 5.6.

![Dielectric Loss vs Frequency](image)

**Fig. 5.6 Variations of dielectric loss with frequency for different SBN30/PU nanocomposites**

However, beyond frequency 100 kHz, all compositions show an increase in dielectric loss with further increase of frequency. The dielectric constant varies from 7.13 to 13.51 at 1 kHz as the SBN30 volume fraction increases from 0 to 0.25 in the matrix, whereas the corresponding variation in dielectric loss is from 0.065 to 0.128. A comparison of the measured dielectric constants for all compositions at frequency 1 kHz with theoretical values is shown in Fig. 5.7. From this figure it is clear that the measured values are in good agreement with corresponding theoretical values.
calculated.

Fig. 5.7 Comparison of theoretical and experimental relative dielectric constants at 1 kHz for SBN30/PU nanocomposites with different volume fractions of SBN30

5.3.4 Pyroelectric coefficients

Pyroelectric coefficients for all the samples with different concentrations of nano SBN30 in PU were measured during heating (Fig. 5.8) as well as cooling cycles (Fig. 5.9). When SBN30 nanoparticles are added to PU the polarization of the composites increase compared to pure PU due to the dipolar contribution from SBN30. It is found that the pyroelectric coefficient during heating increases from 82 µCm⁻²K⁻¹ to 395 µCm⁻²K⁻¹ and during cooling it varies from 79 µCm⁻²K⁻¹ to 380 µCm⁻²K⁻¹ as the SBN30 concentration increases from volume fraction 0 to 0.25. During heating, in addition to the pyroelectric current, a small current due to release of trapped space charges will also be present. During cooling the
Fig. 5.8 Variations of pyroelectric coefficients during heating with temperature

Fig. 5.9 Variations of pyroelectric coefficients during cooling with temperature
Fig. 5.10 Variation of the average pyroelectric coefficient during heating and cooling and Shore A hardness for SBN30/PU nanocomposites with varying volume fraction of SBN30

presence of depolarization currents can be eliminated. That is why during cooling the pyroelectric coefficients are slightly less compared to those during heating. Fig. 5.10 shows the variation of average of the pyroelectric coefficients during heating and cooling for varying volume fractions of SBN30 in PU. The average value of pyroelectric coefficient increases from $81 \mu \text{Cm}^{-2}\text{K}^{-1}$ to $388 \mu \text{Cm}^{-2}\text{K}^{-1}$. As the volume fraction of SBN30 increases, the pyroelectric coefficient increases due to the presence of higher proportion of the ceramic pyroelectric material.

5.3.5 Thermal analysis

Fig. 5.11 shows the variations of photopyroelectric amplitude and phase with frequency, for the volume fraction 0.25 of SBN30 in PU.
Fig. 5.11 Variations of PPE amplitude and phase as functions of frequency for 0.25 volume fraction of SBN30 in PU polymer matrix

Fig. 5.12 Variations of theoretical and experimental thermal conductivity and specific heat capacity of SBN30/PU nanocomposites with varying volume fraction of SBN30
Similar kinds of variations are observed for other volume fractions also. From these amplitude and phase values the thermal parameters are calculated.

Thermal conductivity and specific heat capacity are two other important parameters to be considered for pyroelectric thermal/IR sensor materials. For a good material, thermal conductivity and specific heat capacity should be low in order to enhance their figures of merit. It is found that thermal conductivity for present nanocomposites increases from 0.22 to 0.37 Wm\(^{-1}\)K\(^{-1}\) with increase in filler volume fraction from 0 to 0.25, whereas specific heat capacity correspondingly decreases from 1662 to 1368 Jkg\(^{-1}\)K\(^{-1}\). The variations of thermal conductivity and specific heat capacity with filler concentration are shown in Fig. 5.12. Comparisons with corresponding theoretical values calculated are also shown in this figure. The experimental values follow theoretical ones in both cases.

5.3.6 Pyroelectric figures of merit

The pyroelectric performance of a material is characterized by the relevant figures of merit. Figures of merit are numerical values representing measures of effectiveness, efficiency and performance of the material when used as a transduction device. The figures of merit for high current sensitivity \((F_I)\), high voltage responsivity \((F_V)\) and high detectivity \((F_D)\), which are important for pyroelectric thermal/IR detection applications are calculated [31-34] for each of the SBN30/PU nanocomposites and found that all the figures of merit, in general, increase with increase of filler concentration. \(F_I\) increases from 48 to 283, \(F_V\) from 6.83 to 20.99 and \(F_D\) from 191 to 792 (all in units of \(\times 10^3\) µCm/J) as the filler volume fraction
Fig. 5.13 Variations of normalized pyroelectric figures of merit and normalized inverse Shore A hardness for SBN30/PU nanocomposites with volume fractions of SBN30
increases from 0 to 0.25. In the calculations, values of the dielectric constant and dielectric loss at frequency 1 kHz were used.

Variation of each of the pyroelectric figure of merit normalized to the corresponding value for pure PU, plotted against volume fractions of SBN30 nanopowder, are shown in Fig. 5.13. It can be noticed that the figures of merit increase more or less linearly with filler concentration, which is in tune with mean field approximation [35].

5.3.7 Hardness studies

In the present investigations Shore A scale is used to estimate the hardness of SBN30/PU nanocomposites. As shown in Fig. 5.10, for films of SBN30/PU nanocomposites, increase in Shore A hardness from 40 to 62 has been obtained with increasing volume fractions of SBN30 nanopowder from 0 to 0.25. The variation of inverse Shore A hardness, normalized to the value for pure PU, with varying volume fractions of SBN30, is shown in Fig. 5.13. The inverse Shore A hardness curves meet the figure of merit curves nearly at volume fraction 0.10 of SBN30. Thus, this volume fraction can be considered as one with a good balance between high flexibility and high figures of merit. This curve provides guidelines for the selection of the right composite depending upon the envisaged application.

A comparison of the values of figures of merit reported in this work has been done with the corresponding values reported in literature [22]. For the composite with volume fraction 0.10 of SBN30, the values of $F_I$, $F_V$ and $F_D$, calculated without division by specific heat capacity for direct comparison, are 190, 19.7 and 667.6 $\mu$Cm$^2$K$^{-1}$ respectively, while the corresponding values for TGS (0.43 volume fraction) in P(VDF-TrFE)
composite are 102, 8.3 and 325 respectively, which are the highest reported so far in literature. So these samples hold promise as a high performance detector material.

5.4 Conclusions

SBN30/PU nanocomposites with variable volume fractions could be fabricated as flexible free standing thin films. The pyroelectric, dielectric and thermal properties of various compositions of SBN30/PU nanocomposites are studied. The material figures of merit are determined to evaluate their efficiency for use as pyroelectric detectors. SBN30/PU nanocomposites exhibit high pyroelectric coefficient, low dielectric constant and low thermal conductivity and heat capacity so that they posses comparatively high figures of merit, higher than values reported so far in literature. It is found that the pyroelectric coefficient as well as figures of merit increase by more than 4 times as the volume fraction of SBN30 is increased from 0 to 0.25. In order to understand the changes in flexibility of the polymer with addition of SBN30 nanopowder, Shore hardness measurements are also carried out. The results shown in Fig. 5.13 enable one to identify a composite with right balance between sensitivity and flexibility for the desired sensor applications.
References:


Chapter 5


