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Efficiency of Lead-Free Nanocomposite Films Doped with MWCNT

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ABSTRACT

Polyvinylidenefluoride (PVDF) with excellent pyroelectric and piezoelectric properties such as fast, dynamic response has great potential for use in touch/tactile sensors, infrared detectors and thermal vidicon/imaging devices. Due to the toxicity of the lead based compounds, though they have high efficiencies lead-free materials are preferred for research. PVDF:LiNbO3, PVDF:LiTaO3, and PVDF:BaTiO3 nanocomposites are fabricated with optimal characteristics using the solution casting technique. After characterizing for the best pyroelectric characteristics among these materials, the best material out of these three materials is selected and used the same concentration and weight percentages to make another nanocomposite film doped with multi-walled carbon nanotubes (MWCNT). The objective of this research was to find out the lead free materials efficiency as pyroelectric materials.These lead-free nanocomposites were also characterized using Raman Spectroscopy to get the finger print of these materials and their existence in the composite film. Raman Spectrum of the nanocomposite materials is presented using 785nm laser. Obtained Raman spectrum matches with the literature available. Authors also observed that both microscopic structure and environmental conditions contributed to observed properties. Among all the MWCNT doped nanocomposite materials PVDF:LiTaO3 showed the highest Pyroelectric coefficient which would make the best material to be used in space applications compared to the other materials at test.

Keywords: *PVDF, composite films, dielectric constant, Raman Spectrum, pyroelectric detectors*

INTRODUCTION

There are compounds that are known to have special properties, such as pyroelectricity and piezoelectricity. Pyroelectric compounds are capable of generating voltage in response to changes in temperature, while piezoelectric compounds can generate voltage in response to changes in pressure (1, 3). A pyroelectric thin-film detector is a thermal transducer based on the pyroelectric effect, i.e. when the detector is exposed to infrared radiation, it absorbs radiation, its temperature rises, the rise in the temperature changes the spontaneous polarization, and thus photocurrent is obtained.

These materials are classified as smart materials having applications in various fields of science such as energy harvesting devises. There are numerous applications for these composite films. In the medical field, these films could be used in respiratory monitors as well as in tools to diagnose illnesses such as rheumatoid arthritis, vascular disorders, breast cancer, and diseases of the prostate [3]. In the military, these films could be used in night vision goggles, motion detectors, and detection and tracking of aircraft and missiles [4]. There is also a multitude of environmental applications, such as land-use monitoring; detection of volcanic eruptions, fires, and hot springs; pollution monitoring; meteorology; and investigation of atmospheric phenomena and processes [5]. Pyroelectric infrared sensing devices have several advantages over photon infrared sensors due to its greater sensitivity over a larger spectral bandwidth and greater sensitivity over a wide temperature range without the need of external cooling unlike semiconductor devices, low power requirements, faster response, and cheaper to fabricate. Composite films are of great interest for use in infrared detectors and other technology because they have been shown to have greater pyroelectric and piezoelectric effects than pure films since composite films will possess both polymer properties as well as the bulk material properties. The frequency response of materials and the effects of temperature on physical systems have been major topics of investigation for more than two centuries. Resulting from the advent of nanophysics and new technologies, including microelectronics and high-speed data processing techniques, thermal sensing and imaging have become useful diagnostic tools in the health (medical) industries, in environmental protection usage and in military arenas [6]. Smart materials are solid-state transducers having electrochromic, piezoelectric, pyroelectric, electrostrictive, electroactive, or other actuating and sensing functions. Various smart materials, for use in infrared detector or vidicon and in tensile/ pressure sensing systems, are available in the world and the man made material Polyvinylidene fluoride (PVDF) is of great interest due to its mechanical flexibility and chemical resistance. PVDF is known to have excellent pyroelectric properties, making it a compound with great potential for use in infrared detectors. PVDF is known to have excellent pyroelectric and piezoelectric properties in its β form [7, 9]. Composite films, which contain at least two compounds, have been shown to exhibit more favorable figures of merit than thin films composed of one compound alone [10,13]. In the present work pyroelectric current for various composite films were fabricated and the material which possess the highest pyroelectric current is doped with Multi-walled nanotubes (MWCNT) and characterized for its efficiency as pyroelectric detector. A PVDF thin film was used as a control. In this experiment, composite films composed of PVDF paired with lithium niobate (LiNbO3), lithium tantalate (LiTaO3), or barium titanate (BaTiO3), were fabricated by solution casting. After examining the results LiTaO3 is doped with MWCNT and tested for its characteristics as a pyroelectric device. All three compounds have perovskite structure (ABX3) and belong to the family of oxygen octahedral ferroelectrics (ABO3) [14]. Materials containing perovskites can be chemically manipulated to be dielectric, ferroelectric, magnetoresistive, thermoelectric, electro-optic, semiconducting, conducting, or superconducting (4), which is why these three compounds were selected for use. Incorporating MWCNTs into the polymeric matrices is an attractive method to combine the optical, electrical and mechanical properties of MWCNTs with the advantages of the nanocomposite material [15]. These unique properties of MWCNTs make an ideal reinforcing agent in a number of applications. Multi-walled carbon nanotubes (MWCNTs) consist of sets of SWCNTs having larger diameters [15–17]. The properties depend on the structural perfection and the ratio of Multi-walled nanotubes (MWCNT) consisting of multiple layers of graphite, rolled in onto themselves to form a tube shape structure. The MWCNTs used in the present work are of the outside diameter x length (7-15nm x 0.5-10nm, respectively) exhibit excellent mechanical and electrical properties.

Pyroelectric detectors are thermal detectors and use pyroelectric effect, to detect incident infrared radiation. The pyroelectric effect or pyroelectricity refers to change of internal polarization of a material due to small changes in temperature. Pyroelectric materials are dielectric materials and possess a spontaneous electrical polarization that appears in the absence of an applied electrical field or stress. The ‘pyroelectric’ mode of operation is in the pyroelectric or ferroelectric state of the material i.e. below the Curie temperature of the material (Tc). In the ‘pyroe1ectric’ mode, large changes in the spontaneous polarization with temperature near ferroelectric phase transitions lead to large pyroelectric coefficients. Thus, the sensitivity of detector increases. A pyroelectric detector is a capacitor whose spontaneous polarization vector is oriented normal to the plane of the electrodes. Incident radiation absorbed by the pyroelectric material is converted into heat, resulting in a temperature variation (dT) and thus, the magnitude of the spontaneous polarization. Changes in polarization alter the surface charge of the electrodes, and to keep neutrality, charges are expelled from the surface which results in a pyroelectric current in the external circuit. The pyroelectric current depends on the temperature change with time. Pyroelectric current (Ip) is proportional to Area (A) and rate of change of temperature (dT/dt) of the detecting element.

$$Ip = p.A\frac{dT}{dt} \tag{1}$$

Where p, is the pyroelectric coefficient. Determining the electrical response of a pyroelectric detector requires analysis of the thermal, electrical circuits and optical parameters.

PVDF has a number of attractive properties as used in touch and tactile sensors and in vidicon/ imaging applications. Besides high lateral thermal resolution, desirable conditions are due to PVDF low weight. PVDF's formability occurs into thin sheets between 5µm and 2mm in thickness, with accommodating mechanical properties that provide its usefulness as a material. Nevertheless, there is a need to enhance further PVDF's performance both as a sensor and target for vidicons / imagers. The polymeric, composite films containing BaTiO3, LiNbO3 and LiTaO3 are characterized for their ability to be a pyroelectric detector and the one which proved the best among these three will be doped with MWCNT to enhance the pyroelectric detector property. Research reports indicate that doping the composite material with CNTs (Carbon Nano Tubes) increase the dielectric constant more than carbon black in the microwave frequency due to their high aspect ratio [12-13]. Scientists have also reported that the dielectric constant of the composite films with CNTs and Ag particles is proportional to the thickness of CNTs as well as the weight percentage of them.

Experimental Design and Methodology

Materials and Methodology

PVDF, BaTiO3, LiNbO3 and LiTaO3 powder form were procured from Sigma Aldrich Inc, USA. Ethyl methyl ketone (MEK) also known as 2-Butanone, MWCNTs were also procured from Sigma Aldrich Inc, USA. Several methods of thin film fabrication exist, including sol-gel method, spin coating, and solution casting. In this experiment, solution casting was used to fabricate polymer thin films due to the ease of fabrication and cost effectiveness. This process involves dissolving the polymer (PVDF) in a solvent (MEK), adding the second compound (BaTiO3/LiNbO3/LiTaO3), dispersing the second compound thoroughly by using the magnetic stirrer and heating at a constant rate. For uniform dispersion of the constituents the beaker is placed in the ultra sonic bath for 2-4 hours. After the uniform dispersion of the materials the solution is poured into a petri dish, and allowing the solvent to evaporate (48-72 Hours). Further detail of this process is provided in the experimental section.

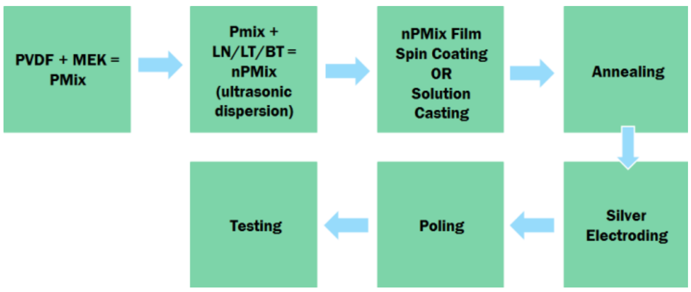

Figure1. *Steps involved in Film fabrication process*

PVDF = Polyvinylidenefluoride, MEK = Methyl Ethyl Ketone, LN = Lithium Niobate, LT = Lithium Tantalate, BT = Barium Titanate

Fabrication

Four samples of 1g PVDF were weighed. Each 0.5 g sample was added to a separate 100 mL beaker containing 20 mL methyl ethyl ketone (MEK) and a small magnetic stir bar. The beakers were placed on a hot plate and the temperature was increased by 5°C every 5 minutes until the temperature reached 80°C.

The temperature was left at 80°C until the PVDF was dissolved and the solution was clear, rather than milky white, and had a gel-like consistency. Throughout heating, the solution was stirred (stir setting approx. 130 rpm). While the PVDF was being dissolved, two sets of 0.05 g samples of $LiNbO_3$, $LiTaO_3$, and $BaTiO_3$ were obtained. Each sample was added to a separate beaker containing the PVDF + MEK 10 ml solution after the PVDF was adequately dissolved. One beaker did not receive a second compound and was used to make a PVDF thin film, which was used as a control. The hot plate was turned off and the solutions were stirred until the $LiNbO_3$, $LiTaO_3$, and $BaTiO_3$ were evenly distributed in their respective solutions. MWCNT was added in the four beakers containing PVDF and PVDF + MEK +$LiNbO_3$/$LiTaO_3$/$BaTiO_3$ and stirred using the magnetic stirrer for 2 hours for the uniform dispersion of the nanotubes into the material. The contents of each beaker were poured into glass petri dishes, which were placed in an oven at room temperature and left overnight. This allowed the solvent to evaporate in uniform conditions (no fluctuations in temperature, humidity, etc.). Throughout the duration of the fabrication process, it is important to ensure that no cross-contamination occurs. The following figure 1 explains the same steps involved in the film fabrication process.

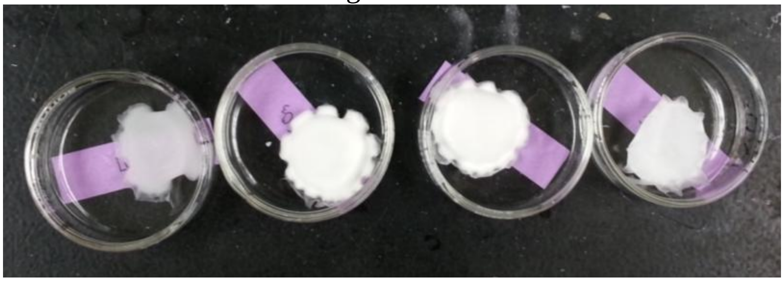

Figure2. *Left to right, PVDF:LiNbO3, PVDF:LiTaO3, PVDF:BaTiO3, and PVDF Films Obtained*

Characterization

All the films were silver coated on both sides of the samples. To measure the pyroelectric current a set-up was designed at Alabama A&M University physics department which includes an Agilent 34970A DMM (Digital Multimeter) with a Type K Thermocouple input for temperature measurement, a Barnant Company Model. 669 Temperature Control Unit with a Type K Thermocouple input for feedback loop control, a Staco, Inc. Type 3PN1010Variac for heater power adjustment, and a PC. All the films were characterized to determine their pyroelectric current. LabVIEW Pyroelectricity Measurement software was used to measure the current produced by the composite films as temperature increased over time. The temperature range for testing was about 25°C to 95°C for all samples. Data was collected by the program every 60 seconds.A simple diagram of the procedure, was explained elsewhere by guggilla et. al.

Results and Discussions

Pyroelectric Analysis

All the thin films were characterized for pyroelectric current and their Raman Spectrum. Figure 3 shows the pure PVDF and PVDF: nanocomposite films' pyroelectric current dependency on temperature variations. All the plots indicate that the pyroelectric current increases with the increase in temperature. PVDF produces the maximum current of the 1.4×10-11Amps at about 90°C, and PVDF:BaTiO3 produces the maximum current of 1.6×10-11Amps at about 90°C. Figure 3 also shows the pyroelectric current produced by PVDF:LiNbO3 as 8×10-13Amps at about 90°C and3.5×10-11Amps at about 90°Cby PVDF:LiTaO3. As shown in figure 3 it is very clear that pyroelectric current generated by PVDF:LiTaO3 film was the maximum among all the samples tested.

Raman Analysis

Figures from 4-8 show the Raman Spectrum of the samples described above. Figure 4 depicts the PVDF Raman spectrum that shows the characteristic peaks at 789 cm-1, 868 cm-1, 1052 cm-1 and 1424 cm-1 which match with the literature reported so far.

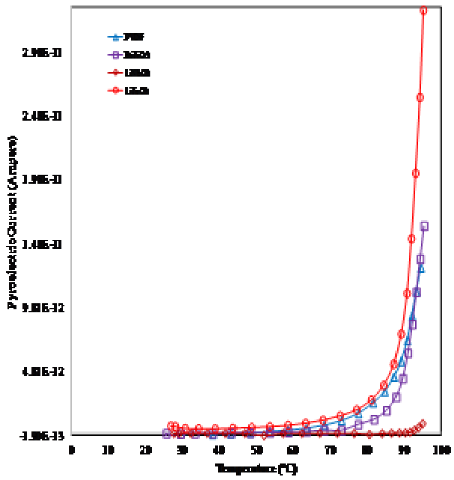

Figure3. *Temperature Vs Current Generated from Pure PVDF and PVDF: $BaTiO_3$/$LiNbO_3$/$LiTaO_3$*

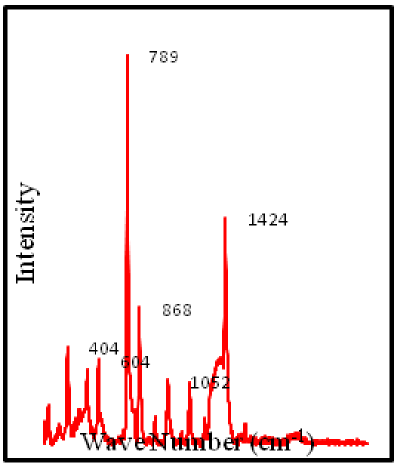

Figure4. *Raman Spectrum of Pure PVDF*

Figure5 shows the PVDF + $BaTiO_3$ Raman spectrum that elevates the characteristic peaks at 820cm^{-1}, 1052 cm^{-1}, 1154 cm^{-1} and 1571cm^{-1} which match with the literature reported so far. Figure 6 shows the Raman spectrum of PVDF+ $LiNbO_3$ that shows the characteristic peaks at 645 cm^{-1}, 822 cm^{-1}, 1033 cm^{-1}, 1158 cm^{-1}, 1358 cm^{-1}, and 1573 cm^{-1} which match with the literature reported so far.

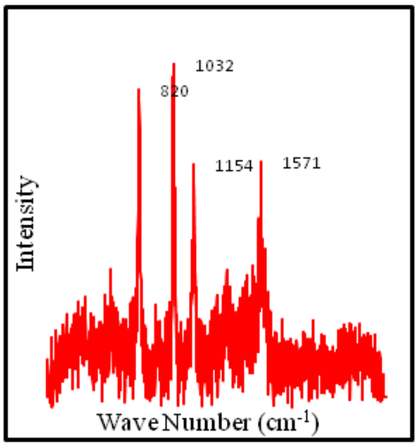

Figure5. *Raman Spectrum of PVDF+$BaTiO_3$*

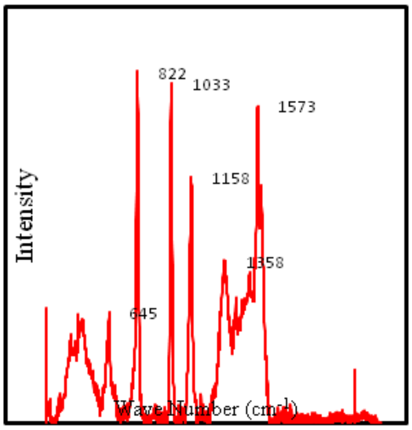

Figure6. *Raman Spectrum of Pure PVDF+LiNbO3*

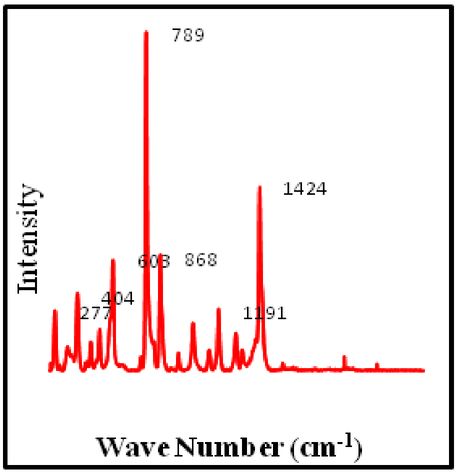

Figure7. *Raman Spctrum of PVDF+$LiTaO_3$*

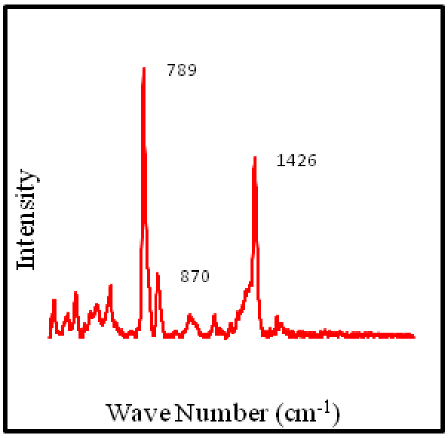

Figure8. *Raman Spectrum of PVDF+$LiTaO_3$+MWCNT*

Figure 7 depicts the PVDF+$LiTaO_3$ Raman spectrum that shows the characteristic peaks at 277 cm^{-1}, 404 cm^{-1}, 603 cm^{-1}, 789 cm^{-1}, 868 cm^{-1},1191 cm^{-1} and 1424 cm^{-1} which match with the literature reported so far. Figure 8 shows the Raman spectrum of PVDF+ $LiTaO_3$+MWCNT that reveals the characteristic peaks at 789 cm^{-1}, 870 cm^{-1}, and 1426 cm^{-1} which match with the literature reported so far. MWCNT should have the characteristic peak at 1426 cm^{-1} for C-C bond and which is evident in our Raman Spectrum.

Conclusion

Lead-free nanocomposite thin films were fabricated successfully using the low cost solution casting technique. All the nanocomposite thin films that were characterized for their electrical and optical properties. Among the pure PVDF and PVDF: BaTiO3, PVDF: LiNbO3, and PVDF:LiTaO3 nanocomposite films PVDF:LiTaO3 generated the maximum pyroelectric current when the temperature and time was varying. With the current research it is evident that there is an alternate for lead-based pyroelectric materials which are most widely used so far. Doing of the Lead-free pyroelectric materials will enhance the pyroelectric properties of the material which is evident in the graphs shown. Lithium Tantalate doped with MWCNT would be a great alternate as a smart material and Raman spectrum shows the C-C bonds in the film fabricated.

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