

Impact of Perovskite Materials in Ferroelectric Polymer

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ABSTRACT

In the recent years, nanocomposites have exhibited a catalytic role in improving electronic and optoelectronic properties of conventional ferroelectric polymers such as Polyvinylidene Fluoride (PVDF). In the present work, we have discovered that PVDF doped with perovskite materials such as calcium titanate (CT) and zinc titanate (ZT) nanoparticles would display improved bandgaps, high absorption, and superior dielectric properties. These features are further complimented by optical studies that display improved absorption and finer spectral analysis.

Keywords

Polyvinylidene Fluoride, Calcium Titanate, Zinc Titanate, Optical Bandgap, Pyroelectric, Dielectric.

Introduction

Polyvinylidene Fluoride (PVDF) has long been a promising ferroelectric polymer in composite matrices for applications in advanced sensors and detectors [1-3]. It is chemically, thermally and mechanically very stable material, which has excellent ferroelectric, pyroelectric and piezoelectric properties. Nanocomposites of electroactive ceramic and a ferroelectric polymer are very appropriate for many applications as their properties can be easily tailored to suit particular performance requirements. It has been extensively studied that the ferroelectric polymers doped with metallic fillers possess higher dielectric constants making them effective in their applications for high-k capacitors. Many research studies have indicated that these outcomes would further thrive by doping pristine PVDF with metallic fillers [4-7] and nanoparticles [8-11]. Additionally, perovskite fillers have also been gaining momentum due to their wide range of applications such as nanogenerators, photovoltaics, supercapacitors, actuators, and energy harvesters [12-15].

Typically, perovskite compounds have a chemical nomenclature of CaTiO_3 , or the family of compounds that exhibit their stoichiometry as ABX_3 . In the past decade, Organo-metal halide (OMH) perovskites have attracted a great deal of interest for applications in high-performance optoelectronic devices due to their higher

absorption coefficients, long-range electron and hole transport and potential to serve as futuristic space solar cells. Indeed, the lead (Pb) based OMH perovskites have exhibited superior photovoltaic (PV) properties, with efficiencies of over 20%, but the presence of lead is least desired for space operations because of its toxicity. As an alternative, the toxic lead was replaced by conventional tin (Sn) as perovskite light absorber. Yet, compared to their Pb-based counterparts, Sn-based perovskites so far show inferior device performance, and they are even more sensitive to degradation because of self-oxidation [16-19].

In this current work, we have investigated on the impact of the most popular perovskites calcium titanate (CaTiO_3) and zinc titanate (ZnTiO_3) as dopants in PVDF polymeric composites. It was observed that both these perovskite doped composites have displayed enhanced optical, electrical and dielectric properties than their pristine PVDF composites.

Experiment

All the materials PVDF, DMF (99.9%), ZnTiO_3 (ZT) & CaTiO_3 (CT) were secured commercially from Sigma-Aldrich. The polymer-composite films were fabricated via solution cast technique. Firstly, 0.5g of the PVDF is dissolved in 20ml of DMF at 60 and 70°C. A requisite amount of ZT and CT compounds are then added to the copolymer solution separately and this mixture is ultrasonically agitated for several hours to break up the agglomerates and disperse nanoparticles uniformly. Then films were dried for 1-2 hours in the oven, at 90°C for the solvent to evaporate.

Optical Studies

The UV-Vis spectroscopy studies were conducted on Hitachi U-2900 dual beam spectrometer spanning wavelength of 100-800nm. All the optical parameters have been derived. The optical properties of the material give information regarding the composition nature of the material. Because molecules absorb different wavelengths of light depending on their structures, monitoring the percentage of absorbance or transmittance can identify the molecular structure of a compound. The testing of samples provided explicit results for absorbance to be higher and transmittance to be lower in doped samples. The doped PVDF Nano composite films have higher transparency than those of pure PVDF thin films in the UV-Visible region with good optical constants.

The study of absorption is nothing but the analysis of the light and electrons interaction. Photon is absorbed when its frequency matches with the excited electron that was allowed to higher states, otherwise the material is transparent to such radiation. Whereas transmittance is the fraction of incident light of a wavelength which passes through a sample and is evaluated using the formula:

$$T = 10^{-A} \quad (1)$$

where, A is the absorption

The absorption coefficient (α) determines how far into a material light of a particular wavelength can be penetrated before it is absorbed and can be evaluated using the formula:

$$\alpha = 2.303 \frac{A}{d} \quad (2)$$

where, d is the thickness in cm and A is $\log\left(\frac{I_0}{I}\right)$ where I_0 is the intensity of the incident beam and I is the intensity of the transmitted beam.

The optical band gap (E_{og}) was determined by analyzing the optical data with the expression of Tauc plot for optical absorption coefficient (α) and the incident photon energy (hv) using the relation:

$$\alpha hv = (Ahv - E_{og})^{n/2} \quad (3)$$

where, A is Absorbance, h is Planck's Constant, ν is Frequency and the value of n is equal to 1 for a direct-gap material and 4 for an indirect-gap material. The plots of $(\alpha hv)^2$ and $(\alpha hv)^{1/2}$ versus hv were drawn using the above equation.

Electrical Studies

The permittivity of a dielectric material is extremely important as the ratio of the imaginary (ϵ'') to the real part (ϵ') of the permittivity is understood to be the dissipation factor. This ratio is important when determining the voltage limit to a capacitor device, and it has an immense impact on the efficiency of the capacitance. Pyroelectricity is the property of specific materials to produce an electric charge from an increase or decrease in temperature. Temperature variations encourage spontaneous polarization which means that changes in temperature can result in a change in dipole moments in a crystal structure.

The real part of the dielectric constant (ϵ')

$$\epsilon' = C_p \epsilon_0 \left(\frac{d}{A}\right) \quad (4)$$

Where, C_p is the parallel capacitance of the sample at chosen signal frequency ω , A is the electrode area of silver electrode, d is the thickness of the sample, $\epsilon_0 = 8.854 \times 10^{-12}$ F/m is the permittivity of vacuum.

The pyroelectric current I_p was measured using the Byer and Roundy Method, and the pyroelectric coefficient (p) was calculated using the relationship:

$$p = I_p \left(\frac{1}{A \cdot dT/dt} \right) \quad (5)$$

where A is the area of the electrode (identical areas for the opposite electrodes used in each sample), and dT/dt is the rate of change of temperature.

Results and Discussions

The optical property of the material gives information regarding the composition nature of the material. Furthermore, since the molecules absorb different wavelengths of light depending on their structures, the molecular structure of a compound can be identified by monitoring the percentage of absorbance or reflectance. The spectra obtained from the spectrometer can not only help identify the bonds between the molecules of the crystal, but can also help us calculate the optical properties that include bandgap energy, optical loss, optical density, dielectric constants, dielectric loss, etc.. The results presented in this research give detailed optical insights about the PVDF electronic structure and the impact of ZT, CT dopants.

The UV-Vis spectroscopy studies have indicated that the perovskite dopant materials CT and ZT have improved the absorbance of PVDF in the visible region. The perovskite materials showcase relatively greater absorption in the visible region and vice versa in the UV region due to the C-C covalent bonds. Extrapolation of the linear portion of the plot to the photon energy axis yielded a direct band gap of 1.53 eV, which is consistent with the literature. The optical bandgap energy is the energy difference between the top of the valence band and bottom of the conduction band. Figure 1 shows the direct and indirect energy gap results. The direct bandgap was found to be 6.55eV for Pure PVDF, 5.75eV for PVDF: ZT and 5.25eV for PVDF: CT. The decrease in the bandgap value is due to the influence of dopants which simultaneously influences the optical properties of the materials. The indirect bandgap was found to be 6.50eV for Pure PVDF, 5.45eV for PVDF: ZT and 4.55eV for PVDF: CT which shows that decrease in the optical indirect bandgap values is due to the dopants.

It is evident from the results that due to the increased irregularity that is caused by doping, there is a small decrease in the optical bandgap values. Thus behavior may be associated with the structural changes occurring after adding the composite material or the dopants. Hence we can conclude that the optical bandgap is dopant dependent. From the direct and indirect bandgap values it is also evident that direct bandgap values are higher than the indirect bandgap values.

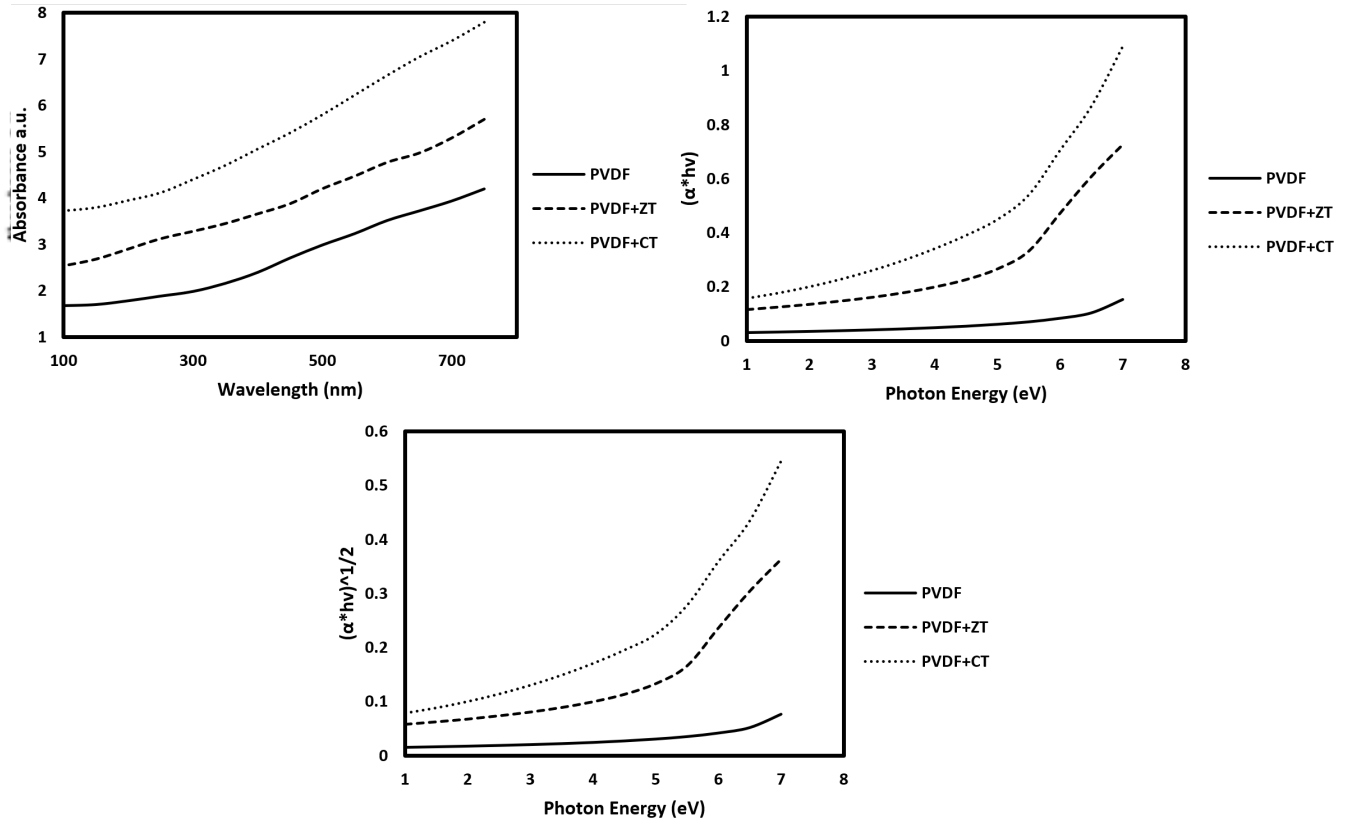


Figure 1: Graphs Illustrating Absorbance Spectra, Direct and Indirect Bandgap for PVDF & PVDF:CT/ZT.

The Raman scans for pure PVDF and PVDF: CT/ZT are shown in figure 2.

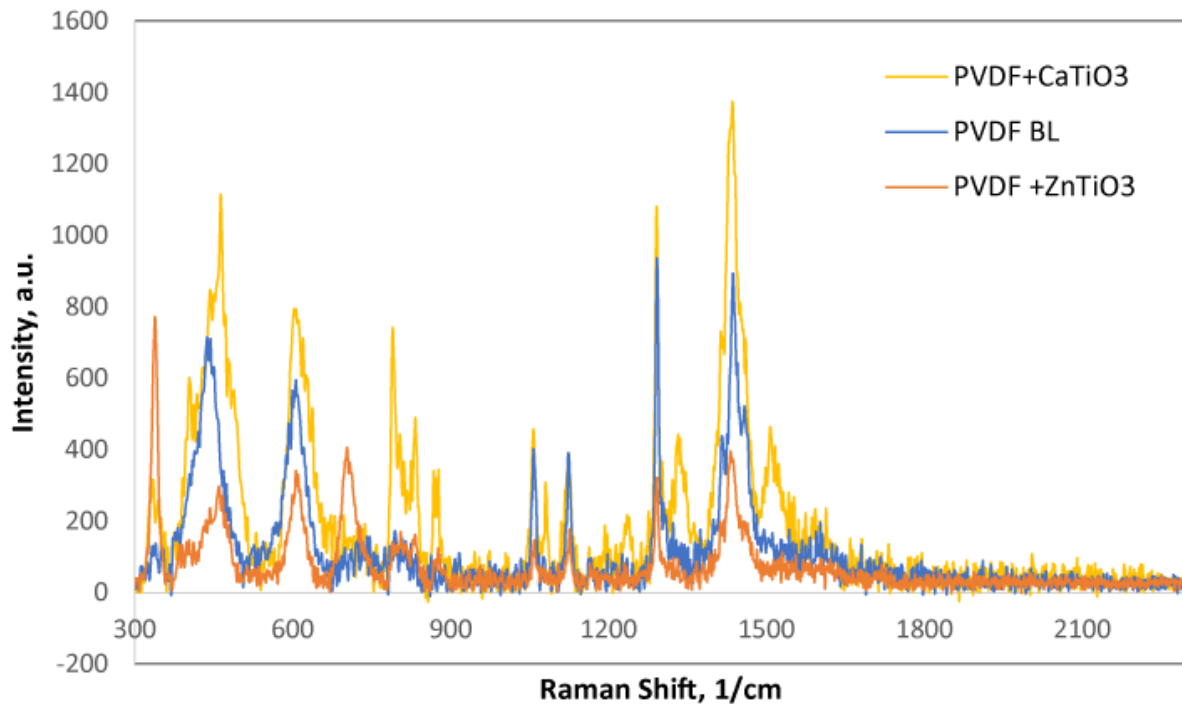


Figure 2: Graph Illustrating Raman Spectra for PVDF & PVDF: CT/ZT.

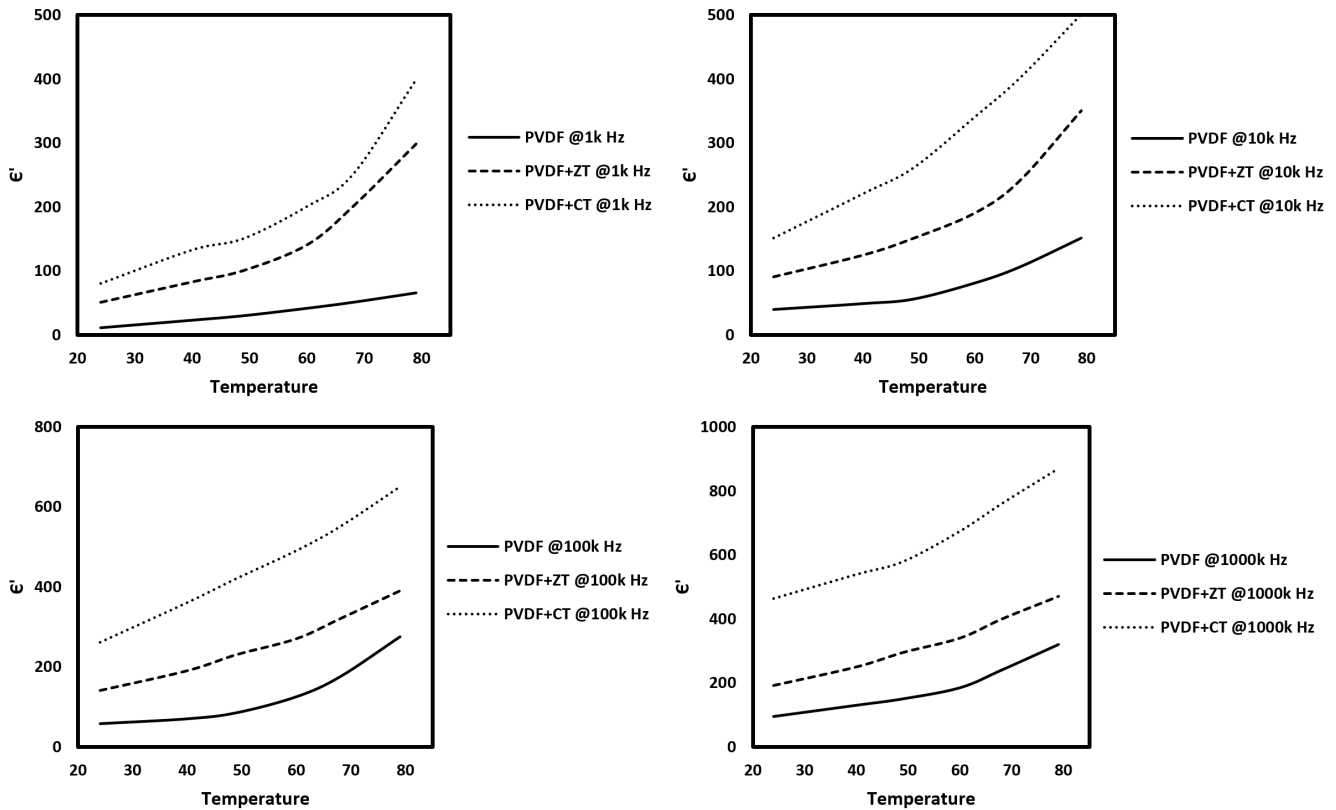


Figure 3: Graph Illustrating Dielectric Constant Vs. Temperature for PVDF & PVDF:CT/ZT

Table below gives us an understanding of Raman peaks. Most of the peaks at the frequencies are corresponding to α and β phase.

Compound	α phase	β phase
PVDF	443 cm^{-1} and 605 cm^{-1}	1293 cm^{-1} and 1436 cm^{-1}
PVDF+ZT	704 cm^{-1}	1433 cm^{-1}
PVDF+CT	464 cm^{-1} and 607 cm^{-1}	1434 cm^{-1}

The dielectric constants of the composites depend not only on the dielectric constant of each phase in the composites but also on their volume fractions, size, porosity and polarizability. The dielectric constant ϵ' was determined from measuring the capacitance C . Figures 3 shows the dielectric constant ϵ' versus the temperature at specific frequencies.

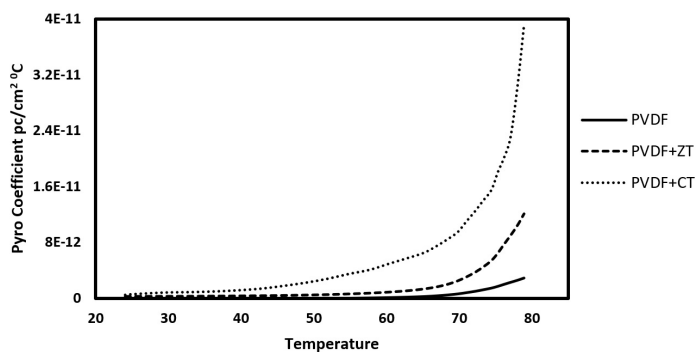


Figure 4: Graph Illustrating Pyroelectric Coefficient Vs. Temperature for PVDF & PVDF:CT/ZT.

Figure 4 shows the temperature dependence of the pyroelectric coefficient (p) of the composite films. It is found that pyroelectric coefficient is high for PVDF doped CT when compared with others. It is also evident that pyroelectric coefficient is higher for doped samples when compared with pure PVDF.

Conclusion

In this research nanocomposite films have been fabricated using the solution casting technique. The main advantage of this technique is that films can be fabricated with low cost, time efficiently and with less effort when compared to ceramic and single crystal fabrication. In our studies, we identified that the impact of traditional perovskite materials namely Calcium Titanate (CaTiO_3)/CT and Zinc Titanate (ZnTiO_3)/ZT in PVDF is significant and warranted promising results especially for sensor applications. The films were characterized for their optical, dielectric and pyroelectric properties as function of composition, frequency, and temperature. Further revealed that the PVDF composites doped with CT have relatively demonstrated superior functionalities than the ZT counterparts. From the results obtained, Absorption seems to be more for PVDF+CT compared to other samples, which also shows that adding of dopants have reduced the direct bandgap from 6.55eV to 5.25eV and from 6.50eV to 4.55eV in indirect bandgap. Thus revealing that the addition of CT nanoparticles can greatly reduce the optical bandgap when compared to ZT. Raman analysis revealed the electroactive β phase of the fabricated films. Dielectric constant ϵ' was investigated as a function of temperature and frequency from an applied signal.

It was observed that an increase in ϵ' occurred with an increase in temperature and dopants in the polymer matrix. The calculated pyroelectric figure of merit of the nanocomposite films was found to be higher than the pure PVDF film. The results have strongly proved the potential of perovskite material fillers in improving the ferroelectric and optical properties of the polymer composites.

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References

1. Matthew E. Edwards, Ashok K. Batra, Ashwith K. Chilvery, et al. Pyroelectric Properties of PVDF : MWCNT Nanocomposite Film for Uncooled Infrared Detectors. *Materials Sciences and Applications*. 2012; 3: 851-855.
2. Young Wan Nam, Woo Nyon Kim, Yong Han Cho, et al. Morphology and Physical Properties of Binary Blend Based on PVDF and Multi-Walled Carbon Nanotube. *Macromol Symposia*. 2007; 249: 478-484.
3. Daniel Guyomar, Gaël Sebald, Elie Lefeuvre, et al. Toward Heat Energy Harvesting using Pyroelectric Material. *J Intell Mater Syst Struct*. 2008; 20: 265-271.
4. Zak AK, Gan WC, Majid WHA, et al. Experimental and theoretical dielectric studies of PVDF/PZT nanocomposite thin films. *Ceramics International*. 2011; 37: 1653-1660.
5. Mago G, Kalyon DM, Fisher FT. Membranes of Polyvinylidene fluoride (PVDF) and PVDF Nanocomposites with Carbon Nanotubes via Immersion Precipitation. *Journal of Nanomaterials*. 2008; 8.
6. Chilvery AK, Batra AK, Thomas M. Investigation on Characteristics of PVDF / ZnO Nanocomposite Films for High-k Capacitors. *Physical Science International Journal*. 2014; 4: 734-741.
7. Chanmal CV. Dielectric relaxations in PVDF/BaTiO₃ nanocomposites. *eXPRESS Polym Lett*. 2008; 2: 294-301.
8. Kim GH, Koo JM, Hwang SS, et al. Relationships between structures and physical properties of PVDF / MWNT composite. 7-8.
9. Matthew E. Edwards, Ashok K. Batra, Ashwith K. Chilvery, et al. Pyroelectric Properties of PVDF : MWCNT Nanocomposite Film for Uncooled Infrared Detectors. *Materials Sciences and Applications*. 2012; 3: 851-855.
10. Tan KS, Gan WC, Velayutham TS, et al. Pyroelectricity enhancement of PVDF nanocomposite thin films doped with ZnO nanoparticles. *Smart Materials and Structures*. 2014; 23.
11. Radovan Vukićević, Peter Hierzenberger, Sabine Hild, et al. Functionalization of Carbon Black Nanoparticles with Poly (vinylidene fluoride). *J Polym Sci Part A Polym Chem*. 2010; 48: 4847-4854.
12. Park KI, Jeong CK, Kim NK, et al. Stretchable piezoelectric nanocomposite generator. *Nano Convergence*. 2016; 12.
13. Richa Pandey, Gangadhar SB, Shivani Grover, et al. Microscopic Origin of Piezoelectricity in Lead-Free Halide Perovskite: Application in Nanogenerator Design. *ACS Energy Lett*. 2019; 4: 1004-1011.
14. Qingguo Chi, Tao Ma, Yue Zhang, et al. Excellent Energy Storage of Sandwich-Structured PVDF-Based Composite at Low Electric Field by Introduction of the Hybrid CoFe₂O₄@BZT-BCT Nanofibers. *ACS Sustain Chem Eng*. 2018; 6: 403-412.
15. Ayesha Sultana, Priyabrata Sadhukhan, Md. Meheboob Alam, et al. Organo-Lead Halide Perovskite Induced Electroactive β -Phase in Porous PVDF Films: An Excellent Material for Photoactive Piezoelectric Energy Harvester and Photodetector. *ACS Appl Mater Interfaces*. 2018; 10: 4121-4130.
16. Ashwith Chilvery, Sanjib Das, Padmaja Guggilla, et al. A perspective on the recent progress in solution- processed methods for highly efficient perovskite solar cells. *Sci Technol Adv Mater*. 2016; 17: 1-9.
17. Hoefler SF, Trimmel G, Rath T. Progress on lead-free metal halide perovskites for photovoltaic applications: a review. *Monatsh Chem*. 2017; 148: 795-826.
18. Filippo De Angelis, Daniele Meggiolaro, Edoardo Mosconi, et al. Trends in Perovskite Solar Cells and Optoelectronics: Status of Research and Applications from the PSCO Conference. *ACS Energy Lett*. 2017; 2: 857-861.
19. Kamat PV, Bisquert J, Buriak J. Lead-Free Perovskite Solar Cells. *ACS Energy Lett*. 2017; 2: 904-905.
20. Roopaa TS, Narasimha Murthy HN, Praveen Kumar VV, et al. Development and Characterization of PVDF Thin Films for pressure sensors. *Mater Today Proc*. 2018; 5: 21082-21090.