ASI

Carbon – Science and Technology

ISSN 0974 – 0546

http://www.applied-science-innovations.com

RESEARCH ARTICLE Received: 18/07/2018, Accepted: 17/01/2019

Synthesis of β, γ- PVDF through electrospinning for piezoelectric force sensing application

Shubhanwita Saha and Dipayan Sanyal *

CSIR-Central Glass and Ceramic Research Institute, 196 Raja S. C. Mullick Road, Kolkata - 700032, India.

Abstract: In the present study, PVDF nanofibers containing β and γ-phases have been synthesized by electrospinning process. An experimental study was conducted for evaluating the high temperature effects on sample precursor preparation as well as PVDF phase transition (*α=>β phase and α=> γ phase*). High temperature melting process was employed to prepare PVDF solution as precursor for electrospinning and a typical process condition was mainatained to draw PVDF nanofiber. Synthesized fibers were characterized by fourier-transfonn infrared spectroscopy (*FTIR*), field emission scanning electron microscopy (*FE-SEM*) and X-Ray diffraction (*XRD*). To measure the sensing performance of the PVDF nanofibers, a piezoelectric force sensor device was constructed using these fibers. The voltage vs current and voltage vs time signals were recorded against calibrated loads using digital oscilloscope. More specifically, it was established that precursors melted at 150°C temperature is essential for producing β+γ mixed crystal based PVDF nanofibers which could generate signals of sufficiently high amplitude at low applied forces consistent with the physical acoustic theory.

Keywords: Polyvinylidene-jluoride (PVDF), electrospinning, piezoelectric force sensor; β, γ PVDF.

---

1 Introduction: During the past two decades, various research concepts have been developed to synthesize polar phase polyvinylidene fluoride (PVDF) due to its good electroactive properties, e. g. piezoelectricity, ferroelectricity, and pyroelectricity, which have a ·wide range of applications. The semi crystalline PVDF represents five separate polymorphs based on distinct chain conformatioi namely α-phases, β-phases, γ-phases, δ-phases and ε-phases which are designated as TGTG' (trans-gauche-trans-gauche), TTTT (trans-trans-trans-trans), TTTGTTTG' (trans- trans-trans-gauche- trans-trans-trans-gauche) respectively **[l]**. Among them, β-phase and γ-phase are most desirable phases for piezoelectric device construction as well as energy harvesting purpose. However, the synthesis of (TITT, TTTG) structure is considered a difficult proposition **[2-3]**. Usually, conversion of α to β-phase is achieved during PVDF crystallization through solution casting where the rate of solvent evaporation plays an important role **[4-6]**. The β-phase formation is favoured under low evaporation rates, whereas the α-phase formation is favoured under high rates of solvent evaporation. Mechanical deformation of α-form is another way of synthesizing β phase based PVDF. In β phase conformation, hydrogen and fluorine atoms are conversely situated on polymer chain. High temperature crystal melting and slow evaporation rate confirm the α- to γ-phase transformation. Specifically, it was recognized that α-form and γ-form PVDF crystals can grow concurrently in a temperature range of 157-162 °C.

Various strategies have been hence employed to get the electroactive phases of PVDF, mostly focusing on the development of specific synthesizing procedures and the addition of particular fillers. Electrospinning is a facile and cost effective technique for synthesizing ultrafme fibers from natural polymer solutions. Over the last decade, several researchers synthesized electrospun PVDF nanofibers for various applications, such as, membrane separation **[7-8]**, energy storage device preparation and so on **[6,9]**. It is reported that β phase containing PVDF nanofibers have been synthesized using electrospinning which offers excellent force sensitivity and flexibility **[10].** The effect of solvent ratio towards the enhancement of β phase crystallinity as well as piezoelectric performance has been demonstrated **[11]**. Recently, a new method **[12]** has been developed by a research group where the synthesis was done in two major steps – high temperature melting followed by slow cooling. In this process, a toy-phases transformation was clearly noticed along with a novel crystal structure phase (γ phase) which exhibited a diffraction pattern like γ- phase and crystal structure similar to α-phase.

In this present study, we report synthesis of polar PVDF phases (β, γ) through electrospinning and characterization of the electrospun PVDF fibers for development of piezoelectric force sensor. Preparation of precursor material plays a key role for synthesis of y phase containing PVDF. The main objective of this research is to study the temperature effect on phase transition as well as the performance of piezoelectric sensitivity. To confirm the effect of temperature on phase transition, synthesized nanofibers were characterized by scanning electron microscopy (SEM), X-Ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR).

1. Experimental

1.1. Materials: Poly(vinylidene fluoride) (PVDF) granules (Mw ≈ 275 000, size 5 mm) were procured from Goodfellow Cambridge Limited, U.K. N, N dimethylformamide (DMF) and Acetone were purchased from E-Merck Chemicals, India.

1.2. Sample Preparation: Measured amount (12 wt %) of PVDF precursor was stirred with a mixed solvent (DMF and acetone - 7:3) at high temperature (150 ◦C) till a homogeneous, dense and transparent polymer solution was formed. After that, it was cooled and stored in ambient temperature for electrospinning. Viscosity of sample was estimated using Anton Paar MCR502 viscometer to ensure ease of injection through the syringe and needle for electrospinning.

1.3. Electrospinning Process: PVDF nanofibers were drawn through electrospinning machine (Super-ES-2, E-spin Nanotech, India) where a 5ml syringe and a rotating drum wrapped with aluminium foil was used as an injector and collector, respectively. Precursor solution was injected through a 5ml syringe and nanofibers were spun for 30 hours. The specific experimental parameters maintained during the synthesis were 0.02 ml/min flow rate, 13 kV applied voltage and 15 cm drum to collector distance.

1.4. Characterization: The structural and morphological investigations of PVDF nanofibers were carried out by Fourier-transform infrared spectroscopy (FTIR) (Perkin Elmer IR Spectrophotometer), X-Ray diffraction (XPERT-PRO PW3071 diffractometer system with Cu Kα radiation (1.54 Å)), field emission scanning electron microscopy (FESEM Carl Zeiss Sigma), equipped with energy-dispersive X-ray (EDS) spectroscopy.

1.5. Piezoelectric Force Sensing: The piezoelectric force sensor was constructed by sandwiching the PVDF nanofibers between two aluminium foils (electrode) and measuring the piezoelectric performance by applying calibrated force on sensor surface with the help of a ITW BISS UNO100 universal testing machine at CSIR-CGCRI shown in Figure 1. Current-voltage and voltage-time characteristic curves

were recorded by a Keithley 2460 Source Meter Unit which has led to a clear understanding on designing of the PVDF force sensor.

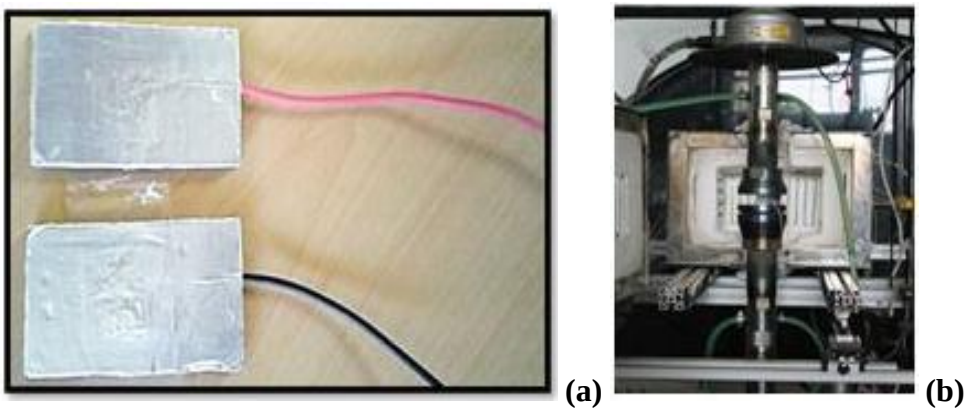

Figure (1): (a) Piezoelectric force sensing arrangements: aluminium electrodes for sandwiching the PVDF nanofibers; (b) ITW BISS UNO100 UTM machine for application of calibrated load.

2. Results and discussion:

2.1 Structural Characterization: XRD and FTIR observation XRD pattern and FTIR spectra of nanofibrous PVDF samples are depicted in Figures 2 and 3, respectively, where the dotted lines signify the particular position of each crystalline phase in the sample. In case of XRD spectra shown in Figure 2, the prominent peaks at 19.2° and 20.4° positions and small peaks at 27.4, 38.1, 39.2° correspond to β-phase and γ-phase **[3]**, respectively. The set of wavenumbers 510, 840, 1279 cm^{-1} **[3]** signify the β-phase and the wavenumbers 776, 832, 1236 cm^{-1} **[3]** signify the γ-phase crystalline structure, respectively, as revealed by the FTIR spectra in Figure 3.

The relative amount of β-phase [F (β)] and γ-phase [F (γ)] is estimated by using the eq. (1) and (2) below where the α, β and γ absorbances are denoted as A_α, A_β and A_γ at 763, 832, 840 position and absorption coefficients are termed as K_α, K_β and K_γ ($K\alpha$=0.365 μm^{-1}, $K\gamma$= 0.15 μm^{-1}; K_β= 6.1 × 10^4 and K_γ = 7.7 × 10^4 cm^2 mol^{-1}), respectively. The estimated values are 0.716 and 0.392, respectively. The result signifies that mixed crystalline structure was found for 12 wt % PVDF sample where the solvent ratio was 7:3.

$$F(\beta) = \frac{A_\beta}{(K_\beta / K_\alpha)A_\alpha + A_\beta} \quad \text{..... (1)}$$

$$F(\gamma) = \frac{A_\gamma}{(K_\gamma / K_\alpha)A_\alpha + A_\gamma} \quad \text{..... (2)}$$

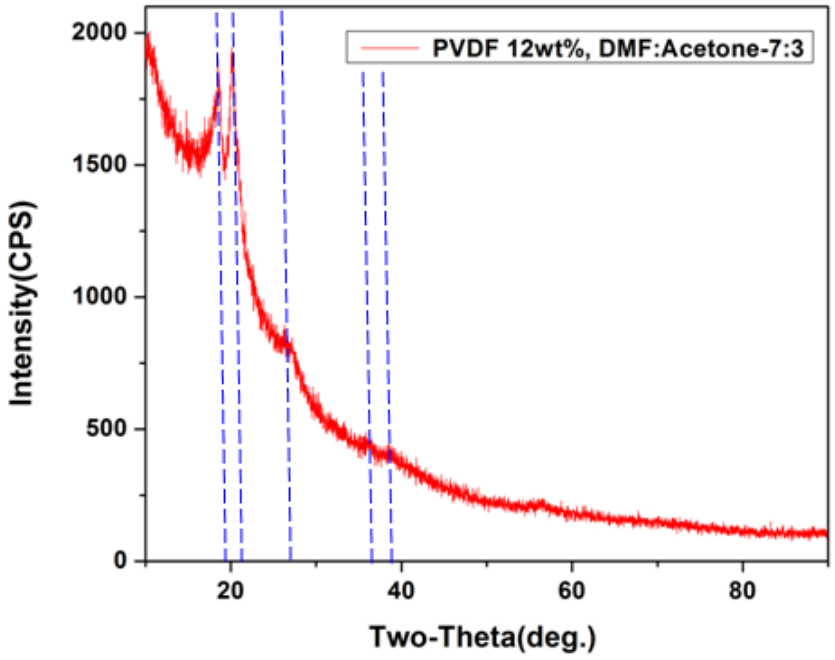

Figure (2). XRD pattern from sample containing 12wt% PVDF and 70% DMF (7:3)

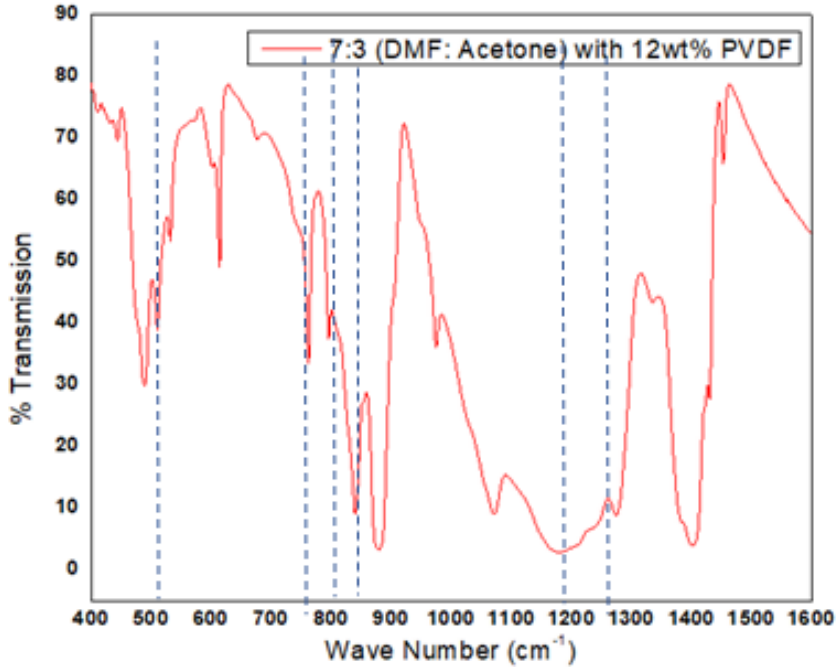

Figure (3): FTIR spectra from the sample containing 12wt% PVDF and 70% DMF (7:3)

2.2. Morphology of nanofibers - FE-SEM observation: Morphology of synthesized fibers as revealed by FE-SEM studies is depicted in Figure 4. PVDF precursors with the solvent ratio of 7:3 with 12 wt % of PVDF produced beads free, thin nanofibers of diameter in the range of 100-107 nm on electrospinning in comparison with other compositions.

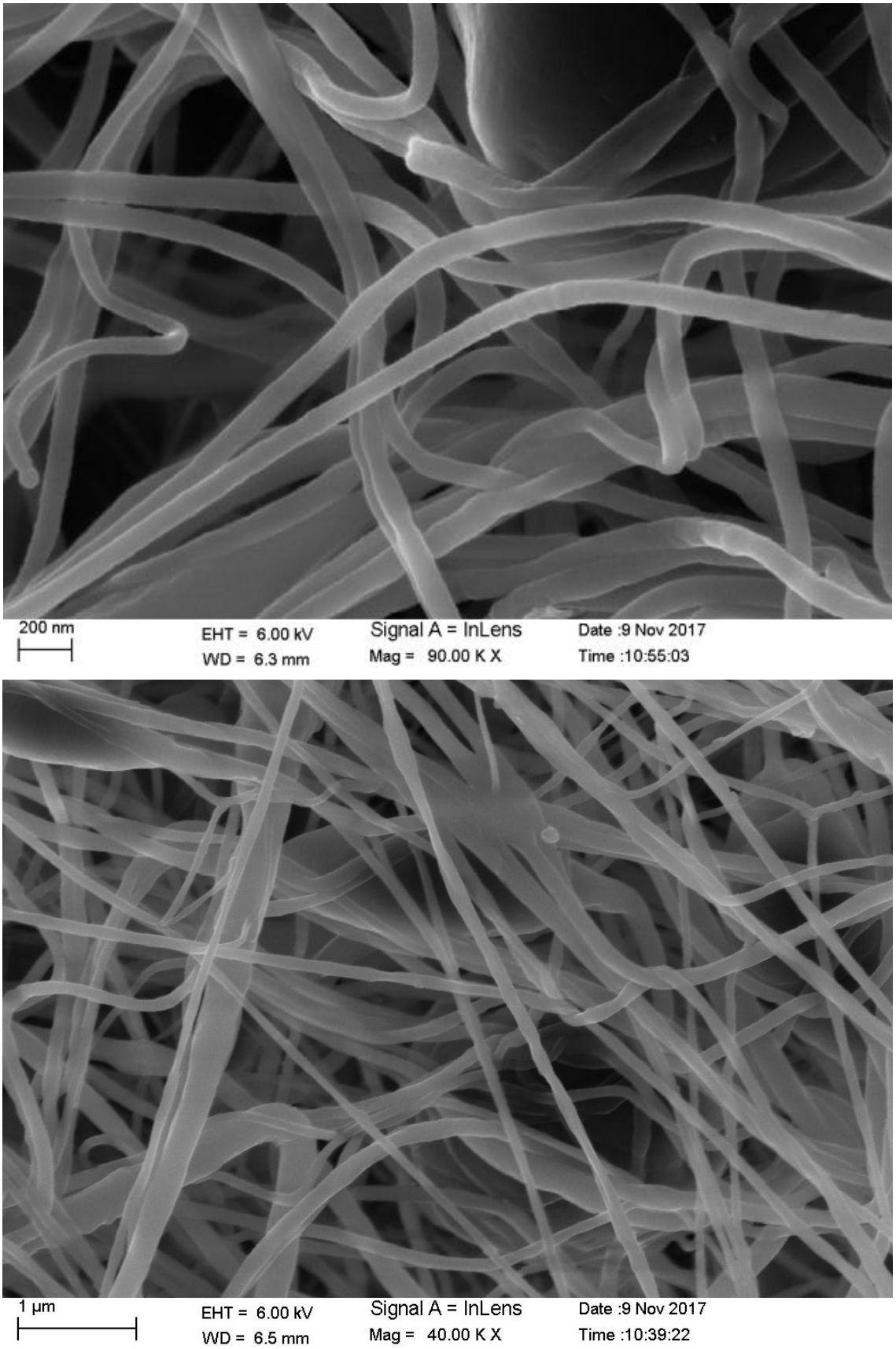

Figure (4): FE-SEM images of PVDF nanofiber.

2.3. Piezoelectric performance measurement and analysis: V vs I characteristic curves were recorded for synthesized PVDF nanofiber which is represented in Figure 5. A mildly non-linear monotonically increasing voltage vs current correlation was observed for this sample.

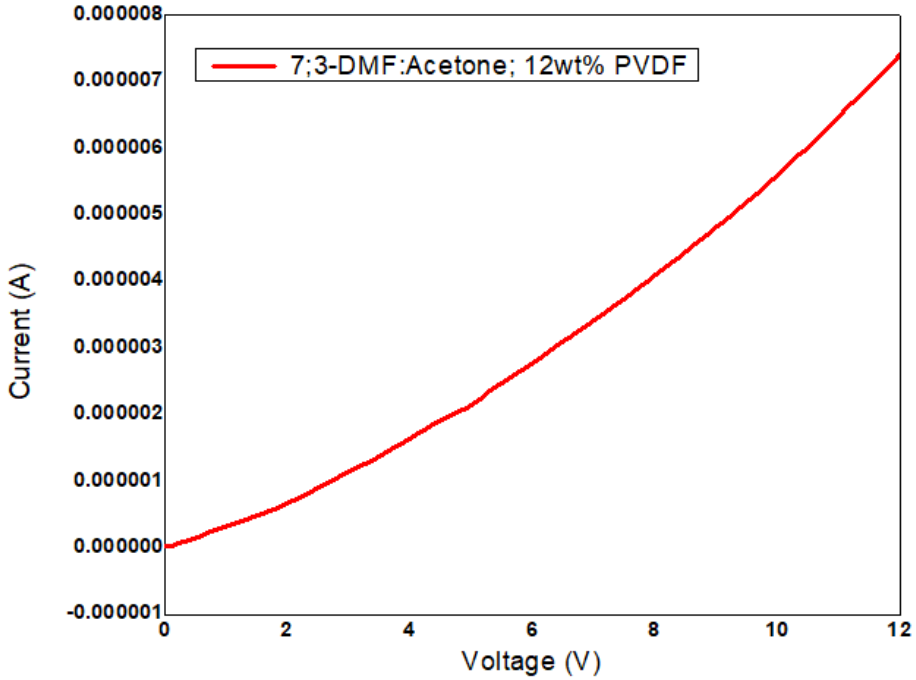

Figure (5): Voltage-Current (V vs I) characteristic curve.

More interestingly, time domain signals as shown in Figure 6 revealed nearly iso-amplitude plot with identical peak to peak time of flight confirming the fixed acoustic velocity of propagation through the medium from the theory of physical acoustics. The time domain signals further reveal sufficiently high amplitudes at relatively low applied pressure.

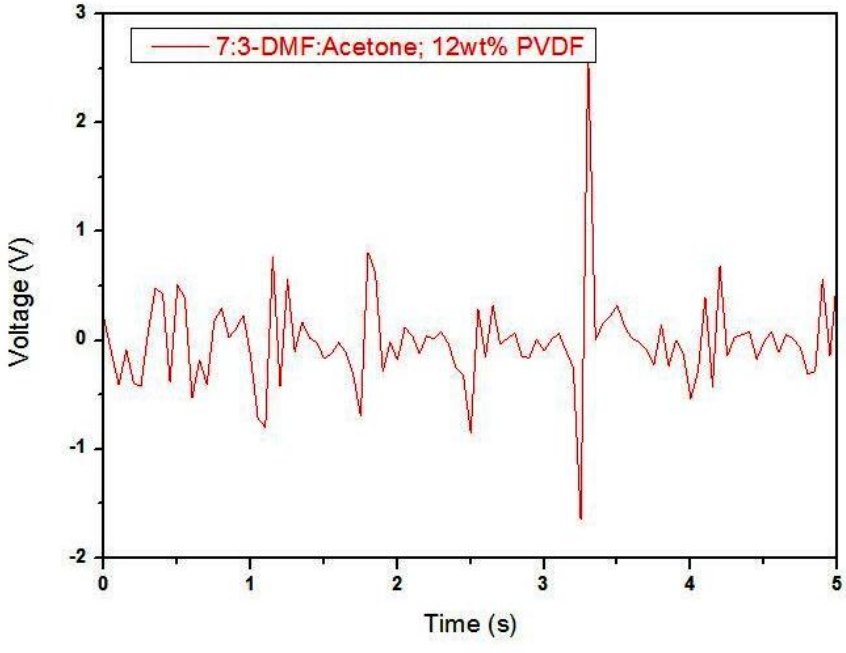

Figure (6): Time vs Voltage characteristic curve

3. Conclusions: In this paper, high temperature melted PVDF precursor based nanofiber was fabricated for development of piezoelectric force sensor. Synthesized fibers were characterized using XRD, FTIR and FE-SEM analysis. Current-voltage plots and time domain (V vs t) signals were also recorded. Specifically, temperature effect on phase transformation was studied in this work. It was established that precursors melted at 150^{o}C temperature is required for producing β+γ mixed crystal based PVDF nanofibers which could generate signals of sufficiently high amplitude at low applied forces consistent with the physical acoustic theory. The study revealed that high temperature melting process is effective for new type of crystal phase formation unveiling a new side of research prospect of force sensing, in future.

4. Acknowledgements: Financial support from CSIR-CGCRI is gratefully acknowledged. Support & encouragement of Dr. K. Muraleedharan, Director, CSIR-CGCRI and several staff and students of Non-Oxide Ceramic & Composite Division, CSIR-CGCR are thankfully acknowledged.

5. References

[1] P. Martins, A.C. Lopes, S. Lanceros-Mendez, Prog. in Pol. Sc. 39 (2014) 683.
[2] Li Mengyuan, H. J. Wondergem, M.-J. Spijkman, K. Asadi, I. Katsouras, P. W. M. Blom and D. M. de Leeuw, Nat. Mater. 12 (2013) 433.
[3] L. Ruan, X. Yao, Y. Chang, L. Zhou, G. Qin and X. Zhang, Pol. 10 (2018) 228.
[4] R. Gregorio, Jr. and M. Cestari, J. Pol. Sc. Part B: Pol. Phy. 32 (1994) 859.
[5] R. Gregorio, Jr. and D. S. Borges, Pol. 49 (2008) 4009.
[6] D. L. Chinaglia, R. Gregorio Jr., J. C. Stefanello, R. A. P. Altafim, W. Wirges, F. Wang and R. Gerhard, J. App. Pol. Sc. 116 (2010) 785.
[7] Y. Liao, R. Wang , A. G. Fane, J. Memb. Sc. 440 (2013) 77.
[8] Y. J. Kim, C. H. Ahn, M. B. Lee and M.S. Choi, Mater. Chem. and Phy. 127 (2011) 137.
[9] S. W. Choi, J. R. Kim, Y. R. Ahn, S. M. Jo and E. J. Cairns, Chem. Mater. 19 (2007) 104.
[10] Y. R.Wang, J. M. Zheng, G. Y. Ren, P. H. Zhang and C Xu, Smart Maters. and Strucs. 20 (2011) 045009.
[11] L. M. M. Costa, R. E. S. Bretas and R. Gregorio, Jr., Mater. Scs. and Apps. 1 (2010) 247.
[12] H. Wang, X. Yang, C. Yan, S. Wang, H. Yang, X. Wang, J. M. Schultz, Pol. (2017) https://doi.org/10.1016/j.polymer.2017.07.004

*****