Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Promising ferroelectric and piezoelectric response of Cr doped ZnO nanofillers incorporated PVDF flexible and laminated nanocomposite system

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S1. Materials and Methods

S1.1. Synthesis of Cr^{3+} ions doped ZnO ($Cr_{0.05}Zn_{0.95}O$) nanoparticles

In this article we have selected two different types of synthesis technique to prepare the Cr^{3+} ions doped ZnO nanoparticles, one is co-precipitation method and another one is hydrothermal method. Cr^{3+} ions doped ZnO nano seeds were synthesised via simple co-precipitation method and the rod-like structure of Cr^{3+} ions doped ZnO nanoparticles have been synthesised via hydrothermal method. In our earlier publication we have discuss about the details of co-precipitation synthesis [1] as well as hydrothermal method [2]. Both the as prepared Cr^{3+} ions doped ZnO nanoparticles synthesized by co-precipitation and hydrothermal method annealed at 400 °C and lastly mortared to obtain the final Cr^{3+} ions doped ZnO nanoparticles.

S2. Results and discussions

S2.1. Theoretical Density Functional Theory calculations

Table: 1 Electrical property calculated by Density Functional Theory

Parameters	CZC	CZH
Dipole moment (Debye)	1.32	7.44851

Quadrapole moment (C m^2)	- 26.39912	- 29.52106
Isotropic polarizability (C m^2 V^{-1})	44.12189	248.9692

S2.2. Geometrical positions of elements

CARTESIAN COORDINATES (ANGSTROEM) (CZC)

Zn	0.160044	1.648698	1.378628
O	1.833116	0.785019	1.218045
Zn	1.590998	0.949587	3.082747
O	-0.081959	1.812846	3.243300

CARTESIAN COORDINATES (ANGSTROEM) (CZH)

Zn	0.580049	1.521871	3.150615
O	1.361890	1.688837	1.557517
Zn	1.711864	0.379310	0.380806
O	-0.151604	1.606131	4.715273

S2.3. FTIR study

In the present article, to understand the modulation and enhancement of the electroactive β-phase of PVDF due to the incorporation of Cr^{+3} doped ZnO nanocomposites prepared by two wet chemical synthesis routes, the FTIR spectroscopy study is performed for all the samples. Figure 1: shows the FTIR spectra of PVDF, CZCP1, CZCP2, CZHP1 and CZHP2, within the range of 1200 cm^{-1} to 400 cm^{-1}. Prominent peaks distinctive of nonpolar α-phase of PVDF which match with CF_2 waging, CF_2 bending, CF_2 bending and skeletal bending, and CH_2 rocking has been observed in the FTIR spectra. Also, distinctive peaks corresponding to CF_2 bending, CH_2 rocking, and skeletal C-C stretching of polar β-phase of PVDF has also been observed in Figure 1. The distinctive peaks of the α- and β- phases are prominent in all the samples. The β-phase fraction [F(β)%] of PVDF, CZCP1, CZCP2, CZHP1 and CZHP2 has been calculated using the Lambert-Beer law,

$$F(\beta) = \frac{A_\beta}{\left(\frac{K_\beta}{K_\alpha}\right)A_\alpha + A_\beta} \tag{1}$$

where, A_α and A_β are the corresponding absorbance values of PVDF, CZCP1, CZCP2, CZHP1, and CZHP2 at 769 and 845 cm^{-1}, respectively, while K_α (6.1×10^4 cm^2 mol^{-1}) and K_β (7.7×10^4 cm^2 mol^{-1}) are the absorption coefficients at the respective wavenumbers. The development of β-phase fraction of CZCP1, CZCP2, CZHP1 and CZHP2 with respect to bare PVDF is depicted in Fig xx. From Fig xx, it is observed that the F(β)% of bare PVDF is ~ 43.86 %. It is also observed that there is a significant enhancement of the F(β)% of the nanocomposite films CZCP1, CZCP2, CZHP1 and CZHP2 as compared to bare PVDF which is shown in Figure 1. The enhancement of the β-phase in the nanocomposite films can be attributed to the interaction of the nanofillers and the CH_2 groups of PVDF, which transforms significant number of PVDF chains to attain the all-trans-planar zigzag (TTTT) conformation hence enhancing the β-phase fraction [5-7]. This enhancement of the electroactive β-phase of PVDF in CZCP1, CZCP2, CZHP1 and CZHP2 will play a significant role in the enhancement of the total polarization response of the nanocomposite films.

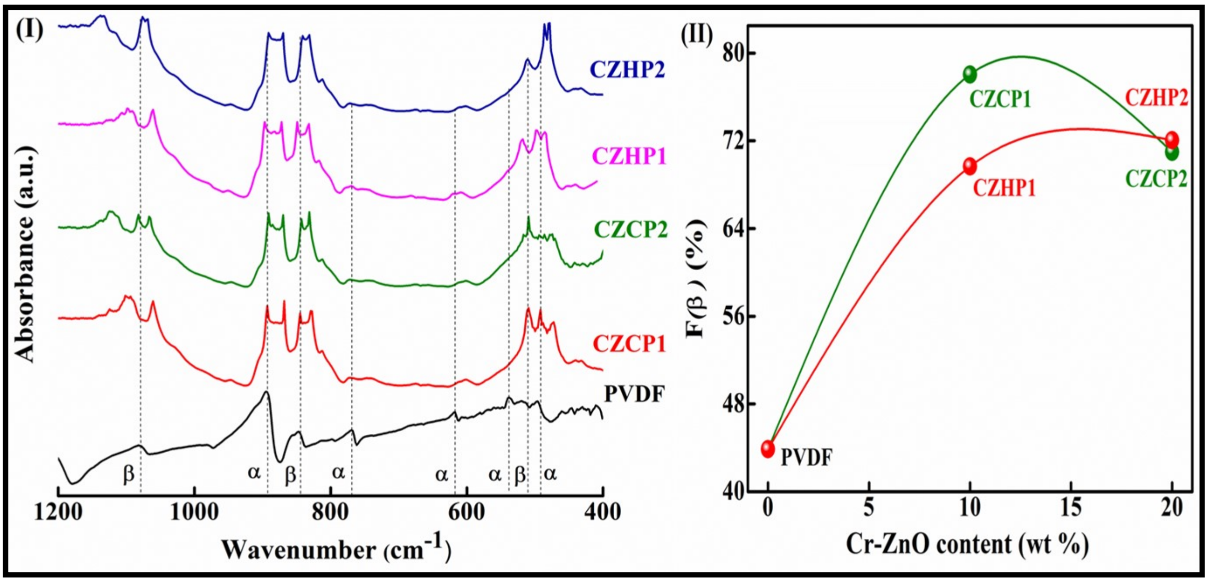

Figure 1: (I) FTIR spectra and (II) β percentage of bare PDVF, CZCP1, CZCP2, CZHP1 and CZHP2 nanocomposite films

S2.4. Calculation of force for piezoelectric energy generation

The amount of force imparted on the device has been calculated by the energy conservation law. At first, we know,

$$mgh = \frac{mv_2}{2} \tag{2}$$

Where m is the mass of a striking object, v is velocity, h is the height of the object from where it falls, and g is the acceleration due to gravity.

Velocity has been calculated in the above equation for the height of 15cm and found to be 1.715 m/s.

Now, the equation of momentum is:

$$mv = (F - mg)\Delta t \tag{3}$$

Therefore, the applied force F is:

$$F = m(\frac{v}{\Delta t} + g)$$

(4)

where Δt is the full width at half maxima (impulsive time) of the output voltage vs the time graph [Figure: 2].

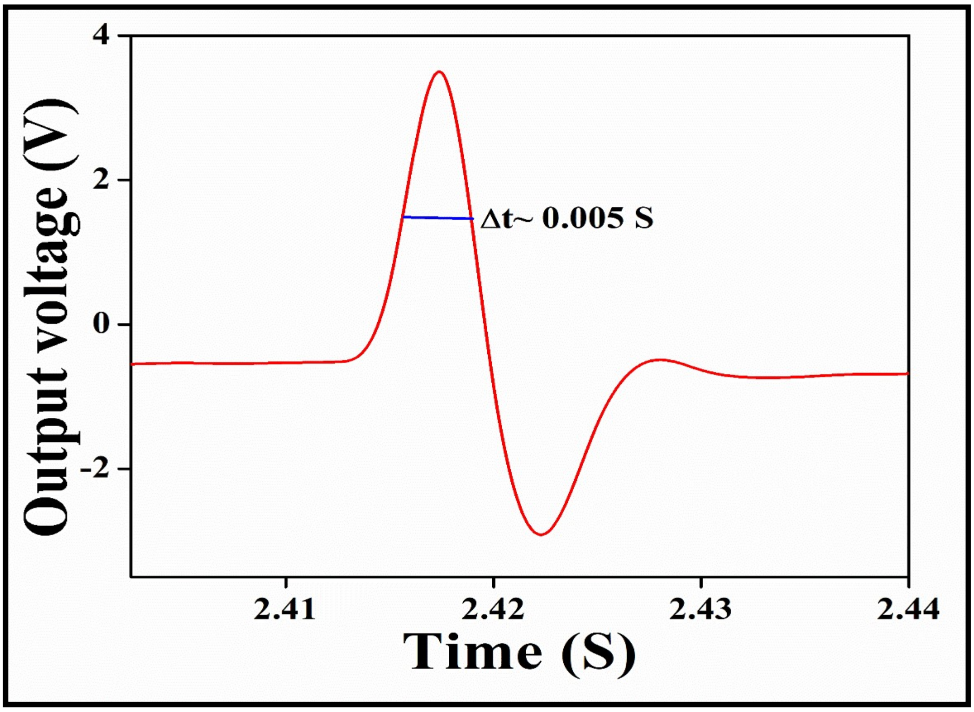

Figure 2: Full width at half maxima (Δt) from the time vs voltage plot of the device

The output piezoelectric voltage has been estimated by exerting force by finger tapping where m is 0.035 kg, v is 1.715 ms^{-1}, h is 0.15 m, g is 9.8 m/s^2, and Δt is 0.005 s. Putting these values into relation, the applied force on the device is found to be 12.35 N.

References:

[1] S. Das, A. Bandyopadhyay, P. Saha, S. Das and S. Sutradhar. *J. Alloys Compd.* 2018, **749**, 1-9.

[2] T. Debnath, T. Chakraborty, A. Bandyopadhyay, K. Das, S. Singh, S. Saha, A. Saha, R. R. Bhattacharjee, S. Das and S. Sutradhar. *Mater. Chem. Phys.* 2023, **296**, 127284.