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Advanced Research in Fluid Mechanics and Thermal Sciences

Spontaneous Polarization and Piezoelectric Tensor of Polyvinylidene Fluoride (PVDF) in α and β Phases

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ARTICLE INFO	ABSTRACT
	Combining the first principles density functional theory (DFT) and non-equilibrium Green's function we have investigated the electronic, dielectric polarization and piezoelectric properties of polyvinylidene fluoride (PVDF) in alpha and beta phases comparatively. PVDF is having a chemical formula $-(C_2H_2F_2)n-$. We have also calculated the dynamical charge properties via Born effective charges. We report the finite value of spontaneous polarization 0.914 C/m^2 and 0.625 C/m^2 for α and β Phases, respectively. These results showed that PVDF is a dielectric material with outstanding electrical response to external stimuli. These findings provide some valuable insight in understanding the quantum mechanical responses of ions and electrons in the nanoscale-materials under external applied field which enable the novel possibilities for next-generation energy materials.

1. Introduction

Fossil and nuclear fuels are the two sources of energy production. Moreover, both of them have their demerits in their own respective way. The main threat is the degradation of fossil fuels and their harmful effect on the environment. On the other hand, only few well developed countries rely on the nuclear energy even though it has an adverse effect in the human health due to high level of nuclear radiation and nuclear waste. Therefore, in the present scenario protecting environment and the renewable energy resources is highly crucial for the sustainable life and to protect mother earth from extinction. The extraction of energy from inorganic materials seems to be motivating in this regard. The manipulation of readily available materials for energy harvesting looks innovating and much greener method. Polyvinylidene Fluoride PVDF ($-CH_2-CF_2-$)n is a semi-crystalline ferroelectric polymer having four noted possible phases termed as the α, β, γ and δ phases. Among, all the known phases α and β looks more promising due to the inherent high dielectric properties which can modulated for energy harvesting such as piezoelectric, ferroelectric and pyroelectric effect [2-5]. As a result, a rigorous research attention has been paid as a greater piezoelectric coefficient is

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associated due to the enhanced electro-mechanical coupling. Various experimental works are in progress for the synthetization of PVDF (α and β). Experimentally, the β-phase of PVDF has been synthesizes when melt and crystallizes above 350 MPa [6-8] and PVDF films exhibit an α-β phase-transition [9-10]. Among the α and β phases, thermodynamically α-phase has been reported to be more stable at ambient pressure and temperature. According to the centro-symmetricity of unit crystal the α-phase is non-polar and exhibit paraelectric behaviour. However, under high mechanical (strain) pressure β-phase is reported to gain higher thermodynamical stability than α-phase [11]. As a matter of fact, that the paraelectric α-phase can be transformed into a ferroelectric β-phase under high strain. The β-phase PVDF behave as a ferroelectric material due to the presence of an intrinsic dipole moment. Free-standing ferroelectric PVDF are readily available in many of the scientific labs (chemical laboratory) but fabrication of ferroelectric PVDF in nanoscale and integration for the practical applications in nano/microelectronic is rather challenging. The higher concentration of polar solvents induces β-PVDF up to certain micrometer thickness but the fraction of the polar phase evaporates along with the solvent [12]. It has been reported that a good ferroelectric property of PVDF can be achieved when synthesizes in presence of an ionic liquid or polymethyl-methacrylate [13-15]. Ferroelectric materials are the key in material characterization due the inherent diverse fascinating functional properties such as a spontaneous polarization, high dielectric coefficient, paraelecric, etc. Thus, ferrolelectric material can be manipulated under external applied field for achieving enhanced electrical, electro-mechanical, opto-electronic and Electro-thermal properties [16-17]. Piezoelectric energy generator as an electrical energy harvesting method from various techniques such as such as mechanical vibration, ultrasonic vibration, sound vibration are green methods for energy production [18]. Piezoelectric materials form an important component in actuators and transducer of sensors which transforms the mechanical pressure into electric pulses [19]. The other possible application comprises of bio-sensors for detecting biological bio-molecules and personal battery which produces electrical energy due to stepping of shoes [20-21]. However, there are some technical difficulties due to low conversion rate and limiting their practical applications. The advancement of nanotechnology and computational techniques have provided an insight in understanding the atomistic-scale interaction and manipulation of specific area for further improvement of piezoelectric materials in energy-related applications.

2. Methodology

Figure 1(a) represents both α and β phases of PVDF. In α-phase once see the carbon chain is formed as an arm-chair in which two F-atoms and two H-atoms are linked to each carbon atom in the same direction. β phase is formed by the zig-zag chain of carbon atoms in which two F-atoms and two H-atoms are linked to two carbon atoms opposite to each other. For the calculation of electronic and piezoelectric properties we have used Virtual Nano Lab Atomistic Tools Kit (VNL-ATK) based on the density functional theory (DFT) within a frame work of linear combination of atomic orbitals (LCAO) [22]. For electron exchange correlation we have adopted a most common functional called generalized gradient approximation (GGA) with PBE parametrization [23].
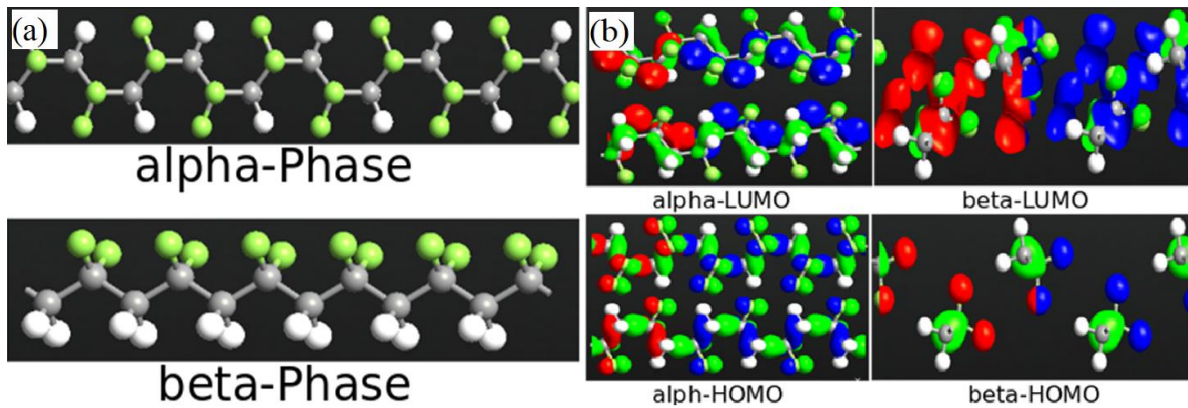
Fig. 1. (a) α and β phases structures of PVDF (b) HOMO and LUMO of α and β phases of PVDF

3. Results

Figure 1(b), represents the 3D view of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for α and β phases structures. The HOMO orbital is mostly composed of C-p and F-p states with small contribution from H-s in both the α and β phases (see Figure 2). However, in β phase the LUMO is contributed mostly by C-p and H-s states. In both α and β phases we have obtained a very high value of direct band gap, which can be seen from the electronic band energy plot (Figure 2(b)). The HOMO is represented by valence band maxima (VBM) and LUMO is conduction band minima (CBM). The calculated value of VBM and CBM along the same symmetry (Γ-Γ) are -3.46 eV and 3.46 eV, respectively for the α-phase. Similarly, the respective values of VBM and CBM are -3.076 eV and 3.076 eV in the case of β-phase. The presence of Fermi energy exactly at the middle of the energy band gap is a signature of intrinsic semiconductor. Therefore, both the α and β PVDFs are the direct semiconductors with wide band gap values 6.95 eV and 6.15 eV, respectively. The presence of F-p states is more in the valence region due to the larger p-orbital. The electron transport is related to the charge mobility and effective masses (m*) of the holes and the electrons. The lower value of effective mass gives high charge mobility due to the inverse relationship. The effective masses can be calculated from the parabolic fit of the energy band near to Fermi level. The flat band at the top of the valence region of the α-phase gives very high value of the hole effective mass $m^*_h = 35.30$ (m_e) which predict slower motion of the holes. Whereas, in the α-phase the effective mass of electron is $m^*_e = 0.426(m_e)$. The respective effective masses for the electrons and the holes in the β phase are $0.48(m_e)$ and $0.46(m_e)$ (see Table 1). For the analysis of bonding nature for both the α and β phases structures we have calculated the electron localized function (ELF) as shown in Figure 2(a). It is the matter of fact that the larger degree of ELF is represented by higher degree of electron pairing corresponds to covalent bond and smaller ELF denoted by ionic and metallic bonds. Refer to Figure 3(a) for both the α and β phases we have observed a small degree of ELF between the C-C bond. The displacement of atoms in ferroelectric perovskites and distortion of their unit cells induces polarization.
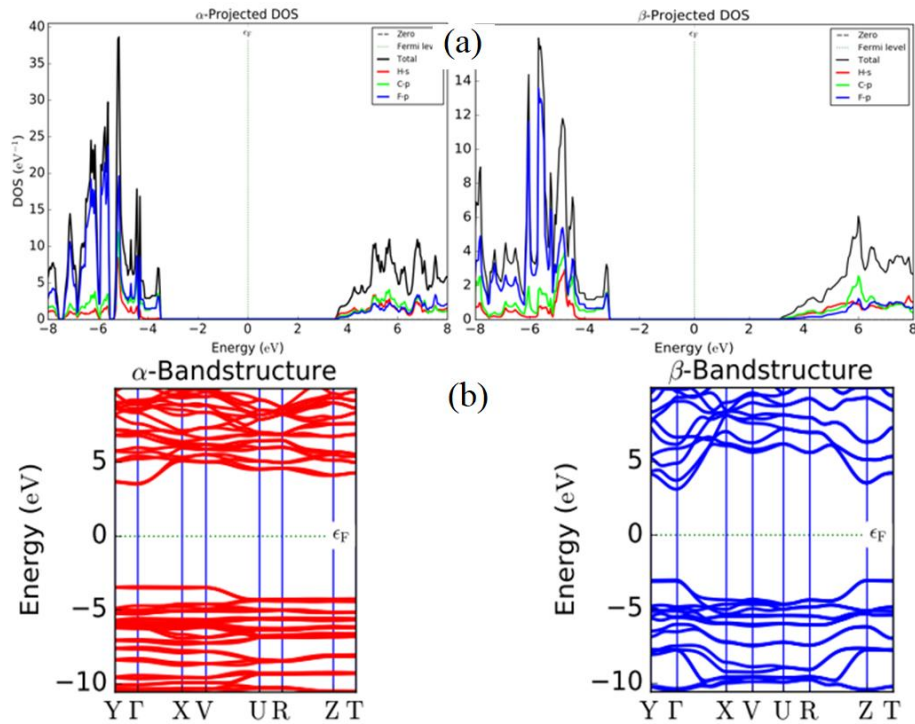
Fig. 2. (a) Total and partial density of states (DOS) of α and β phases and (b) Energy band structure of α and β phases
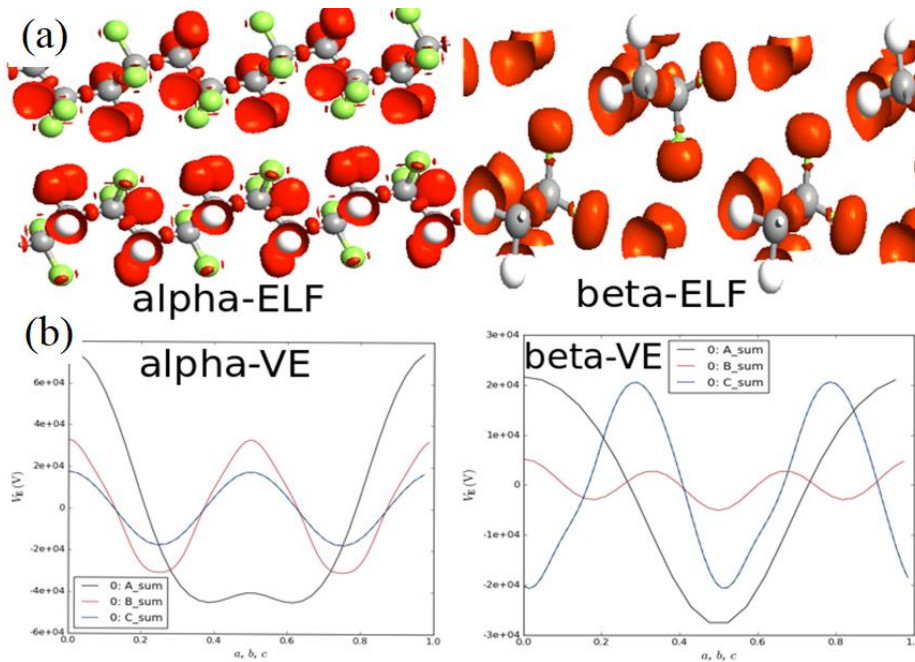
Fig. 3. (a) The electron localization function (ELF) of α and β phases and (b) Electrostatic potential of α and β phases along a, b, c axes

Table 1
Calculated effective masses (m*) and energy band gap for α and β phases

Phases	α	B
HOMO/VBM (eV)	-3.476	-3.076
LUMO/CBM (eV)	3.476	3.076
m^*_h (m_e)	-35.30	-0.460
m^*_e (m_e)	0.426	0.481
Band gap (eV)	6.953	6.152

The calculation of the Born effective charges Z* helps in analysis of the dipolar contribution in relation to the lattice dynamics in polar compounds [24]. The Born effective charges Z* indirectly helps in estimating the spontaneous polarization and piezoelectric effect. The calculated results of Born effective charges are tabulated in Table 2. The effective charges of C atoms vary from -0.45 (e) to 1.69 (e) falls within the range of -4 (e) to 4 (e) in the case of α-phase along x and z-axis, respectively (Table 2). For F-atom the Z* values are -0.73(e) to -1.39 (e) close to its actual valence charges -1. This results in charge transfer from Carbon to Florine atom. On the contrary, the Born charges of H-atom is very less as compared to +1 (e). This reflects the charge transfer from hydrogen to Carbon. However, the sensitivity of covalent bond is prominent due to the presence of small ELF between C-C atoms. Similar explanation may follow for the β phase as well. Thus, the essence of bonding in both α and β phase is a mixture of covalent as well as ionic. The calculated dynamical Born effective charges are in qualitative agreement with the previous results [25]. Which can also be seen from the ELF-figure as displayed in Figure 3(a).

Table 2
Calculated born effective charges Z* (e) for α and β phases

Phases	C			F			H		
	X	Y	Z	X	Y	Z	X	Y	Z
-α	-0.18	-0.21	-0.45	-0.43	-1.11	-0.71	0.15	0.06	0.107
	1.69	1.50	1.41	-1.35	-0.39	-0.43	0.13	0.15	0.08
-β	1.39	1.80	1.62	-0.46	-0.14	-0.42	0.073	0.089	0.212
	-0.59	-0.16	-0.18	-0.46	-0.51	-1.27	0.062	0.156	0.052

Any crystalline semiconductor/insulator of two or more sublattices with centro-symmetricity possesses a macroscopic polarization which can be manipulated to give novel piezoelectric properties. However, the large value of piezoelectric effect for practical application is still a big hurdle. For obtaining a large piezoelectric behaviour a material should have the movable ions having high value of effective charges under applied strains. The application of uniaxial-strain produces a spontaneous polarization with induced electric field to exhibit piezoelectric coefficient. The total macroscopic polarization (P_t) is calculated as the sum of the electronic polarization (P_e) and the ionic polarization due to strain (P_i) given by Eq. (1).

$$P_t = P_e + P_i \tag{1}$$

The piezoelectric tensor [26] is expressed as Eq. (2)

$$\rho_{\delta\alpha} = \frac{\Delta P_\delta}{\Delta \varepsilon_\alpha} \tag{2}$$

Here, $\rho_{\delta\alpha}$ has been calculated by taking a finite displacement method and P_t is calculated from Berry-phase approach [26]. The calculated values of total macroscopic polarization values are 0.914 C/m^2 and 0.625 C/m^2 for α and β Phases, respectively. Also, the values of piezoelectric constants for α and β Phases are 0.0207 C/m^2 and -0.271 C/m^2, respectively. Our result is in good agreement with the previously obtained result 0.18 C/m^2 [27]. But the result obtained from isotropic continuum dielectric theory was underestimated 0.086 C/m^2 [28,29], incorporating the pairs of point charges at each lattice point and taking Coulomb the result to 0.127 C/m^2 [30]. Moreover, from the force fields molecular simulation the value has been enhanced to 0.140 C/m^2 [31]. The other value reported by using the quasi-harmonic lattice dynamics at 0K is 0.182 C/m^2 [32] and from a rigid-dipole model is 0.131 C/m^2 [33].

4. Conclusions

In summary, we have calculated the electronic and piezoelectric properties polarization of the planar arm-chair α-phase and the planar-zigzag β-phase of polyvinylidene fluoride (PVDF) by density functional theory within LCAO potential and GGA. In addition, we have calculated the spontaneous polarization for both the phases from Berry-phase approach. From finite displacement of the polarization the dynamical Born effective charges are computed for each atom. These effective charges denote nature of bond, carbon-carbon bond is covalent in nature, Carbon-Flourine bond is polar and Carbon-Hydrogen bond is less polar in nature. Finally, analysing the effective charges the system under our investigation exhibits mixture of ionic and covalent bondings. The calculated piezoelectric constants are in good agreement with the previous results reported from different approaches.

Acknowledgement

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