



Stability, phonon dispersion and specific heat of solid poly(vinyl alcohol) using density functional theory



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ABSTRACT

The present paper reports a systematic theoretical study of structural, electronic, vibrational and thermal properties of solid poly(vinyl alcohol) (PVA) in the orthorhombic and monoclinic structures. Our results on phonon dispersion curves confirm that PVA is dynamically stable in both orthorhombic and monoclinic structures as claimed by the X-ray diffraction study. However, total energy is minimum in the case of orthorhombic structure and hence orthorhombic is more favorable phase of PVA. We also report the electronic band structure for PVA in both structures and obtained a good agreement between present and available data. The dielectric constant has also been reported and discussed. We have also calculated the temperature dependent specific heat at constant volume, C_v and discussed its behavior. There is a reasonably good agreement between the experimental and our calculated data.

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1. Introduction

In recent years, Poly(vinyl alcohol) (PVA: $[-CH_2-CHOH-]_n$), a hydrophilic semicrystalline polymer has attracted much attention from material science, chemistry and condensed matter physics researchers due to its excellent biocompatibility, nontoxicity, electrical, optical, mechanical and vibrational properties. PVA has very high dielectric strength, good charge storage capacity and dopant dependent electrical and optical properties. This makes PVA an important member for polymer composites. In general, the polymers are fundamentally different from conventional inorganic materials due to their highly anisotropic quasi one dimensional structure. The diffusion of molecules/atoms into the structure due to its weak inter chain binding is easy while strong inter-chain carbon–carbon bonds maintain the integrity of the polymer. Therefore, any lattice modification in the bonding and position of atoms will bring modification in the structure and composition of the polymer and thus bring sufficient changes in the properties. These properties have paved a way to its use in a wide range of applications ranging from cosmetics to food to packaging materials to pharmaceuticals. Despite its great importance and uses, there are many issues in PVA which are yet to be addressed for its use and

applications. One of such long awaited issues is the structure of poly(vinyl alcohol) [1–3]. The first comprehensive X-ray analysis of PVA showed that the PVA has a pseudo-orthorhombic cell [1], while Bunn [2] in a later study proposed a monoclinic unit cell with two molecules. In another study, Colvin [3] has shown that no single unit cell can adequately account for all the observed reflections in X-ray analysis of PVA and hence system comprises two crystal structures: monoclinic and orthorhombic. First principles calculation based on density functional theory [4] has been an effective method for the study of structural, electronic, dynamical, mechanical and dielectric properties of polymers [5–7]. The phonon calculations in the complete Brillouin zone is a method to indicate the dynamical stability of a compound in a particular structure. Furthermore, the lattice dynamics or vibrational spectroscopy plays an important role in probing the conformational changes through confirmationally sensitive modes. The usual vibrational spectroscopic techniques such as infrared absorption (IR) or Raman spectrum for polymers are very complex and cannot be unrevealed without the full knowledge of dispersion curves.

In this paper, we present a systematic theoretical results from ab initio calculations on solid PVA in orthorhombic and monoclinic structures. Of particular interest is to investigate lattice dynamical properties such as phonon dispersion curves, phonon density of states and lattice specific heat of PVA in both the structures and shed some light on the structure of PVA. Further, we report energetics, structural, electronic, thermal and dielectric properties

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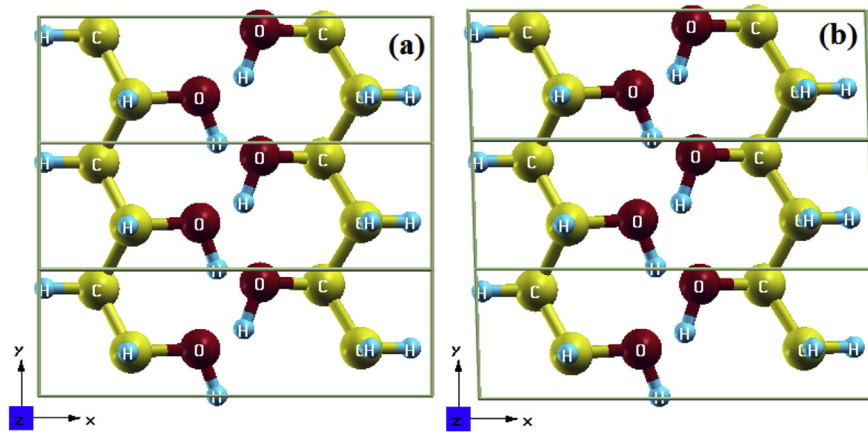


Fig. 1. Optimized structure of PVA (a) orthorhombic and (b) monoclinic structure.

Table 1
Lattice parameters, Dielectric constant and Total energy of PVA in monoclinic and orthorhombic structure.

PVA	Monoclinic structure		Orthorhombic structure	
	Present work	Expt.	Present work	Expt.
a (Å)	7.88	7.81 ^a , 7.79 ^c	7.91	7.82 ^b , 7.93 ^c
b (Å)	2.56	2.52 ^a , 3.795 ^c	2.563	2.52 ^b , 2.975 ^c
c (Å)	5.56	5.51 ^a , 5.325 ^c	5.55	5.60 ^b , 5.27 ^c
β	9140'	9142 ^a , 96 ^c	–	–
Dielectric const. ϵ_{∞}	2.4, 2.67, 2.3	2.6 ^d	2.37, 2.64, 2.26	2.6 ^d
Total energy (Ry/atom)	–8.487063	–	–8.487326	–

^a [2].

^b [1].

^c [3].

^d [19].

which may help in understanding the charge transport behaviors in PVA and enable one to design the devices based on this material (Polymer).

2. Computational details

All calculations for solid PVA have been performed using density functional theory with generalized gradient approximation (GGA) using Perdew–Burke–Ernzerhof (PBE) [8] parameterization of exchange correlation as implemented in the Quantum Espresso Code [9]. The plane wave ultrasoft pseudo potential method is adopted to describe the interaction between electrons and ions. For the Brillouin zone integration we use $8 \times 8 \times 8$ sampling mesh within Monkhorst–Pack scheme [10]. Kohn–Sham wave functions were represented with a plane wave basis with energy cutoff 50 Ry and charge density cutoff 500 Ry. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) method is used for geometry optimizations. The force on each atom is converged up to 0.1 eV/Å for all optimizations. Phonon calculations are performed within framework of self-consistent density functional perturbation theory (DFPT) [11] which allows the use of only the unit cell to calculate the phonons at any wave vector. The DFPT calculates full dynamical matrices through the linear response of electrons to a static perturbation included by the ionic displacements.

The thermodynamic functions of a solid can be calculated using phonon density of states which is an important dynamical property as its computation needs frequencies in the entire BZ [12–15] and can be defined as

$$g(\omega) = \frac{1}{N} \int_{BZ} \sum_j \delta[\omega - \omega_j(q)] dq \quad (1)$$

where N is normalization constant that $\int g(\omega) d\omega = 1$, $g(\omega) d\omega$ is the ratio of the number of eigenstates in the frequency range ($d\omega = \omega + d\omega - \omega$) to the total numbers of eigenstates and $\omega_j(q)$ are phonon modes. This means that the density of states expresses the way energy is distributed among the various branches of phonon modes in the crystal. Using equation (1), the phonon contribution to Helmholtz free energy ΔF , the phonon contribution to the internal energy ΔE , the constant volume specific heat C_v and the entropy S with temperature T can be calculated using harmonic approximation as given in Refs. [15–17].

3. Results and discussions

In our calculations, we first optimized the PVA in orthorhombic and monoclinic structures through total energy calculations. The completely relaxed structures of PVA in both the phases are presented in Fig. 1. We have already reported lattice parameters, bond lengths and other structural and electronic properties of PVA in monoclinic phase in our preliminary study [18]. Table 1 presents the optimized cell parameters, total energy and dielectric constant together with the available experimental data [1–3,19] which depicts an excellent agreement between present and available experimental data. A very small difference (almost nil) in the lattice parameters of both the systems suggests the possibility of the presence of both the structures as concluded by Colvin [3]. The lower total energy of the orthorhombic phase suggests

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