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Prediction of new polymorph of glycine and study of electronic and dielectric properties: A first-principles study

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ABSTRACT

First-principles calculations based on Density Functional Theory have been done on an important Amino acid Glycine. Its structure has been simulated and variable cell calculations based on energy minimization technique give a new polymorph of Glycine showing triclinic unit cell with lattice parameters a=4.15Å, b=14.30Å, c=5.53Å, α=97.35deg, β=101.65deg and γ=98.46deg. Volume of the unit cell is found to be 313.8Å^3. Band gap in case of this polymorph of Glycine comes out to be 3.43eV. This value is in the range exhibited by Non-linear Optical (NLO) materials. The value of dielectric constant comes out to be 2.30, 2.29 and 2.61 along X, Y and Z axes respectively and its average value comes out to be 2.4. Molecular packing in this polymorph of Glycine is similar to that in case of α-Glycine. © 2016 Trade Science Inc. - INDIA

KEYWORDS

Glycine;
Dielectric constant;
Electronic density of states;
First-principles calculations;
Amino acid;
NLO material.

INTRODUCTION

Amino acids are biologically important organic compounds made from amine (-NH2) and carboxylic acid (-COOH) functional groups, along with a side-chain specific to each amino acid. The key elements of an amino acid are carbon, hydrogen, oxygen, and nitrogen, though other elements are found in the side-chains of certain amino acids. Glycine (C2H5NO2) is structurally the simplest amino acid. It has no center of chirality. Glycine can exist as a neutral molecule in the gas phase and it exists as a zwitterion in solution and in the solid state.

In the solid state, glycine crystallizes in three forms (α, β and γ) which have been studied by x-ray[1-3] and neutron diffraction[4-6]. The α form consists of hydrogen bonded double layers of molecules which are packed by van der Waals forces. The unstable β form, whose single molecular layers possesses an internal arrangement the same as the α form, readily transforms into the α form in air[2]. The γ form crystallizes with a trigonal hemihedral symmetry. While the γ form is stable at room temperature, it is reported to irreversibly get converted to the α form upon heating above 165^{0}C.

Glycine has several commercial applications such as flavor masking and enhancement, pH buffering and stabilization applications in antiperspirants, cosmetics, and toiletries. It has pharmaceutical applications and even used as a chemical intermediate[7]. Glycine has also gained importance in astrophysics as it is also the object of interstellar spec-

troscopic searches[8] to help answer the question of whether the seeds of life were created in space or on earth.

Taylor, R.E.[9] has applied C-13 CP/MAS technique and carried out experiments on three polymorphic structures of Glycine. P. Langan et. al.,[10] have studied the crystal structure of α-Glycine in the temperature range 288-427 K using neutron diffraction and have claimed that the molecular structure does not change significantly and the putative crystallographic phase transition associated with anomalous electrical behaviour in this temperature range is not observed. L. Li and N. RodrIguez-Hornedo[11] have carried out studies on the growth kinetics of Glycine crystals from aqueous solution.

It has been found that any little modification in the structure and composition of a material will bring in sufficient changes in the properties of the material[12, 13]. Thus it is important to study the structure of the materials and look at the parameters which can be altered to get a better material for technological applications. First-principles calculation based on Density Functional Theory[14] has been proved to be an effective tool in the study of structural, electronic and dielectric properties of organic materials[15, 16]. Amino acids have attracted the scientific community in various aspects. With this in view, structure of Glycine has been simulated using First-principles calculations based on Density Functional Theory and computation of Electronic density of states and Dielectric constant have been done and the results have been reported in the present paper.

COMPUTATIONAL DETAILS

Several codes are available for the theoretical structure simulation[17]. The density functional theory approach has emerged as a well established computational method. It has been widely employed to arrive at the conformations of a large number of molecular systems. The practical applicability and sophistication of DFT is strongly sensitive to the good choice of exchange–correlation function along with the appropriate basis set.

Quantum espresso is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modelling. It is based on density-functional theory, plane waves, and pseudopotentials. Author has used plane wave self consistent field (PWSCF)[18] implementation of density functional theory (DFT), with a Local density approximation (LDA)[19] to exchange correlation energy of electrons and ultrasoft pseudopotentials[20], to represent interaction between ionic cores and valence electrons. Kohn-Sham wave functions were represented with a plane wave basis with an energy cutoff of 30 Ry. Integration over Brillouin zone was sampled with a Monkhorst-Pack scheme[21] with appropriate k point mesh and occupation numbers were smeared using Methfessel-Paxton scheme[22] with broadening of 0.03 Ry. The structure was relaxed to minimize energy.

RESULTS AND DISCUSSION

In the present study, the unit cell of Glycine was first simulated using "Avogadro"[23]. Later, atomic positions of the molecules have been used in the plane wave self consistent field calculations.

The structure was subjected to variable cell calculations based on energy minimization technique of Quantum espresso. Relaxed and the optimized values of the unit cell parameters thus arrived at through minimization of energy are; a=4.15Å, b=14.30Å, c=5.53Å, α=97.35deg, β=101.65deg and γ=98.46deg. Volume of the unit cell is found to be 313.8Å^3. This comes out to be a Triclinic lattice [with space group P1(1)] with four molecules per unit cell. This turns out to be a new polymorph of Glycine as the other three polymorphs are not showing Triclinic lattice with four molecules per unit cell. But the α-Glycine shows the monoclinic lattice with four molecules per unit lattice. "scf"" calculation was done using the final atomic positions obtained after relaxing the structure using the program 'pw.x' of Quantum espresso.

Completely relaxed structure of the unit cell was visualized using the program "XcrysDen"[24] and the structure of unit cell of new polymorph of Glycine as seen along X-axis, Y-axis and Z-axis are shown in Figures 1, 2 and 3 respectively. The bond lengths and bond angles in the relaxed structure of new polymorph of Glycine have been tabulated in TABLES 1 and 2 respectively. The molecular packing is very

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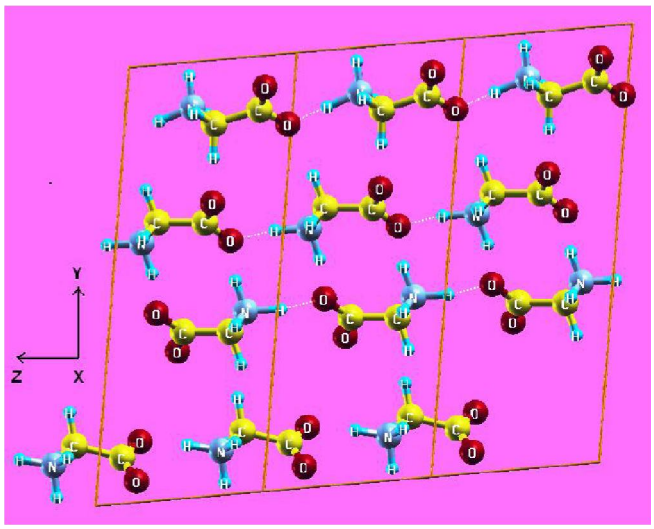

Figure 1 : Structure of unit cell of new polymorph of glycine and packing of molecules as viewed along X-axis

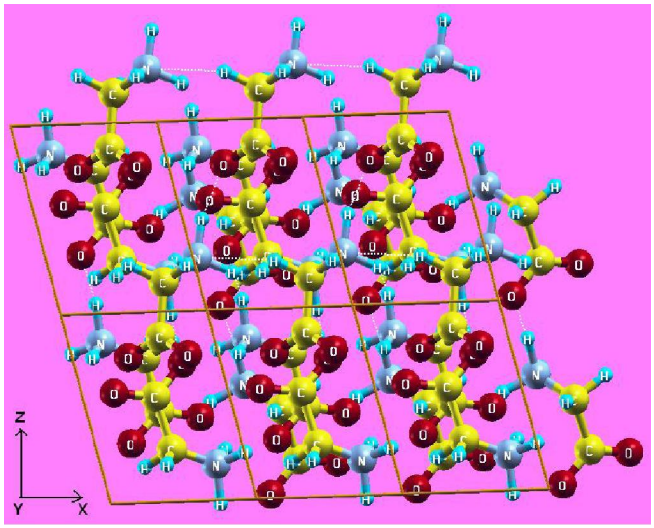

Figure 2 : Structure of unit cell of new polymorph of glycine packing of molecules as viewed along Y-axis

much similar to that found for α-Glycine[1].

It has also been observed in Glycine that on the (011) faces, both oxygen atoms of the carboxyl group are normal to the faces which provides good binding sites for polar water molecules[25]. The zwitterionic glycine molecules align end to end, with the second layer antiparallel to the first. There are four molecules per unit cell. The molecular packing in the structure simulated by First-principles calculation based on DFT of the present study is matching well with the molecular packing shown by R.E. Marsh [1].

EDOS calculation

Electron Density of States (EDOS) has been computed in new polymorph of Glycine using Elec-

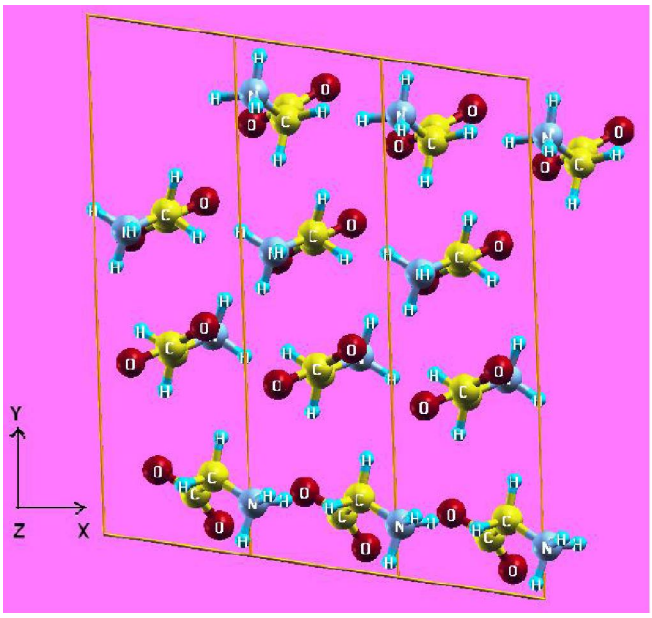

Figure 3 : Structure of unit cell of new polymorph of glycine and packing of molecules as viewed along Z-axis

tronic structure calculation code of Quantum espresso. EDOS in new polymorph of Glycine has been shown in Figure 4. Band gap in new polymorph of Glycine is found to be 3.43eV. This is close to the value of the Band gap found in NLO materials. First-principles calculations in Beta Alanine have given a value of 4.47eV as the Band gap[26]. Band gap in case of 2-Chloro-3-Chloro-Phenyl-Benzamide has been found to be 3.08eV[13].

Dielectric constant

Dielectric constant of the material has been computed in case of new polymorph of Glycine. The

TABLE 1 : Bond lengths in new polymorph of glycine

Bond	Bond length (Å)
C – H	1.09 – 1.13
C – N	1.42
C – C	1.55
N – H	1.04 – 1.15
C – O	1.25 – 1.27

TABLE 2 : Bond angles in new polymorph of glycine

Bond	Bond angle (deg)
C – C – O	111 – 121
C – C – H	104 – 112
N – C – C	115 – 122
N – C – H	102 – 110
H – C – H	102 – 107
O – C – O	126 – 128

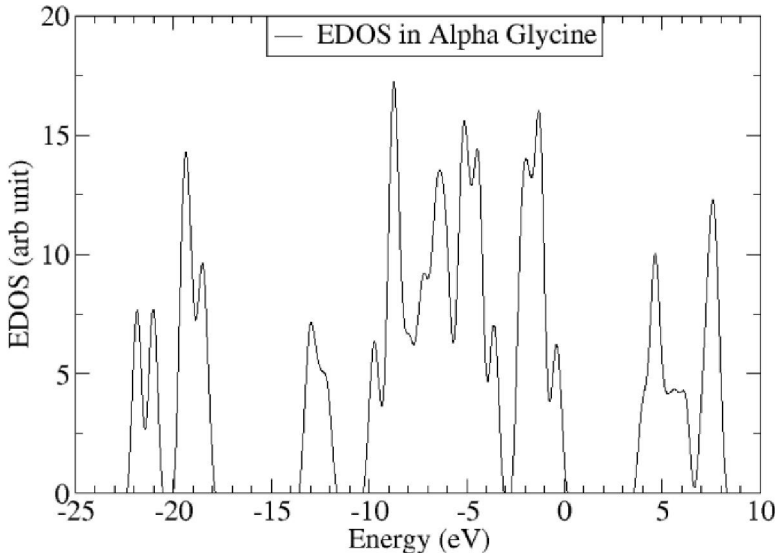

Figure 4 : Electron density of states in new polymorph of glycine

value of dielectric constant in new polymorph of Glycine comes out to be 2.30, 2.29 and 2.61 along X, Y and Z axes respectively and its average value comes out to be 2.4. L-Alanine - another important amino acid and NLO material shows an average dielectric constant of 2.2[26].

CONCLUSIONS

The molecular packing in the simulated and optimized structure of new polymorph of Glycine is matching close to the structure of α-Glycine reported in the literature. Band gap in case of new polymorph of Glycine comes out to be 3.43eV. The value of dielectric constant in new polymorph of Glycine comes out to be 2.30, 2.29 and 2.61 along X, Y and Z axes respectively and its average value comes out to be 2.4.

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