Structural and electronic properties of Diisopropylammonium bromide molecular ferroelectric crystal

A Alsaad*1, I A Qattan2, A A Ahmad1, N Al-Aqtash3 and R F Sabirianov3

1Department of Physics, Jordan University of science and technology, P. O. Box 3030, Irbid 22110, Jordan.
2Department of App. Math. and Sci., Khalifa University of Sci., Tech. & Res., P.O. Box 127788, Abu Dhabi, UAE.
3Department of Physics, University of Nebraska at Omaha, Omaha, NE 68182, USA.

*email: alsaad11@just.edu.jo

Abstract: We report the results of ab-initio calculations based on Generalized Gradient Approximation (GGA) and hybrid functional (HSE06) of electronic band structure, density of states and partial density of states to get a deep insight into structural and electronic properties of P21 ferroelectric phase of Diisopropylammonium Bromide molecular crystal (DIPAB). We found that the optical band gap of the polar phase of DIPAB is ≈ 5 eV confirming it as a good dielectric. Examination of the density of states and partial density of states reveal that the valence band maximum is mainly composed of bromine 4p orbitals and the conduction band minimum is dominated by carbon 2p, carbon 2s, and nitrogen 2s orbitals. A unique aspect of ferroelectric phase is the permanent dipole within the material. We found that DIPAB has a spontaneous polarization of 22.64 µC/cm² consistent with recent findings which make it good candidate for the creation of ferroelectric tunneling junctions (FTJs) which have the potential to be used as memory devices.

1. INTRODUCTION

Investigation of molecule-based ferroelectrics [1, 2, 3, 4, 5, 6, 7, 8, 9] revealed that a simple organic salt, Diisopropylammonium Chloride (DIPAC) displays the highest Tc among the known molecule-based ferroelectrics (Tc = 440 K). It undergoes a reversible phase transition from a high-temperature paraelectric phase (2/m) to a low-temperature ferroelectric one (2m). Its ferroelectric activity occurs below the Tc with a large spontaneous polarization P, ≈ 8.9 µC/cm², comparable with those of organic polymers such as Poly (Vinylidene Difluoride) (PVDF, ≈ 8 µC/cm²) and Nylon-11 (≈ 5 µC/cm²). This molecule is quite remarkable, with some of the key properties that are comparable with the most common inorganic crystals.

Previously reported molecule-based ferroelectrics usually show low Tc and small P values that extremely limit their practical applications. Ferroelectricity, involves the relationship of dielectric and elastic behavior in highly nonlinear, anisotropic, and polarizable, deformable crystals. It was found that crystals of Seignette (Rochelle) salt behave like a ferromagnet (They show the hysteresis of polarization and undergo phase transitions from the polar to the nonpolar phase) [10, 11, 12, 13].
It has been found that some organic molecules show a capacity as an organic substitute to today’s silicon-based semiconductors [14] demonstrate properties that make them well appropriate to a wide range of applications in memory, sensing and low-cost energy storage. Switchable large polarization of ferroelectrics has made them suitable for electronics applications such as capacitor, sensor, and data storage, as well as to electromechanical and optical devices [15, 16]. For “order-disorder-type” ferroelectrics, the sum of permanent dipole moments of polar ions determines the polarization, while the product of relative displacement and charge of the ions had been the classical picture of the polarization for the “displacive-type” ferroelectrics. The macroscopic polarization of ferroelectrics can be described using Berry phase quantum mechanical approach [17, 18]. This fact is especially important for the displacive-type ferroelectrics having some orbital hybridization between ions [19, 20].

In this perspective, ab-initio calculations based on Berry phase have been intensively used for the understanding of the dielectrics. For instance, the displacive-type ferroelectric oxides have an amplified macroscopic polarization via the orbital hybridization between the occupied $p$-orbitals of oxygen and the empty $d$-orbitals of transition metals [21]. Molecular ferroelectrics are highly desirable for their easy and environmentally friendly processing, light weight, and mechanical flexibility. It has been found that Diisopropylammonium Bromide (DIPAB) is an organic crystal that is made from Bromine, a natural element isolated from sea salt, mixed with carbon, hydrogen and nitrogen. Researchers dissolved the elements in water and evaporated the liquid to grow the crystal. Because the molecule contains carbon, it is organic, and its pivoting chemical bonds allow it to flex. It was found to be a ferroelectric with a spontaneous polarization of $23 \mu C/cm^2$ [of the order of that of Barium Titanate (BTO)], high Curie temperature of 426 K (above that of BTO), large dielectric constant, and low dielectric loss.

DIPAB exhibits fairly good piezoelectric response and well-defined ferroelectric domains. These characteristics make it a molecular alternative to perovskite ferroelectrics and ferroelectric polymers in sensing, actuation, data storage, electro-optics, and molecular or flexible electronics.

2. COMPUTATIONAL METHODS

First-principles density functional theory [22, 23] simulations are used in our study. The electronic structure was calculated using the Projector Augmented Wave (PAW) method [24] as implemented in the Vienna ab initio simulation package VASP [25]. The Generalized Gradient Approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) form [26] was used for the exchange-correlation functional. Hybrid Fock exchange/density functional theory functional have shown to be very successful in describing a wide range of molecular properties. A hybrid functional [27] that evaluate the Fock exchange in real space was introduced. We used the hybrid functional HSE06 to calculate the electronic and optical properties of DIPAB.

Our results indicate that the hybrid functional indeed often improve the description of these properties. We set the plane-wave-cut-off energy to 400 eV. We used a 4 x 4x 4 Monkhorst-Pack grid to minimize the computation time. Instead of the all-electron electron-ion potential norm-conserving pseudopotentials were used. The relaxed atomic positions were followed by minimizing the total energy (i.e., as small as $10^{-6}$ eV), and the Hellmann-Feynman forces. These forces were as small as 0.003eV/Å at convergence in the unit cell of all different electronic structure relaxations that have been performed.
3. RESULTS AND DISCUSSIONS

3.1. Structural properties of the $P2_1(\alpha)$ ferroelectric phase of DIPAB crystal

Table 1. The structural properties and spontaneous polarization of polar monoclinic $P2_1(\alpha)$ phases of DIPAB ferroelectric molecular crystal.

| Parameter               | $P2_1(\alpha)$ phase |
|-------------------------|----------------------|
| Empirical formula       | C$_6$H$_{16}$BrN     |
| Space group             | $P2_1$               |
| Lattice parameter a (Å) | 7.799                |
| Lattice parameter b (Å) | 8.067                |
| Lattice parameter c (Å) | 7.584                |
| $\alpha^\circ$          | 90                   |
| $\beta^\circ$           | 116.231              |
| $\gamma^\circ$          | 90                   |
| Equilibrium volume $V$ (Å$^3$) | 443.30          |
| Spont. polarization $P_s$ ($\mu e/$cm$^2$) | -22.64             |

As shown in table 1, we employed XRD-derived structural parameters as initial structure in our ab-initio calculations [28]. We performed gradient-descent optimization of the structure. The obtained lattice parameters are presented in table 1. The relaxed structures are very close to the experimentally observed ones.
When a dielectric is placed in an electric field, it becomes polarized, producing a dipole with a dipole moment given by the product of the charges and their separation distance. The polarization is then defined as the dipole moment per unit volume. If the dielectric is non-central-symmetric like the one shown in figure 1(a) (i.e., $P2_1(\alpha)$ polar phase of DIPAB), a relatively large piezoelectric strain proportional to electric field is possible. As can be seen from table 1, the magnitude of spontaneous polarization of $P2_1(\alpha)$ phase of DIPAB is 22.64 $\mu_{\text{C}}/\text{cm}^2$. This is quite remarkable and indicate that this molecular ferroelectric crystal could be used as an alternative for some perovskite materials in a wide range of application.

3.2. Band structure and density of states

For a better understanding of the electronic and optical properties of DIPAB, the investigation of electronic energy band structure can be useful. The calculated band structures of ferroelectric DIPAB using GGA method is shown in figure 2. The band structure has been computed and the high symmetry directions on the surface of the irreducible BZ are plotted. The Fermi level is set to zero. The obtained band gap of $P2_1(\alpha)$ polar phase is found $\approx 5$ eV using GGA method (figure 2). To the best of our knowledge, we are not aware of any experimental or theoretical works that reported the electronic band structure of DIPAB. Furthermore, the density of states (DOS) and the partial density of states (PDOS) of monoclinic $P2_1$ DIPAB are shown in figures (3-9). The DOS and PDOS plots give a quick qualitative picture of the electronic structure of a material and sometimes they can be related directly to the electronic transitions and experimental spectroscopic results.
As can be clearly seen, the valence band maximum is mainly composed of Br 4p orbitals and the conduction band minimum is dominated by C 2p, C 2s, and N 2s orbitals. The figures indicate that the interband transitions are mainly from the valence bands of Bromine (Br) atoms to the conduction bands of Carbon (C) and Nitrogen (N) atoms. Examining the total density of states using GGA and HSE06 methods, we found that the optical band gap obtained using HSE06 is $\approx 6$ eV, while that obtained using GGA method is $\approx 5$ eV consistent with value of the optical band gap obtained from the electronic band structure plot using GGA method. Our results indicate that using HSE06 hybrid pseudopotentials rather than GGA method leads to a higher optical band gap. This is due to the fact that GGA underestimates the optical band gap.

**Figure 2.** Calculated electronic energy band structure of $P2_1$ polar DIPAB using GGA method.
Figure 3. The total density of states (DOS) of $P_{21}$ polar DIPAB calculated using GGA (Blue) and HSE06 Hybrid functional (Red).

Figure 4. The partial density of states (PDOS) of Bromine $4p$ orbitals of $P_{21}$ polar DIPAB.
Figure 5. The partial density of states (PDOS) of Carbon \(2p\) orbitals of \(P2_1\) polar DIPAB.

Figure 6. The partial density of states (PDOS) of Carbon \(2s\) orbitals of \(P2_1\) polar DIPAB.
Figure 7. The partial density of states (PDOS) of Nitrogen $2p$ orbitals of $P2_1$ polar DIPAB.

Figure 8. The partial density of states (PDOS) of Nitrogen $2s$ orbitals of $P2_1$ polar DIPAB.
CONCLUSIONS

In summary, we present *ab initio* calculations of the electronic energy band structure, density of states, partial density of states and spontaneous polarization of the polar DIPAB molecular crystal. We found that the optical band gap of polar DIPAB is $\approx 5$ eV indicating that the material is a dielectric. The density of states and partial density of states reveal that the major interband transitions in ferroelectric DIPAB occur from the valence band of bromine to the conduction bands of carbon and nitrogen atoms in polar DIPAB. Examining the total density of states using GGA and HSE06 methods, we found that the optical band gap obtained using HSE06 is $\approx 6$ eV, while that obtained using GGA method is $\approx 5$ eV. Furthermore, we report results on spontaneous polarization of non central-symmetric polar ferroelectric phase of DIPAB. We found that polar DIPAB exhibits a spontaneous polarization of 22.64 $\mu C/cm^2$, indicating that this remarkable ferroelectric molecule could be used as an alternative for some pervoskites in a wide range of piezoelectric applications, electronics applications such as capacitor, sensor, and data storage, as well as to electromechanical and optical devices. To the best of our knowledge, our results on electronic and ferroelectric properties of the polar phase of DIPAB crystal are the first to be reported. We hope that our findings can pave the way for further experimental investigations on electronic, piezoelectric and optical properties of this remarkable molecule.

ACKNOWLEDMENTS

The authors would like to acknowledge the technical and financial support provided by the faculty of scientific research at Jordan University of Science and Technology (JUST), and by Khalifa University of Science and Research (KUSTAR), UAE.
References

[1] Q Ye, Y.-M Song, G.-X Wang, K Chen, D.-W Fu, P W H Chan, J.-S Zhu, S D Huang, R.-G Xiong 2006 J. Am. Chem. Soc. 128 6554.
[2] H.-Y Ye, D.-W Fu, Y Zhang, W Zhang, R.-G Xiong, S D Huang 2009 J. Am. Chem. Soc. 131 42.
[3] W Zhang, R.-G Xing, S D Huang 2008 J. Am. Chem. Soc. 130 10468.
[4] D.-W Fu, Y.-M Song, G.-X Wang, Q Ye, R.-G Xiong, T Akutagawa, T Nakamura, P W H Chan, S D Huang 2007 J. Am. Chem. Soc. 129 5346.
[5] W Zhang, L.-Z Chen, R.-G Xiong, T Nakamura, S D Huang 2009 J. Am. Chem. Soc. 131 12544.
[6] W Zhang, H.-Y Ye, H.-L Cai, J.-Z Ge, R.-G Xing, S P D Huang 2010 J. Am. Chem. Soc. 132 7300.
[7] T Hang, W Zhang, H.-Y Ye, R.-G Xiong 2011 Chem. Soc. Rev., 40 3577.
[8] H.-L Cai, W Zhang, J.-Z Ge, Y Zhang, K Awaga, T Nakamura, R.-G Xiong 2011 Phys. Rev. Lett. 107 147601.
[9] G.-C Xu, W Zhang, X.-M Ma, Y.-H Chen, L. Zhang, H.-L Cai, Z.-M Wang, R.-G Xiong, S Gao 2011 J. Am. Chem. Soc. 133 149.
[10] J Valasek, “Piezoelectricity and Allied Phenomena in Rochelle Salt” 1921 Phys. Rev. 17 [4] 475-81.
[11] J Valasek, “Piezoelectric Activity of Rochelle Salt Under Various Conditions” 1922 Phys. Rev. 19 478-91.
[12] J Valasek, “Properties of Rochelle Salt Related to the Piezoelectric Effect” 1922 Phys. Rev. 20 639-64.
[13] J Valasek, “Dielectric Anomalies in Rochelle Salt” 1924 Phys. Rev. 24 [5] 560-68.
[14] Da-Wei Fu, Hong-Ling Cai, Yuanming Liu, Qiong Ye, Wen Zhang, Yi Zhang, Xue-Yuan Chen, Gianluca Giovannetti, Massimo Capone, Jiangyu Li, Ren-Gen Xiong 2013 SCIENCE vol 339, 425-428.
[15] K Uchino, Ferroelectric Devices 2000 (Marcel Dekker, NewYork).
[16] M E Lines and A M Glass, Principles and Applications of Ferroelectrics and Related Materials 1977 (Oxford University, New York).
[17] J F Scott 2007 Science 315 954.
[18] R D King-Smith and D Vanderbilt 1993 Phys. Rev. B 47 1651.
[19] R Resta 1994 Rev. Mod. Phys. 66 899.
[20] R E Cohen 1992 Nature (London) 358 136.
[21] T Egami, S Ishihara, and M Tachiki 1993 Science 261 1307.
[22] G Giovannetti et al 2011 Proximity of iron pnictide superconductors to a quantum tricritical point. Nat. Commun. 2 398.
[23] P Hohenberg, W Kohn, Inhomogeneous electron gas 1964 *Phys. Rev.* **136** (3B), B864.

[24] J P Perdew, J A Chevary, S H Vosko, K A Jackson, M R Pederson, D J Singh, and C Fiolhais 1992 *Phys. Rev. B* **46** 6671.

[25] G Kresse, D Joubert 1999 *Phys. Rev. B* **59** 1758.

[26] J P Perdew, K Burke, M Ernzerhof 1996 *Phys. Rev. Lett.* **77** 3865.

[27] HSE03, J Heyd, G E Scuseria, and M Ernzerhof 2003 *J. Chem. Phys.* **118** 8207.

[28] Anna Piecha, Anna Gągor, Ryszard Jakubas and Przemysław Szklarz 2013 “Room-temperature ferroelectricity in diisopropylammonium bromide” *Cryst. Eng. Comm.* **15** 940-944.