J Materiomics xxx (2017) 1–5

Contents lists available at ScienceDirect

J Materiomics

journal homepage: www.journals.elsevier.com/journal-of-materiomics/

Journal of
Materiomics

Modelling of the electronic and ferroelectric properties of trichloroacetamide using Monte Carlo and first-principles calculations

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ARTICLE INFO

Article history:
Received 27 September 2016
Received in revised form
24 November 2016
Accepted 21 December 2016
Available online xxx

Keywords:
First-principles study
Monte Carlo
Trichloroacetamide
TCAA
Organic ferroelectrics

ABSTRACT

The electronic structure and ferroelectric mechanism of trichloroacetamide were studied using first principles calculations and density functional theory within the generalized gradient approximation. Using both Bader charge and electron deformation density, large molecular spontaneous polarization is found to originate from the charge transfer cause by the strong “push-pull” effect of electron-releasing interacting with electron-withdrawing groups. The intermolecular hydrogen bonds, N—H···O, produce dipole moments in adjacent molecules to be aligned with each other. They also reduce the potential energy of the molecular chain threaded by hydrogen bonds. Due to the symmetric crystalline properties, however, the polarization of trichloroacetamide is mostly compensated and therefore small. Using the Berry Phase method, the spontaneous polarization of trichloroacetamide was simulated, and good agreement with the experimental values was found. Considering the polarization characteristics of trichloroacetamide, we constructed a one-dimensional ferroelectric Hamiltonian model to calculate the ferroelectric properties of TCAA. Using the Hamiltonian model, the thermal properties and ferroelectricity of trichloroacetamide were studied using the Monte Carlo method, and the Tc value was calculated.

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1. Introduction

In the past decades, organic ferroelectric materials have attracted increasing attention because of their large number of potential applications, especially with respect to bionic devices [1–4]. Single-component organic ferroelectrics with low-molecular-mass usually have many benefits, including low toxicity, mechanically flexibility, and environmental friendliness. These highly desirable properties makes them promising candidates for the commercial fabrication of flexible and lightweight functional ferroelectric devices using conventional processing techniques like spin-coating, spray-coating, inkjet printing, and vapor-phase deposition [1,5]. So far, very few single-component low-molecular-mass organic ferroelectric molecules have been discovered [1]. The rareness of organic ferroelectric molecules hinders the development of organic ferroelectrics both theoretically and experimentally. Although most of the organic compounds in the Cambridge Structure Database have been studied already to predict and find organic ferroelectric molecules, only one organic molecule with poor ferroelectric properties, cyclohexane-1,1′-diacetic acid, was found [6]. Despite being an anti-ferroelectric, the polarization mechanism of the proton transfer of this squaric acid [7] is particularly interesting with regard to its homologous series of organic compounds [1]. Croconic acid (4, 5-dihydroxy-4-cyclopentene-1, 2, 3-trione, $H_2C_5O_5$) was first reported as a proton-transfer type single-component organic ferroelectric [8], for which the large polarization is generated by charge transfer (CT) via the hydrogen bonds. Collective site-to-site transfer of protons dramatically reduces the polarization-flip energy, which facilitates flipping of the polarization [9].

Trichloroacetamide (TCAA) is another single-component low-molecular-mass organic ferroelectric at room temperature [10–12]. As shown in Fig. 1(c), there are two carbon atoms in each TCAA molecule. One is bonded to an oxygen atom and an amino (NH_2) group, and the other one links three chlorine atoms forming

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Peer review under responsibility of The Chinese Ceramic Society.

http://dx.doi.org/10.1016/j.jmat.2016.12.005
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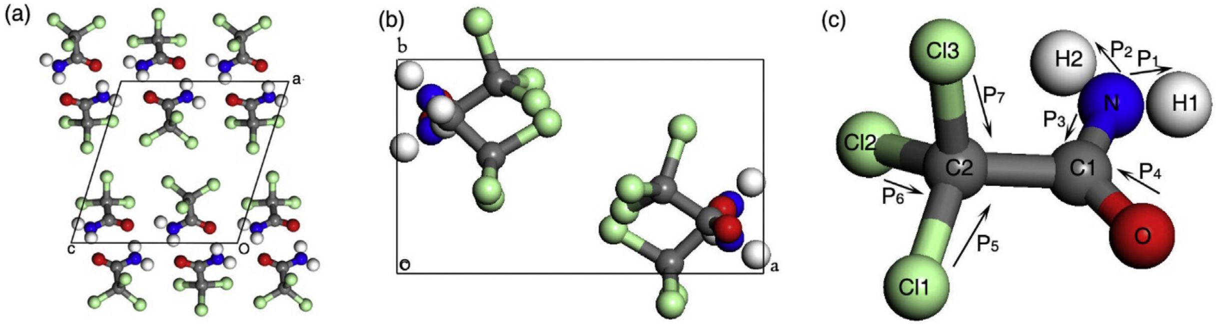

Fig. 1. Crystal of the FE structure of TCAA viewed along the b-axis (a) and c-axis (b). Molecule of TCAA and the schematic diagram of the dipole moment components (c).

trichloromethyl (CCl_3). However, unlike the other order-disorder type ferroelectric materials, TCAA has two slightly different molecules in its ferroelectric (FE) phase that originate from the differently oriented trichloromethyl (CCl_3) [10].

Because of the different orientations of trichloromethyl (CCl_3), there are two different molecules in the FE phase (62% and 38%), and three different molecules in the paraelectric (PE) phase (51.8%, 27.6%, and 20.6%). The ferroelectric TCAA with its high Curie temperature of 355 K and small polarization of 0.2 $\mu C\ cm^{-2}$, shows polarization reversal in an electric field as low as 7.5 $kV\ cm^{-1}$. It shows an even smaller coercive field (4 $kVcm^{-1}$) than other ferroelectric materials like croconic acid, which has a small coercive field of 11 $kV\ cm^{-1}$ [11,12]. There are few theoretical studies of its ferroelectric mechanism that determine its properties and device applications. In this paper, we investigate the ferroelectric and thermal properties of TCAA with respect to its molecular and electronic structure. We found that TCAA undergoes a polarization reversal though the rotation of certain groups. This reversal mechanism can significantly reduce the coercive field. The outcomes of this study may provide new ways to find potential single-component organic ferroelectrics of the group-rotation type, which have a low coercive field and good switch performance.

This paper is organized into three sections. In the theoretical methods section, we provide the details of our calculation. In the results and discussion section, the density of states (DOS), electron density, deformation charge density and Bader charge of TCAA are calculated to simulate polarization using first principle calculations and the Berry phase method. A Hamiltonian-model-based structure of TCAA was built, according to our first principle calculation results. The Curie temperature was obtained using the Monte by Carlo method. Its value is consistent with earlier research [9]. A summary is given in the fourth section.

2. Theoretical methods

TCAA has several structures both in the PE and FE phase. For simplification, we only present the detailed study of one FE structure with 62% occupancy and one PE structure with 51.8% occupancy. The TCAA crystal in the FE structure, which is plotted in Fig. 1, is an orthorhombic phase with space group P21 without an inversion center. We calculated the DOS, charge density, and deformation charge density of TCAA using the Vienna ab-initio Simulation Package (VASP). The first principles calculations were performed using density functional theory (DFT) with a generalized gradient approximation (GGA). For the self-consistent calculations, the Γ-centered Monkhorst-Pack scheme was used to generate the K points in the Brillouin zone [13]. A plane-wave cut-off of 550 eV and a k-point grid of 7 × 13 × 7 were used in our calculation. The convergence criterion for the total energy was 10^{-4} eV, and the force convergence criterion was assumed to be 0.01 eV/Å for the optimization of the lattice parameters. Based on the experimental data (collected from X-ray diffraction in the Cambridge Crystallographic Data Center) of a = 10.4368 Å, b = 5.80040 Å, and c = 10.1922 Å [10], the optimized lattice parameters are a = 10.7708 Å, b = 5.9860 Å, and c = 10.5184 Å. The deviation of the optimized lattice parameters a, b, and c from the experimental values is about 3.2%.

3. Results and discussion

3.1. Ferroelectric mechanism

The total density of states (DOS) and the partial density of states (PDOS) of the TCAA FE phase are shown in Fig. 2. The calculated indirect band gap is 4.25 eV. The valence bands mainly consist of the *1s* orbital of H, *2p* orbitals of N, O, C and Cl, while the bottom of the conduction band contains *2p* orbitals of N, O, C and Cl. The three chlorine atoms have nearly the same PDOS, which indicates the presence of a π conjugation bond among the three chlorine groups. As shown in Fig. 2, both hydrogen and nitrogen atoms have similar PDOS peaks in the valence band, and the hydrogen atoms have hardly any PDOSs at the bottom of the conduction band. This indicates an ionic bond characteristic between the hydrogen and nitrogen atoms as well as the stronger covalent bond components in the N—C and O—C bonds.

The deformation density maps show the difference between the electron density of the molecule and the electron density of the independent atom model (IAM): $\rho - \rho IAM$ [14]. The electron

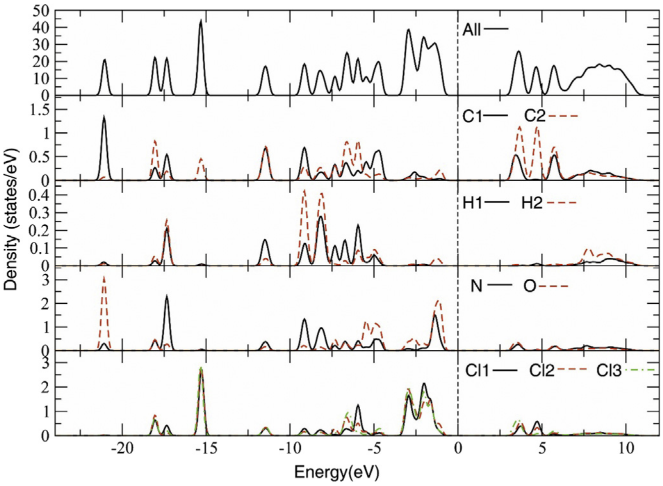

Fig. 2. DOS and PDOS of TCAA.

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