AN INVESTIGATION OF STRUCTURAL AND ELECTRONIC PROPERTIES OF ZIRCONOLITE (CaZrTiO₇) USING DENSITY FUNCTIONAL THEORY

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Abstract: Zirconolite (CaZrTiO₇) has been acknowledged as the favourable candidate for high level radioactive waste immobilisation due to its effectiveness in aqueous durability, chemical flexibility, waste loading and radiation tolerance. In this study, the structural and electronic properties of zirconolitethave investigated using Density Functional Theory (DFT) within generalized gradient approximation (GGA) as implemented in Quantum ESPRESSO (QE). It was found that the zirconolite structure is stable. The calculated electronic band structure of zirconolite shown along a high symmetry direction and the energy range of band structure is plotted from 0.00 eV to 3.0 eV, the energy separation between the conduction band maximum and valence band minimum occurred at the R and T points, indicating that zirconolite is an indirect band gap material with an approximate value of 2.90 eV energy gap, this value is consistent with previous DFT result but less than the experimental result whichrevels the material’s semi-conductivity. The calculated density of the state (DOS) shows the domination of different states in both the valence band and the conduction band while projected density of the state (PDOS) indicates s-orbital of Zr, s-orbital of Ca and p-orbital of Ti atoms are responsible for material properties in the valence band near the Fermi level. The type of chemical bond and charge transfer between the anions and the cations was examined by charge density distribution.

Keywords: DFT, CaZrTiO₇, zirconolite, immobilisation, electronic properties

Introduction

Nuclear energy has been utilised in different fields, comprising of defence, aerospace, power generation, health care, industry and agriculture (Zhao et al., 2018; Du and Jiang, 2017). The long-lived radioactive waste generated from nuclear fuel cycle has been persistent issue of nuclear energy. Nuclear waste is categorised into low-level waste (LLW), intermediate level waste (ILW) and high-level waste (HLW) based on it is activity and half-lives present (Mulroue and Duffy, 2011). Reprocessing and direct disposal in Geological Disposal Facility (GDF) without reprocessing (Once through nuclear fuel cycle) are the two possible available alternatives for treating spent nuclear fuel (Wattal, 2017). Reprocessing process involves removal of plutonium (Pu) and uranium (U) for reuse in mixed oxide fuel (MOX) and then fission products (FPs) and minor actinides (MA: Np, Am, Cm) immobilisation in a highly durable glass or ceramic, stored in an interim storage and disposed of in or direct disposal in GDF spent nuclear waste (Wattal, 2017). Currently around 30% of spent fuel are reprocessed globally generating high quantity of high-level liquid radioactive wastes (HLLW) comprising of long-lived radionuclides with half-lives ranging from thousands to million years (MA: ¹⁵²Cs, ⁹⁰T, ⁹⁴Zr…). MA and Pu are the major causes for long term radiotoxicity of HLW (Ma et al., 2018). Consequently, HLW must be isolated from biosphere for public and environmental protection (Zhao et al., 2018).

High-level radionuclides immobilisation within a chemically durable and radiation resistant waste forms has been considered as unique separation method (Ma et al., 2018). A possible effective radionuclides immobilisation that would confine radionuclides migration into the environment via underground water was proposed using multi-barrier concept which entails of wasteform, container, engineered barrier and geological barrier (Zhao et al., 2018). The bubble formation due to hydrogen gas within the cement matrix leads to reduction in mechanical strength. As such a solid matrix of borosilicate glass is used for HLW. The use of ceramics matrices for HLW encapsulation was proposed over borosilicate glasses due to its higher retention of actinides elements in leach tests as well as naturally occurring ceramic materials (Mulroue and Duffy, 2011; Gilbert et al., 2010). In addition, low thermal stability of glass attributed to its failure in actinides waste disposal (Zhang et al., 2019). Alternatively, SYNROC, a synthetic rock which was derived at the Australian Nuclear Science and Technology Organisation (ANSTO) was proposed to replace borosilicate glasses (Mulroue and Duffy, 2011). SYNROC has various compositions designed for each waste form. SYNROC-C derived by Ringwood in 1981 consists of zirconolite (CaZrTiO₇), pyrochlore (A₂B₂O₇) and hollandite (BaAl₂Ti₆O₁₆) compositions for HLW encapsulation (Ringwood et al., 1981).

Zirconolite is the most suitable actinide-bearing phase among synroc minerals (Mulroue and Duffy, 2011), (Zhang et al., 2019). It was preferred due to its efficiency in aqueous durability, chemical flexibility, waste loading and radiation tolerance (Ma et al., 2018; Caurant et al., 2010). Furthermore, zirconolite crystalline structure exists naturally retaining many minor actinides and lanthanides (Lumpkin et al., 2004; Rossell, 1980). It has been used industrially as main hosting phase for intermediate-level waste (Ma et al., 2018).

Furthermore, Zirconolite is derived from anion-deficient fluorite structure with general formula of CaZr₂Ti₆O₁₆ with 0.8 < x < 1.37 (Begg et al., 1998). it also entails of corner-linked layers of TiO₆ octahedra separated disconnected by Ca and Zr planes’ atoms. Three lattices of zirconolite were occupied by titanium with two that are octahedrally attached to oxygen while the third is fivefold coordinated to oxygen separately as shown on Fig. 1 (Begg et al., 1998). Zirconolite develop five polytypic forms due to its nature of anion-deficient derivative of fluorite structure (Ma et al., 2018) such as zirconolite-2M (monoclinic, C2/c) (Rossell, 1980), zirconolite-4M (monoclinic, C2/c) (Hadley et al., 2005), zirconolite-3T (trigonal), zirconolite-3O (orthorhombic), zirconolite-6T (trigonal) (Coelho et al., 1997; Smith and Lumpkin, 1993). Zirconolite-2M is the predominantly studied structure among polytypes for actinides immobilisation, while zirconolite-6T crystal was only detected
Structural and Electronic Properties of Zirconolite Using Density Functional Theory

intergrown within zirconolite-3T crystal without comprehensive structural information (Smith and Lumpkin, 1993; Ma et al., 2018). Previous studies proposed the construction of these polytypes by stacking hexagonal tungsten bronze (HTB) and Ca/Zr layer in various orientation (Ma et al., 2018).

Ab-initio methods established on typical density functional theory (DFT) offer suitable means for the calculation and characterization of the material’s ground-state properties such as atomic configuration and total energies (Abdullahi et al., 2018). The aim of this article is to reveal the structural and electronic properties of Zirconolite ceramic using Density Functional Theory (DFT) within generalized gradient approximation (GGA) implemented in Quantum ESPRESSO (QE).

Computational Details
Computational method
The calculations are performed on the \(2 \times 2 \times 2\) supercells model of the primitive unit cell of zirconolite (\(\text{CaZrTi}_2\text{O}_7\)) based on first principle calculation using density functional theory (DFT). Quantum ESPRESSO simulation package were implemented. The Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) pseudopotential has been applied for the exchange-correlation potential approximation (Perdew et al., 1996). Maxfessel-Paxton smearing method has been employed for integrals. The brillouin zone integration is achieved using Monkhorst-Pack scheme (Monkhorst and Pack, 1976) with \(6 \times 6 \times 6\) k-points grids for all materials. Fixed supercell dimensions were used all over the calculations while Broyden-Fletcher-Goldfarb-Shannon (BFGS) algorithm was used for total atomic positions relaxation until acting atomic forces are lower than 0.001eV/Å.

Results and Discussion
Convergence test
Performing convergence test calculation prior to principal calculation is a basic requirement of any DFT calculation using DFT code. The results presented below represent the convergence testes with respect to plane wave kinetics energy cut-off and k-points mesh for zirconolite crystal (\(\text{CaZrTi}_2\text{O}_7\)).

Convergence Test Results of \(\text{CaZrTi}_2\text{O}_7\)
Figure 2 shows the convergence result for the zirconolite for the energy cut-off (E-cut (Ry)) with respect to total energy (E_total (Ry)). The graph illustrates the total energy varies considerably with respect kinetic energy cut-off with turning points at 20 Ry and 30 Ry. However, the total energy remains almost constant within the kinetic energy cut-off range of 40-60 Ry (Table 1). This indicates a well-converged kinetic energy cut-off. As such, 40 Ry is taken as an optimized value for the kinetic energy cut-off (E-cut (Ry)) for the zirconolite compound.

Table 1: Convergence test of \(\text{CaZrTi}_2\text{O}_7\) total energy with respect to kinetic energy cut-off of the plane wave

<table>
<thead>
<tr>
<th>S/N</th>
<th>Kinetic energy cut-off (Ry)</th>
<th>Total energy (Ry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>-2332.42911354</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>-2510.07378884</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>-2565.77283074</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>-2569.44117006</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>-2569.57268693</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>-2569.60249898</td>
</tr>
</tbody>
</table>

Furthermore, Fig. 3 illustrates the change of the total energy with respect to the k-points mesh within the range of \(2 \times 2 \times 2\) to \(12 \times 12 \times 12\) k-points maintain the about the same total energy, which implies less effect on zirconolite’s total energy and indicates well-converged k-point. Therefore, \(6 \times 6 \times 6\) k-point is regarded as an optimized k-point value for zirconolite compound.

Fig. 1: Schematic illustration of the Zirconolite-2M structure consisting of two HTB and Ca/Zr layers (Ma et al., 2018)

Fig. 2: The convergence of total energy with respect to the kinetic energy cut-off

Fig. 3: The convergence of the total energy with respect to the k-points grids

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Table 2: Convergence of the total energy with respect to the k-points mesh of CaZrTiO₄

<table>
<thead>
<tr>
<th>S/N</th>
<th>k-points mesh</th>
<th>Total energy (Ry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 x 2 x 2</td>
<td>-2569.44015841</td>
</tr>
<tr>
<td>2</td>
<td>4 x 4 x 4</td>
<td>-2569.4417006</td>
</tr>
<tr>
<td>3</td>
<td>6 x 6 x 6</td>
<td>-2569.44129866</td>
</tr>
<tr>
<td>4</td>
<td>8 x 8 x 8</td>
<td>-2569.44129764</td>
</tr>
<tr>
<td>5</td>
<td>10 x 10 x 10</td>
<td>-2569.44128591</td>
</tr>
<tr>
<td>6</td>
<td>12 x 12 x 12</td>
<td>-2569.44130387</td>
</tr>
</tbody>
</table>

Fig. 4: The bulk structure of simulated. Zirconolite red (small dark) spheres show oxygen ions, grey (large grey spheres show Zr ions) and cyan (large cyan) spheres show Ca ions and blue (large blue) spheres show Ti ions

Structural properties of the zirconolite CaZrTiO₄

The structural properties of the zirconolite CaZrTiO₄ with the space group of P1 was simulated as shown on Fig. 4. The zirconolite structure exhibits triclinic geometry with corner-linked layers of TiO₆ octahedra separated by Ca and Zr plane’s atoms. Three lattices of zirconolite were occupied by titanium with two that are octahedrally attached to oxygen while the third is fivefold-coordinated site. The Ca and Zr atoms interlayer are eightfold and sevenfold coordinated to oxygen separately (Begg et al., 1998). The triclinic crystal structure relates to the primitive unit cell was adopted in this work. The supercell consists of 2 x 2 x 2 supercell (Fig. 4). The optimized crystal parameters of the supercell are α = 7.286 Å, β = 7.315 Å, c = 11.477 Å and α = 80.977°, β = 80.849°, γ = 60.608°.

Electronic properties

Electronic properties calculations are crucial in predicting the electronic properties such as band structure, density of state (DOS), projected density of state (PDOS) and charge density distributions of a solids (Afif et al., 2020). Most of the reported research in the literature on the CaZrTiO₄ are experimental. A generalized gradient approximation Perdew-Burke-Ernzerhof and generalized gradient approximation (PBE-GGA) were utilized for electronic properties calculation. The calculated electronic band structure of zirconolite compound (CaZrTiO₄) is shown on Fig. 5 in triclinic phase using PBE-GGA. 11 high symmetry points were selected (Γ’-X |Y’-F’-Z’ | R’ |T’-F’ | U’ |V’-V’). (Yoyo et al., 2017; Setyawan and Stefano, 2010) and the band structure energy is plotted between 0.00 eV to 3.0 eV. The Fermi level of the crystal band structure is indicated by the zero (0 eV) on the energy scale. The calculated band structure for CaZrTiO₄ within PBE-GGA shows the presence of both Valence Band Maximum (VBM) and Conduction Band Minimum (CBM) at R₂ and T₂ points. The energy separation between VBM and CBM at these symmetry points reveals that the material has indirect band gap. The calculated band gap energy of the material is 2.90 eV, which is 0.70 eV less than the experimentally found value of 3.6 eV (Mulroue and Duffy, 2011; Yuga et al., 2009). In addition, the result also is in agreement with the previously simulated calculated band gap of 2.8 eV as shown on Table 3 (Mulroue et al., 2011). This is ascribed to the generally known band gap underestimation generated by erroneous handling of electron-exchange in typical DFT (Idris et al., 2020).

Table 3: Calculated bandgap for CaZrTiO₄ with previous first principle calculation and experimental data

<table>
<thead>
<tr>
<th>Method</th>
<th>Bandgap (eV)</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental data</td>
<td>3.60</td>
<td></td>
</tr>
<tr>
<td>(Mulroue and Duffy, 2011; Yuga et al., 2009)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work PPE-GGA</td>
<td>2.90</td>
<td>0.70</td>
</tr>
<tr>
<td>DFT-PBE (Mulroue and Duffy, 2011)</td>
<td>2.80</td>
<td>0.80</td>
</tr>
</tbody>
</table>

In order to understand the nature of the energy gap more clearly, total density of state (DOS) and projected density of state (PDOS) as well as charge density distribution of zirconolite were studied. Figs. 6 and 7 generally showed the presence of high peaks at the valence band and low peaks at the conduction band. The valence band of zirconolite comprised of three regions, the lowest occurrence of valence band between -58.2 eV and -40 eV due to the contribution of the Ti-3s, Zr-4s and Ca-3s orbitals, the intermediate occurrence of valence band between -34.5 eV and -191.10 eV which is the highest peak region due to the domination of the Ti-3p, Zr-4p, Ca-3p orbitals with the minor contribution of the Ti-4s, O-2p, Ca-4s, Ca-4p and Zr-5p orbitals and the highest occurrence of valence band which is just below the Fermi level between -6.2 eV and -2.0 eV which...
is the lowest peak dominated by O-2p orbital with the minor contribution of O-2s, Ti-3d, Zr-4d and Ca-4s. Furthermore, the DOS and PDOS (Figs. 6 and 7) are zero between -2 eV and 0.9 eV which implies unavailable states for occupation, as such this can be considered as band gap which is calculated as 2.9 eV. The occupied conduction band between 0.9 eV to 3.9 eV consists of combined hybridization of Ti-3d, O-2s, O-2p, orbitals and minor contribution of Ca-4s, Ca-4p and Zr-4s orbitals.

Figure 8 shows that the shape of charge distribution along the cations (Ca$^{2+}$, Zr$^{4+}$, Ti$^{4+}$) are spherical, signifying charge transfer between the atoms. Therefore, the cations make ionic bonding due to transfer of charges to O atoms. The thermometer from Fig. 8 shows that the magenta colour develops the highest charge (+1.4106) which relates to the maximum charge accumulation. Thus, Zirconium (4s) atom has the greatest charge distribution than other atoms. The Oxygen (2s) atom with the red colour has a weaker charge density (+0.0013) while the Titanium has a moderate charge density. This implies that the Zirconium has the smallest ionic radius and greatest charge distribution compared to the rest of the atoms.

**Conclusion**

The structural and electronic properties of zirconolite, a promising compound and complicated ceramic for high level radioactive waste encapsulation, was investigated using Quantum ESPRESSO code within DFT. A generalized gradient approximation (PBE-GGA) approximation was applied to calculate the total energy. The Structure of the zirconolite CaZrTi$_2$O$_7$ was found to be stable against decomposition and it is also near the experimental and theoretical calculations. The electronic properties of the material show that the energy separation between the Conduction Band Minimum (CBM) and Valence Band Maximum (VBM) at the R$_2$ and T$_2$ points which indicated calculated indirect band gap nature and the band gap value of 2.90 eV. The result is in agreement with the theoretical calculated value and less than the experimental value due to the known concern of DFT. In addition, the density of state (DOS) and projected density of state (PDOS) calculated indicated that the dominations of different states in both the valence band and the conduction band as well as orbital contributions, the peaks predominate in the valence band compared to conduction band. The disposition of chemical bond and charge transfer between the anions and the cations were examined by the charge density distribution calculation which shows the ionic nature of bond and zirconium as the largest charge density.
Acknowledgments

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Conflict of Interest

Authors have declared that there is no conflict of interest reported in this work.

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