Ab initio study of intrinsic defects in zirconolite

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Zirconolite, CaZrTi₂O₇, is a proposed ceramic for the use in disposal of highly active nuclear waste. Density functional theory (DFT) has been used in conjunction with a random search technique to identify the stable interstitial sites for the intrinsic defects in zirconolite. There is a significant dependence on charge states for the vacancy defect structures, with the formation of an O_2 molecule in certain charge states of Ti and Zr vacancies. The low coordination of the oxygen ions provided sites on which DFT localized holes associated with the cation vacancies. The Frenkel defect energies calculated from the combination of the vacancy and interstitial formation energies show that the oxygen defects have a strong dependence on the chemical environment with a range of 1.5 eV between the oxygen Frenkel pair energies.

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I. INTRODUCTION

The proposed method for the long-term storage of highlevel radioactive waste is the encapsulation of the waste in a ceramic matrix, followed by storage in an underground repository.¹ One such ceramic, which has many of the properties thought to be favorable for waste storage, is zirconolite (CaZrTi₂O₇). Zirconolite is one of the components of SYNROC, a synthetic rock composed of a number of ceramics that is able to incorporate the long-lived radioactive actinide species (Pu,U).^{2–4}

The decay of the encapsulated radioisotopes in a ceramic will modify the microstructure by the creation of defects and, possibly, amorphization. The alpha particle emitted from these elements will create lattice displacements, as well as a large number of excited electrons. The alpha particle dissipates its energy into the electronic system producing excited electrons and holes, which are able to trap at defect sites in ceramic materials. It has been shown recently that trapping of holes and electrons at defects in MgO has a significant effect on their properties.⁵ The long timescale durability of the material will depend on the evolution of the microstructure over periods of hundreds or even thousands of years, well beyond the timescale of experimental measurements. A detailed understanding of the properties of defects is, therefore, a necessary starting point for the prediction of the long-term durability of the encapsulating ceramics.

There have been few modeling studies of zirconolite to date due to the complex crystal structure. Classical molecular dynamics simulations of low-energy cascades have been performed on uranium-loaded zirconolite, and displacement energies have been calculated.⁶ Experimental analysis of the material has included electron microscopy of natural zirconolite containing actinide species,⁷ x-ray diffraction (XRD) of synthesized zirconolite containing Pu or its surrogate Ce,^{8–10} ion beam studies,² x-ray absorption studies (XAS),¹¹ leaching studies,^{12,13} and the behavior of He inside the crystal.^{14,15}

In this paper we use density functional theory (DFT) to calculate the fundamental properties of intrinsic point defects (vacancies and interstitials) in zirconolite. The complex crystal structure of zirconolite makes it challenging to predict the stable configurations of interstitial ions, therefore we use the *ab initio* random structure search (AIRSS) technique. AIRSS has been used successfully for locating novel crystal structures^{16–18} and has been shown to be proficient in deducing point defect structures.^{19,20} We investigate the effects of trapped charge on the defect conformations and formation energies.

II. COMPUTATIONAL METHOD

Zirconolite has a monoclinic crystal structure consisting of rows of 6- and 4-fold coordinated Ti-O polyhedra separated by alternating layers of Ca and Zr ions (Fig. 1).

The crystal structure was obtained from XRD experiments performed by Rossell.²¹ Zirconolite can exist in a number of different stoichiometries, 21,22 CaZr_xTi_{3-x}O₇, where 0.80 < x < 1.37, but a value of x = 1 has been used in this research to minimize the size of the simulation cell. Experimental studies of zirconolite have detected a 5-fold coordinated Ti ion instead of the 4-fold coordinated Ti ion in the ideal structure. Our modeling studies suggest that this could be related to the nonstoichiometry of the experimental sample. Substituting one Zr ion per unit cell for Ti (x = 0.875) results in the substitutional Ti ion becoming 5-fold coordinated. A unit cell with an excess of Zr (x = 1.125), created by substituting one Ti ion per unit cell for a Zr ion, results in the two 4-fold coordinated Ti polyhedra in the same layer as the extra Zr ion becoming 5-fold coordinated. Therefore CaZr_{1.25}Ti_{1.75}O₇ must have the two extra Zr ions in different Ti layers to remove the 4-fold coordinated Ti polyhedra.

The periodic plane wave DFT calculations were performed using the VASP code^{23,24} with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional,²⁵ Projector Augmented Wave (PAW) pseudopotentials, and a single *k*-point sampling of the Brillouin zone at the Γ point, corresponding to a minimum Brillouin zone sampling of 0.07 Å⁻¹ with a basis set containing plane waves up to an energy of 600 eV. A 1×2×1 supercell containing 176 ions was used in this work. Relaxation of the cell volume resulted in relaxed lattice parameters that are in reasonable agreement with those obtained by Rossell using XRD experiments (Table I).²¹ The defects were then



FIG. 1. (Color online) Structure of bulk zirconolite projected in the [010] direction. Red (small dark) spheres show oxygen ions, gray (large gray) spheres show Ti ions, white spheres show Zr ions, and green (small gray) spheres show Ca ions.

introduced into this cell and the structure relaxed with the lattice parameters fixed.

A. Interstitial defects

The complicated crystal structure of zirconolite presents problems for modeling interstitial point defects because it is difficult to predict the stable configurations. In this study an efficient random search technique, AIRSS, was employed to identify energy minima. Interstitial atoms were placed randomly within the simulation cell, and the ionic positions were structurally relaxed within VASP. Once a local minimum is located the process is repeated until the required number of minima are found, then the local minima are sorted by energy. The lowest energy interstitial sites were identified from 100 random searches for each interstitial defect. This involved insertion of an additional atom with the number of electrons corresponding to the desired charge state at randomly generated coordinates in an 88 ion unit cell. The 89 ions were relaxed until all the forces were less than 0.1 eVÅ⁻¹ using the pseudopotentials Ca($3p^6 4s^2$), Zr(4d 5s5p), Ti($3d^3 4s^1$), and O($2s^2 2p^4$) (with a maximum of 283 eV of kinetic energy used in the pseudopotential) to describe the atoms. The 20 lowest energy configurations resulting from the 100 searches were identified, and these were further relaxed until the forces were less than 0.01 eVÅ⁻¹. The lowest energy interstitial configuration was identified from these 20 searches. The interstitial was inserted into the larger 176 ion supercell, and the ions relaxed until the forces were

TABLE I. Lattice parameters calculated by DFT and compared to experimental XRD values obtained by Rossell. $^{21}\,$

Lattice parameter	DFT PBE (Å)	Experimental (Å)	% Error
a	12.09	12.45	2.89
b	14.14	14.55	2.82
c	11.08	11.39	2.72
Volume (Å ³)	1862.82	2028.12	8.15



FIG. 2. (Color online) Partial DOS of bulk zirconolite. Red (thick dark) show oxygen p orbitals, green (light thin) show titanium d orbitals, and blue (dark thin) show zirconium d orbitals.

less than 0.01 eVÅ⁻¹ using the pseudopotentials Ca($3s^2$ 3 p^6 $4s^2$), Zr(4d 5s 5p), Ti($3d^3$ $4s^1$), and O($2ss^2$ 2 p^4) (with a maximum of 700 eV of kinetic energy used in the pseudopotentials) to describe each atom. The interstitial energies from this larger cell were used to calculate the Frenkel defect energies.

B. Vacancies

The vacancies were created by removing the corresponding lattice ion from the 176 ion cell before relaxing all the ions, with the lattice vectors fixed, until the forces were less than $0.01 \text{ eV}\text{Å}^{-1}$ on each atom. The number of electrons in the cell was adjusted to obtain the required oxidation state. Each vacancy species was studied with a charge ranging from 0 to the formal charge of the vacancy (i.e., for the Ti vacancy the Ti atom was removed and 0, 1, 2, 3, or 4 electrons added to the cell). The VASP code introduced a neutralizing background charge when the system was not charge neutral.

III. RESULTS AND DISCUSSION

The band gap calculated for zirconolite in the current simulations was 2.8 eV, which is 0.8 eV less than the experimentally obtained value of 3.6 eV.²⁶ This is in line with the general tendency of DFT to underestimate band gaps in insulators.^{27,28} A study of the partial density of states (DOS) has shown that the edge of the valence band is constructed from the *p* orbitals from the oxygen ions, while the conduction band edge is constructed from Ti *d* orbitals (Fig. 2).

A. Interstitials

The lowest energy configuration of the neutral oxygen interstitial is dependent on the size of the simulation cell and, therefore, the defect concentration. A $\langle 111 \rangle$ dumb-bell interstitial was the lowest energy configuration identified within the 88 ion cell, with a lattice oxygen from a 6-fold coordinated Ti polyhedron forming the second atom of the split interstitial [Fig. 3(a)]. The oxygen dumb-bell has also



FIG. 3. (Color online) The relaxed configuration of the O^0 interstitial in (a) an 88 unit cell and (b) a 176 supercell. The purple (large dark) spheres show the interstitials ion. Partial DOS from (c) the 88 unit cell and (d) the 176 supercell. The upper and lower parts for this, and subsequent DOS plot represent values for spin-up and spin-down electrons, respectively.

been identified as the lowest energy configuration for a neutral oxygen interstitial in a number of oxides.^{5,29–31} In zirconolite the oxygen atoms of the dumb-bell have a separation distance of 1.5 Å, and Bader analysis³² of the relaxed structure shows that -0.48e is transferred from the lattice oxygen to the interstitial, resulting in a charge of -0.57e on both oxygen atoms of the dumb-bell. The formation of the oxygen dumb-bell creates a defect level which resides 0.29 eV above the valence band maximum [Fig. 3(c)]. However, a different interstitial configuration was formed in the 176 ion cell. In the larger cell the interstitial results in the increase in the coordination of two 6-fold coordinated Ti ions to 7-fold coordinated, with the maximum Ti-O bond length defined as 2.2 Å. The interstitial also increased the coordination of all the 4-fold coordinated Ti, with three increasing to 6-fold coordination and the remaining five to 5-fold coordination [Fig. 3(b)]. Two unoccupied defect levels form in the band gap 0.40 eV and 0.69 eV above the valence band for this defect configuration [Fig. 3(d)].

AIRSS located a defect structure for the singly charged oxygen interstitial that was not dependent on the cell size. The oxygen ion binds to a 4-fold coordinated Ti polyhedron producing a defective 5-fold coordinated Ti polyhedron [Fig. 4(a)]. Bader analysis shows that no significant electron density is redistributed due to these displacements. The defect level created by the O⁻ interstitial is 0.54 eV above the valence band [Fig. 4(b)]. The doubly charged oxygen interstitial was found to be unstable as it relaxed to the same configuration as the singly charged interstitial with the extra electron delocalized over the cell.

The calcium interstitial was inserted in two different charge states, the neutral and +2e, but Bader analysis of the resulting configuration shows that the neutral interstitial lost its electrons, giving a charge state of +1.4e, indicating that the calcium interstitial is only stable in the doubly charged state. The double charged interstitial also had a charge of +1.4e, 0.2e less than the lattice Ca ions. The Ca interstitial resides in the $\langle 010 \rangle$ channels, that run through zirconolite [Fig. 5(a)]. The formation of the calcium interstitial does not result in the formation of a defect level in the band gap of zirconolite, because the valence and conduction bands are not constructed from Ca orbitals.

The titanium interstitial was also studied in the neutral and the formal charge (+4e) states, however, in both of these cases the electron distribution was such that the resulting interstitial had a charge of +2e, with the neutral interstitial electron density equal +1.4e and the quadruply charged +1.8e. AIRSS



FIG. 4. (Color online) (a) The relaxed configuration of the O⁻ interstitial in the 176 ion supercell and (b) the partial DOS.



FIG. 5. (Color online) The relaxed configuration of (a) the Ca^{2+} and (b) the Ti^{2+} interstitials located in the $\langle 010 \rangle$ channel.

was then performed on the doubly charged Ti interstitial, and the stable interstitial site was found to be in the $\langle 010 \rangle$ channels [Fig. 5(b)] close to the position of the Ca interstitial, with a Bader charge of +1.6e. The Ti interstitial results in the formation of two singly occupied defect levels in the band gap 2.04 eV and 2.23 eV above the valence band (Fig. 6).

A similar procedure for the zirconium interstitial found that it also exists only in the doubly charged oxidation state, with Bader charge of +1.7e and 2.2e for the neutral and quadruple charged interstitials, respectively. However, in this case AIRSS located an interesting lowest energy structure. The additional zirconium ion displaces a 6-fold coordinated Ti ion from its lattice site and resides on the Ti site. The displaced Ti-lattice ion becomes an interstitial ion (Fig. 7). This displaced Ti ion resides in the same position as the Ti interstitial describe above, and both have the same Bader charge of +1.61e. The bond distances within the polyhedron increase with the substitution of a Zr for a Ti ion, with one of the O ions displaced away from the polyhedron causing the Zr to be 5-fold coordinated. The substitution of a Ti ion by a Zr ion has been observed previously in pyrochlores³³ and Zr-doped TiO₂.³⁴ The substitutional Zr/Ti-interstitial configuration is 0.27 eV more stable than the next lowest energy configuration, which is the Zr interstitial located in the (010) channel.

B. Vacancies

There are seven different oxygen chemical environments in zirconolite, and vacancies in four of these environments have



FIG. 6. (Color online) Partial DOS of the Ti²⁺ interstitial.



FIG. 7. (Color online) (a) The relaxed configuration of the Zr^{2+} interstitial, where the Zr ion has displaced a lattice Ti ion into the $\langle 010 \rangle$ channel. (b) The partial DOS for the defect configuration.

been studied here to observe trends in the oxygen vacancy behavior. The four environments studied were an oxygen ion that bridges two 6-fold coordinated Ti polyhedra in the (010)direction; an oxygen ion that bridges a 6-fold coordinated Ti polyhedron; a Zr ion (1.99 Å Zr-O), another oxygen ion from a 6-fold coordinated polyhedron bridging a Zr ion (2.14 Å Zr-O); and finally a 3-fold coordinated oxygen ion that bridges two 6-fold coordinated polyhedra in the (100) direction and a Zr ion. The local environment of the vacancy had little effect on the localization of the excess electrons generated from the neutral vacancies, as one of the electrons localized on the Ti ion that the oxygen was bonded to and the other localized on a Ti ion in the same or in an adjacent row. This localization of the excess electrons is similar to that found in anatase (TiO_2) .³⁵ The exception to this was the fourth environment in which one electron localized between the neighboring Ti ion in an adjacent row and a Zr ion, and the other electron localized on another neighboring Ti (Fig. 8). The localization of the excess electron from the singly charged vacancy is consistent for the different environments, where the electron localizes on the Ti ion that the oxygen was coordinated to. The second environment is an exception to this behavior as the excess electron localizes between the Ti and Zr ions from where the oxygen ion was removed. Analysis of the electronic DOS, calculated using the Gaussian smearing approximation, for the oxygen vacancies found that only the neutral defects result in the creation of a defect level in the band gap. The defect levels were constructed from Ti d orbitals with a contribution from the Zr d orbitals for the fourth environment. The energy of



FIG. 8. (Color online) The 0.06 e ${\rm \AA}^{-3}$ isosurface of the $V_{\rm O}{}^0$ in the fourth environment.



FIG. 9. (Color online) Partial DOS of the neutral oxygen vacancy in the fourth environment.

these defect levels are 2.66 eV, 2.25 eV and 2.01 eV above the valence band for the first, second, and fourth oxygen (Fig. 9) environment, respectively. A single defect level is also found for a neutral oxygen vacancy in anatase.³⁵

The neutral calcium vacancy localized the two holes present on two oxygen ions. One of the oxygen ions is next to the vacancy site, while the other oxygen ion is the top of a 6-fold coordinated polyhedron, in which the bottom of the polyhedron is next to the vacancy site. Both of these oxygen ions are 2-fold coordinated. There are no defect levels created in the band gap due to the presence of the vacancy. The singly charged vacancy also localizes the hole state on a 2-fold coordinated oxygen. The localization of the hole does not result in a defect level being created in the band gap nor is a defect level present for the doubly charged vacancy.

The zirconium vacancy showed significant charge-state dependence on the observed defect structure, summarized in Table II. The neutral defect results in the formation of an oxygen molecule below the vacancy site. The bond distance of this O_2 molecule was 1.24 Å, which compares to 1.22 Å for a free O_2 . The phonon frequency of this molecule is 37.99 THz compared to the 45.18 THz for the free molecule (1267.10 cm⁻¹ and 1507.09 cm⁻¹, respectively) showing that the molecule has a weaker covalent bond than the free O_2 molecule. Analysis of the isosurface showed that there was

TABLE II. Summary of the effect of charge localization on the defect structure of the Zr vacancy.

Charge state	Defective structure		
V ⁰ Zr	O_2 molecule 6 × 5-fold coordinated Ti 1 × 6-fold coordinated Ti		
V_{Zr}^{-}	5×5 -fold coordinated Ti 2×6 -fold coordinated Ti		
V^{2-} Zr	5×5 -fold coordinated Ti 1 × 6-fold coordinated Ti		
V^{3-} Zr	6×5 -fold coordinated Ti		
V^{4-}_{Zr}	5×5 -fold coordinated Ti		



FIG. 10. (Color online) Isosurface $(-0.01 \text{ eV}\text{Å}^{-3})$ of the 6-fold coordinated Ti neutral vacancy showing electron density between the oxygen atoms viewed along the (001) direction.

electron density in between the two oxygen atoms, similar to that shown in Fig. 10, indicating that a covalent bond has formed. The vacancy also leads to the displacement of a 4-fold coordinated Ti polyhedron by 0.83 Å out of the Ti row towards the vacancy. The defect structure results in the creation of a defect level 2.28 eV above the valence band constructed from Ti *d* orbitals (Fig. 11). The oxygen molecule gives rise to a defect level 2.36 eV below the valence band.

The charged Zr vacancies do not result in the formation of an oxygen molecule. The 6-fold coordinated polyhedron below the vacancy has become 5-fold coordinated with the oxygen ion moving toward the vacancy site for the singly charged vacancy. The distance between the Ti and O ion has increased from 1.89 Å in the bulk to 2.65 Å in the defective structure. The doubly charged vacancy delocalizes the two holes on four oxygen ions surrounding the vacancy. These four oxygen ions are all 2-fold coordinated in the defect structure, bridging a 6-fold coordinated Ti and a Zr ion. The triply charged defect delocalizes the hole over two 2-fold coordinated oxygen ions, which bridge a Ti and Zr. The localized holes are on oxygen



FIG. 11. (Color online) Partial DOS of the neutral Zr vacancy.

Charge state	1st environment	2nd environment	3rd environment	
$\overline{V^0_{Ti}}$	O ₂ molecule	6-fold coordinated Ti	3×5 -fold coordinated Ti	
V ⁻ _{Ti}	O_2 molecule	6-fold coordinated Ti	2×5 -fold coordinated Ti	
V ²⁻ _{Ti}	-	6-fold coordinated Ti	3×5 -fold coordinated Ti	
V ³⁻ Ti	5-fold coordinated Ti	6-fold coordinated Ti	1×5 -fold coordinated Ti	
V^{4-}_{Ti}	5-fold coordinated Ti	6-fold coordinated Ti	1×5 -fold coordinated Ti	

TABLE III. Summary of the effect of charge localization and chemical environment, as described in text, on the defect structure of the Ti vacancies.

ions that are the same side of the vacancy and are separated by the Zr/Ca row. The quadruply charged vacancy has no holes associated with this vacancy, and thus a delocalized state is prevented. The 4-fold coordinated polyhedron is displaced from the Ti row in these charged vacancies by 0.69 Å, 0.68 Å, 0.69 Å, and 0.85 Å for the singly, doubly, triply, and quadruply charged vacancy, respectively. There are no defect levels present in the band gap for any of these charged vacancies.

There are three different chemical environments for the titanium ions, and the relaxed vacancy structure is strongly dependent on the environment, as Table III shows. In the first environment the neutral and singly charged vacancies result in the formation of an oxygen molecule within the vacancy site, similar to that of the neutral zirconium vacancy, with bond lengths of 1.25 Å and 1.24 Å, respectively. The phonon frequencies of these molecules are 37.05 THz and 37.59 THz $(1235.90 \text{ cm}^{-1} \text{ and } 1253.86 \text{ cm}^{-1})$ for the neutral and singly charged vacancies, respectively. The isosurface of the neutral vacancy is shown in Fig. 10 at $-0.01 \text{ eV}\text{\AA}^{-3}$ and clearly shows electron density in the middle of the two oxygen atoms. This build up of electron density indicates that a covalent bond has formed. The molecule formed by the singly charged vacancy has a similar electron density to that of the neutral vacancy O₂ molecule. The higher charged vacancies do not result in the formation of an oxygen molecule; however, the triply and quadruply-charged vacancies lead to the formation of a 5-fold coordinated Ti polyhedron at the expense of the 4-fold coordinated polyhedron next to the vacancy.

The vacancy in the second Ti environment causes the formation of a 6-fold coordinated Ti polyhedron from the 4-fold coordinated polyhedron next to the vacancy site in all of the charge states. The quadruply charged vacancy gives rise to defect levels in the band gap formed from oxygen p orbitals at 0.15 eV and 0.28 eV above the valence band (Fig. 12). The 4-fold coordinated vacancy results in the formation of a 5-fold coordinated Ti polyhedron from the other 4-fold coordinated Ti polyhedron in the Ti row for all vacancy charge states. An additional 5-fold coordinated Ti polyhedron is formed in the Ti row below the vacancy in the neutral and doubly charged state. The presence of the doubly charged or lower-charged vacancies forms an oxygen dumb-bell in the adjacent Ti row by two bridging oxygen ions at the expense of a 6-fold coordinated polyhedron. The presence of the 4-fold coordinated Ti vacancy results in the formation of three 5-fold coordinated Ti polyhedra when the vacancy is neutral or doubly charged.

It is rare that DFT is able to describe hole localization in oxide materials;³⁶ however, it has been observed to correctly localize hole states at low coordinated sites on the MgO surface.³⁷ Analysis of the oxygen coordination in zirconolite shows that the oxygen ions are either 2- or 3-fold coordinated and thus providing sites for holes to localize. The calcium and first Ti vacancies localize holes on 2-fold coordinated oxygen ions, while the second Ti vacancy localizes the holes on only 3-fold coordinated oxygen ions. The Zr and the 4-fold coordinated Ti vacancy localizes the holes on both 2- and 3-fold coordinated oxygen ions.

1. Vacancy defect formation energies

The formation energy of the vacancy defects has been calculated to determine the stable charge state of the vacancy and the results are summarized in Table IV. The formation energy is calculated using (1) and is with respect to the chemical potential of the element and the electrons.

$$E_f(\mu_x, E_F) = (E_v - q\Delta V) - E_B + \mu_x + qE_{\text{VBM}} + q\Delta E_F$$
(1)

Here E_f is the formation energy, E_v is the energy of the cell containing the vacancy, $q\Delta V$ is the potential alignment correction,³⁸ E_B is the energy of the bulk cell, μ_x is the chemical potential of the isolated element in a vacuum ($\mu_x = E_x$, with the oxygen atom in a triplet state), $E_{\rm VBM}$ is the energy of the valence band maximum, and E_F is the Fermi level which acts as an electron reservoir and is set to the valence band maximum in these calculations.



FIG. 12. (Color online) Partial DOS quadruply charged Ti vacancy in the second environment.

TABLE IV. Summary of the formation energy for the vacancies in different charge states in bulk zirconolite. The formation energies are with respect to the chemical potential of the isolated atom in vacuum and the electron chemical potential set to the valence band maximum. The numbers in bold show the most stable charge state for each vacancy.

Charge state	O bridging two 6-fold coordinated Ti	O short Ti Zr bridge	O long Ti Zr bridge	3-fold coordinated bridging O	Ca	Zr	6-fold coordinated Ti	6-fold coordinated Ti	4-fold coordinated Ti
Neutral (eV)	3.75	5.78	5.04	5.43	8.16	20.4	17.89	17.36	18.58
Singly charged (eV)	1.1	2.99	2.58	1.43	7.84	20.94	18.02	16.69	18.37
Doubly charged (eV)	-1.32	0.49	-0.2	-1.19	7.90	19.35	17.54	16.33	18.46
Triply charged (eV)						19.17	17.32	16.60	16.35
Quadruply charged (eV)						19.05	17.66	16.91	16.48

Table IV shows that for this position of the E_F the neutral defects are the least stable for all species apart from the Zr vacancy, which is 0.5 eV more stable than the singly charged defect. The chemical environment of the 6-fold coordinated Ti has an effect on the stable vacancy charge state with the Ti in the 6-fold coordinated row favoring the triply-charged state, while the Ti in the alternating row favors the doubly charged state. The value of E_f for the oxygen vacancies are in good agreement with the formation of oxygen vacancies in ZrO_2 .³⁹

C. Frenkel defects

The energies of the isolated interstitials and vacancies were used to calculate the Frenkel pair energies, Eq. (2), for each species present in zirconolite. The Frenkel pair energies are summarized in Table V. Only the neutral O pairs are considered here.

$$E_{\rm FP} = (E_i - q\,\Delta V) + (E_v - q\,\Delta V) + (2E_B) \,, \qquad (2)$$

where $E_{\rm FP}$ is the Frenkel defect energy, E_i is the energy of the cell containing the interstitial, E_v is the energy of the cell containing the vacancy, $q\Delta V$ is the potential alignment correction,³⁸ and E_B is the energy of the bulk cell.

Table V shows that the Frenkel defect energies are relatively low and that they are consistent with other complex materials, with the oxygen Frenkel pair energies ranging from 2.8-5.3 eV in pyrochlores⁴⁰ and a Zr Frenkel pair energy of 11.16 eV in zircon.⁴¹

TABLE V. Frenkel pair energies of the species within zirconolite. *denotes energy of Zr interstitial located in (010) channel is used to calculate the Frenkel pair energy. Refer to the text for more description of oxygen vacancy sites.

Frenkel pair	Defect energy (eV)
$\overline{O^0 + two}$ 6-fold coordinated Ti bridging V_0^0	1.15
O^0 + Ti Zr short bridging V_0^0	3.18
O^0 + Ti Zr long bridging V_0^0	2.44
O^0 + 3-fold coordinated bridging V_0^0	2.83
$Ca^{2+} + V_{Ca}^{2-}$	1.97
$Zr^{2+} * + V_{Zr}^{2-}$	8.22
Ti^{2+} + 1st 6-fold coordinated V_{Ti}^{2-}	5.11
Ti^{2+} + 2nd 6-fold coordinated V_{Ti}^{2-}	3.98
Ti^{2+} + 4-fold coordinated V_{Ti}^{2-}	6.03

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IV. CONCLUSIONS

We have used DFT to study intrinsic defects in zirconolite, a complex ceramic that is a promising candidate for encapsulating high-level radioactive waste. The complex crystal structure and the range of possible defect oxidation states mean that this material is challenging to study using both experimental and modeling techniques.

We have used an efficient random search technique to identify the lowest energy conformation for interstitials in the zirconolite unit cell. This method enabled the identification of stable defect structures that would have been difficult to predict by traditional methods. The neutral O interstitial resulted in the removal of the 4-fold coordinated Ti polyhedra, whereas the O^- interstitial increased the coordination of a Ti ion from 4 to 5. The Ca and Ti interstitials favor sites in the $\langle 010 \rangle$ channels between the ions, whereas the Zr interstitial displaced a Ti ion from its lattice site to form a substitutional Zr ion and a Ti interstitial.

Vacancies in zirconolite were also shown to have interesting structures, which were sometimes strongly dependent on the oxidation state. In particular the neutral Zr vacancy resulted in the formation of an O_2 molecule, whereas the singly charged vacancy did not result in molecule formation, but it did cause significant displacement of one oxygen atom on a neighboring 6-fold coordinated Ti ion. Oxygen molecules were also observed to form near some Ti vacancies, those associated with the 6-fold coordinated Ti ion, but not in others.

The chemical environment of the O vacancies was found to have a strong effect on the formation energies of oxygen Frenkel pairs, which range between 1.15 eV and 3.18 eV for different chemical environments. The low Frenkel pair formation energies could explain why zirconolite requires a small number of displacements per atom (dpa) to become amorphous,² as the defects are relatively stable. *j.mulroue@ucl.ac.uk

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