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**Atomistic simulation of defects and thermal
conductivity in oxides**

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Abstract

Atomic scale computer simulation techniques are used to predict the thermal conductivity and defect properties in Li_2O and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics. Li_2O represents a simple model system while $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is a complex layered oxide ceramic with potential engineering applications due to its highly anisotropic thermal conductivity.

The efficacy of the available pair potential models for Li_2O are evaluated by comparing with experimental properties such as lattice parameters, elastic constants, thermal expansion and bulk modulus. Other properties, such as the Li ion superionic transition temperature, activation energy and diffusion coefficients for lithium diffusion are also compared with experimental data. The empirical potential set of Chroneos *et al.* [1] was found to best replicate the experimental diffusion data; therefore this potential was used to calculate the reaction energies of the intrinsic disorder properties and then used in the investigation of the thermal properties of Li_2O .

The thermal conductivity of Li_2O was calculated using the velocity exchange methodology within molecular dynamic simulations. The calculated thermal conductivity was compared to experimental data. A number of corrections have been suggested to improve the agreement between the simulated thermal conductivity and the equivalent experimental value. These corrections and the underlying physics are also discussed within the context of Li_2O .

The extent of the isotope effect on thermal conductivity was investigated by comparing a supercell, in which there is a random distribution of ^6Li and ^7Li atoms, to a supercell where all the atoms are given a fractional average mass. The results show that the effect of a non-homogeneous distribution of Li mass can lead to a significant decrease in the thermal conductivity at low temperatures but this effect gradually decreased up to the superionic transition temperatures, where it disappears altogether.

Two different structures have been proposed for low temperature $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, one with a monoclinic space group (B1a1) and the other with a very similar structure

but an more symmetric orthorhombic space group (B2cb). A combination of empirical pair potential and first principles density functional simulations are employed to compare the two structures. Both techniques suggest the monoclinic structure has the lower energy of the two candidate structures. The enthalpy of formation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is calculated using first principles simulation. The macroscopic properties of a material are determined by the concentration and behaviour of point defects such as vacancies and interstitials. Therefore, density functional theory (DFT) simulations were performed to investigate the formation energies and defect volume of vacancy defect in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

The pair potential set of Islam *et al.* [2] and Snedden *et al.* [3] which replicate the structural properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ were used to predict the anisotropic thermal conductivities of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ in x , y and z direction. The sound velocity and mean free paths were calculated and used to explain the temperature independent thermal conductivity in the z direction and the anisotropic thermal conductivity. Finally, the Debye temperature as a function of temperature was computed.

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Dedication

To Hongbao Lu and Yinshan Fu

My Dear Grandfather and Grandmother

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Chapter 1

Introduction

In daily life, a system is normally assessed from a macroscopic point of view in terms of measurable properties such as temperature, pressure, and bulk modulus. However, a material is, in fact, composed of an enormous number of atoms. With the fast development of computational processing power and algorithm development, one can use basic physical rules to model the atoms in the system; that is called atomistic simulation. Atomistic simulation is particularly useful for examining nano scale processes that are impenetrable to experiment as well as explaining the underlying mechanisms responsible for macroscopic properties such as mass and heat transport. In addition, atomistic simulation can investigate proposed theories or models to see whether they will predict the correct macroscopic properties (for example, the concept of minimum thermal conductivity).

The general structure of this thesis is organized as follows: it starts with the introduction of basic concepts such as crystal structure and defects, solid state diffusion, heat transfer and thermal conductivity. Then in the chapter 2, the methodology of classical simulation (both static and dynamic) and quantum mechanical simulation (Density Functional Theory) are reviewed. In the chapter 3 and chapter 4, the influences of fast lithium ionic diffusion and defects (isotope effect) on the thermal conductivity of Li_2O are calculated and analysed. The

mechanical properties, diffusion mechanisms and intrinsic defect disorders are also investigated. In chapter 5 and chapter 6, the low temperature structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is determined. The formation enthalpy and defect formation energies are calculated. The origin of the anisotropic thermal conductivity and low thermal conductivity are investigated. Finally, the thesis ends with conclusions and further work.

1.1 Crystal structure and defects

The structure of a crystal is comprised of a basis and lattice. The lattice is a regular array of points in space and the basis represents the selection of atoms to be attached to each lattice point. Crystals fall into 7 lattice systems by reference to crystal axes, their angles and relative length: cubic, hexagonal, tetragonal, orthorhombic, rhombohedral, monoclinic and triclinic. The 7 lattice systems correspond to the only distinct shapes that can be infinitely tessellated in 3D space without leaving any empty space. Bravais found that there are 14 distinct lattices [4, 23].

A space group is set of a mathematical operators system that describes the symmetry inherent in a crystal structure. It is a combination of the translational symmetry of a unit cell and the point group symmetry operations of reflection, rotation, inversion and improper rotation, screw axes and glide planes. There are a total of 230 unique space groups. The details of space groups can be found in a standard crystallography text book [24].

Any imperfection in a crystal is called a defect. Defects are important in determining many macroscopic properties such as diffusion rate, thermal conductivity, electrical conductivity. There are two types of defect disorder processes, extrinsic and intrinsic. The incorporation of a foreign atom into the crystal structure is called an extrinsic defect. Conversely, defects that occur in the structure without

the introduction of foreign atoms are known as intrinsic.

Intrinsic defect disorder processes include Frenkel, Schottky and antisite reactions. The Frenkel reaction proceeds when an atom is transferred from a lattice site to an interstitial position. A Schottky reaction occurs by transferring an atom from a lattice site in the interior to a lattice site on to the surface of the crystal [4]. The anti site reaction occurs when two different atoms swap their lattice sites. At high concentrations, isolated defects can form clusters.

1.1.1 Kröger-Vink notation

Defects are usually reported using Kröger-Vink notation [25]. The notation is a convention used to describe the net electrical charge and lattice position of point defect species in crystals [25]. The notation is written as M_S^C where M is the species or vacancy (V). S indicates the lattice site that the species occupies, which can be an interstitial site (i) or an atom lattice site. C is the electronic charge species relative to the site; $(\bullet)$ for positive charge, $(')$ for negative charge, $(\times)$ for neutral charge. Examples for MO where M is a divalent cation are given in Table 1.1.

Table 1.1: Example of Kröger-Vink notation for MO.

Defect	Kröger-Vink notation
Cation interstitial	$M_i^{\bullet\bullet}$
Oxygen interstitial	$O_i^{\prime\prime}$
Cation vacancy	$V_M^{\prime\prime}$
Oxygen vacancy	$V_O^{\bullet\bullet}$
Oxygen on cation site	$M_O^{\bullet\bullet\bullet}$

1.2 Solid state diffusion

Diffusion describes the movement of particles from a high concentration to a low concentration region, as defined by Fick's law [26].

$$J_D = -D \frac{\partial C}{\partial z} \quad (1.1)$$

where, J_D is the flux of the atoms, D is the diffusivity and $\frac{\partial C}{\partial z}$ is a concentration gradient. In this example diffusion is driven by a concentration gradient but other driving force such as a temperature gradient may also promote diffusion. Diffusion occurs by Brownian motion [27], a kind of random walk motion. The atoms, owing to a Boltzmann distribution of their energies, are subject to thermal movements of a statistical nature. These statistical fluctuations are the source of the stochastic motions of the atoms. [28].

The diffusivity, D , is related to the mean square displacement of the particles (MSD) as described by Einstein [29],

$$D = \frac{\langle \mathbf{R}^2 \rangle}{2t} \quad (1.2)$$

where $\mathbf{R}$ is the total displacement of an atom after many individual steps and t is time, which needs to be long enough that the atoms starts to undergo random collisions. For three dimension and a sufficiently long time, the equation can be further written as,

$$D = \frac{\langle \mathbf{R}^2 \rangle}{6t} \quad (1.3)$$

Eq. 1.3 suggests that the MSD increases linearly with time for a diffusing atom. The diffusivity can be plotted as a function of temperature. A discontinuity in the diffusivity vs. temperature plot, will indicate if a superionic transition has occurred, whereby the atoms starts to diffuse much faster. The point defects reviewed previously are important for diffusion processes since they promote

mass transport [28]. Since point defect diffusion is thermally activated, diffusivity will obey the Arrhenius equation [30],

$$D = D_0 \exp\left(\frac{E_a}{k_B T}\right) \quad (1.4)$$

where D is the diffusivity obtained from the slope of diffusivity against temperature, D_0 is a pre-exponential factor, the maximum diffusion coefficient at infinite temperature, E_a is the activation energy for the atom jump, T is the temperature.

1.3 Heat and Thermal Conductivity

1.3.1 Fourier's law

Energy transferred due to a temperature difference (other than performance of mechanical work) is called heat, denoted as Q . When two regions of a material are held at different temperatures, heat can flow from a high temperature to a low temperature region, this is known as heat conduction. The fundamental law of heat conduction is based on the observation of experiments [31]. It can be written as

$$\frac{\partial Q}{\partial t} = -kA \frac{\partial T}{\partial z} \quad (1.5)$$

where k is thermal conductivity, $\frac{\partial T}{\partial z}$ is the temperature gradient in the direction of conduction which will be referred to as the z direction. Heat flux (J) is defined as $\frac{\partial Q}{\partial t A}$. Therefore we can rewrite Eq.1.5 as,

$$J = -K \left(\frac{\partial T}{\partial z} \right) \quad (1.6)$$

This equation is called Fourier's law [32].

1.3.2 Thermal transport theory

Introduction to the phonon

The general motion of a system can be expressed as the superposition of normal modes. The energies of the normal modes of a crystal are quantised: the energy in a normal mode of angular frequency ω can only have a value of $(n + \frac{1}{2})\hbar\omega$, where n is any positive integer; $2\pi\hbar$ is the Planck constant and $\frac{1}{2}\hbar\omega$ is the ground state energy. The quantum of energy $\hbar\omega$ is associated with an elementary excitation called a phonon. Thus, a phonon is a quantum of crystal vibrational energy [33].

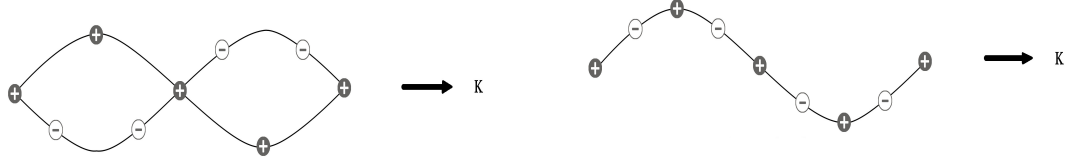
A phonon is a quasi-particle because it does not carry real physical momentum. However, for practical purposes a phonon acts as if it had momentum $\hbar\mathbf{K}$, where $\mathbf{K}$ is its wave vector. In crystals, there are two kinds of phonons: acoustic and optical as shown in Fig. 1.1. Optical phonon modes have a dipole which couples to the electric field of the photon. The positive and negative vibrate against each other, but their centre of mass is fixed. Conversely, the acoustic phonon modes do not and cannot couple to a photon. The atoms and their center of mass move together. Heat energy is mainly transferred by acoustic phonons. In this thesis, the speed of sound is approximately the speed of the acoustic phonon.

Phonon gas

Heat is transmitted by phonons, which are considered to be like a random moving gas of particles. Then from the kinetic theory of gases, thermal conductivity k can be approximated as,

$$k = \frac{1}{3}Cvl \quad (1.7)$$

v is speed of sound, which can be approximated using the Young's modulus of the



(a) Optical phonon.

(b) Acoustical phonon.

Figure 1.1: (a) Optical phonon. (b) Acoustical phonon. Optical and acoustical waves in a diatomic lattice for the two modes. The figure is the reproduction of Kittel's book. [4]

material (the stiffness of the bonding), l is the mean free path of phonons between collisions and C is specific heat. Debye proved that C is proportional to T^3 at low temperature and is almost constant at high temperature [34].

Conduction of heat through a lattice is facilitated by phonon motion through the lattice. Four processes can impede this motion and lead to a reduction of the thermal conductivity. These are phonon-phonon scattering, mass-difference impurity scattering (isotope effect), impurity scattering (due to point defects), grain boundary scattering and electron-phonon scattering.

Phonon-phonon scattering interactions can be considered as a three-phonon process, written as,

$$K_1 + K_2 = K_3 + G \quad (1.8)$$

where K_1 , K_2 and K_3 are wave vectors and G is the reciprocal lattice vector. When $G \neq 0$ this phonon process is called an umklapp process (umklapp is German meaning fold). The only meaningful phonon K values lie in the first Brillouin

zone, so that any long K produced in a collision must be brought back into the first zone by addition of a reciprocal lattice vector, G [4]. As a consequence, there is no longer conservation of phonon momentum. This process is the main origin of thermal resistivity in a perfect single crystal. When $G = 0$ this phonon process is called the normal process; its energy and momentum are both conserved and the phonon flux does not decay across the bulk material and this results in a thermal resistance of zero in a defect free, infinite crystal. Above the Debye temperature (the highest temperature that can be achieved by a single normal mode wave), a substantial portion of all phonon collisions are umklapp processes which requires high thermal energy.

For a typical perfect single crystal, at very low temperature, the umklapp process is not significant. The grain size effect is dominant, therefore $k = CvD$ where D is the diameter of the specimen. The thermal conductivity k increases with T^3 because $C \propto T^3$ [34]. The thermal conductivity reaches a peak and decreases due to anharmonic phonon scattering (umklapp process) proportional to $1/T$. At very high temperature, the thermal conductivity reaches a minimum and becomes independent of temperature, where C and v are almost constant and l is comparable to atomic spacing [35].

Chapter 2

Methodology

Atomistic simulations can fall into two broad categories: classical and quantum simulations.

In classical simulations, atoms are modelled as interacting charged ions, where the detailed electronic structure is not computed exactly. Instead interactions between ions are usually empirically derived by fitting to physical properties such as lattice parameter and elastic constants for a specific system. This suggests the transferability of the potentials can be limited; as it is fitted to a specific system there is no guarantee it will be appropriate for a different system. Despite these limitations, classical simulations can be very useful for predicting macroscopic properties of large systems. In this thesis, the thermal conductivity of a material has to be calculated using classical simulations because a large system is required. Quantum mechanical simulations can describe the electronic structure of the atoms by solving the Schrödinger equation. Although many simplifications are made, quantum mechanical methods are still very computationally intensive and thus can not yet be used to predict properties such as thermal conductivity.

In this thesis, both static and molecular dynamic classical simulations are performed. However, only static quantum mechanical simulations are performed. The simulation codes used are GULP [36], DLPOLY [37] , LAMMPS [38] and

CASTEP [39]. Gulp and CASTEP are used for static classical and quantum mechanical simulations respectively. DLPOLY and LAMMPS are both classical molecular dynamic codes, with LAMMPS used for thermal conductivity calculation due to its inclusion of conductivity calculation algorithms [40].

2.1 Classical simulation

The classical simulation methods carried out in this thesis employed the Born model [41, 42], which assumes the crystal to be an infinite, periodic array of points. The total energy of such a crystal is summed over all the ion interactions, which is expressed as,

$$\Phi_{(r_1 \dots r_n)} = \sum_{i,j}^n \Phi_2(r_{ij}) + \sum_{i,j,k}^n \Phi_3(r_{ijk}) + \sum_{i,j,k,l}^n \Phi_4(r_{ijkl}) + \dots \quad (2.1)$$

where $\Phi_2(r_{ij})$ is the interaction energy between pair of ions i and j at a separation of r_{ij} . $\Phi_3(r_{ijk})$ and $\Phi_4(r_{ijkl})$ are the interactions between ion triplets and quartets respectively. The sum of the pairwise interactions is the major contribution to the lattice energy for ionic materials and higher order interactions are ignored, this is known as the pair-potential approximation [43]. As a result, the Eq. 2.1 becomes

$$\Phi_{(r_1 \dots r_n)} = \sum_{i,j}^n \Phi_2(r_{ij}) \quad (2.2)$$

The term $\Phi_2(r_{ij})$ will be written as $E_{ij}(r_{ij})$ to specially represent a pair potential energy.

2.1.1 Coulombic potential

Charged ions interact with each other due to the Coulombic force. The interaction energy for an ion pair is given as,

$$E_{ij}^{\text{Coulomb}} = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (2.3)$$

where q_i and q_j are charges on ions i and j separated by the distance r_{ij} . ϵ_0 is the permittivity of free space.

From Eq. 2.3, it can be seen that the magnitude of the interaction energy diminishes with $1/r_{ij}$ and therefore converges slowly. As a result, it is computationally intensive to sum the true interactional energy of the system because a great number of ion-ion interactions for each ion need to be considered. The Ewald [44] summation was employed to solve the problem. The details of the derivation is beyond the scope of this thesis, but can be found in Kittel's book and Tosi's paper [45, 46]. However, the main success of this method is that through a transformation into reciprocal space, the sum of electrostatic potentials experienced by a single ion from all other ions can be made to converge more quickly.

Two like charged ions repel each other while two oppositely charged ions attract each other. For the two oppositely charged ions, E_{ij}^{Coulomb} will approach negative infinity when the separation r_{ij} is very small, as suggested by Eq. 2.3. This is physically incorrect because the nuclear-nuclear repulsion and overlap of electron clouds cause a sharp increase in the energy due to the Pauli exclusion principle, which states that no two fermions can occupy the same quantum state [47]. For this reason short range potentials are incorporated to deal with the failure of the Coulomb potential at small separations.

2.1.2 Short range potential

Born and Landé [48] first described the short range potential energy as a repulsive energy to account for the overlapping of electron clouds and nuclear-nuclear interaction using:

$$E_{ij}^{BL} = \frac{b}{r_{ij}^n} \quad (2.4)$$

where b and n are the constants derived to reproduce the equilibrium ionic separation.

With the development of quantum mechanics, another more general potential form was introduced by Born and Mayer [41],

$$E_{ij}^{BM} = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) \quad (2.5)$$

where A_{ij} and ρ_{ij} are adjustable parameters specific to pairs of interacting species.

At intermediate to small separations, there is a weak attractive force between atoms from instantaneously induced dipoles arising due to fluctuations of electron positions. To account for this, London [49, 50] determined that the interaction energy of the ions is proportional to r^{-6} . Therefore, for the charged ions, the attractive term is written as,

$$E_{ij}^{\text{London}} = -\frac{C_{ij}}{r_{ij}^6} \quad (2.6)$$

where C_{ij} is a variable.

By incorporating the Born Landé model Eq. 2.4 and London interaction Eq. 2.6, the Lennard-Jones potential form is reached.

$$E_{ij}^{\text{LJ}} = \frac{b}{r_{ij}^n} - \frac{C_{ij}}{r_{ij}^6} \quad (2.7)$$

By incorporating the Born Mayer model Eq. 2.5 and London interaction Eq. 2.6, the Buckingham potential form is reached [51].

$$E_{ij}^{\text{Buck}} = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \quad (2.8)$$

The Buckingham potential is the short range potential form used in the studies presented herein. The pair potential parameters are reported and verified in the later chapters.

Evaluation of the short-range energy is computationally intensive (due to the exponential and r^6 terms). Thus, to reduce this burden, the short-range energy is only evaluated to a pre-fixed value, the cut-off. A cut-off of 20 Å for the Buckingham potential is sufficiently large because beyond this value the influence of short range potential on the total interactional energy is negligible.

When the separation of pair ions is very small, then the Buckingham potential will drop again unphysically, because the C/r_{ij}^6 in London interaction term decreases more rapidly than the exponential term increases, see Fig. 2.1. This leads to the ions collapsing onto each other. This usually happens when investigating radiation damage, which is not my interest. As such, this situation did not occur in these studies.

2.1.3 Total energy of the system

The total potential energy between ion pairs is the sum of the Coulombic potential and the short range potential energy. In this research, sum is over pairs of ions i, j of interaction energy E_{ij}^{Combine} so that the Coulombic potential and Buckingham potential, are written as

$$E_{ij}^{\text{Combine}} = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \quad (2.9)$$

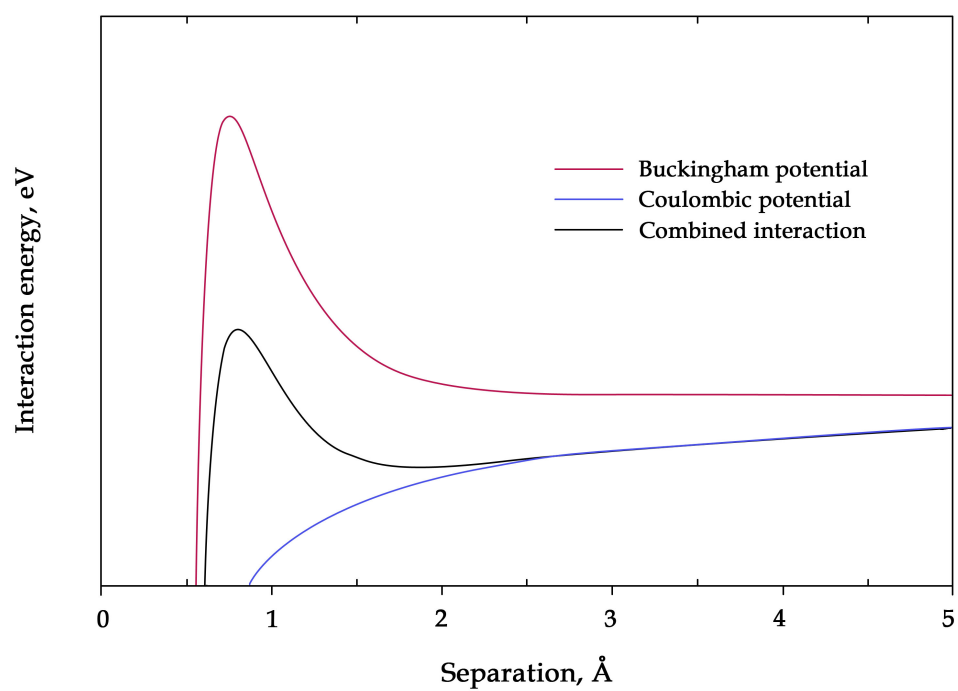


Figure 2.1: The overall pair potential and its relation to the long range Coulombic interaction and short range Buckingham potential for $\text{La}^{3+} - \text{O}^{2-}$ [5, 6].

Therefore, the total energy of the system is

$$E_{\text{system}} = \sum_i^n \sum_{j>i}^n E_{ij}^{\text{combine}} \quad (2.10)$$

2.1.4 Shell model

The Dick and Overhauser shell model [52] is used to mimic ionic polarization. This enables charged ions to form a dipole distortion subject to the electrical field from surrounding ions. In this way, many body effects are included into the simulations. For a cation, the shell model is not necessary because electrons are tightly bound to the nucleus and so cations are not very polarisable.

In the shell model, an ion is modelled as a positively charged core (with charge X) connected to a negatively charged massless shell (with charge Y) by a harmonic spring of force constant, k . Formal charges are used in this thesis, therefore $X + Y = \text{oxidation state}$. The core and shell can move to simulate dielectric polarisability. An isolated ion has a polarisability α given by

$$\alpha = \frac{1}{4\pi\epsilon_0} \frac{Y^2}{k} \quad (2.11)$$

where k is the spring constant; and ϵ_0 is permittivity of free space. X , Y and k are parameters derived to fit the dielectric constant of the material to be modelled.

The core and shell react to the external electrical field. Fig 2.2 (a) demonstrates that without an external electrical field, the core and shell are centered on the same point. Fig 2.2 (b) shows that when subjected to the electrical field, however, the core and shells can move and are not centred on the same point, as a result of this distortion a dipole is induced

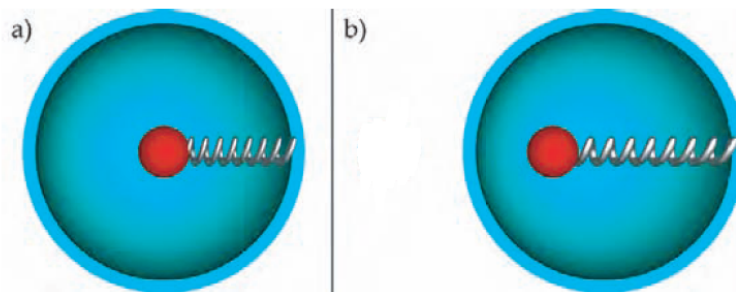


Figure 2.2: Representation of the shell model. a) shows an ion not subjected to an electrical field. b) shows an isolated ion with shell showing polarisation subjected to an external electrical field. The core and shell move to replicate the dipole. [7].

2.2 Energy minimization

In classical and quantum mechanical simulations, prior to any further calculations, the structure should be relaxed to an equilibrium state. This is achieved by minimising the system's energy to a local minimum.

The Newton-Raphson method is employed in the simulations reported here; a basic description is presented next. The energy of the 2 dimensional potential surface after one minimisation step can be written as Eq. 2.12 using Taylor's series,

$$E(x + \delta x) = E(x) + \delta E(x) = E(x) + \frac{dE(x)}{dx} \delta x + \frac{1}{2} \delta x \frac{d^2 E(x)}{dx^2} \delta x \quad (2.12)$$

where δx and δE are an infinitely small movement and associated energy change. The first derivative of energy with respect to distance ($\frac{dE(x)}{dx}$) is the force and second derivative of energy with respect to distance ($\frac{d^2 E(x)}{dx^2}$) is strain. When energy minimization is achieved,

$$\delta E = \frac{dE(x)}{dx} \delta x + \frac{1}{2} \delta x \frac{d^2 E(x)}{dx^2} \delta x = 0 \quad (2.13)$$

giving

$$\delta x = -2 \frac{\left(\frac{dE(x)}{dx} \right)}{\left(\frac{d^2 E(x)}{dx^2} \right)} \quad (2.14)$$

In 3D the second derivative is defined as Hessian matrix, H

$$\delta x = -2H^{-1}g \quad (2.15)$$

where g is the gradient vector. In the large system, calculation and inversion of the Hessian matrix is very computer intensive. Therefore a simplification method proposed by Broyden, Fletcher, Goldfarb and Shanno (BFGS) [53] is used to update H^{-1} .

There are two conditions for energy minimisation: constant volume and constant

pressure. Under constant volume conditions, the lattice energy is minimized by rearranging positions of the ions in the fixed volume cell. Under constant pressure conditions, the cell parameters are also allowed to vary.

2.3 Defect energy calculation

Two approaches have been used in calculating defect energies: the supercell method [54] and Mott-Littleton method [55]. In this thesis, the supercell method is used for quantum mechanical simulations while the Mott-Littleton method is employed in classical simulations.

2.3.1 Supercell approach

A supercell is a repeating unit consisting of more than one primitive cells. The defect is introduced into the supercell. The energy of the defective supercell can also be calculated using energy minimization techniques.

For instance, when a vacancy is introduced into a perfect crystal, the resulting defect energy is the energy difference between a perfect cell and defective cell plus the chemical potential of the atom removed. In the classical simulations, the energies are calculated via the interaction energies between ions and the ion can be considered to move to infinity, as a result the chemical potential energy of the ion removed is zero. For quantum mechanical simulations, the more exact electronic energy of the displaced atom is computed, and the chemical potential is not zero (usually depends on the detailed conditions) and can not be omitted, this will be discussed in Sec. 5.5.3.

Due to the nature of the periodic method used in the simulations, the energy of self-interaction of the defect will be included inappropriately. This can be solved by increasing supercell size so that the self-interaction energy between

defect images are negligible. However, for large systems carried out in quantum mechanical simulations, large supercells (more atoms) will result in a tremendous increase of computing power required.

2.3.2 Mott-Littleton approximation

This method potentially avoids the self-interaction of defect in the supercell method. In this method, a defect or cluster of defects are placed close to the centre of a spherical region of space and two outer concentric spherical regions in an infinite lattice are defined, as shown in Fig. 2.3.

In region I, the interaction energy (E_I) is calculated explicitly using long range and short range potentials until energy minimisation has been achieved.

Region II starts from the edge of region I and extends to infinity. The region II is divided into region IIa and region IIb. In the region IIa, the energy (E_{IIa}) is calculated explicitly but atoms are moved from their perfect lattice site using the force from the polarisation due to the defect. The polarization is given [43, 55] by,

$$P(r) = \frac{q\mathbf{x}}{4\pi r^3} \left(1 - \frac{1}{\varepsilon}\right) \quad (2.16)$$

where , r is the separation and $\mathbf{x}$ is displacement vector in region I, V is the unit cell volume and ε is the static dielectric constant.

In region IIb, for computational reasons, the perturbations are assumed to be quasi-harmonic, and the energy is given as,

$$E_{IIb} = \frac{1}{2} \mathbf{A} \mathbf{y}^2 \quad (2.17)$$

where $\mathbf{y}$ is the coordinates and $\mathbf{A}$ is the force constant.

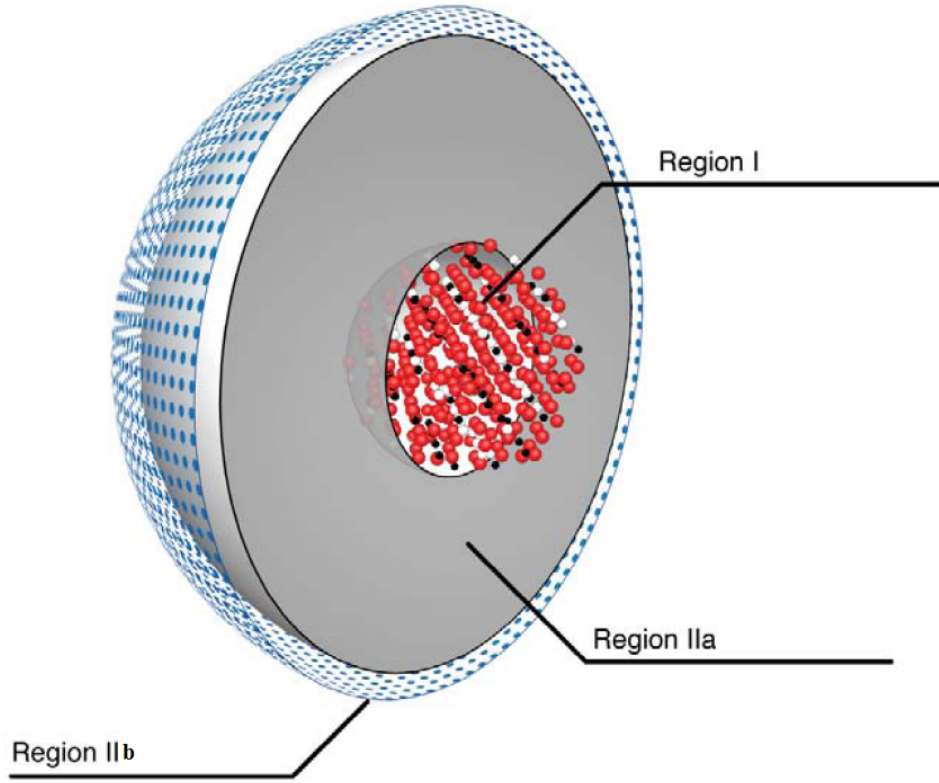


Figure 2.3: Representation of Mott-Littleton regions [8]. In the region I, the ions move explicitly under energy minimisation using derived pair potentials. The gray sphere refers to region IIa where the ions move according to polarisation force. The blue dots referred to region IIb where the ions are extended to infinity.

The defect energy is given,

$$E_{\text{defect}} = E_I + E_{\text{IIa}} + E_{\text{IIb}} \quad (2.18)$$

The size of region I was chosen such that no appreciable change in the defect energy if the region size is increased further.

2.4 Molecular dynamics simulation

The thermal conductivities of materials are investigated in this thesis. Heat is transferred through a crystal via atomic vibration which usually vary as a function of temperature. This is a dynamic process, which means that static techniques such as energy minimisation discussed before are not appropriate simulation methods. Molecular dynamics allows the time evolution of a system to be simulated and temperature effects to be considered, which makes it suitable for thermal conductivity calculations. Before moving onto the specific details of the thermal conductivity measurement algorithm, the fundamental physical ideas and assumptions behind molecular dynamics are reviewed.

The basic physics of MD simulations is to solve Newton's equation of motion in order to predict the behaviour of ions. Newton's second law of motion is given as

$$\mathbf{a}_i(t) = \frac{\mathbf{F}_i(t)}{m_i} \quad (2.19)$$

where m_i is the mass of ion i , $\mathbf{a}_i$ and $\mathbf{F}_i$ are the acceleration and force exerted on the ion as a function of t . As the MD simulations described here are based on classical physics, atom masses are considered to be constant with relativistic effects being ignored.

The potential energy (Φ_i) of an ion is the interaction energy due to the other ions in the system. In this thesis, the pair potential energies with short range Buckingham potentials are employed.

Newton's law of motion from Eq. 2.19 is rewritten as

$$\frac{\partial \Phi_i}{\partial \mathbf{r}_i} = -m_i \frac{\partial^2 \mathbf{r}_i}{\partial t^2} \quad (2.20)$$

where $\mathbf{r}_i$ is the coordinate of atom i .

Considering the large number of mutual time dependent interactions in the sys-

tem, Eq. 2.20 is usually not solved analytically. Instead, during MD Newton's laws of motions are numerically integrated with respect to time.

In a MD simulation, an ion is assigned an initial velocity with a random direction and a statistical magnitude that is to represent temperature according to the Boltzman distribution. The ion is assigned an initial position from the crystallographical information.

Given the knowledge of an ion position and velocity at time t , the position and velocity at later time $t + \delta t$ can be calculated, where δt is a small time increment usually referred as the MD timestep. The velocity Verlet integration method is used in this research and detailed description can be found in the paper by Swope *et al.* [56]. The equations governing the algorithm allow the position $\mathbf{r}_i$, and velocity $\mathbf{v}_i$ of an ion i to be established as,

$$\mathbf{r}_i(t + \delta t) = \mathbf{r}_i(t) + \delta t \mathbf{v}_i(t) + \frac{1}{2} \delta t^2 \mathbf{a}_i(t) \quad (2.21)$$

$$\mathbf{v}_i(t + \delta t) = \mathbf{v}_i(t) + \frac{1}{2} \delta t [\mathbf{a}_i(t) + \mathbf{a}_i(t + \delta t)] \quad (2.22)$$

where δt needs to be small enough to accurately describe atom trajectories. The time step used in this research is 1 fs (10×10^{-15} s). Eq. 2.21 and Eq. 2.22 can be solved iteratively in δt increment until the desired simulation time is achieved, with all the motion of ions solved as discussed before.

It is necessary to relate the positions and velocities of ions at the atomic scale (so called microstates of the system) to macroscopically measurable properties such as temperature and pressure. This is achieved through statistical mechanics using a concept: the ensemble. A thermodynamic ensemble represents all the accessible different microstates with the same properties. For instance, all the microstates corresponding to the same number of ions, volume and energy, is a NVE ensemble. All the microstates corresponding to the same number of ions, volume and temperature, is a NVT ensemble. Constant temperature is

achieved by allowing the system to exchange energy with an imaginary heat bath [57, 58]. All the microstates corresponding to the same number of ions, volume and temperature, is a NPT ensemble. Constant pressure is achieved by allowing the cell volume to vary [59, 60]. Macroscopic properties should in principle be obtained from an ensemble average. Assuming that the allowed microstates have the same probability of occurring; each trajectory of the MD simulation can be regarded as one equal-probability microstate; the Ergodic hypothesis can be applied that states the time average over the microstates is equal to the ensemble average of all the possible microstates. This is why time average is usually used in MD simulations to obtain a correct ensemble average.

2.5 Thermal Conductivity Measurements

The thermal conductivity measurement method used in this thesis is a non-equilibrium molecular dynamic (NEMD) method. The NEMD method has been used to predict the thermal conductivity of amorphous silica [61, 62] Yttria-stabilized zirconia (YSZ) [63], Lennard-Jones systems [64] and carbon nanotubes [65].

The following method was one of the NEMD methods, initially proposed by Muller *et al.* [40]. The simulation system is partitioned into "hot" and "cold" slabs. A constant heat flux is imposed by exchanging velocities of ions in these slabs, the resultant temperature gradient can be generated; see Fig. 2.4. The thermal conductivity can then be computed based on Eq.1.6, Fourier's law. Energy Q' moves from the cold slab to the hot slab. The velocity of the same type ions are exchanged. The algorithm proceeds by selecting the highest velocity ion in the cold slab and the lowest velocity in the hot slab. These velocities are exchanged if the highest velocity ion in the cold slab is higher than the lowest velocity ion in the hot slab. This is always possible as the Maxwell Boltzmann distribution of

atomic velocities is much wider than the difference of the mean velocities in the two slabs. When the pair of ions have the same mass, the total energy and linear momentum are conserved in the system. More than one pair of ions can exchange velocities, that is the lowest and highest velocities pair and the second lowest and greatest velocities pair.

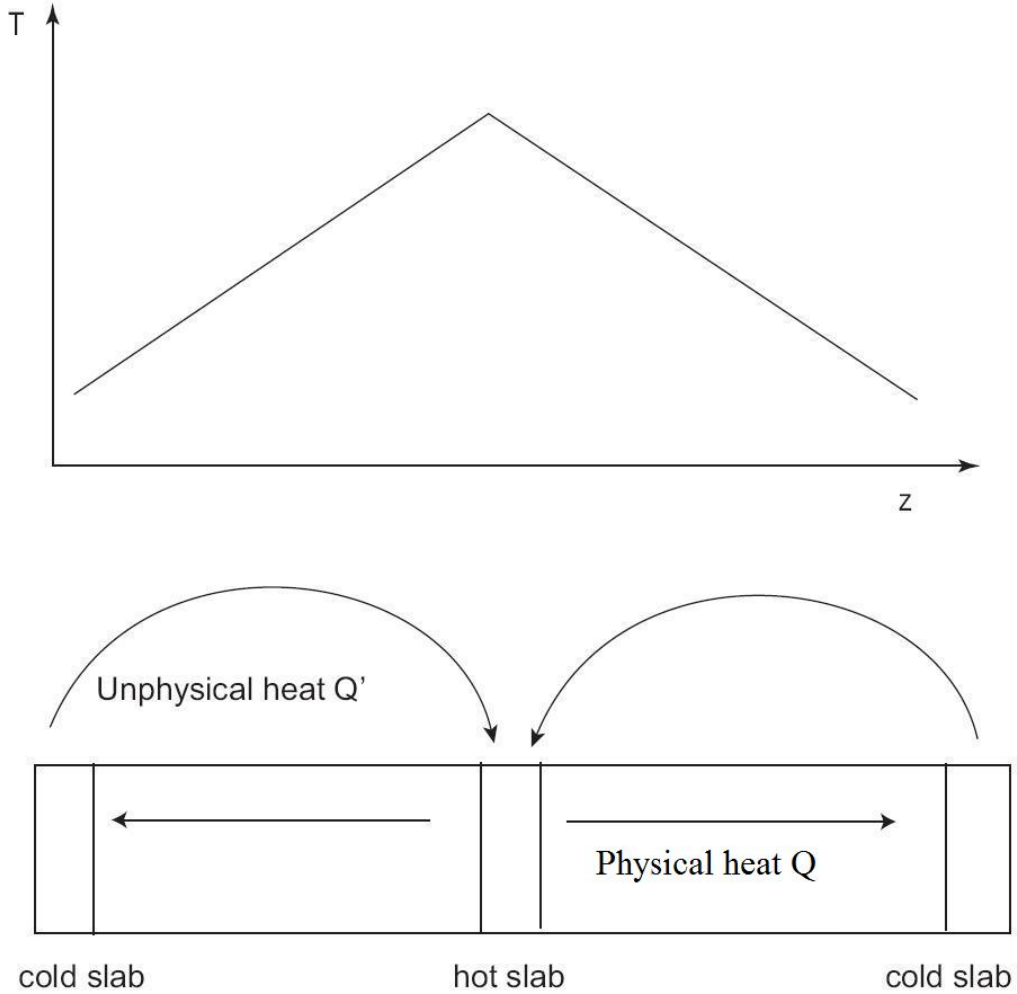


Figure 2.4: Illustration of unphysical energy flow Q' (It is termed unphysical energy because this energy is due to artificially swap kinetic energy of ions by computer algorithm), heat flow Q and temperature gradient ($\frac{dT}{dz}$) along the z direction. Q will later be expressed in terms of kinetic energy and $\frac{dT}{dz}$ are required by Eq. 2.28.

Since the total energy is conserved, the unphysical energy perturbation introduced by the swap should flow back from the hot slab to the cold slab by heat conduction

mechanism. When the steady state is reached, the heat Q has the same magnitude but opposite direction to the unphysical energy Q' .

$$Q = -Q' \quad (2.23)$$

The unphysical energy can be exactly obtained by summing up the "quanta" of energy transported by velocities exchanged as follows,

$$|Q| = |Q'| = \frac{1}{2} \sum_{\text{transfer}} \frac{m}{2} (\mathbf{v}_{\text{hot}}^2 - \mathbf{v}_{\text{cold}}^2) \quad (2.24)$$

The heat flux is then

$$\mathbf{J} = \frac{1}{2At} \sum_{\text{transfer}} \frac{m}{2} (\mathbf{v}_{\text{hot}}^2 - \mathbf{v}_{\text{cold}}^2) \quad (2.25)$$

where, m is the mass of the ion; t is the total simulation time, v_{hot} and v_{cold} are the lowest velocity ion in hot slab and highest velocity ion in cold slab respectively. The factor $1/2$ comes from the periodicity of the simulation system because the energy can be dissipated in both directions.

The kinetic energy of all the ions are computed individually in the MD simulations. The simulating system can be partitioned into many layers. The local temperature of a partitioned layer, T_{layer} , can be calculated using,

$$\frac{3Nk_{\text{B}}T_{\text{layer}}}{2} = \frac{1}{2} \left\langle \sum_i^N m \mathbf{v}_i^2 \right\rangle \quad (2.26)$$

where N is the total number of ions in the layer and $\mathbf{v}_i$ is the velocity of ion i and the angle brackets denote the averaging operator over time. Therefore, a linear response temperature gradient $\frac{dT}{dz}$ can be calculated, as illustrated in Fig. 2.4.

The temperature gradient $\frac{dT}{dz}$ and the heat flux $\mathbf{J}$ are all obtained. The thermal conductivity along the z direction k is,

$$k = -\frac{\mathbf{J}}{\frac{dT}{dz}} \quad (2.27)$$

The practical working formula is

$$k = - \frac{\frac{1}{2At} \sum \frac{m}{2} (\mathbf{v}_{\text{hot}}^2 - \mathbf{v}_{\text{cold}}^2)}{\frac{dT}{dz}} \quad (2.28)$$

The number of velocity swapping pairs and swapping rate are chosen carefully. Too many swapping pairs or too high a swapping rate will lead to non linear temperature gradients. Conversely if their values are too small, the resulting temperature variance will mix with noise.

The method has advantages such as [40],

- The total energy and linear momentum are constant.
- The resulting temperature gradient is well defined and rapidly convergent.

2.6 Thermal conductivity correction for MD simulation

As previously mentioned, when phonons travel through a material, they can be scattered by several mechanisms: anharmonic phonon-phonon scattering, phonon-impurity scattering (isotope, point defects and etc), phonon-electron scattering and phonon-boundary scattering (grain boundaries, dislocations etc.).

In this thesis, ceramic materials were considered, in which electrons are tightly bonded to the nuclei, therefore, the phonon-electron scattering contribution to thermal conductivity was neglected. The atomic computer simulation techniques allow the impurity level of the system to be precisely controlled, which means the phonon-impurity scattering can be evaluated accordingly. The contribution to thermal conductivity due to phonon-boundary and anharmonic phonon-phonon scattering were corrected for when using MD simulation.

2.6.1 Phonon boundary scattering effect

In the velocity exchange method, phonon scattering occurs at the interfaces of the hot and cold slab, where atomic dynamics was altered by the simulation algorithm. Unless the simulation cell length is significantly larger than the phonon mean free path, phonon scattering from the hot and cold slab interface can limit the thermal conductivity [66]. Increasing the cell size to this condition resulted in significant increase of computing time. This finite size effect was discussed and a solution proposed by Schelling *et al.* [62] using the following relationship,

$$\frac{1}{k} \propto \frac{1}{L_z} \quad (2.29)$$

where L_z is the length of simulation cell. Thus, here the thermal conductivity of different simulation cell sizes has been calculated at a given temperature using MD simulation. Then, the infinite size bulk thermal conductivity at this particular temperature can be obtained by the extrapolation of the thermal conductivity values to $\frac{1}{L_z} = 0$. This infinite size bulk thermal conductivity is then comparable to the experimental single crystal thermal conductivity.

2.6.2 Phonon-phonon scattering effect

If phonons do not interact with other phonons in an infinite defect free system, the lattice thermal conductivity is infinite. This ideal harmonic system is not accurate for real crystals.

Thermal expansion is a result of the anharmonicity of the phonon-phonon scattering in real crystals. The thermal expansion coefficient α , is written in terms of the specific heat C and bulk modulus B as,

$$\alpha = \frac{\gamma C}{B} \quad (2.30)$$

where γ is the Grüneisen parameter, the measure of the anharmonicity. γ is the mean value of γ_i which measures the rate of change of the frequency of vibration of mode i with the volume of the crystal [67].

For a given phonon, many other phonon modes can interact with it and therefore the interaction of the transition probability over all possible modes is complicated for any model and beyond the scope of this thesis. An estimate of the lattice thermal conductivity in terms of the Grüneisen parameter was given by [68],

$$k \sim \frac{24}{10} \frac{4^{1/3}}{\gamma^2} \left(\frac{k_B}{h} \right) MV \frac{T_D^3}{T} \quad (2.31)$$

where T_D is Debye temperature, M and V are the atomic weight and volume per atom.

Through the dependence of the Grüneisen parameter, Eq. 2.30 and Eq. 2.31 can be related as,

$$k = \chi \frac{1}{B\alpha^2} \frac{CT_D^3}{T} \quad (2.32)$$

And χ is a constant,

$$\chi = \frac{24 \times 4^{1/3} k_B MV}{10h} \quad (2.33)$$

The specific heat C is considered to be a constant obeying the Dulong-Petit limit at sufficiently high temperature and the Debye temperature T_D is assumed to be the same for simulated and experimental results at all temperatures. When the pair potential does not perfectly reproduce the bulk modulus B and the thermal expansion α , this will result in a deviation of the simulated thermal conductivity from the experimental thermal conductivity.

2.7 Quantum mechanical simulation

Quantum mechanical simulation aims to replicate the macroscopic physical properties and behaviours of solids by describing the wave functions of nuclei and electrons in a closed system, that is, by solving all Schrödinger equations [69], as shown Eq. 2.34.

$$\hat{H}\Psi_{\text{system}} = E\Psi_{\text{system}} \quad (2.34)$$

where Ψ_{system} is all the wave functions of electrons and nuclei in the system. Then,

$$\hat{H} = \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r}) \quad (2.35)$$

where $\hat{H}$ is the non-relativistic Hamiltonian operator, and $\mathbf{R}$, $\mathbf{r}$ are the sets of nuclei and electronic coordinates respectively. $\hat{T}_N$ and $\hat{T}_e$ denote the kinetic energy operators of nuclei and electrons. $\hat{V}_{eN}$ is the potential energy operator due to electrons nuclei interactions, $\hat{V}_{NN}$ is the potential energy operator due to nuclei nuclei interactions and $\hat{V}_{ee}$ is the potential energy operator for the electron electron interactions. The individual term can be written as

$$\hat{T}_N(\mathbf{R}) = - \sum_i \frac{\hbar^2}{2M_A} \nabla_i^2 \quad (2.36)$$

$$\hat{T}_e(\mathbf{r}) = - \sum_A \frac{\hbar^2}{2m} \nabla_A^2 \quad (2.37)$$

$$\hat{V}_{eN}(\mathbf{r}, \mathbf{R}) = - \sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} \quad (2.38)$$

$$\hat{V}_{NN}(\mathbf{R}) = - \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} \quad (2.39)$$

$$\hat{V}_{ee}(\mathbf{r}) = - \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad (2.40)$$

where ∇ is the Laplace operator, a second order differential operator with respect to

x, y and z . $\hbar$ is the reduced the Planck constant, $\frac{\hbar}{2\pi}$. r_{Ai} , R_{AB} and R_{ij} are the distances between nuclear-electron, nuclear-nuclear and electron-electron respectively. A and B are elements of $\mathbf{R}$ (the nuclei) and i and j are the elements of $\mathbf{r}$ (the electrons). The atomic number is Z , the charge of an electron is e . The nuclear mass and electron mass are M_A and m respectively.

Eq. 2.35 can be energy minimized with respect to $\mathbf{R}$ and $\mathbf{r}$ to achieve the ground energy state, which is an approximation (0 K) to describe the physical properties of materials. However, to calculate all the electron-nuclei, nuclei-nuclei electron-electron interactions is extremely computationally intensive. There are a few further approximations such as the Born-Oppenheimer approximation [70], density functional theory [71, 72], Blochs theorem [73], k point sampling, plane wave energy cut off, and pseudo potentials to be implanted in the practical simulations employed in this thesis.

2.7.1 Born Oppenheimer approximation

Born [70] states the nuclei are much heavier and slower moving particles, compared to the electrons. These large differences make the nuclei appear immobile relative to the movement of electrons. This realisation allows us to separate the Hamiltonian into nuclei and electronic part for simplification.

2.7.2 Density functional theory

In density functional theory, DFT, the ground energy state of a many electron system is estimated subject to approximations [9]. DFT assumes each electron is in an effective potential generated by all the other electrons and nuclei. This converts the problem into solving a set of one electron Schrödinger as shown in equation:

$$\hat{H}_e \Psi = [\hat{T}_e + \hat{V}_{\text{ext}} + \hat{U}] \Psi \quad (2.41)$$

where $\hat{H}_e$ is the electronic Hamiltonian, Ψ is wavefunction of the electron. $\hat{T}_e$ is the kinetic energy operator of the electron. $\hat{V}_{\text{ext}}$ is the external potential operator due to the presence of nuclei or some other possible external field and $\hat{U}$ is the effective potential energy operator due to electron electron interactions. In fact, this approximation is used in most quantum mechanical methods.

The DFT is based on two simple principles [71]

1. The total energy of a system of electrons and nuclei is a unique function of the electron density.
2. The variation principle can be used to find the ground state energy of the system. The variational minimum of the energy is exactly equivalent to the ground state energy of the system.

These two principles result in two basic theorems [74] in Eq. 2.42-2.44,

$$E(n) = \int \hat{V}_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n] \geq E_0 \quad (2.42)$$

$F[n]$ is a function accounting for T_e and U ,

$$F[n] = \min_{\Psi \rightarrow n} \langle \Psi^* | \hat{T}_e + \hat{U} | \Psi \rangle \quad (2.43)$$

where the minimum is taken over all wave function of electrons, Ψ . The Bra-ket notation ($\langle \parallel \rangle$) is used. The total ground state energy E_0 then can be written as a function of the electron density $n(\mathbf{r})$ as,

$$E_0 = \int \hat{V}_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n] \quad (2.44)$$

The great advantage of DFT is that the total energy is written in terms of a functional of the electron density $n(\mathbf{r})$, which is only dependent on the positions

of the electrons. The $n(\mathbf{r})$ at a position $\mathbf{r}$ is given by $n(\mathbf{r}) = \sum_i^N |\Psi_i(\mathbf{r})|^2$, where in the ground state, the sum runs over the N lowest eigenvalues, and N is the number of non-interacting electrons moving in the effective potential [75].

The practical tool for the DFT is Kohn-Sham equation [72], written as,

$$F[n(\mathbf{r})] = \hat{E}_k[n(\mathbf{r})] + \hat{E}_H[n(\mathbf{r})] + \hat{E}_{xc}[n(\mathbf{r})] \quad (2.45)$$

where $\hat{E}_k$ is the electron kinetic energy operator defined as the kinetic energy of a system of all non-interacting electrons, $\hat{E}_H$ is the Hartree Coulomb term energy operator and $\hat{E}_{xc}$ is the exchange correlation energy functional operator.

In the Kohn-Sham equation, the Kohn-Sham potential V_{ks} defined as

$$V_{ks} = \frac{\partial}{\partial n(\mathbf{r})} (\hat{E}_H[n(\mathbf{r})] + \hat{E}_{xc}[n(\mathbf{r})]) = V_H + \frac{\partial \hat{E}_{xc}[n(\mathbf{r})]}{\partial n(\mathbf{r})} \quad (2.46)$$

where V_H is the average of the Coulomb potential between electrons and all other charged particles in the system, called the Hartree potential.

2.7.3 Exchange-Correlation energy function

The exchange correlation energy physically involves separating electrons with the same spin (exchange energy) and with opposite spin (correlation energy) [74]. Thus the actual calculation is complicated, and is usually approximated in some ways in terms of electron density.

E_{xc} (Eq. 2.45) is most widely approximated using either the local density approximation (LDA) [72] or the generalized gradient approximation (GGA) [76].

LDA assumes a slowly varying density electron gas, therefore,

$$E_{xc}^{\text{LDA}}[n] = \int n(\mathbf{r}) \varepsilon_{xc}(n(\mathbf{r})) d\mathbf{r} \quad (2.47)$$

where $\varepsilon_{xc}(n)$ is the exchange-correlation energy per electron in a uniform gas of density n . The assumption is not quite approximate, because the electron density is much higher near the nuclei. However, it works well in many cases, especially where only weaker interaction between valence electrons are important.

The graded functional was developed to take into account the non-uniform electron density around atoms, termed GGA. The approximation is given

$$E_{xc}^{\text{GGA}}[n] = \int f(n(\mathbf{r}), \nabla n(\mathbf{r})) d\mathbf{r} \quad (2.48)$$

where $f(n(\mathbf{r}), \nabla n(\mathbf{r}))$ is a function of electron charge density, n , and its derivative.

In this thesis, the GGA exchange correlation function is used for all the quantum mechanical simulations.

2.7.4 Bloch's theorem

It is not possible to describe all the electronic wave functions across the entire lattice of the solid, therefore the crystal lattice is assumed to be periodically repeated supercells. The behaviour of electronic waves is then described in the first Brillouin zone (the primitive cell in reciprocal space) for mathematical convenience.

Bloch's theorem states each electronic wave function in a crystal, can be written as a product of a cell-periodic part and a wave like part [73, 77],

$$\Psi_j(\mathbf{r}) = f_i(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \quad (2.49)$$

where $e^{i\mathbf{k}\cdot\mathbf{r}}$ is the space part and $f_i(\mathbf{r})$ is the cell-periodic part. The cell periodic part can be expanded using a discrete set of plane waves. Therefore, each electronic wave can be written as a sum of plane waves

$$\Psi_j(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{K}+\mathbf{G})\cdot\mathbf{r}} \quad (2.50)$$

where $\mathbf{G}$ are the reciprocal lattice vectors and the exponential term is a plane wave of wave vector $\mathbf{k}$.

2.7.5 K-point sampling

Bloch's theorem changes the calculation of the electronic wave functions across the infinitely periodic supercell to calculating electronic wave functions at an infinite number of $\mathbf{k}$ -points within the first Brillouin zone [9]. The first Brillouin zone is sampled at a particular set of $\mathbf{k}$ -points determined by the Monkhorst-Pack method [78] that creates a uniform grid in $\mathbf{k}$ space (avoiding the infinite array problem by offering an approximation - a representative set of points). Inadequacy of $\mathbf{k}$ -point sampling can result in a large error in the total energy of the system. Conversely, too dense a $\mathbf{k}$ -point sampling regime is very computationally intensive. Therefore, the electronic potential and total energy needs to be converged with increasing $\mathbf{k}$ point sampling within reasonable computational time and cost.

2.7.6 Plane wave energy cutoff

In principle, the electronic wave function at each $\mathbf{k}$ point is expanded by an infinite set of discrete plane waves. However, plane waves with lower kinetic energy play a more important role than those with higher kinetic energy. Therefore a finite set of plane waves is established by truncation at a sufficiently high energy cutoff to offer a good approximation. Again the plane wave cut-off must be investigated for convergence.

2.7.7 Pseudo potential

The electrons of atoms can be grouped into core electrons (near nuclei) and valence electrons (the outer shell electrons). Describing the all electron wave functions

by using a set of plane waves is very computationally expensive. Especially if a very large number of plane waves is required to describe core electron wave functions which oscillate rapidly due to large variation of electron density in this region close to the nucleus. Since the valence electrons mainly determine the properties of the material, the accuracy of the core electron wave function is less important. Therefore, the core electron wave function can be approximated to a simple wave function and non-diverging core electron potential as shown in Fig. 2.5. Outside the core radius, pseudo potential are constructed to be exactly the same as the true potentials for replicating the valence state. The detailed theory to derive the pseudopotential is beyond the scope of this thesis, but can be found in Yin *et al.* [79]. Vanderbilt *et al.* [80] provides an approach to generate a ultra-soft pseudopotentials in the core, which enables a reduction in the plane wave energy cutoff.

In this thesis, the ultra-soft pseudopotential sets are used in first principles simulations.

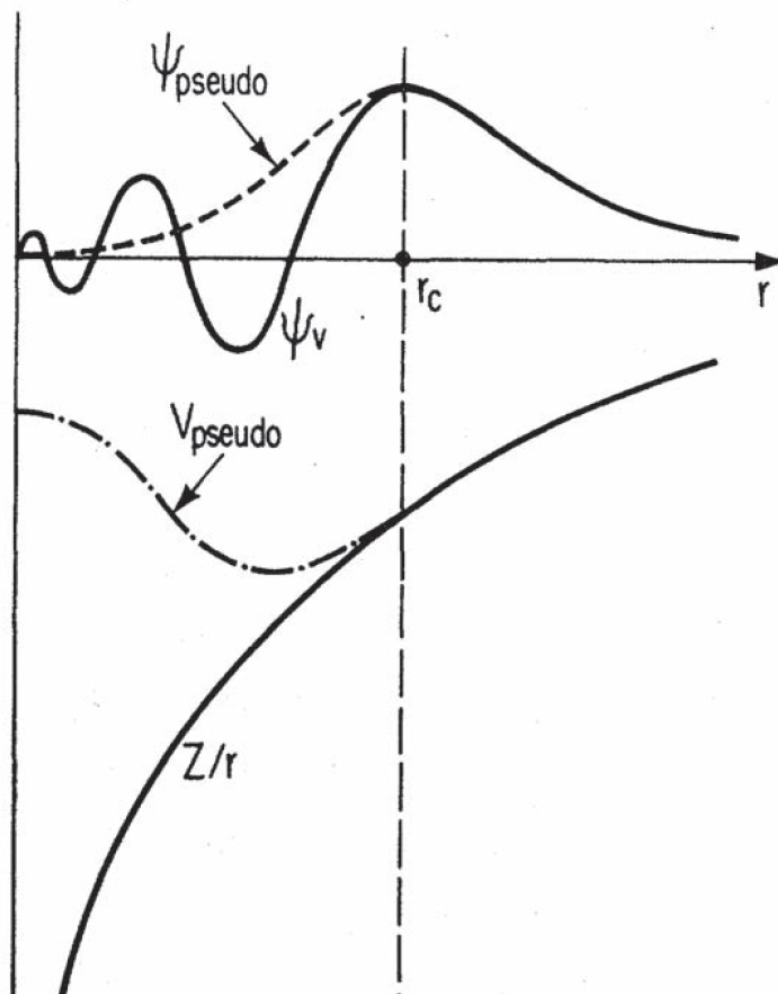


Figure 2.5: Schematic illustration of all electron (solid line) and pseudoelectron (dashed lines) potentials and their corresponding wave functions. The pseudopotential replicates the true potential above r_c . [9]

Chapter 3

A comparison of interatomic pair potentials for Li_2O

3.1 Introduction

Lithium oxide (Li_2O) is an inorganic chemical compound. Li_2O pellets can be obtained by a sintering process under vacuum conditions while single crystals may be grown from a sintered rod in an argon atmosphere by the floating-zone melting technique [10, 81].

Li_2O has several technologically significant applications in light, portable electronic device such as laptops, iPads and mobile phones that rely on rechargeable lithium-ion batteries that possess a high energy density and no memory effect [82]. $\text{CoO} - \text{Li}_2\text{O}$ and $\text{SnO} - \text{Li}_2\text{O}$ can be used as coating materials for lithium battery anodes to provide mobile lithium ions [82, 83]. Another recent application is CO_2 retention. The absorption rate of CO_2 depends on the available lithium ions to form Li_2CO_3 . The rate increases significantly when lithium ions starts to move away from their original lattice sites at around the fast ion transition temperature [84]. For these applications, lithium diffusion plays an important role and its behaviour and properties will be investigated in this chapter.

3.2 Crystal structure

α -phase Li_2O adopts the cubic antiferroite crystal structure with the $Fm\bar{3}m$ (No. 225) space group. An illustration of the α phase Li_2O is given in Fig.3.1. In α phase Li_2O , the Li^+ ions occupy $8c$ Wyckoff site and the O^{2-} $4b$ Wyckoff sites. O^{2-} ions are arranged in a face centre cubic (fcc) array with coordination number of 8 whilst Li^+ are in a simple cubic array with a coordination number of 4 [85].

Lazicki *et al.* [86] observed a reversible phase change from the cubic antiferroite α phase to the orthorhombic β anticotunnite phase, Pnma (No.62) at 50 GPa at room temperature, using X ray diffraction and Raman spectroscopy. Kunc [87] confirmed the transition of the β phase structure at 36.9 GPa using *ab initio* calculations. They also predicted the transition to the densely packed Ni_2In structure, $\text{P6}_3/\text{mmc}$. (No.194) structure at 135 GPa [88].

A number of empirical potential sets have been derived for modelling this system. In this chapter, these potentials will be assessed for their ability to reproduce the physical properties of α phase Li_2O .

3.3 Previous studies

3.3.1 Thermal expansion

Hull *et al.* [17] measured the lattice parameter (a) of Li_2O as a function of temperature in the range of $293\text{K} < T < 1603\text{K}$ and fitted to a cubic polynomial equation of the form $a = m_0 + m_1(T - 293) + m_2(T - 293)^2$, where m_0 , m_1 and m_2 are fitted constants. Their fitted equation was given as :

$$a(\text{nm}) = 0.4611 + 1.283 \times 10^{-5}(T - 293) + 2.729 \times 10^{-12}(T - 293)^3 \quad (3.1)$$

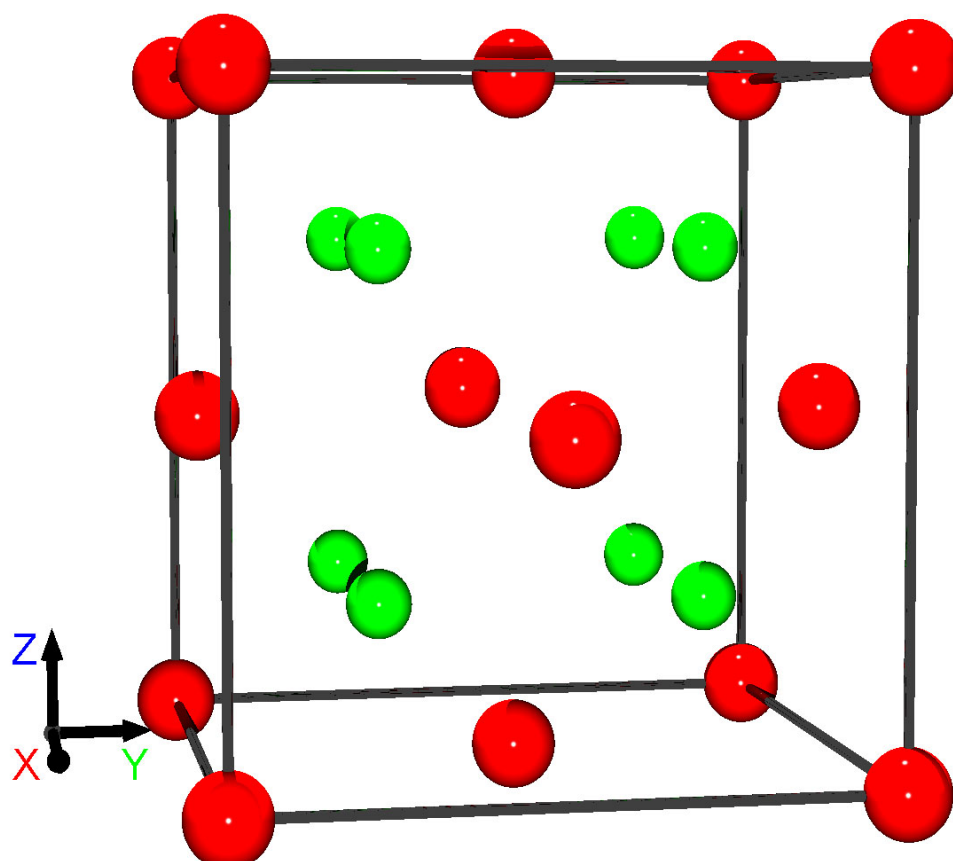


Figure 3.1: The α phase structure of Li_2O under ambient pressure. The red spheres are oxygen and green spheres are lithium.

Eq. 3.1 is divided by a constant term m_0 at 293 K and differentiated with respect to T yielding a linear thermal expansion coefficient as :

$$\alpha_m(\text{K}^{-1}) = 2.782 \times 10^{-5} + 1.775 \times 10^{-11}(T - 293)^2 \quad (3.2)$$

If a simpler relation of the type $a = m_0 + m_1(T - 293)$ is fitted to the lattice parameter in the low temperature range $293 < T < 1273$, an average value of $\alpha_m(\text{K}^{-1}) = (32.9 \pm 0.04) \times 10^{-6}$ can be determined.

3.3.2 Fast and slow ions

The diffusivity of the constituent ions of Li_2O has been extensively investigated by experimental and theoretical methods such as tracer ion diffusion, ionic conductivity and nuclear magnetic resonance (NMR), in addition to static and dynamical simulations. The values obtained for the activation energy of Li^+ ion diffusion varied significantly, probably due to the existence of impurities in experimental samples and inherent difficulties associated with the different measuring methods.

Oishi *et al.* [10] employed ^6Li as a tracer in diffusion experiments. Two polycrystals were used, one with a natural abundance and the other one enriched with ^6Li . The self-diffusion of Li^+ was determined from the distribution of the isotope ratio measured by mass spectroscopy between the two Li_2O polycrystals. They interpreted the low temperature region (below 1200 K) as extrinsic diffusion with an activation energy of 1.01 eV, which only included the migration energy of Li^+ . Conversely, the high temperature region (above 1200 K) was regarded as intrinsic diffusion with a 2.52 eV activation energy, which included the migration energy of Li^+ and the Li Frenkel defect formation energy. Mousa *et al.* [89] used NMR to investigate Li^+ ion diffusion. The Li^+ ion conductivity was determined from the ^7Li relaxation rate under a magnetic field. Their measured extrinsic and intrinsic

energies were 0.55 eV and 1.3 eV respectively. Ohno *et al.* [81] measured the conductivity of single crystal and sintered pellets (polycrystal) of Li_2O using the two terminal technique, with an AC impedance bridge in an argon atmosphere. The Li^+ ion activation energies for extrinsic diffusion was 0.4-0.5 eV and the activation energies for intrinsic diffusion were 1.2-1.3 eV. The difference between activation energy in single crystal and pellets was not found to be significant. However, the humidity (i.e. the concentration of OH^- impurity) had a relatively large influence on the activation energy between the extrinsic diffusion region. This may explain the large difference in activation energy between different experimental results. Fracchia *et al.* [90] calculated the lithium diffusivity via mean square displacement within molecular dynamic simulations. As the MD simulation used a perfect cell, the activation energy encompassed the Li vacancy formation energy and migration energy, hence it should correspond to the intrinsic region in the experiments. The Arrhenius equation was used to calculate the activation energy and a value of 1.5 eV was obtained.

Akiyama *et al.* [91] employed ^{18}O as a radioactive tracer. The self-diffusion coefficient for oxygen ions was much smaller than that of Li ions. The activation energy was interpreted for the intrinsic oxygen diffusion, which was the sum of the formation energy of the Schottky trio, oxygen Frenkel pair and the migration energy for oxygen. The calculated oxygen activation energy was 3.61 eV.

From the current literature, Li^+ is a fast ion with significant diffusion at high temperature in the high temperature region, while O^{2-} is a slow ion with much less significant diffusion before fully melting.

3.3.3 Li^+ ion diffusion mechanism

Static simulations employing the pair potential of Chadwick *et al.* [92] suggested that the most likely mechanism for Li^+ ion diffusion was via a cation vacancy and

that Frenkel disorder was more energetically favourable than Schottky disorder. The vacancy diffusion model was later experimentally supported by Strange *et al.* [93]. The values of the diffusion coefficients of vacancy and interstitial diffusion model were both calculated using data from NMR and AC conductivity measurements. The diffusion coefficients of the vacancy diffusion model were in good agreement when using both techniques, while those of the interstitial diffusion model were different, suggesting that vacancy diffusion was a better model because of the consistency.

Farely *et al.* [85] employed neutron diffraction to investigate Li^+ ion diffusion. They claimed that below 1073 K the observed Bragg peak intensity can be well fitted using the antiferroite structure. Above this temperature, the time averaged disordered structure consists of interstitial lithium ions occupying mean positions very close to the midpoint between two nearest-neighbour lithium sites. The empty cubo-octahedral interstitial sites were therefore not the best fitting model at high temperature. Fracchia *et al.* [90] carried out molecular dynamics simulations on Li_2O . Their results suggest direct migration mechanism along the $\langle 100 \rangle$ family of directions is not the dominant mechanism. Therefore a more complicated diffusion mechanism should exist. Pfeiffer *et al.* [94] also employed molecular dynamics simulations to investigate Li^+ ion diffusion. They did not observe Li^+ fast ion diffusion for their perfect crystal up to a temperature of 1200 K. One possible explanation was that their simulation time was too short (8 ps) to observe Li^+ ion diffusion. Goel *et al.* [95] employed molecular dynamics simulations and observed Li^+ fast ion diffusion in a perfect crystal at around 1000 K. They identified from their MD trajectory that the Li^+ ion moves from one tetrahedral site to another tetrahedral site via the cubo-octahedral interstitial site. Hayoun *et al.* [96] observed a number of Li^+ ion diffusion pathways in their MD trajectories and grouped them into two families according to their path. In the first family, the Li^+ ion jumped following a direct path along the $\langle 100 \rangle$ between two nearest Li atom sites whereas in the second family the Li^+ ion traveled along $\langle 111 \rangle$

directions through the cubo-octahedral site. The calculated migration enthalpy for direct diffusion is lowest, at 0.29 eV. The diffusion path between two nearest neighbour Li atom sites was found to be dominant especially at temperatures below 1400 K.

Oda *et al.* [97] employed MD and found Li^+ ion diffusion was promoted if the system contained Li defects such as Li vacancies and Schottky type defects. This was expected as the Li ions can diffuse to the existing defects, avoiding the energy to create a vacancy.

Elastic properties

In 1988, Hull *et al.* [17] employed inelastic neutron scattering to obtain the energy of acoustic phonon modes in α -phase Li_2O between 293 and 1603 K. From the slopes of the phonon energy dispersion curves, the cubic elastic stiffness constants were then obtained. The C_{11} elastic constant experienced a sharp decrease at around 1350 K due to the onset of the fast lithium fast ion transition.

In 2006, Li *et al.* [15] employed *ab initio* Hartree-Fock simulations to investigate the elastic properties of Li_2O . Their results were in good agreement with experimental data. They found, at zero pressure, the elastic constants and bulk modulus decreased monotonically over the temperature range from 0 to 1100 K. When $T > 1100\text{K}$, C_{12} was converging to zero, consistently with the fast ion transition temperature.

3.4 Potential sets

The success of any classical simulation requires good quality, transferable inter atomic (short range) potentials. An inter atomic potential can be derived by empirical fitting to experimentally determined properties or by fitting to the

potential energy curves evaluated by quantum mechanical calculations. In the present study, three different potential models were used and compared. Potentials from Allan *et al.* [98] and Chroneos and Busker [1] were empirically fitted to experimental properties, i.e. lattice parameters or elastic constants. Fracchia *et al.* [90] derived the pair potential by fitting the variation in energy as a function of relative displacements of oxygen and lithium sublattices obtained from periodic *ab initio* Hartree-Fock simulations. All three potentials employed formal charges and were fitted in the form of a Buckingham type potential model, with the parameters shown in Table 3.1.

Table 3.1: Potential parameter sets for Li₂O.

	Interactions	A (eV)	ρ (eV)	C (eV.Å ⁶)
Allan <i>et al.</i> [98] Potential A	Li ⁺ - O ²⁻	525.95	0.3010	0.0
	O ²⁻ - O ²⁻	22764.3	0.1490	20.37
Chroneos and Busker[1] Potential B	Li ⁺ - O ²⁻	828.01	0.2793	0.0
	O ²⁻ - O ²⁻	9547.96	0.21916	32.0
Fracchia <i>et al.</i> [90] Potential C	Li ⁺ - O ²⁻	653.84	0.285723	0.0
	O ²⁻ - O ²⁻	0.0	1.0	-76.651

The O²⁻ shell parameters are shown in Table 3.2.

Table 3.2: The O²⁻ shell model parameters.

	Shell charge (e)	k (eV Å ⁻²)
Potentials A and C [90, 98]	-2.9769	47.6908
Potential B [1]	-2.04	6.30

All results obtained from the simulations will be compared to the available data in the literature, both experimental and theoretical. This is essential in providing validation of the potential models.

3.5 Results and discussion

3.5.1 Validation of potentials

Perfect lattice

The code used here was the General Utility Lattice Program (GULP). The perfect unit cell was relaxed to zero stress using energy minimization under constant pressure conditions, that is, during relaxation both atom positions and cell parameters were able to change. Predicted lattice and elastic properties of the relaxed structure are compared with the experimental and theoretical data found in literature in Table 3.3.

The lattice parameter, a , as predicted by potential C was closest to the experimental value. Nevertheless, the lattice parameters obtained using the other two potential sets were still acceptable. The elastic constants C_{11} and C_{14} were in good agreement with experimental and *ab initio* simulation results. However, the elastic constant C_{12} was not in good agreement with the experimental data. This was due to the consequence of the Cauchy relation operating in these simulations. The Cauchy relation reduces the number of independent elastic constants by applying additional symmetry, for the cubic system, it implies that $C_{12} = C_{44}$. The relationship holds as long as the potential energy is approximated using only a pair potential. This is due to the centrosymmetric nature of the potential, whereby the energy is only dependent on the separation between ions, additional discussion is provided by Elcoro *et al.* [99]. The bulk modulus, calculated using $B = \frac{C_{11} + 2C_{12}}{3}$ was therefore not accurate as a consequence of the inaccurate C_{12} . Conversely, the Hartree Fock and DFT simulations replicate the elastic C_{12} and bulk modulus well.

Table 3.3: Comparison of perfect lattice parameters and mechanical properties of Li₂O for potential sets *A*, *B*, *C*, *ab initio* Hatree-Fock [15], DFT[16] and extrapolation from experiment data [17].

	Experiment	Hatree-Fock	DFT-LDA	<i>A</i>	<i>B</i>	<i>C</i>
<i>a</i> (Å)	4.55	4.53	4.57	4.62	4.62	4.55
<i>C</i> ₁₁ (GPa)	217	238	237	251	263	274
<i>C</i> ₁₂ (GPa)	24	16	28	61	76	70
<i>C</i> ₄₄ (GPa)	68	66	68	61	75	70
Bulk modulus (GPa)	88	89	94	124	139	138

3.5.2 Bulk modulus

The bulk modulus was determined from MD simulations performed using DLPoly. The $10 \times 10 \times 10$ supercell size system (12000 atoms) was equilibrated for 10 ps under different hydrostatic pressures, that is 0, 10, 20, 30, 40 50 katm at a series of temperatures. The hydrostatic pressures chosen were all sufficiently below the phase transition pressure in given literature [86, 88]. The hydrostatic pressure is plotted as a function of volume at the desired temperature as shown in Fig. 3.2. The volume decreased linearly with increasing pressure. The bulk modulus, *B* is calculated as

$$B = -V \frac{dp}{dV} \quad (3.3)$$

where *V* is the average volume. In this example, *V* is the average volume at 0 GPa and 1173 K, $\frac{dp}{dV}$ was the gradient between hydrostatic pressure and cell volume, obtained from Fig. 3.2.

The same simulation procedures were employed to obtain bulk modulus at different temperatures, i.e. 293 K, 523 K, 773 K, 973 K, 1273 K, 1373 K and 1473 K as shown in the working example before. The bulk modulus simulated using potentials *A*, *B* and *C* as a function of temperature were compared with experimental data in Fig. 3.3. The experimental bulk modulus decreased linearly with increasing temperature, as reported by Hull [17]. The linear expression then was fitted into the relationship between bulk modulus and temperature. The correla-

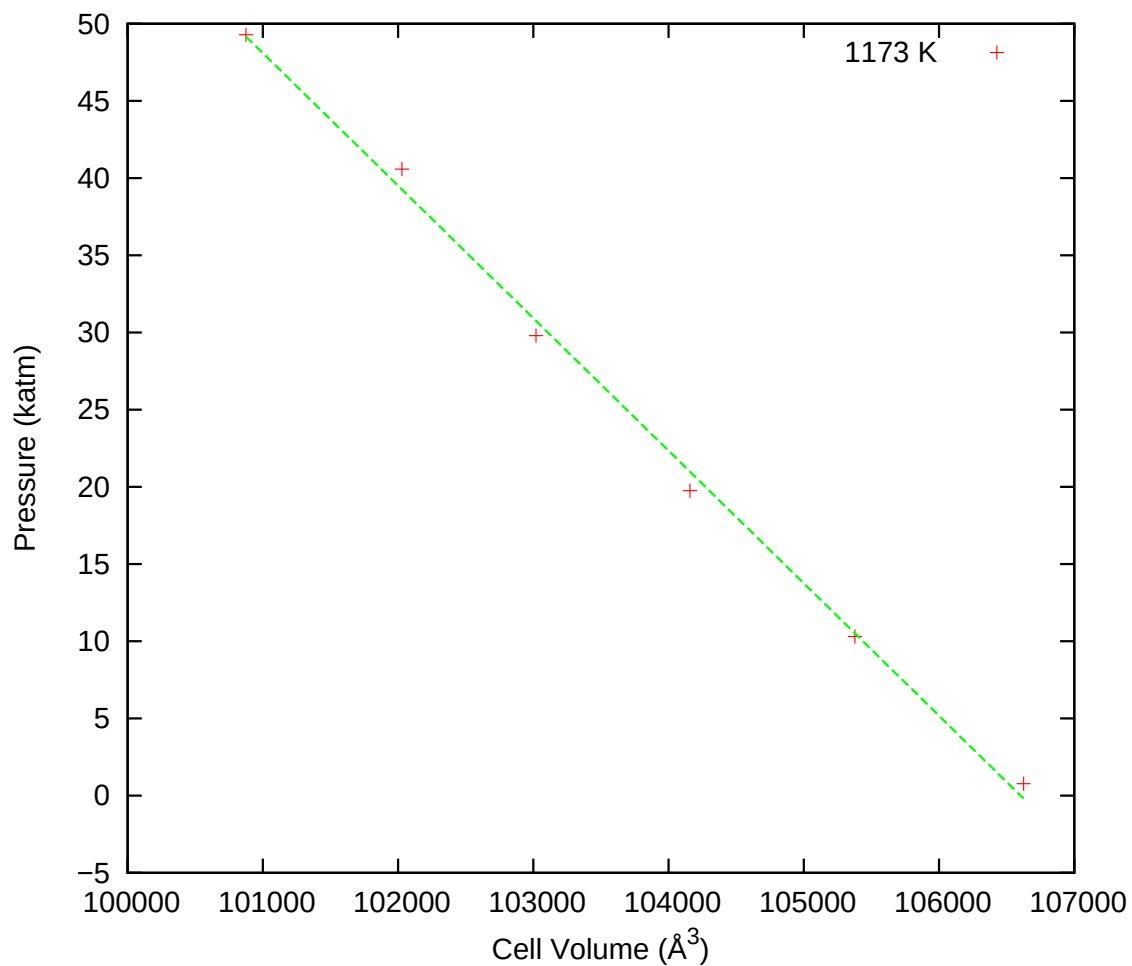


Figure 3.2: The pressure-volume diagram of Li_2O using potential A at 1173K. The equation of the state is $p = -0.0086V + 915.14$, where p is pressure in katm and V is the cell volume in $\text{\AA}^3$.

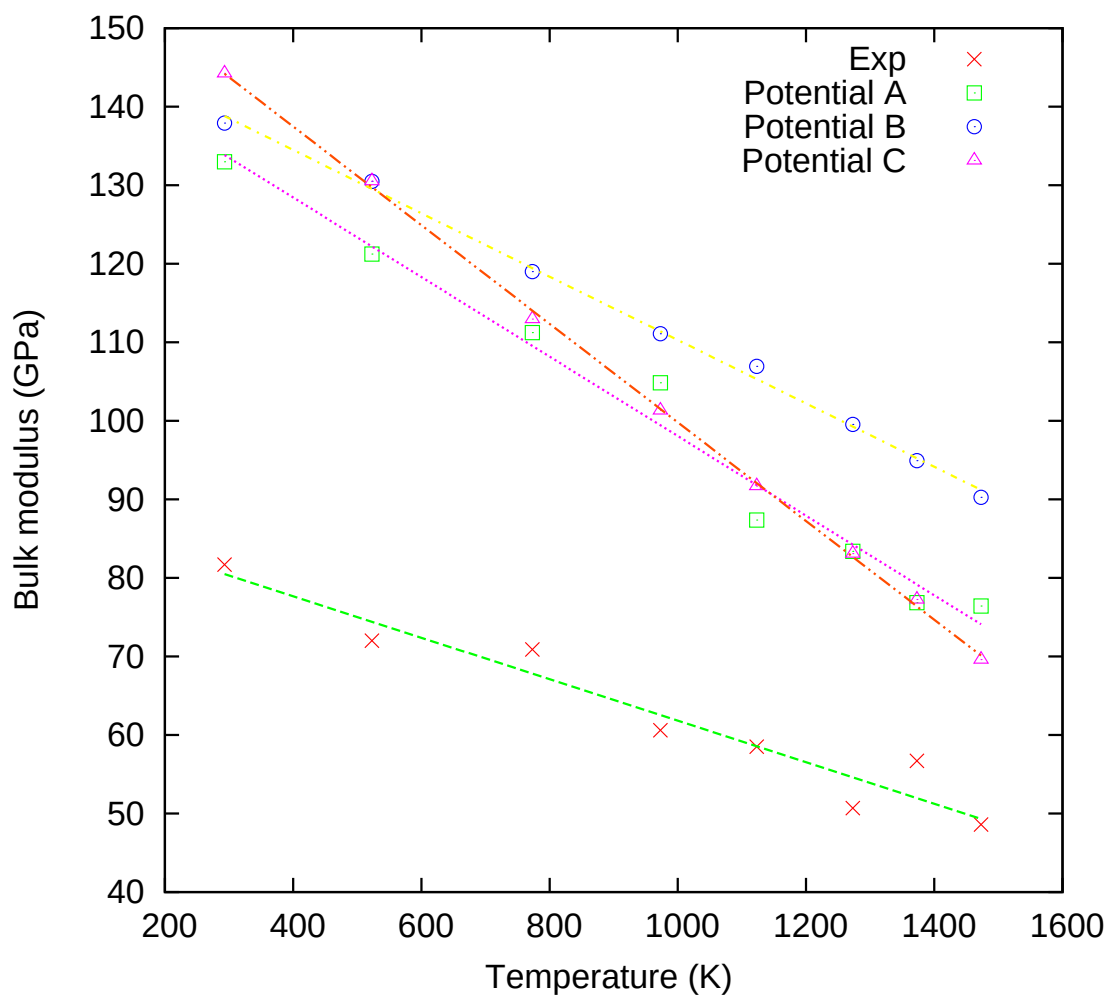


Figure 3.3: Comparison of Li_2O bulk modulus as a function of temperature using potentials A, B and C with experimental data.

tion coefficient, R^2 was calculated to give a measure of the reliability of a linear relationship between pressure and bulk moduli. The linear expressions were calculated as,

$$B_{\text{Exp}} = -0.026T + 88.23 \quad (3.4)$$

$$B_{\text{A}} = -0.051T + 148.69 \quad (3.5)$$

$$B_{\text{B}} = -0.040T + 150.63 \quad (3.6)$$

$$B_{\text{C}} = -0.063T + 162.59 \quad (3.7)$$

The simulated bulk modulus decreased linearly with increasing of temperature, the gradients all being around a factor of two larger than the experimental value. The possible reason was that the full charge model used in the simulation, caused stronger bonding compared to the experimental data.

Overall the potential sets can reproduce the general trend of the bulk modulus with increasing temperature despite the overestimation. Comparing the gradient of bulk modulus vs temperature, potential B was the closest.

3.5.3 Thermal expansion

The $10 \times 10 \times 10$ supercell was equilibrated at zero pressure and a series of temperatures (NPT condition) for 10 ps. The lattice parameters were averaged over the last 5 ps of the simulation and plotted as a function of temperature and compared with experimental data [17] in Fig. 3.4.

The simulated lattice parameters can be fitted using two different expressions according to different temperature ranges, which are compared with available experimental data.

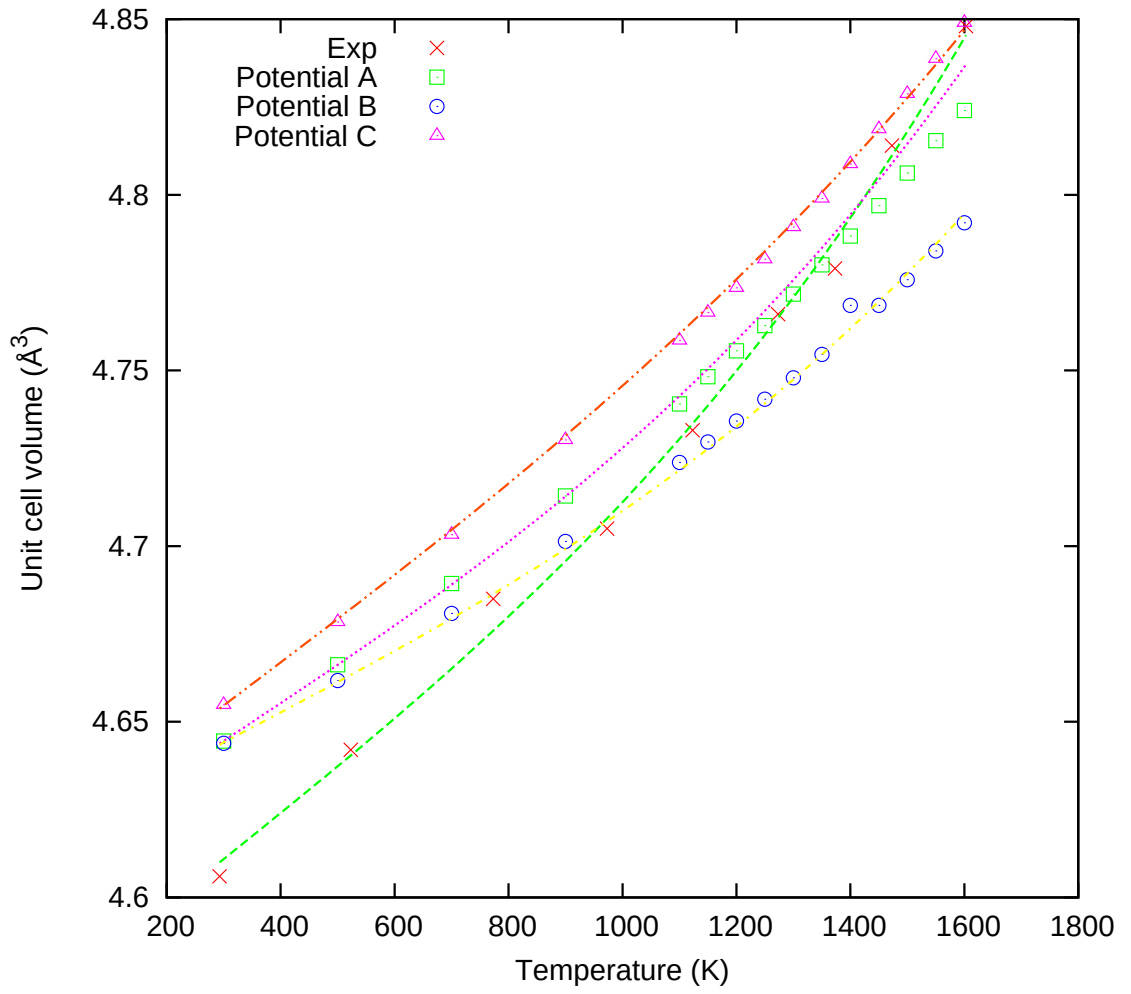


Figure 3.4: Comparison of experimental and simulated thermal expansion of Li_2O using potential A, B and C. The simulation supercell is $10 \times 10 \times 10$ unit cells.

For the temperature range $273 \text{ K} < T < 1600 \text{ K}$

$$a = m_0 + m_1(T - 293) + m_2(T - 293)^3 \quad (3.8)$$

where, T is the temperature, a is the lattice parameter and m_0 and m_1, m_2 are constants.

The fitted expressions for the lattice parameters are given below:

$$a_{exp}(nm) = 0.461 + 1.28 \times 10^{-5}(T - 293) + 2.73 \times 10^{-12}(T - 293)^3 \quad (3.9)$$

$$a_A(nm) = 0.464 + 1.07 \times 10^{-5}(T - 293) + 2.35 \times 10^{-12}(T - 293)^3 \quad (3.10)$$

$$a_B(nm) = 0.464 + 0.85 \times 10^{-5}(T - 293) + 1.78 \times 10^{-12}(T - 293)^3 \quad (3.11)$$

$$a_C(nm) = 0.465 + 1.23 \times 10^{-5}(T - 293) + 1.47 \times 10^{-12}(T - 293)^3 \quad (3.12)$$

The linear thermal expansion coefficient can be obtained by dividing through by the constant term m_0 and differentiating with respect to T . The linear thermal expansion coefficient as determined using potentials A, B and C and experimental data are listed below:

$$\alpha_{exp} = 2.78 \times 10^{-5} + 1.78 \times 10^{-11}(T - 293)^2 \quad (3.13)$$

$$\alpha_A = 2.31 \times 10^{-5} + 1.52 \times 10^{-11}(T - 293)^2 \quad (3.14)$$

$$\alpha_B = 1.83 \times 10^{-5} + 1.15 \times 10^{-11}(T - 293)^2 \quad (3.15)$$

$$\alpha_C = 2.65 \times 10^{-5} + 0.94 \times 10^{-11}(T - 293)^2 \quad (3.16)$$

All three potential sets predict that the cell expanded with the temperature. The simulated lattice parameters at room temperature were all close to experimental data, with a discrepancy of less than 1%. In the low temperature region ($T <$

1300 K), illustrated in Fig. 3.4, the deviation of lattice parameter from experiment was smallest simulated using potential set B. In the high temperature region ($T > 1300$ K), potential set A can best reproduce the lattice parameter. The change of lattice parameter ($\frac{da}{dT}$) becomes steeper at higher temperature. This trend is more pronounced in the results obtained using potential sets A and C than potential set B.

For the low temperature range ($273 \text{ K} < T < 1300 \text{ K}$), the lattice parameter were considered to increase linearly with temperature, therefore the data can be fitted with a more simple expression,

$$a = m_0 + m_1(T - 293) \quad (3.17)$$

Equations for the linear relationship fitted to the results obtained with potential sets A, B and C are listed

$$a_{exp}(nm) = 0.461 + 1.58 \times 10^{-5}(T - 293) \quad (3.18)$$

$$a_A(nm) = 0.464 + 1.27 \times 10^{-5}(T - 293) \quad (3.19)$$

$$a_B(nm) = 0.464 + 1.05 \times 10^{-5}(T - 293) \quad (3.20)$$

$$a_C(nm) = 0.465 + 1.36 \times 10^{-5}(T - 293) \quad (3.21)$$

The thermal expansion coefficients were then independent of temperature, and are listed in Table 3.4. The results suggested that potential C offered the best description of thermal expansion at low temperature.

In summary, the simulated thermal expansion and its trend were reproduced well in the temperature range from 300-1600 K using all potential sets. At low temperature, potential set B was the best potential to replicate the lattice parameters. At high temperature, the lattice parameter matched to experiment better using potential sets A and C. The thermal expansion coefficient can be considered as

Table 3.4: Comparison of experimental and simulated thermal expansion coefficients at low temperature $273\text{ K} < T < 1300\text{ K}$.

Low temperature thermal expansion coefficient $\alpha(K^{-1})$	
Experiment[17]	3.29×10^{-5}
Potential A	2.73×10^{-5}
Potential B	2.25×10^{-5}
Potential C	2.91×10^{-5}

temperature independent at low temperature, where potential C offered the best agreement with experiment.

3.5.4 Diffusion

The diffusivity of Li^+ and O^{2-} were calculated from their mean square displacements (MSD) whose assumptions and mechanisms were described in Sec 1.2. The superionic transition temperature (Li fast ion diffusion) and activation energies were determined from an Arrhenius plot of these diffusivities.

Diffusivity and related properties calculation

The molecular dynamics simulations were carried out in a $10 \times 10 \times 10$ Li_2O supercell of 12,000 atoms using a short-range cut off distance of $10\text{ \AA}$. Individual molecular dynamics simulations were performed in the temperature range 700 K to 1600 K. For each simulation a period of 10 ps NPT dynamics was performed in order to relax the super cell and obtain the average equilibrated volume. After each NPT simulation, a long simulation was then restarted under NVT conditions with the average equilibrated volume for 300 ps. The relatively large supercell provided an unbiased conduction process while the long time NVT dynamics provided good statistics.

The MSDs were calculated for a range of temperatures from 700 K to 1600 K. The

MSDs as a function of time for O^{2-} and Li^+ ions were plotted in Fig. 3.5 and Fig. 3.6 respectively. Fig. 3.5 shows that the O^{2-} ion MSD was time independent across the whole temperature range. Therefore the O^{2-} ions did not migrate and the sublattice can still be identified at high temperatures. In Fig. 3.6, at low temperature the Li^+ ion MSD was also time independent. However, at high temperatures, Li^+ ions MSDs increased linearly with time. This implies that Li^+ ions were no longer vibrating around their lattice site but moving away from their sites, to the extent that Li^+ ions were undergoing fast ionic diffusion.

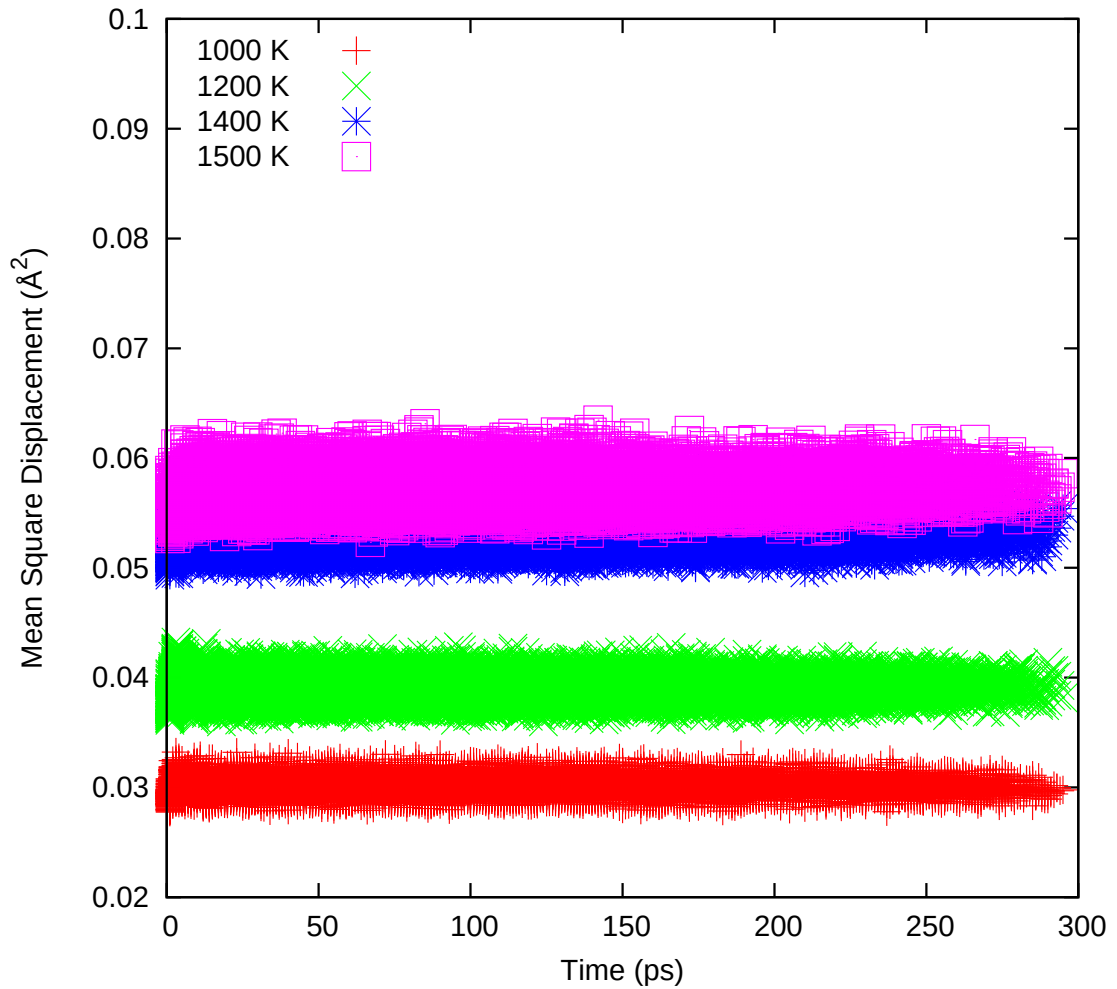


Figure 3.5: Mean square displacement as a function of simulation time for O^{2-} diffusion simulated using potential B.

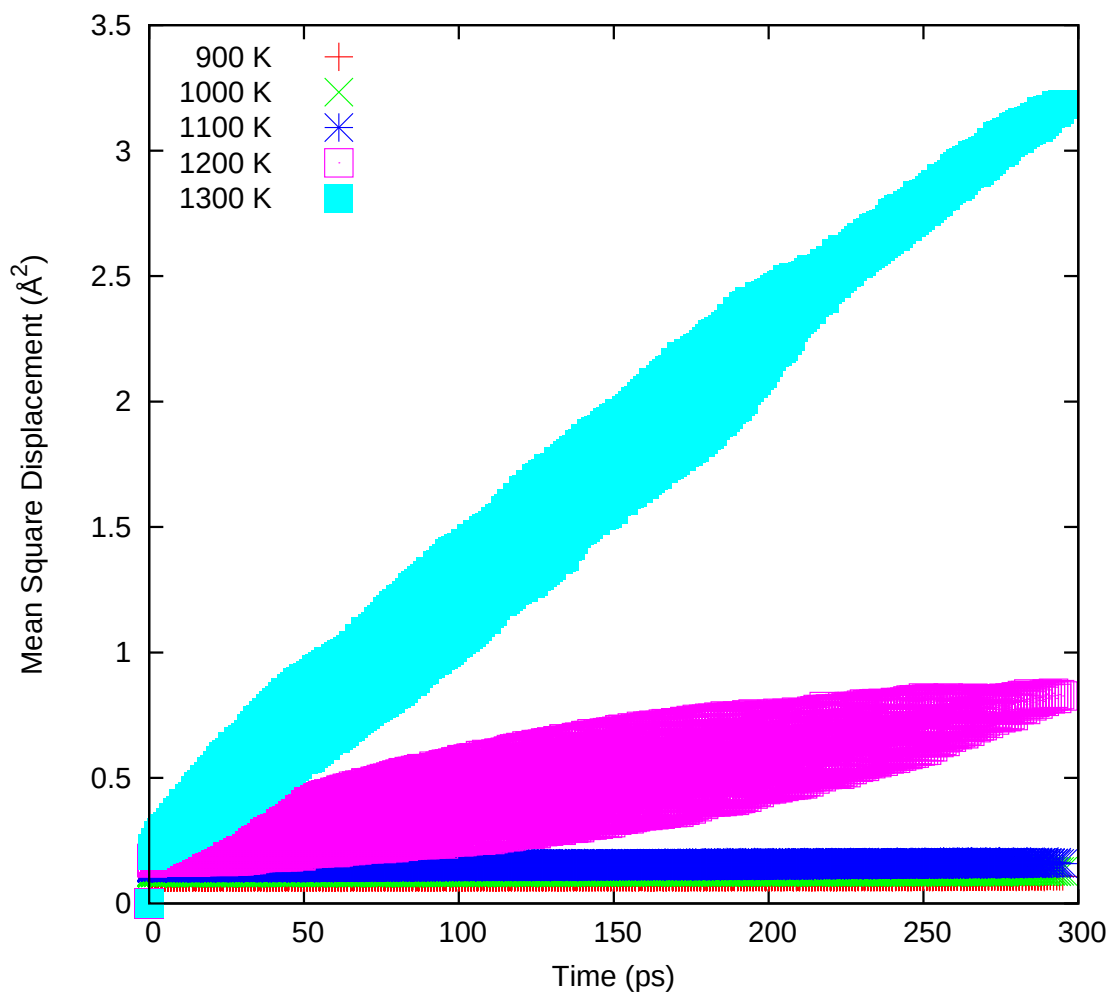


Figure 3.6: Mean square displacement as a function of time for Li^+ diffusion simulated with potential B.

Lithium diffusivity was obtained from the gradient of MSD vs time plot and the natural logarithm of the diffusivity was plotted as a function of reciprocal temperature alongside experimental results in Fig. 3.7. The experimental diffusivities [10] were digitized and converted to the same units for comparison. In the low temperature range, the simulated diffusivity was not in good agreement with the experimental diffusivity. The reason may be that Li^+ ion diffusivities below the transition temperature are very low, and so the errors in the experiments and simulations may be more influential. In the high temperature range, potential set B exhibited the best match to the experimental diffusivities. Since potential B can best replicate the experimental ionic diffusivity, it was then chosen to model another thermal property: thermal conductivity of Li_2O . This potential will be used to predict the thermal conductivity of Li_2O in the next chapter. Of course, thermal and ionic conductivities are quite different processes. However, they are both testing the potential interactions away from equilibrium (at least for higher temperatures).

In Fig. 3.7, all the potential sets reproduce the Li^+ fast ion transition, where the diffusivity increases dramatically above a certain temperature. This fast ion transition temperature can be estimated from the graph. The simulated fast ion transition temperature was around 900-1000 K, agreeing reasonably well with experimental transition temperature, around 1100-1200 K [10, 17].

The activation energy for Li^+ ion fast ion diffusion was calculated using the Arrhenius relationship, details can be found in Sec 1.2.

$$D = D_0 \exp\left(\frac{E_a}{k_B T}\right) \quad (3.22)$$

where E_a is the activation energy. Because the perfect structure of Li_2O was simulated in the MD simulations, the activation energy consists of the the energy required to create a Li vacant site and to move Li^+ ion around in the cell.

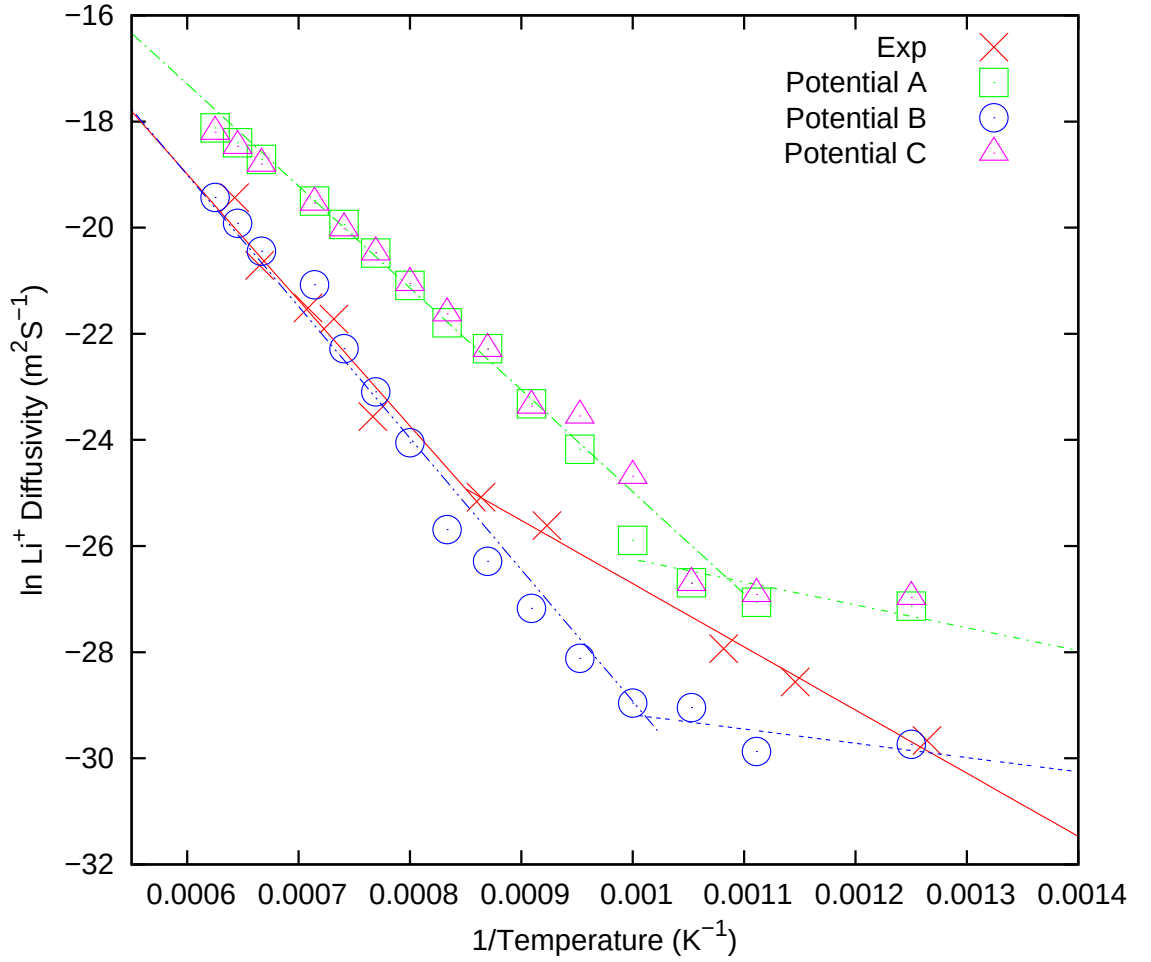


Figure 3.7: The natural logarithm of diffusivities of Li_2O obtained using potential sets A, B and C are plotted as a function of reciprocal temperature alongside experimental results [10]. The lines are provided as a guide to the eye.

The activation energies simulated using potential sets A, B and C can be compared with a number of experimental and theoretical activation energies. They are: 1.3 eV [89], 1.4 eV [81], 1.5 eV [90], 2.33 eV [92], 2.52 [10], 3.02 eV [93]. The activation energies display a significant variation due to different measuring methods, impurity, humidity and pair potentials used. As a result, the simulated results using different potential sets were mainly compared to the experimental activation energy measured by Oishi *et al.* [10] as shown in Table 3.5. This is because they obtained the activation energy via diffusivity and Arrhenius equation, in an analogous manner to the MD simulation method used here. In addition, Oishi *et al.* provide a complete diffusivity data set as a function of temperature for

comparison [10]. The activation energy for potential set B was found to be closest to the Oishi *et al.* value.

Table 3.5: The comparison of an Li^+ ion activation energy using potentials *A*, *B* and *C* and experimental result.

	Literature	Potential A	Potential B	Potential C
E_a (eV)	2.52 [10]	1.50	2.54	1.56

Li^+ diffusion mechanism

Given that potential B gave the best match to the experimental diffusivities and intrinsic activation energy, this potential was used to investigate the Li^+ ion diffusion mechanisms. In order to identify lithium diffusion pathways, a long scale MD simulation under NVT conditions with a small time step and many trajectories are required. The long scale simulation can ensure that the MSD is larger than the possible diffusion distance, that is the Li^+ ion site to cubo-octahedral interstitial site (1.95 Å) and the distance between two nearest Li ion sites (2.40 Å). Employing a small time step and recording atom positions frequently ensures that details of the diffusion pathway were observable.

The $10 \times 10 \times 10$ Li_2O supercell containing 12,000 atoms was first equilibrated under NPT dynamics for 10 ps. The MD production simulation was performed under NVT conditions for 500 ps. As the Li^+ MSD was constantly less than the possible diffusion distance below the superionic transition temperature, the Li^+ diffusion mechanism was only investigated above the superionic transition temperature.

Above the superionic transition temperature, Li^+ ion diffusion was observed, and the diffusion pathways are illustrated in Fig. 3.8a-3.8d. Two different types of diffusion mechanism were observed, in agreement with Hayoun’s observation [96]:

1. The Li^+ ions diffuse along $\langle 111 \rangle$ directions, creating an cubo-octahedral

interstitial at (0.5 0.5 0.5) and leaving its initial site vacant before moving onto another available vacancy. If the Li^+ ion falls back recombining with its vacancy, diffusion does not occur. Diffusion occurs only if a Li^+ ion enters a different vacant site, such as (0.75 0.75 0.25), (0.25 0.75 0.75) or (0.75 0.75 0.75), shown in Fig. 3.8a-3.8c. At high temperatures, the cell is distorted and distances between the interstitial site and the three possible vacancy sites are no longer equal, then a Li^+ ion will move towards the closest vacancy of the three sites.

2. The Li^+ diffuses along a $\langle 001 \rangle$ direction and enters an empty nearest neighbour Li^+ site. At high temperature, this distance can actually be longer than that shown in Fig. 3.8d due to the distortion of the structure, which could make the diffusion via the cubo-octahedral interstitial site favourable.

Li^+ ions, in principle, diffuse to the nearest available vacancy. However, due to the distortion of the lattice at high temperature, it may not diffuse to the nearest vacant site according to the α Li_2O structure in the energy minimized state.

After the 500 ps NVT simulation at 1400 K, a further simulation was performed using NVT conditions for 10 ps. A timestep of 1 fs was employed and the trajectory was recorded at each step. These trajectories were mapped back into a single unit cell. Li^+ density contour plots in plane (1 0 1) and (0 0 4) planes illustrate the diffusion process; see Fig. 3.10-3.9. In Fig. 3.9, the Li^+ density is high (red) at the cubo-octahedral site, suggesting the presence of a stable interstitial site. This agrees with the previous MD trajectory observation that Li^+ stayed at the octahedral site before it diffuses to other possible vacancies. By comparison the Li^+ density between two adjacent sites is low (white color), suggesting that there are no intermediate interstitial sites between two adjacent lithium sites, in disagreement with Farley *et al.* [85] who suggested Li^+ occupies a middle point between two adjacent lithium sites. Li^+ diffuses directly to the adjacent vacancy, see Fig. 3.10.

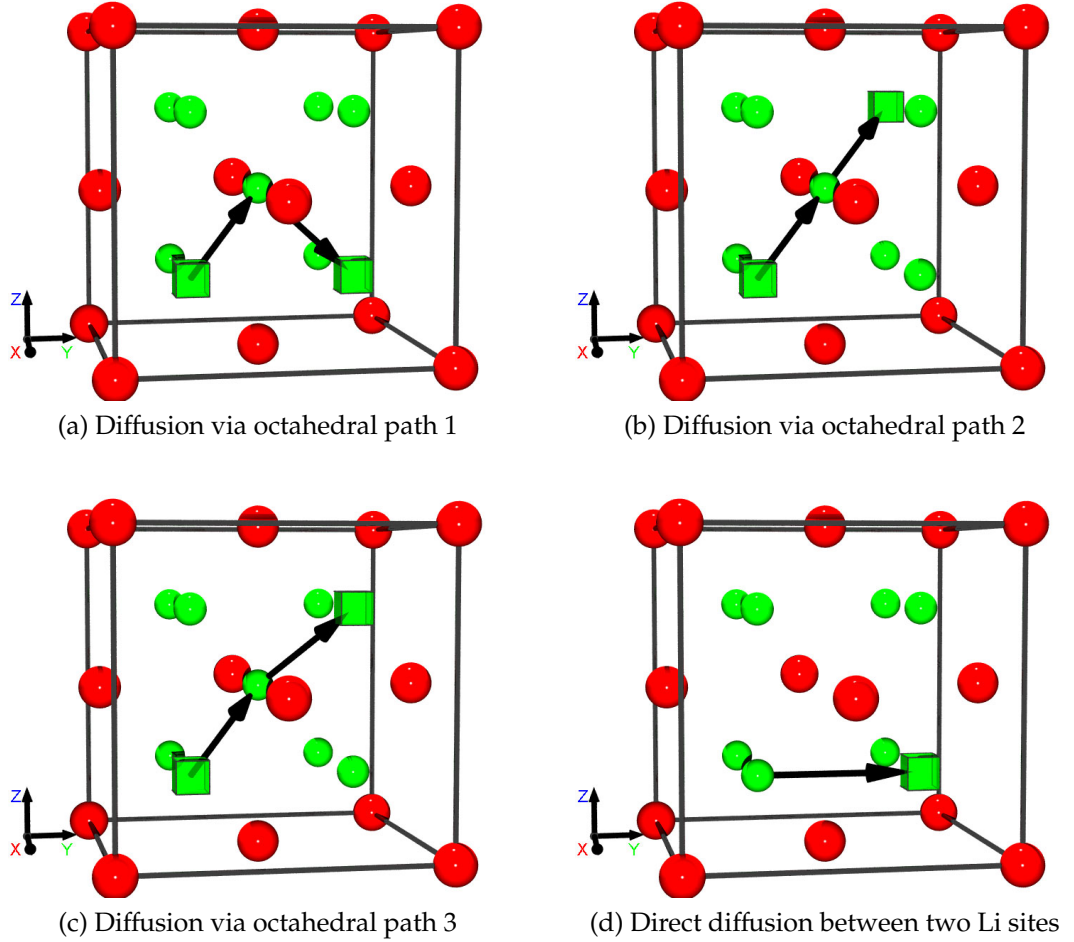


Figure 3.8: The diffusion mechanisms were observed at 1400 K. The red and green spheres represent oxygen and lithium respectively. The green cubes represent lithium vacancy. Diffusion via the cubo-octahedral site are: (a) Li ion diffuses via the cubo-octahedral site (0.5 0.5 0.5) and enters (0.75 0.75 0.25). (b) Li ion diffuses via octahedral site (0.5 0.5 0.5) and enters (0.25 0.75 0.75). (c) Li ion diffuses via octahedral site (0.5 0.5 0.5) and enters (0.75 0.75 0.75). (d) Direct diffusion sees an Li^+ ion moving directly onto a neighbouring site.

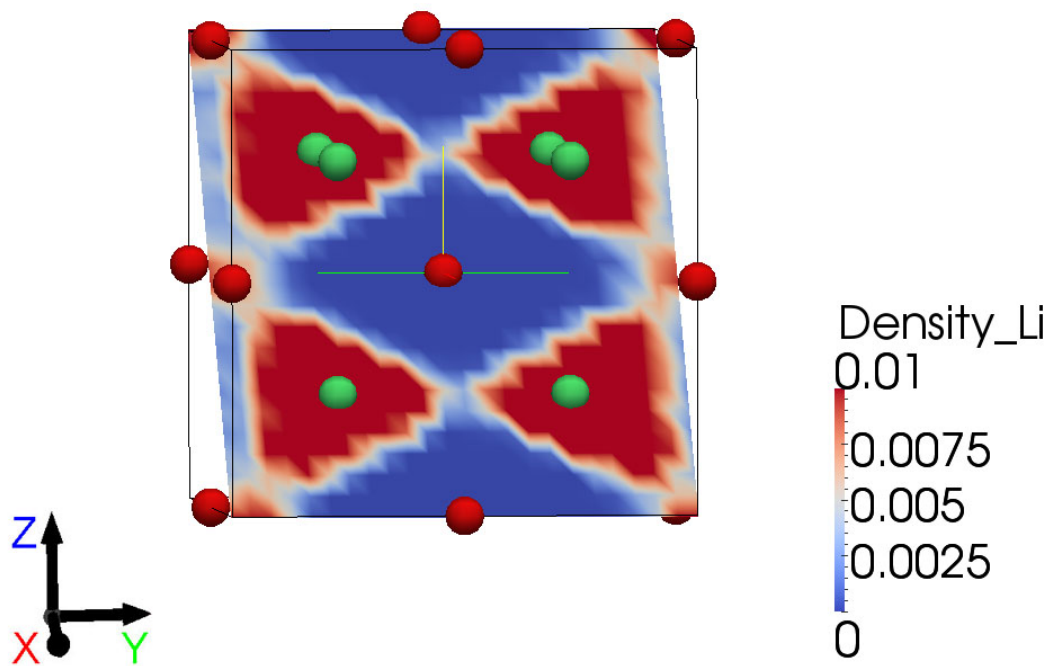


Figure 3.9: The Li^+ contour plot of Li_2O for the plane (1 0 1) at 1400 K viewed along the x direction. The structure is shown half a unit cell displaced with respect to the structure shown in Fig. 3.1. The red and green spheres represent oxygen and lithium ions respectively. The density unit is $\text{ion}/\text{\AA}^3$.

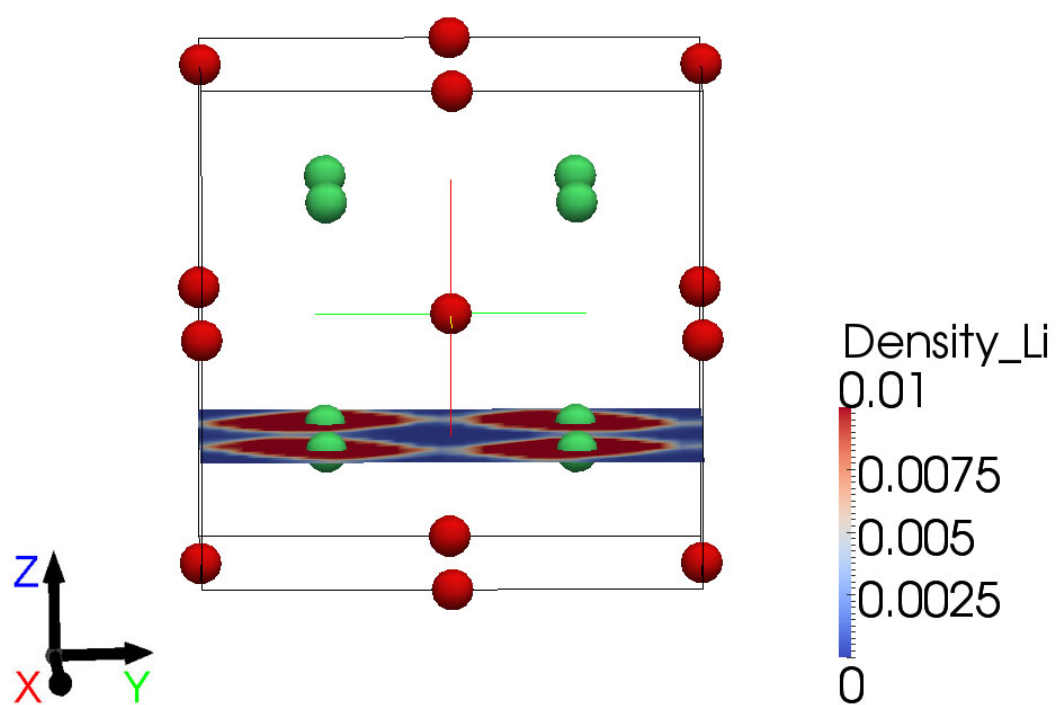


Figure 3.10: The Li^+ contour plot of Li_2O the $(0\ 0\ 4)$ plane at 1400 K viewed along the x direction. The structure is shown half a unit cell displaced with respect to the structure shown in Fig. 3.1. The red and green spheres represent oxygen and lithium ions respectively. The density unit is $\text{ion}/\text{\AA}^3$.

3.5.5 Defects and defect disorder process

Within the framework of lattice statics, defect energies can be calculated using the Mott-Littleton approximation. In the Mott-Littleton approximation, the lattice is divided into spherical regions of increasing radius, as described in the Sec. 2.3.2. The size of the spheres is an important consideration in determining the defect energy, therefore, it is essential to ensure the energy is converged with respect to the region I and region IIa radii. A large region IIa size, 30 Å, was chosen. The region I size was then increased to obtain the converged defect energy. For example, the defect energy of a Li vacancy converged for region I size greater than 12 Å (region IIa size of 30 Å), is accurate to 0.01 eV, see Fig. 3.11. The remaining defect simulations employed these the same region sizes.

Table 3.6 shows the defect energies for the simple intrinsic defects in Li₂O. Also included in the table are the defect energies of the defect clusters. The clustered defects, $\{V'_{\text{Li}} : V^{\bullet\bullet}_{\text{O}} : V'_{\text{Li}}\}^{\times}$ and $\{\text{Li}^{\bullet}_i : \text{O}''_i : \text{Li}^{\bullet}_i\}^{\times}$ have three different configurations. Each oxygen ion is surrounded by a cube with a Li ion at each vertex. The different configurations of $\{V'_{\text{Li}} : V^{\bullet\bullet}_{\text{O}} : V'_{\text{Li}}\}^{\times}$ are illustrated in Fig. 3.12 by focusing on the cube surrounding a simple O²⁻ ion. For the two lithium and one oxygen interstitial sites, the structure is presented as a standard unit cell; see Fig. 3.13.

In Table 3.6, the processes of adding an extra ion or clusters of ions are more energetically favourable than the processes of removing an ion or a cluster. This is because the structure is not closed packed, exhibiting a readily available cubo-octahedral interstitial site in the structure. However, it is the complete defect reactions, reported below that are important when discussing thermodynamic processes.

Considering the tri-vacancy sites, the most energy favourable process is that which involves the two V'_{Li} defects with the largest separation between them. The least energy favourable process has the vacancies adjacent to each other. Because the

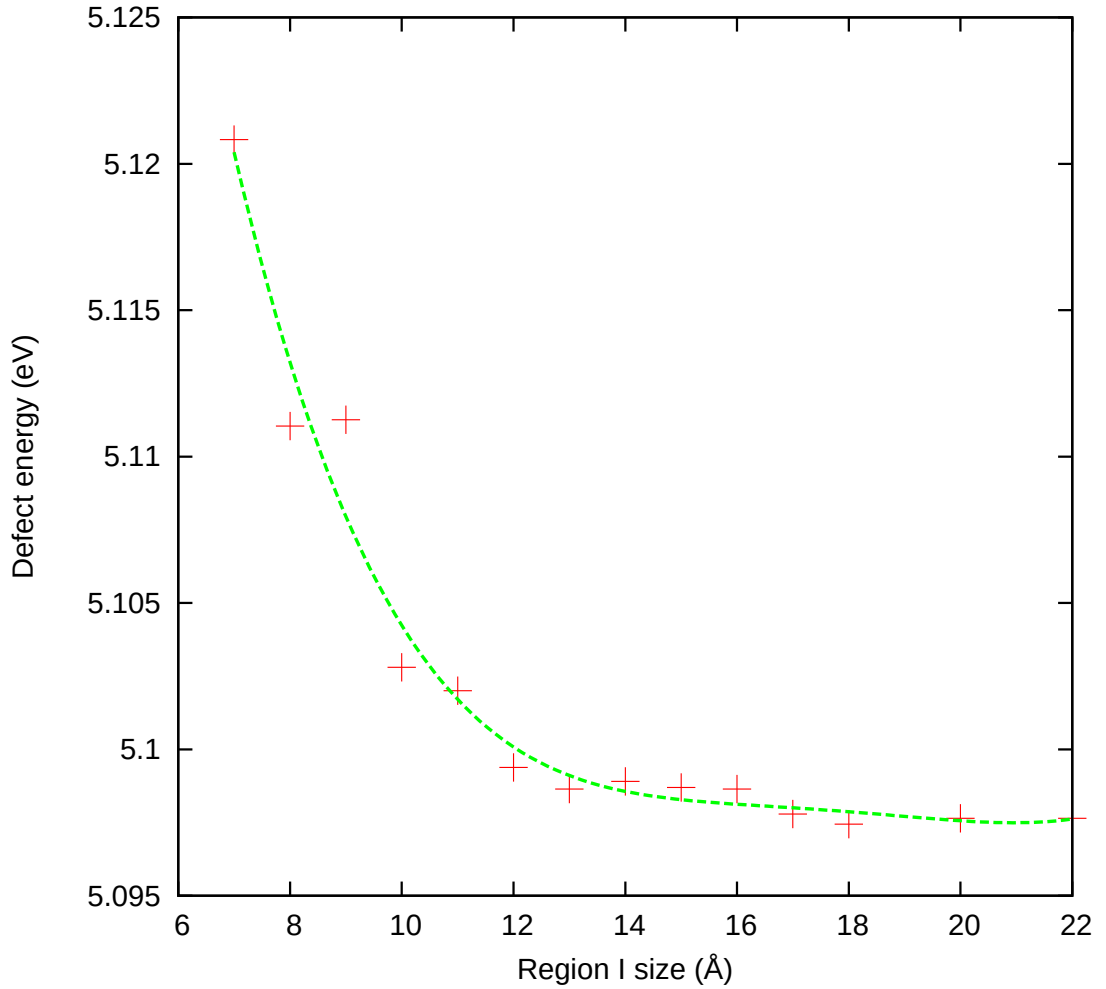


Figure 3.11: Defect energy of a Li vacancy as a function of region I size. The line is a guide to the eyes.

simulation is a static energy minimization, kinetic energy need not be considered. The distance between V'_{Li} defects and the $V_{\text{O}}^{\bullet\bullet}$ defect are same in all three different configuration, therefore the potential energy between V'_{Li} defects and $V_{\text{O}}^{\bullet\bullet}$ are also the same. The only difference is the potential energy between two V'_{Li} defects, which can be written $V(r) = \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$ where ϵ_0 is the permittivity of free space; r_{ij} is the distance between two V'_{Li} defects and e is electron charge. According to this equation, the potential energy is inversely proportional to the separation between two charged defects. The larger the separation, the smaller the energy required to create such defects configuration, hence more energetically favourable. The same reason applied for triple interstitial structure.

The equations for Frenkel, Schottky and anti-site disorder are given in Eq.3.23-3.31.

The clustered defects are also considered in these disorders process. The reaction energies calculated from the equations are compared with available experimental and theoretical results listed in Table 3.7. The calculated Frenkel, Schottky and anti-site disorder energies are generally in good agreement with literature values. Of all the types of disorders considered, antisite disorder is the highest energy process and the Li Frenkel disorder process is the most energetically favourable. This is not surprising given that the Li sublattice becomes superionic.

If the products are clustered, the reaction energies for all the equations are lowered. This means that clustered defects are more energetically favourable and more likely to occur in these disorders at thermal equilibrium, providing the defect concentrations are high enough to overcome configurational entropy (that favours isolated defects). Only Li Frenkel disorder was observed in the previous MD trajectories, suggesting that the Lithium Frenkel process is kinetically favourable as well. The Li^+ ion leaves its lattice site and enters the nearest cubo-octahedral interstitial site, creating the metastable clustered defect $\{\text{Li}_i^\bullet : V_{\text{Li}}'\}^\times$.

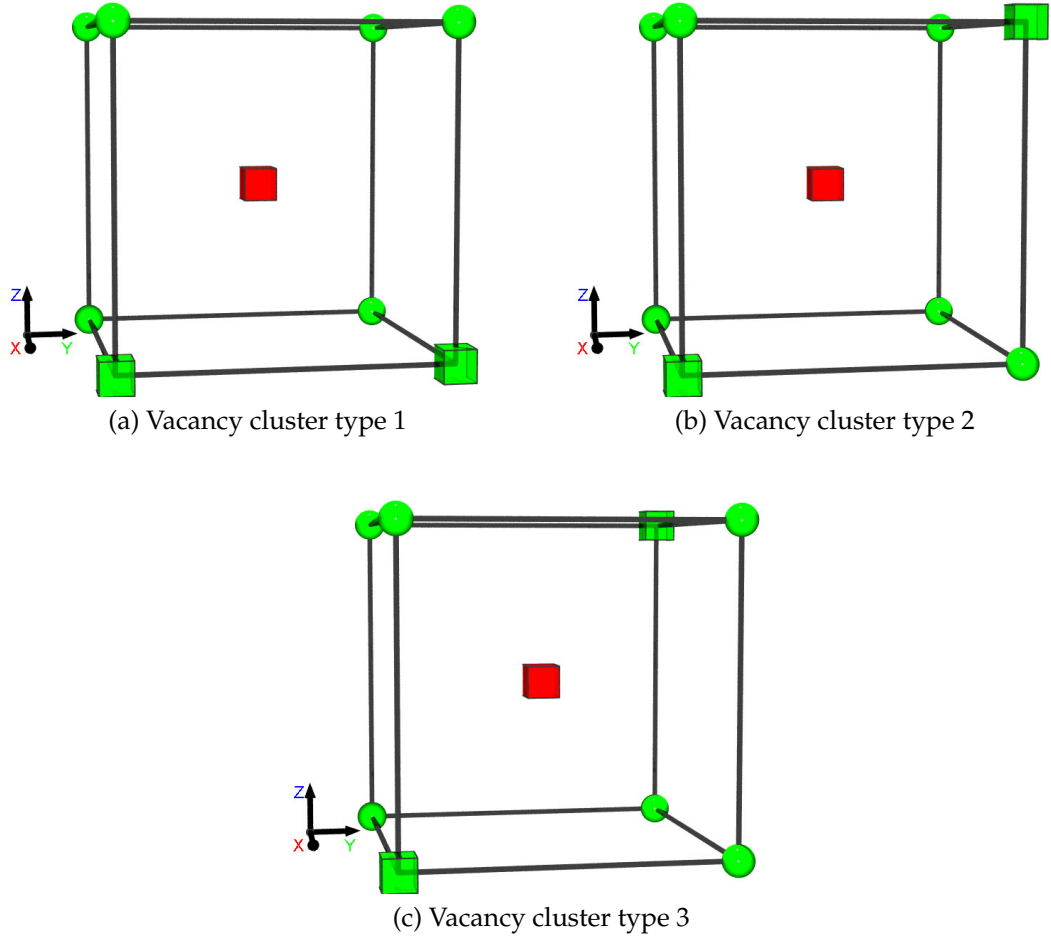


Figure 3.12: $\{V'_{\text{Li}} : V_{\text{O}}^{\bullet\bullet} : V'_{\text{Li}}\}^{\times}$ defect cluster configurations. The green spheres and cubes are Li ions and Li vacancies while red cube is the oxygen vacancy. The structure is obtained via shifting half a unit cell with respect to the structure shown in Fig. 3.1 and only part of the structure is shown (i.e. a Li cubic with an oxygen in the centre).

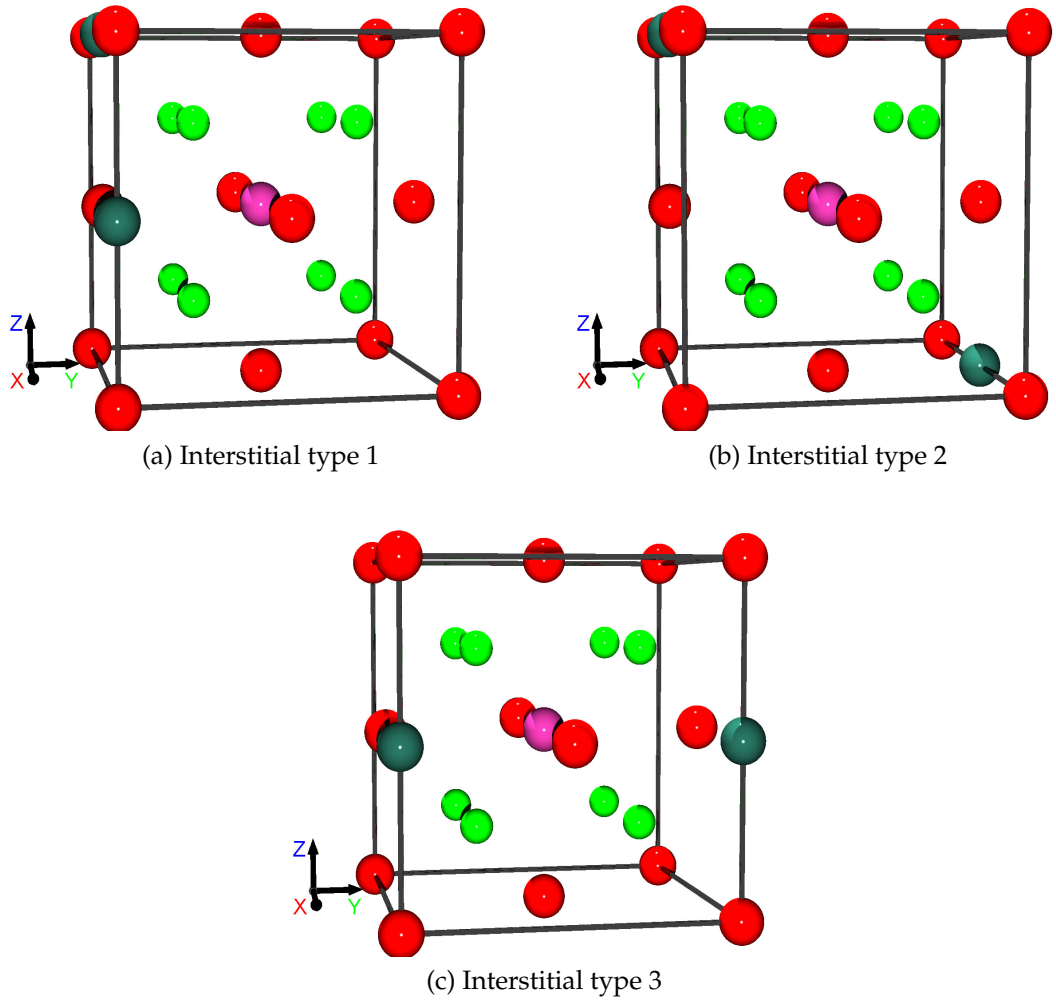


Figure 3.13: $\{\text{Li}_i^\bullet : \text{O}_i'' : \text{Li}_i^\bullet\}^\times$ cluster configurations. The red and green spheres are oxygen and lithium ions. The violet red and dark green spheres are the interstitial oxygen and lithium ions.

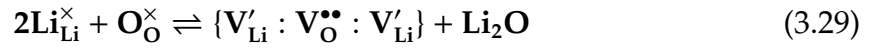
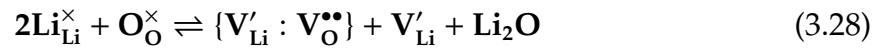
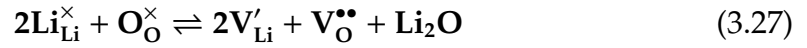
Table 3.6: Dilute limit isolated defect and clustered defect energies (enthalpy of formation of isolate and clustered defect) in Li_2O . Simulations were carried out using the Mott-Littleton method via potential B.

Defect	Potential set B (eV)
V'_{Li}	5.10
$V_{\text{O}}^{\bullet\bullet}$	26.98
$\text{Li}_i^{\bullet}$	-2.25
O_i''	-16.96
O_{Li}'''	-9.29
$\text{Li}_{\text{O}}^{\bullet\bullet\bullet}$	28.86
$\{\text{Li}_i^{\bullet} : \text{O}_i''\}$	-20.80
$\{V'_{\text{Li}} : V_{\text{O}}^{\bullet\bullet}\}$	30.36
$\{\text{Li}_i^{\bullet} : V'_{\text{Li}}\}$	2.02
$\{\text{O}_i^{\bullet\bullet} : V_{\text{O}}''\}$	5.70
$\{\text{Li}_{\text{O}}^{\bullet\bullet\bullet} : \text{O}_{\text{Li}}'''\}$	10.92
$\{V'_{\text{Li}} : V_{\text{O}}^{\bullet\bullet} : V'_{\text{Li}}\}$ type 1	34.61
$\{V'_{\text{Li}} : V_{\text{O}}^{\bullet\bullet} : V'_{\text{Li}}\}$ type 2	34.19
$\{V'_{\text{Li}} : V_{\text{O}}^{\bullet\bullet} : V'_{\text{Li}}\}$ type 3	34.09
$\{\text{Li}_i^{\bullet} : \text{O}_i'' : \text{Li}_i^{\bullet}\}$ type 1	-23.76
$\{\text{Li}_i^{\bullet} : \text{O}_i'' : \text{Li}_i^{\bullet}\}$ type 2	-23.94
$\{\text{Li}_i^{\bullet} : \text{O}_i'' : \text{Li}_i^{\bullet}\}$ type 3	-23.89

Frenkel reactions,



Schottky reactions



Anti-site reactions



Table 3.7: The reaction energies for defect disorder processes using potential B with available experimental and previous simulation results for Li_2O .

Reaction	Potential set B (eV)	Exp(eV)	Simulated (eV)
Li Frenkel	2.85	2.1[85], 2.53[93]	2.12[93], 2.55[100], 2.2[101]
Li Frenkel clustered	2.02		
O Frenkel	10.02	8.31[100]	
O Frenkel clustered	5.70		
Schottky	5.90		5.15[92], 5.8[100]
Schottky two vacancies clustered	4.17		
Schottky three vacancies clustered	2.80		
Antisite	19.58		

3.6 Conclusion

All three potential sets can reproduce the experimental lattice parameters and elastic constants C_{11} and C_{44} of Li_2O . All the potential sets overestimated the bulk modulus as a result of overestimating C_{12} due to the centrosymmetric nature of the pair potential. Potential set B best replicated the relationship between bulk modulus and temperature. The thermal expansion coefficients were predicted to be almost constant (linear thermal expansion) at low temperature using all potential models. At low temperature, potential set B gave the smallest deviation of lattice parameter while compared to experiment potentials A and C gave the better matching at high temperature.

Only Li^+ ions were observed to diffuse at high temperature within the observation time. The transition from a non-conducting material to conducting, occurred in the range 1100-1200 K and is referred to as a superionic transition. The activation energy, including the formation of Frenkel defects and migration energy, for potential B was 2.54 eV, which was closest to the experimental data. In addition, potential B best reproduced the diffusivity, therefore potential set B should be able to reproduce the best thermal conductivity. The lithium site can diffuse either via the cubo-octahedral interstitial site or directly to an adjacent lithium ion site. The lithium ion contour plot confirmed the interstitial at cubo-octahedral site and ruled out the possible interstitial sites between two adjacent lithium ion sites [85].

Considering the tri-interstitial and tri-vacancy defects, two lithium ion vacancies or interstitials with furthest separation was the most energetically favourable, and vice versa. According to the calculation, Frenkel disorder was the most energy favourable disorder process and anti-site was least energy favourable. Clustering of ions were more energy favourable than individual ions; that could explain the clustered $\{\text{Li}_i^\bullet : V_{\text{Li}}'\}$ defect observed in the MD trajectory.

Chapter 4

Isotope effect on thermal conductivity for Li_2O

4.1 Introduction

Nuclear fusion is prospectively one of the cleanest, greenest and safest future sources of energy. The most practical and promising fusion reaction is the deuterium-tritium (D-T) reaction. The supply of deuterium is virtually unlimited (abundant as it is found in sea water), and thus it can meet man's energy consumption needs for the next millennium. There are however many remaining scientific and engineering obstacles to solve prior to commercialization of the nuclear fusion. In this regard, Li_2O is a potential blanket breeding material for providing the tritium essential for the fusion process but has possible advantages and disadvantages in this application. This chapter will concentrate on the thermal conductivity of Li_2O , a key issue for any material in an energy application.

In several Helium Cooled Pebble Bed (HCPB) fusion power plant models, such as the European SEAFP model (Safety and Environmental Assessment of Fusion Power), or the American model ARIES-IV, Li_2O has been selected for tritium

production [102]. It has also been considered as the reference breeder material for the ceramic breeder blanket of Japanese fusion reactors [102].

When the Li_2O is irradiated with neutrons, the following two fission reactions Eq. 4.1 and Eq. 4.2 occur, where tritium is bred to sustain the deuterium-tritium fusion process Eq. 4.3.



For the ${}^6\text{Li}$ reaction, where the tritium can be generated by slow neutrons, Li_2O is a good candidate because it has low volatility, high melting temperature and a high density of lithium. The last factor suggests that Li_2O may achieve a tritium breeding ratio greater than unity without the need for ${}^6\text{Li}$ enrichment and Be neutron multipliers [17]. As a solid, its thermal expansion is similar to the structural material such as steel, leading to a higher degree of compatibility than liquid breeder blankets materials. The solid blanket is also safer than proposed liquid breeder blanket due to its low chemical reactivity with air or water in case of accidents[103].

The main disadvantage of a potential solid breeder is its low power density (power per unit volume) due to low thermal conductivity compared to liquid breeder blankets [103]. The low power density could potentially make a nuclear fusion power station economically unattractive.

For fusion applications, Li_2O has been considered in two forms: pellets (block) and pebble bed. Li_2O pellets could theoretically result in a higher thermal conductivity than pebble beds. However, Li_2O pellets are very sensitive to thermal stresses

and would prohibit the use of pellets for high power applications [103]. This is why Li₂O pebble beds have been considered.

The effective thermal conductivity of the pebble beds can be influenced by many parameters such as filling gas, gas pressure, bed deformation, bed packing fraction, pebble size and surface roughness, helium thermal conductivity and last but not the least, the thermal conductivity of Li₂O itself [104]. Therefore, the aim of this chapter is to investigate the thermal conductivity of Li₂O and in particular, to estimate the impact of isotopic effects and the possible implications for future fusion performance.

4.2 Previous studies

Measurement of thermal conductivity

The thermal conductivity of Li₂O has been previously measured experimentally. Takahashi *et al.* [105] investigated the porosity dependence on thermal conductivity in the temperature range of 573-1173 K. The reported data could be described by the relationship:

$$k = 1/(A + BT) \quad (4.4)$$

where T is absolute temperature. The parameters A and B were determined to be:

$$A = 2.2D^{-1.94} \quad (4.5)$$

$$B = 0.01784D^{-1.94} \quad (4.6)$$

where D is the ratio of the bulk density to the theoretical density. The relationship between theoretical thermal conductivity (K_T), porosity (P) and thermal conductivity with porosity (K_M) obeying the generalized Loeb equation [106] $K_M = K_T(1 - \gamma P)$, γ being 1.70 and obeyed the modified Maxwell-Eucken Equa-

tion [107, 108, 109] $K_M = K_T(1 - P)(1 + \beta P)$, where β is the pore correction factor ranging from 1.81 (at 473K) to 1.32 (at 1173 K).

Subsequently, Ethridge *et al.* [11] expanded the thermal conductivity data between 373-1173 K. Ethridge then adjusted both his data and that of Takahashi to 100% density using the Maxwell-Eucken equation $(1 - P)/(1 + \beta P)$ and made a comparison. Fig. 4.1 shows the thermal conductivity as a function of temperature adjusted to a density of 100%. In the range where data is available from both authors, there was a good agreement between the two datasets. There was only minimal indication of the errors associated with each dataset, see Fig.4.1 error bars, however, the data appeared to agree within the error from the two different experimental investigations.

As Li_2O will be subjected to neutron irradiation in fusion reactors, the influence of irradiation on thermal conductivity needs to be considered. A significant decrease in thermal conductivity was observed at low temperatures (e.g. 300 K) in irradiated Li_2O , resulting from radiation induced lattice damage [11]. At high temperature (> 700 K), the thermal conductivity was close to that of the unirradiated material because the influence of irradiation effects can be ignored compared to intrinsic behaviour i.e. Li ion superionic diffusion [11]. By consequence, the damage due to irradiation is not significant since the working temperature of the breeder material is typically higher than 700 K. As a result irradiation effects were not explicitly considered in the simulations presented in this chapter.

The thermal conductivity of Li_2O may be influenced by the random distribution of isotopes (^6Li and ^7Li) over lattice sites, producing a stronger scattering of phonons. The fluctuation in atomic mass across the crystal lattice gives rise to thermal resistance and was first considered theoretically by Pomeranchuk [110]. Experimentally the isotope scattering effect was first observed in germanium [111]. Assuming that Umklapp scattering dominates (the three phonon process caused thermal resistivity due to unconserved momentum) over the entire

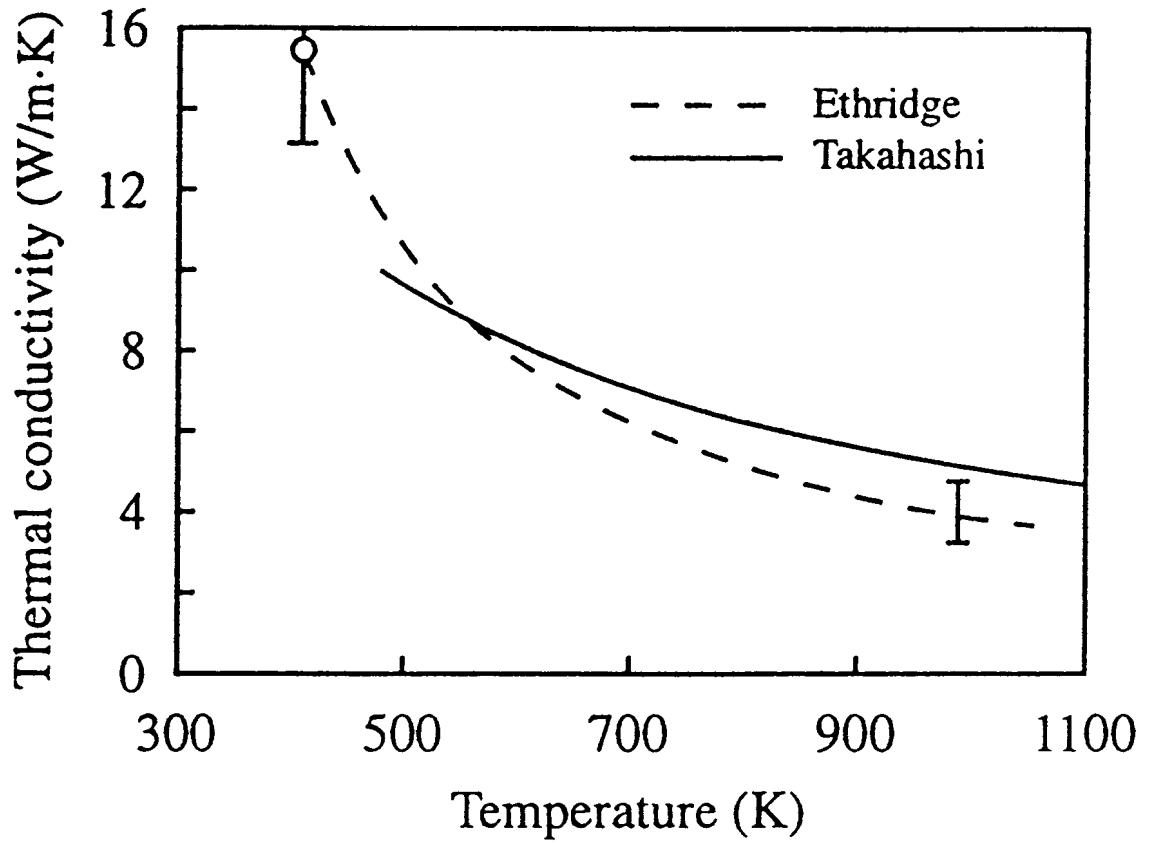


Figure 4.1: Comparison of thermal conductivity for unirradiated Li_2O at 100% theoretical density [11] due to Maxwell-Eucken equation. Ethridge calculated error bars in the data sets.

frequency range, Ambegaokar [112] showed in the Debye approximation, that thermal resistance W_{iso} due to isotope disorder g can be expressed as

$$W_{\text{iso}} = \frac{\pi g \Omega T_D}{6 v_D^2 \hbar} \quad (4.7)$$

where Ω is atom volume; T_D is Debye temperature and v_D is Debye velocity. For mass-fluctuation scattering, the scattering rate is proportional to the isotope disorder parameter, [113] :

$$g = \sum_i f_i (1 - M_i/M_{\text{av}})^2 \quad (4.8)$$

Where f_i is a concentration of the i -th isotope with mass M_i and $M_{\text{av}} = \sum_i f_i M_i$ is an average atomic mass.

Significantly for the present study, there has been no experimental or computer simulation based investigation of the isotope effect on thermal conductivity for Li_2O .

4.3 Results and discussion

4.3.1 Comparison of experimental and simulated thermal conductivity

The thermal conductivity of Li_2O was calculated using the velocity exchange method, as described in Sec 2.5. The positions and velocities sampled from the canonical (NVT) and isothermo-isobaric(NPT) ensembles are generated.

The thermal conductivities for different supercell sizes were calculated. The supercell size systems were: $5 \times 5 \times 30$ (9000 atoms), $5 \times 5 \times 40$ (12000 atoms), $5 \times 5 \times 60$ (18000 atoms) and $5 \times 5 \times 75$ (22500 atoms). Each system was equilibrated

under NPT condition for 5 ps and then under NVT conditions for a further 4 ps at a series of temperatures. Then, the highest velocity Li atom in the cold slab and lowest velocity Li atom in the hot slab had their velocity exchanged every 10 fs. A similar process was performed on the oxygen ions. The heat flux J was calculated in terms of the difference of kinetic energy of the atom pairs in the hot and cold slabs using Eq. 2.25. The atoms outside the slabs moved according to Newton's second law of motion. Over a period of 100 ps, during which atom velocities in the hot and the cold slabs were exchanged, a temperature profile along the z axis was induced. The profile was obtained from many different individual layer temperatures, using Eq. 2.26. In Eq. 2.26, the kinetic energies of atoms in the layer were time and space averaged (50 ps and $5a \times 5a \times 1 \text{ \AA}^3$ respectively). The temperature profiles of different average temperatures for a $5 \times 5 \times 60$ system are shown in Fig. 4.2. For all the averaged temperatures, linear temperature profiles were obtained. This represents a better approach than the direct method, where a non linear temperature profile is found near the hot source[63]. The thermal conductivity was then calculated via Eq. 2.28, using the calculated heat flux (in terms of kinetic energy) and temperature profiles.

In a previous simulation study, considering the thermal conductivity of UO_2 , Watanabe *et al.* applied a correction to their data for phonon-boundary (finite size) and phonon-phonon scattering effects [114]. These were found to help improve their results especially below 750 K. In order to obtain similar improvements, these corrections are now explored here. The phonon-boundary effect was introduced in in Sec 2.6.1.

The thermal conductivity of Li_2O using potential B was calculated for different cell sizes: $5 \times 5 \times 30$, $5 \times 5 \times 40$, $5 \times 5 \times 60$ and $5 \times 5 \times 75$ supercell. The results were plotted as $1/k$ vs $1/L_z$ in Fig. 4.3.

Recall Eq. 2.29:

$$\frac{1}{k} \propto \frac{1}{L_z}$$

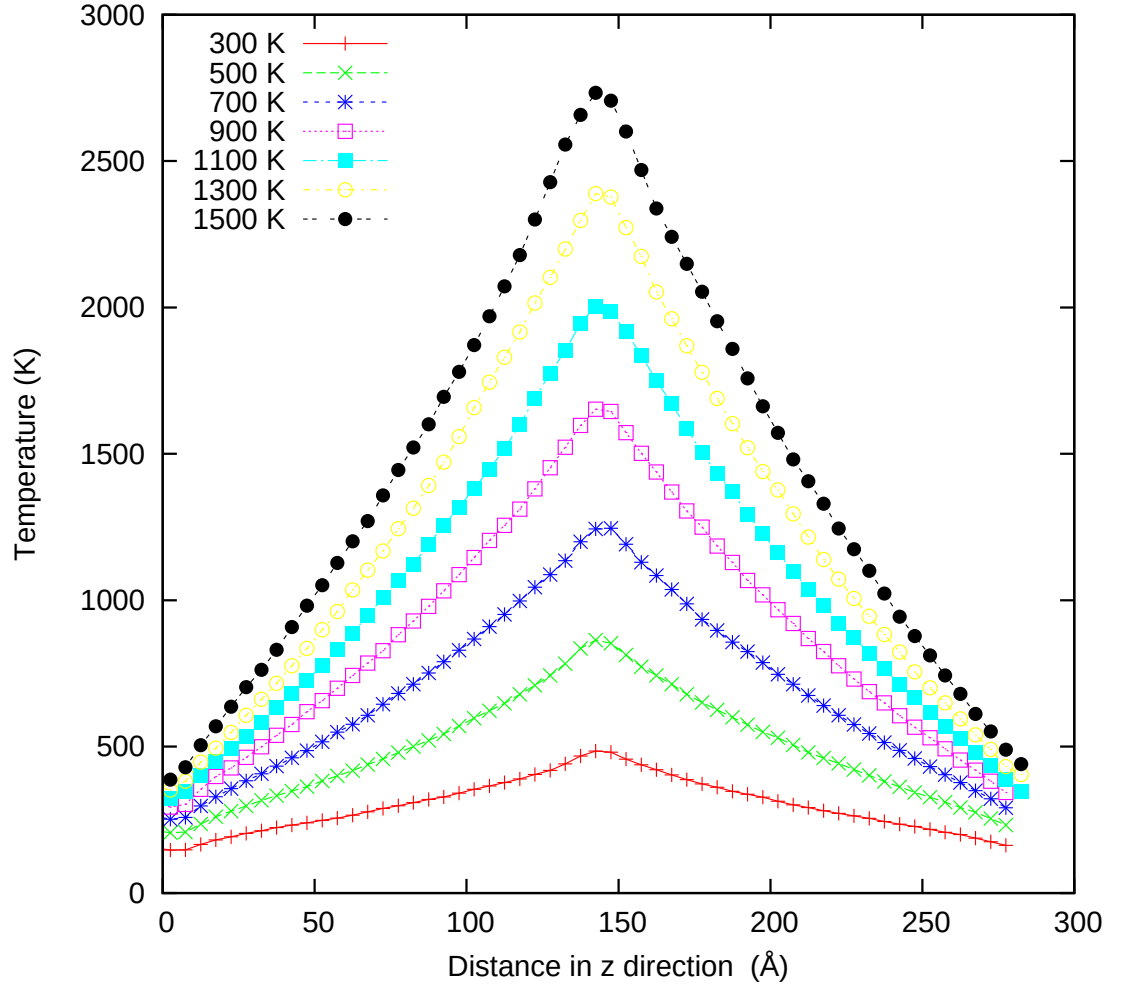


Figure 4.2: Temperature profile for a $5 \times 5 \times 60$ system at different average temperatures, using potential B. The highest temperature region is the hot slab and lowest temperature region is the cold slab.

To correct for the finite size of the simulated systems, the infinite thermal conductivity k_∞ was obtained by extrapolation to $1/L_z = 0$ in Fig. 4.3 (i.e. the y-axis intercept). The infinite size bulk thermal conductivity can be used as a good approximation for comparison with the thermal conductivity of the experimental specimen.

Watanabe [114] *et al.* analysed anharmonicity of the crystal lattice arising due to phonon-phonon interactions in experimental and simulated systems. The details of which were introduced in 2.6.2. Their results allow the effects of phonon-phonon interaction to be identified.

Recall the equation Eq. 2.32,

$$k = \chi \frac{1}{B\alpha^2} \frac{C_v T_D^3}{T}$$

Here it is assumed that experimental and simulated systems had the same Debye temperature T_D . The heat capacity C_v remains almost constant at sufficient high temperature (above 600K) [115]. These two constants will be cancelled out by k_B/k_{exp} .

In Sec 3.5.3 and Sec 3.5.2, the expression for bulk modulus B and linear thermal expansion coefficients α as predicted by potential B were calculated,

$$B_{\text{Exp}} = -0.026T + 88.23 \quad (4.9)$$

$$B_B = -0.040T + 150.63 \quad (4.10)$$

$$\alpha_{\text{Exp}} = 2.78 \times 10^{-5} + 1.78 \times 10^{-11}(T - 293)^2 \quad (4.11)$$

$$\alpha_B = 1.83 \times 10^{-5} + 1.15 \times 10^{-11}(T - 293)^2 \quad (4.12)$$

For a cubic system, the thermal expansion coefficient is three times the linear thermal expansion coefficient, $\alpha \sim 3\alpha_{\text{linear}}$. Therefore substituting bulk modulus

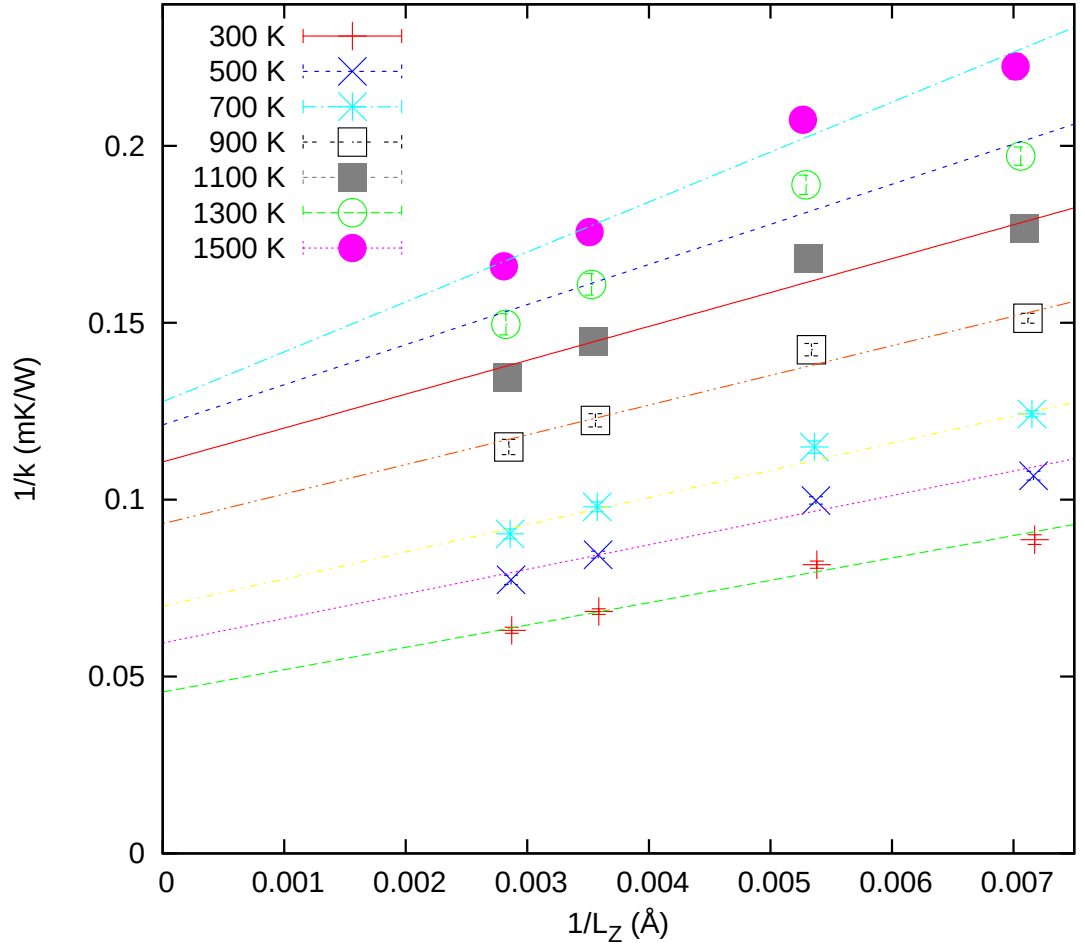


Figure 4.3: Size dependence of thermal conductivity for potential B.

and linear thermal expansion coefficients into Eq. 2.32 gives:

$$k_{\text{exp}} = \chi \frac{1}{9(-0.0263T + 88.23)[2.78 \times 10^{-5} + 1.78 \times 10^{-11}(T - 293)^2]^2} \frac{C_v T_D^3}{T} \quad (4.13)$$

$$k_B = \chi \frac{1}{9(-0.0398T + 150.34)[1.83 \times 10^{-5} + 1.15 \times 10^{-11}(T - 293)^2]^2} \frac{C_v T_D^3}{T} \quad (4.14)$$

where χ , C_v and T_D were regarded as constant and at each different temperature, the anharmonic correction was made by k_B/k_{exp} . Watanabe *et al.* did not consider the temperature dependence for static bulk modulus and thermal expansion in the correction, while in the present calculation, these properties were expressed as a function of temperature. This should yield better results since these properties are temperature dependent.

The experimental[11], largest cell size ($5 \times 5 \times 75$), infinite size, infinite size with anharmonic correction to thermal conductivity all as a function of temperature, are plotted in Fig. 4.4. The experimental data from Ethridge *et al.* was chosen for comparison because it has a wider temperature range.

All the simulated thermal conductivities reproduced a similar trend to the experimental results: it showed a steeper slope at low temperature which decreases with increasing temperature. The simulated thermal conductivity was expected to be higher than the experimental thermal conductivity because the possible non-stoichiometry and microstructure defects in the experimental sample act as phonon scattering centres. In addition, the full charge model used in the simulations can also overestimate the strength of bonding, resulting in a higher thermal conductivity.

The largest cell thermal conductivities were higher than the experimental data at high temperature, as expected, whilst at low temperature the simulated thermal conductivity appeared to be lower than experiment. However, due to the large error quoted for the experimental data, it is difficult to judge if this difference is particularly significant. It does not, by any means reduce the relevance of the

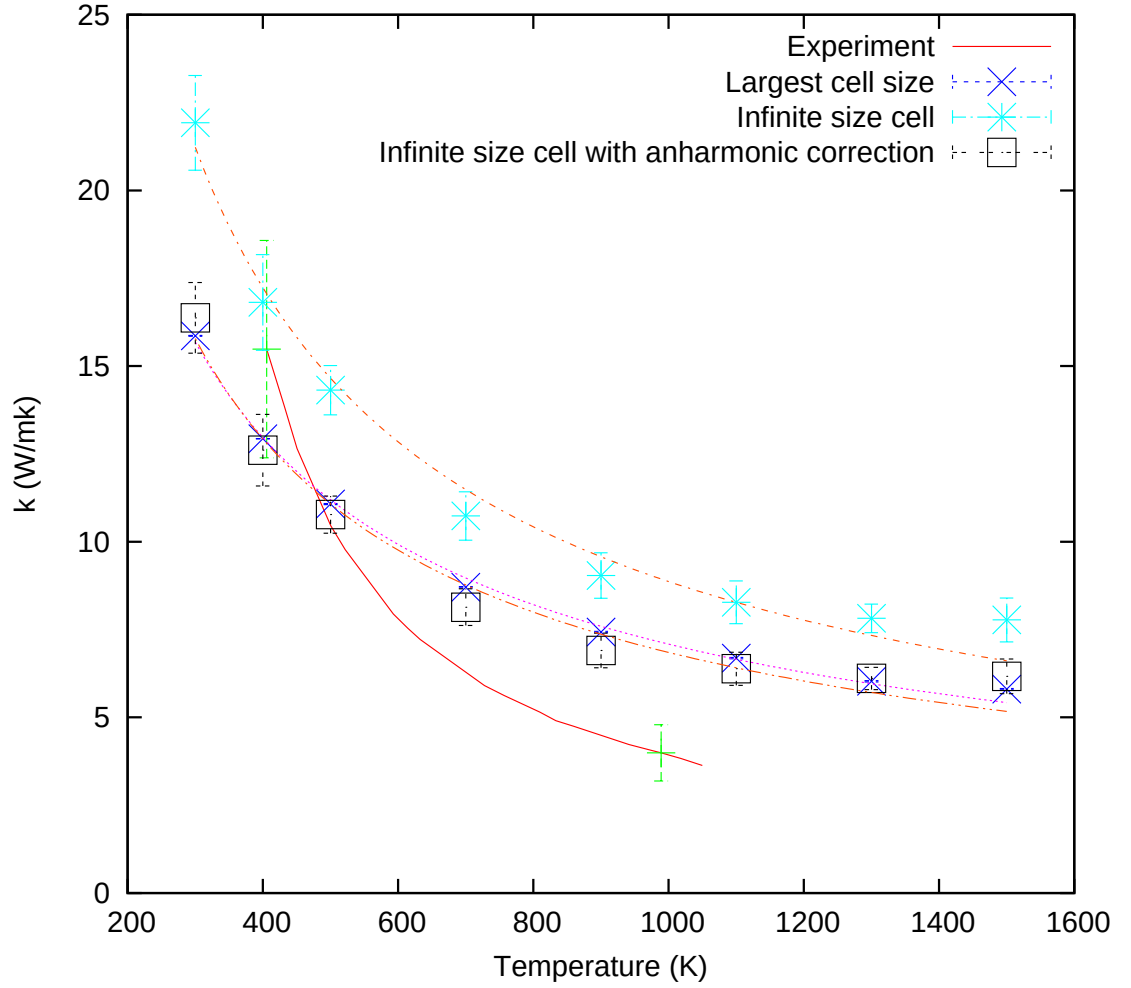


Figure 4.4: Comparison of experimental, largest cell size ($5 \times 5 \times 75$), infinite size and infinite size with anharmonic correction thermal conductivities generated using potential B. The lines were fitted to $k \propto T^n$.

predictions presented here.

The infinite size thermal conductivity systematically overestimated the experimental thermal conductivity. This was because the experimental specimen was not a single crystal but a sintered polycrystalline material, which exhibited a lower thermal conductivity due to scattering at grain boundaries.

If the potentials had failed to reasonably reproduce the lattice anharmonicity, the deviation of simulated thermal conductivity from experimental data could be very large, as occurred in the UO_2 simulations [114]. Unless the potentials were specifically derived to represent anharmonicity (bulk modulus and thermal expansion), a deviation in thermal conductivity is inevitable. The anharmonic effect may have a large influence on thermal conductivity and affect the accuracy of the present simulated model. Applying an anharmonic correction, the simulated thermal conductivity did show a better match to the experimental thermal conductivity (see Fig. 4.4). However, the improvement was not significant as the general trend had not been altered and the absolute difference in thermal conductivity at the same temperature was not very large.

Due to the lack of high quality experimental thermal conductivity data and the simplified simulation system used (i.e. single crystal rather than polycrystalline and lacking in defects), the simulated thermal thermal conductivity was unlikely to perfectly fit the experimental results. Including both finite size and anharmonic effect corrections can improve the matching of experimental results to some degree. However, the corrections haven't changed the general trend of the simulated thermal conductivity as shown in Fig. 4.4, the thermal conductivity decreased fast at low temperature, slowed down at medium temperature and converged at high temperature. Therefore, for the following isotope calculations, the largest cell size $5 \times 5 \times 75$ thermal conductivity was used to analyse the underlying mechanisms, without application of these corrections.

4.3.2 Isotope effect on thermal conductivity

Natural Li consists of two stable isotopes, 7.5% ^6Li and 92.5% ^7Li [116]. ^6Li and ^7Li both can be used to breed tritium in fission reactions. During operation it is likely that the $^6\text{Li} : ^7\text{Li}$ ratio would change due to the difference in the ^6Li and ^7Li neutron capture cross section (^6Li is easier to transmute) and this will result a change in thermal conductivity. The thermal conductivity of the breeder material in a reactor is an important design consideration, therefore understanding how it varies with isotopic ratio and temperature is of potential technological significance. To this end, molecular dynamics simulations were used to investigate these effects.

Two sets of simulations were performed: in the first, termed the discrete mass system, Li isotopes with discrete masses of 6 and 7 were distributed randomly across the Li sub-lattice in the correct proportion to obtain the desired average mass. In the second, termed as the average mass system, all Li ions were assigned an average Li mass appropriate for the isotopic ratio. For example, for $^6\text{Li} : ^7\text{Li}=1 : 9$, the mass was 6.1. This was performed to highlight the need to consider thermal conductivity at the atomic level to fully understand isotopic effects. The thermal conductivity of these $5 \times 5 \times 75$ supercells were then calculated four times and the standard deviations are plotted in Fig. 4.5 at 300 K, 600 K, 900 K, 1200 K and 1500 K.

Fig. 4.5a shows a thermal conductivity comparison of the average mass system and discrete mass system at 300 K. The thermal conductivity of the average mass system decreased linearly with increasing average atomic weight. The pure structure of ^6Li had the highest thermal conductivity. While the thermal conductivity of the discrete mass system showed a curve where the small thermal conductivities were found when ^6Li and ^7Li isotopes had the same or close proportion and the large thermal conductivities were found for pure ^6Li and ^7Li lattice structures. The same trends were observed at 600 K and 900 K in Fig. 4.5b and Fig. 4.5c but at a lower thermal conductivities. In 4.5d and Fig. 4.5e, the quadratic curve of the

discrete mass system disappeared and its thermal conductivities became close to that of the average mass system.

The quadratic curve relationship between thermal conductivity of the discrete mass system and atomic weight has been explained by Ambegaokar [112] in terms of isotope disorder parameter. Recall the expression of isotope disorder parameter Eq. 4.8. From the equation, the isotope disorder parameter can be calculated and is plotted as a function of average atomic weight (bottom axis) and isotope ratio (top axis) in Fig. 4.6. This suggested there is a quadratic relationship between isotope disorder parameter and ^7Li - ^6Li isotope ratio (also average atomic weight). As the isotopes were randomly distributed, the isotope disorder parameter was highest (most disordered) at a ^7Li : ^6Li ratio of 1 : 1 and lowest for pure ^7Li or ^6Li structures.

The thermal resistance (reciprocal of thermal conductivity) and isotope disorder parameter can be related. Recall the expression for thermal resistance Eq. 4.7. At a given temperature, the thermal conductivity ($1/W_{\text{iso}}$) is inversely proportional to the isotope disorder parameter (g), hence:

$$\sigma = \frac{1}{w_{\text{iso}}} \propto \frac{1}{g} \quad (4.15)$$

where g has quadratic relationship with ^7Li - ^6Li isotope ratio. The thermal conductivity of the discrete mass can broadly reproduce this quadratic relationship at low temperature as illustrated in Fig. 4.5a-4.5c.

For the purposes of understanding thermal conductivity, the crystal lattice can be considered as a system of harmonic oscillators joined by springs. When heat is added, the oscillators vibrate and energy can be transmitted through the crystal lattice in the form of waves. If an infinite periodic system is defect free and oscillating system are perfect harmonic oscillators, consequently the system has a single vibrational mode (phonon mode), with no wave destruction, and the ther-

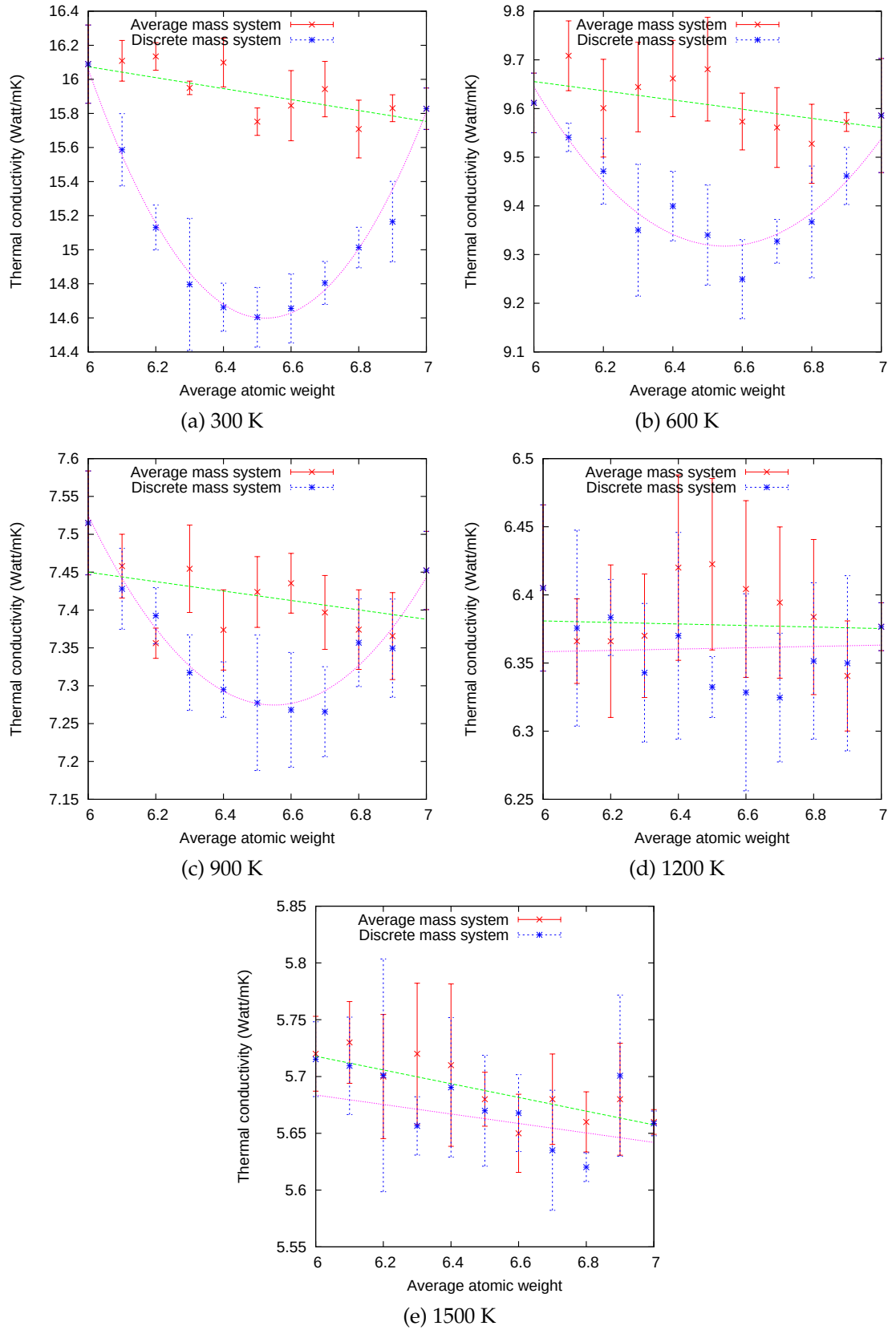


Figure 4.5: Comparison of the thermal conductivity of the average mass system and discrete mass system of randomly distributed ^6Li , ^7Li isotopes at 300 K, 600 K, 900 K, 1200 K and 1500 K using the $5 \times 5 \times 75$ unit cell.

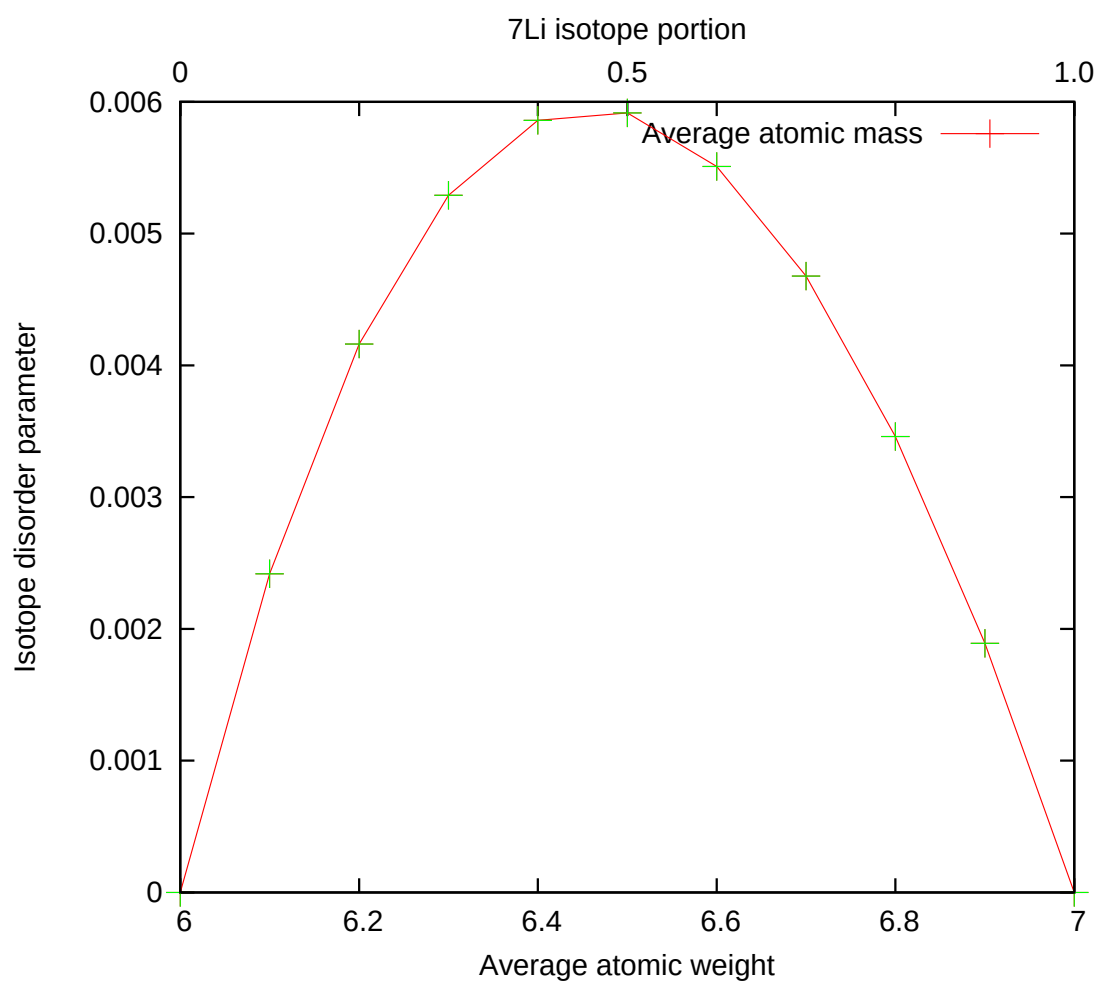


Figure 4.6: The isotope disorder parameter was plotted as a function of average atomic weight (bottom x axis) and as a function of ^7Li portion (top axis).

mal conductivity will be infinite. When the crystal structure consists of more than one type of atom, there is more than one vibrational mode. The introduction of isotopes will also increase the number of vibrational modes. In a lattice containing different isotopes, the atomic mass varies from site to site. The amplitude and resonant frequency of atoms with different masses are therefore different. This means that there is more than one type of normal mode wave in the crystal lattice. These waves can be out of or different in phase, reducing the ability to transfer heat and hence reduces the thermal conductivity. In modern physics, each normal mode of the lattice is a phonon. The number of phonons increases with the degree of isotope disorder and also phonons interact more often.

The linear relationship between thermal conductivity of average mass system and average atomic weight at a fixed temperature can be explained. In theory, the thermal conductivity can be calculated via integration of the transition probability over all possible modes for all the phonons. The process is very complicated but a simple estimate has been given in the form [67]

$$k \propto \frac{MVT_D}{T\gamma^2} \quad (4.16)$$

where V is the volume occupied by one atom, assumed to be same for ${}^6\text{Li}$ and ${}^7\text{Li}$ and M is the atomic weight. T_D is the Debye temperature and T is the temperature. γ is Grünsein constant. At a fixed temperature, V , T_D , T and γ are all constant and thermal conductivity is proportional to the atomic weight directly.

A crude linear relationship between thermal conductivity of the average mass system and average atomic weight can be identified in all the temperature ranges considered.

In Fig. 4.7, the thermal conductivity difference between the average mass system of Li mass at 6.5 and the isotope mass system of equal proportion ${}^6\text{Li}$ - ${}^7\text{Li}$ was plotted as a function of temperature. The thermal conductivity difference

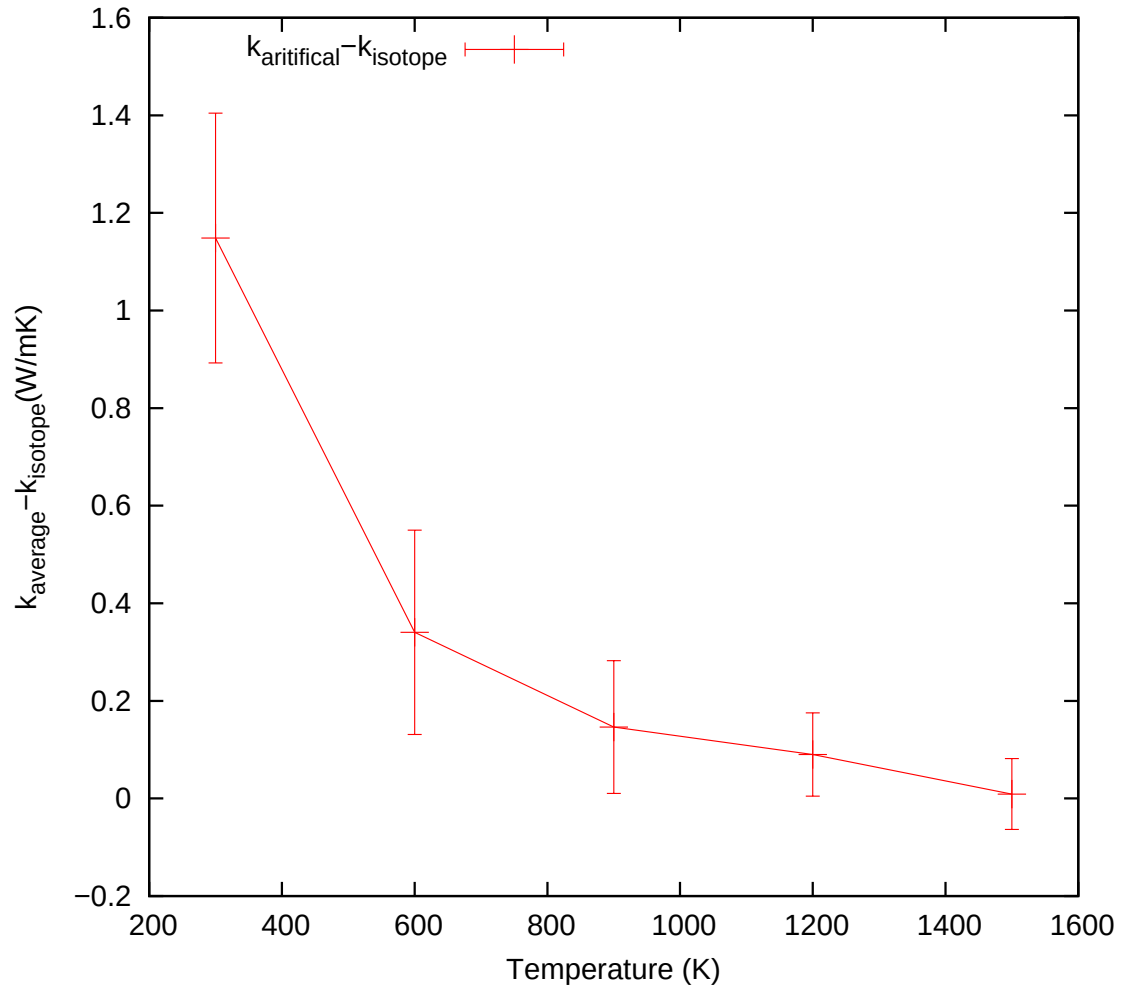


Figure 4.7: The thermal conductivity difference between the average mass system of Li mass at 6.5 and discrete mass system of equal proportion ${}^6\text{Li}$ - ${}^7\text{Li}$ was plotted as a function of temperature.

decreased gradually with rising temperature and approached zero above 1000 K. This temperature was close to the Li ion superionic transition temperature, calculated using potential set B in Sec. 3.5.4. This can be interpreted as: below the transition temperature, the isotope scattering effect has large influence on thermal conductivity. While above the transition temperature, structural disorder (Li fast ion diffusion) becomes more dominant. In the Li diffusion process, Li atoms move away from its original lattice site, creating Frenkel defects and then enter adjacent Li sites. For a given site, ^6Li or ^7Li can occupy the site at different instants. When this site is averaged over the simulation time, this creates the same effect as a Li ion of average mass sitting at the site. Therefore the thermal conductivity difference becomes similar at high temperatures.

4.3.3 Conclusion

MD simulation was able to replicate the experimental thermal conductivity and its trend of Li_2O in a reasonable agreement with and without applying finite size and anharmonicity corrections. The thermal conductivity of the average mass system decreased linearly with increasing average atomic weight. The isotope ratio had a significant effect on thermal conductivity below the Li ion superionic transition temperature. There was a quadratic relationship between thermal conductivity of the discrete mass system. At a fixed temperature, the thermal conductivity decreased to a minima when ^6Li and ^7Li had a ratio of 1 : 1 (average atomic weight 6.5). The maximum thermal conductivity can be found for pure ^6Li . This is a consequence of phonon scattering due to the isotope disorder. The isotope disorder effect was most dominant at low temperature but disappeared above Li ion superionic transition temperature. This was because the structural disorder effect (Li ion diffusion) overwhelmed the isotope disorder effect on thermal conductivity. On a given Li site, the average mass system and discrete mass system would have same mass when averaging over time. As a result, the different system showed similar thermal conductivity and trend.

In a nuclear fusion reactor, a high thermal conductivity blanket breeding material is an advantage and therefore enriched ^6Li could be considered as an option to improve the thermal efficiency at the operating temperature at around 700 K, below the fast ion transition temperature, despite its expensive cost (In the most case, ^6Li is always enriched to improve the tritium breeding ratio). At even higher temperature, the isotope effect needn't be considered because their thermal conductivities were similar to a artificial assigned Li mass.

Chapter 5

Structure and vacancy defects in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

5.1 Introduction

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is regarded as a promising candidate material for non-volatile random access memories due to its ferroelectric property [117]. Other possible applications of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ are as a thermal barrier coating and shielding due to its strong thermal anisotropy.

A conventional synthesis of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is via a solid state reaction of Bi_2O_3 and TiO_2 [118]. The high processing temperature in the reaction usually results in the loss of Bi. More recently, a number of wet-chemical methods based on processes such as sol-gel have been developed to avoid this problem [119].

5.2 Crystal structure

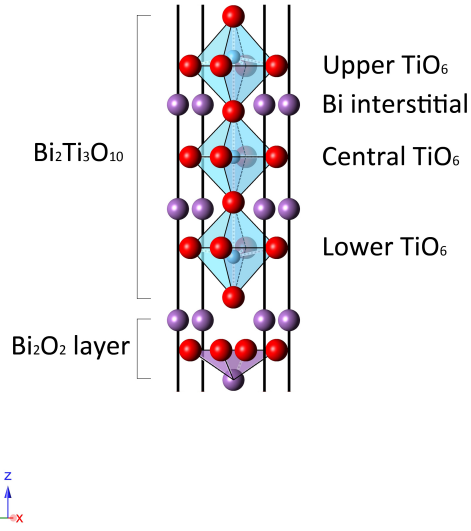
The Aurivillius structure typically consists of alternating fluorite like layers $(\text{M}_2\text{O}_2)^{2+}$ and perovskite like layers $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}^{2-})$ where $n = 1 \sim 8$ layers), M

is generally Bi^{3+} , the A type atom is a group II or lanthanide metal and the B type atom is a d^0 transition element [120]. When $n = 3$, the A type atom is Bi and the B type atom is Ti, the Aurivillius phase is $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

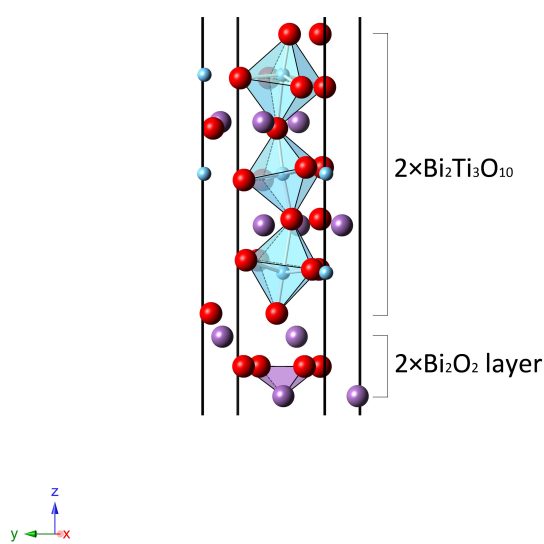
The structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ can be written as $(\text{Bi}_2\text{O}_2)(\text{Bi}_2\text{Ti}_3\text{O}_{10})$. In the $(\text{Bi}_2\text{O}_2)^{2+}$ layer, the Bi^{3+} ion has four nearest oxygen ions forming a square pyramid [121]. The perovskite like layers are in the middle, formed with TiO_6 octahedra between which the Bi^{3+} ions sit in 12-fold cuboctahedral coordinated sites.

The parent structure is a tetragonal structure $I4/mmm$ (space group number 139) above the Curie temperature of 948 K [14]. When the temperature is decreased, the structure transforms to either a low symmetry orthorhombic structure with the B2CB (space group number 41) or a very similar monoclinic structure with the B1A1 (space group number 7). The tetragonal, orthorhombic and monoclinic unit cell structures are shown in Fig. 5.1a-5.1c. For ease of comparison, only half unit cell structures are shown, i.e. one formula unit of the tetragonal structure and two formula units of the orthorhombic/monoclinic structure. The main differences between the tetragonal structure (at high temperature) and the orthorhombic/monoclinic structures (at low temperature) are as follows:

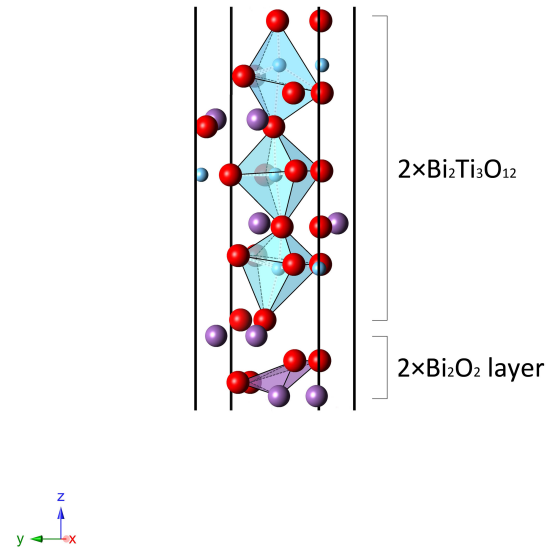
1. The lattice parameter $a_{\text{orthorhombic/monoclinic}} \approx b_{\text{orthorhombic/monoclinic}} = \sqrt{2}a_{\text{tetragonal}}$.
2. There are two formula units in the tetragonal unit cell ($\text{Bi}_8\text{Ti}_6\text{O}_{24}$) whilst there are four formula units ($\text{Bi}_{16}\text{Ti}_{12}\text{O}_{48}$) in the orthorhombic/monoclinic unit cell.
3. TiO_6 octahedra are more tilted in an orthorhombic/monoclinic structure; the Bi^{3+} interstitial atoms in the perovskite layers and the atoms in Bi_2O_2 layers are also displaced as a result of losing symmetry below the Curie temperature.
4. More symmetry group operations have disappeared in the monoclinic structure compared to the orthorhombic structure.



(a) Tetragonal structure.



(b) Orthorhombic structure.



(c) Monoclinic structure.

Figure 5.1: (a) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with the tetragonal structure. (b) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with the orthorhombic structure. (c) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with the monoclinic structure. Each structure shows a half unit cell and viewed along x direction with slight tilting. The red, blue and purple spheres are the oxygen, titanium and bismuth ions respectively.

This phase transition is accompanied by a ferro-paraelectric transition. Hervoches *et al.*[122] claimed that the predominant driving force for the ferroelectric transition lies with the unsatisfactory coordination of the Bi^{3+} ion in the perovskite block of the tetragonal phase. The Bi^{3+} ions tend to optimize their bonding to the neighbouring oxygen atoms. Therefore for optimal bonding, the bond Valence Sum for the metal site would be its oxidation state, that is 3.0 for Bi. The Bond Valence Sum (BVS) [123] is a method to estimate oxidation states. The valence of an atom is the sum of the surrounding individual bond valences, which can be calculated from the observed bond lengths. The calculations suggest the BVS for Bi increases from 2.22 above the Curie temperature to an optimal value of 3.0 in the low temperature phase.

In 2003, Lightfoot *et al.* [120] reported there was no intermediate phase between the ferro-para electric transition. This was based on following pieces of evidence:

1. A discontinuous change in the c parameter as a function of temperature in the Curie temperature range, suggesting a first order structural transition.
2. A sharp and discontinuous change in Bi-O bond lengths near the Curie temperature.

In the same year, Zhou [13] reported the possible existence of an intermediate phase based on very high resolution powder diffraction and smaller temperature intervals (7 K). There was a continuous change of c parameter as a function of temperature. Their program, ISOTROPY [124], confirmed that, under a non-first order transition, a direct orthorhombic to tetragonal transition could not exist. The possible intermediate phases had space groups Fmm2 and Cmca.

As mentioned previously, there are two candidate space groups for the low temperature phase of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, B1a1 and B2cb. There has been much discussion in the literature about which space group offers the best description of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ at low temperature, that is are reviewed below.

Aurivillius, who first described the room temperature structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, reported that the symmetry was not higher than orthorhombic [125]. The assertion that $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ exhibited an orthorhombic structure was supported by the X-ray powder diffraction studies of Subbarao *et al.* [126]. Hervoches *et al.* [122] employed neutron powder diffraction to investigate the structure. They found it was not possible to obtain a stable refinement of the monoclinic model due to very high pseudo-symmetric correlations associated with the subtle tilts of the TiO_6 octahedra. Therefore, they suggested that the orthorhombic structure was a better choice. Chakraborty *et al.* [121] studied the low temperature structure by Rietveld refinement of the neutron diffraction data from 15 to 300 K. They arrived at the same conclusion: that the orthorhombic structure was a better fit.

Rae *et al.* [127] reported a monoclinic structure at room temperature using electron diffraction, as the loss of the b -glide plane was observed. Jeon *et al.* [22] performed a structural analysis using X-ray diffraction. The monoclinic (M-model) and the orthorhombic model (O-model) were assumed and Rietveld refinement was carried out. The goodness of fit indicators for M-model and O-model are 1.09 and 1.43 respectively, which suggested that the monoclinic structure was a more suitable model at room temperature. Kim [128] applied the same Rietveld refinement, except using neutron diffraction and arrived the same conclusion. Du *et al.* [119] carried out a Raman study of the structure. They found two broad Raman bands centred at 57 and 93 cm^{-1} , which broke into several peaks at 90 K. Their result indicated that monoclinic structure existed at a much lower temperature. Shrinagar *et al.* [129] employed first principles simulations to determine the low temperature structure. They found the energy of the monoclinic structure was lower than for the orthorhombic structure, however the difference was very small. They also argued that the unit cell parameters, fractional coordinates, density of states and band structure of the two structures were very similar, meaning it would be very difficult to differentiate between the two structures using experimental techniques.

5.3 Defects and doping

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has been regarded as a promising candidate for non-volatile random access memory due to its ferroelectric properties. For such applications, high Curie temperature, large remanent polarization, low coercive field, low polarization fatigue and low leakage current are required. The type of vacancy defects (V_{Bi}''' , $V_{\text{O}}^{\bullet\bullet}$ and $V_{\text{Bi}}''' - V_{\text{O}}^{\bullet\bullet}$) and their distribution may have an influence on the polarization properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The defects act as space charges that hinder polarization switching, resulting in a reduction of remanent polarization, polarization fatigue and an increase of leakage current. These effects can be more pronounced if the defects are mobile and aggregate to form clusters [130, 131]. Spontaneous polarization due to external field (ferroelectricity) only occurs below Curie temperature for possible applications, therefore the defects behaviours (vacancy or doping) were investigated in the low temperature orthorhombic/monoclinic phase.

Oxygen vacancies act as strong pinning points for polarisation switching [131], reducing the remanent polarization and the polarization fatigue. The oxygen vacancies in the perovskite layers are more effective at hindering the polarization than those in the $(\text{Bi}_2\text{O}_2)^{2+}$ layer, because the perovskite layer controls the polarization [131]. Oxygen vacancies were observed by X-ray photoelectron spectroscopy in both the perovskite layer and $(\text{Bi}_2\text{O}_2)^{2+}$ layer however oxygen vacancies were preferentially sited in $(\text{Bi}_2\text{O}_2)^{2+}$ layer [132, 133]. Empirical pair potential simulations found the oxygen vacancies in the $(\text{Bi}_2\text{O}_2)^{2+}$ layer had the lowest energy, in agreement with X-ray phototelectron studies. [3]. Hashimoto *et al.* [134] conducted first principles calculations on oxygen vacancies in the orthorhombic structure. They found the +2 charged oxygen vacancies were likely to occur in the $(\text{Bi}_2\text{O}_2)^{2+}$ layers and charged oxygen vacancies were not stable. They also found that the oxygen vacancies in the $(\text{Bi}_2\text{O}_2)^{2+}$ layer greatly altered the polarization. Growing the crystal in high oxygen pressure can suppress the oxygen vacancy formation, hence enhancing the polarization properties [135].

The $V_{\text{Bi}}''' - V_{\text{O}}^{\bullet\bullet}$ vacancy complex can also hinder polarization switching [136]. To eliminate the V_{Bi}''' , doping with Ln^{3+} on the A site has been considered. The doping structure $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLZ) has a larger remanent polarization (defined as the magnitude of polarization at $E=0$), a small cohesive field (defined as the horizontal intercept of the hysteresis loop or the field at $P=0$) and a high fatigue resistance [137, 138]. Similar results have been observed for doping with other lanthanide ions, such as Nd^{3+} , Pr^{3+} , Sm^{3+} and Gd^{3+} [139, 140, 141, 142]. Doping with Ln^{3+} decreases the Curie temperature [143]. Snedden *et al.* [3] employed pair potential lattice static simulations to investigate the Ln^{3+} (Yb, Gd, Nd and La) dopant properties in the orthorhombic structure. They concluded that Ln^{3+} doping in Bi_2O_2 is most energetically preferred at the dilute limit. Another way to eliminate the oxygen bismuth vacancy complex $V_{\text{Bi}}''' - V_{\text{O}}^{\bullet\bullet}$ is to substitute higher-valent cations such as V^{5+} and W^{6+} for Ti^{4+} at the perovskite B-site and to achieve charge neutrality by incorporation of oxygen into $V_{\text{O}}^{\bullet\bullet}$ defects. This effectively removes the $V_{\text{O}}^{\bullet\bullet}$, leading to large remanent polarization but a large cohesive field [136]. In general, A-site substitution suppresses the V_{Bi}''' defect while B site substitution compensates for $V_{\text{O}}^{\bullet\bullet}$. A-site substitution currently is a more prominent method of improving ferroelectric properties than the B-site substitution.

5.4 Potential sets

There have been no potential models derived specifically for the study of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Therefore, the empirical pair potentials are taken from studies of related Bi, Ti, and O containing systems. Pair potential parameters for the Bi-O, Bi-Bi and O-O interactions were taken from the Bi_2WO_6 structure, which is the simplest Aurivillius structure [144]. A number of different Ti-O potentials were investigated for their efficacy. The different Ti-O potentials were termed A, B and C. Potential set A is taken from potential set C and modified to fit the lattice parameters of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ in the low temperature orthorhombic structure [3]. Potential B was modified from

a study of SrTiO_3 interfaces that reproduced mixed oxide structural parameters [145]. Potential C was derived from the binary oxide TiO_2 , from the cohesive energy and structure [146]. The potentials sets are shown in Table 5.1. The shell model parameters have been taken from Snedden *et al.* [3], as shown in Table 5.2.

Table 5.1: Pair potential sets used in simulations.

	A (eV)	ρ (Å)	C (eV Å ⁶)
Bi-O [144]	49529.35	0.2223	0.000
Bi-Bi [144]	24244.50	0.3284	0.000
O-O [144]	9547.96	0.2192	32.00
Ti-O [3] (Potential A)	2549.4	0.2989	0.000
Ti-O [145](Potential B)	2131.04	0.3038	0.000
Ti-O [146](Potential C)	760.47	0.3879	0.000

Table 5.2: Shell model parameters.

		Shell charge (e)	k (eV Å ⁻²)
Bi	8.31	-5.31	359.55
Ti	1.11	2.89	39.5
O	0.04	-2.04	6.3

5.5 Results and discussion

5.5.1 Phase determination using pair potential and first principles simulation

The $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ structure was energy minimized under constant pressure conditions, starting from the experimental tetragonal structure[122] using all the three potential sets with and without shell parameters. Simulations were performed without shells to allow a comparison with MD simulations where shells are omitted for computational reasons (as the shell has no mass, it will develop unphysical velocity). The lattice parameters, angles, energies per formula unit, space group and sign of phonon frequency are shown in Table 5.3. The space group was

determined using Materials Studio [147], with 0.5Å tolerance for atom positions. For the same potential set, the simulation with shell parameter yielded a slightly lower energy, suggested a more energetically favourable structure. This is expected as the inclusion of the shell allows the crystal more degrees of freedom to rotate octahedra. The potential sets, with and without shell parameter, can generally reproduce the experimental lattice parameters and space group. The potential models without shell parameter replicated the lattice parameter a and b better. The potential sets with shell parameter replicated the c lattice parameter better. Imaginary phonon modes (negative phonon frequency) were found using all the potential sets, both with and without shell parameter. This suggested the current structure was unstable, which was expected because there exists a more energetically favourable structure at low temperatures. The tetragonal structure was a local energy minimum structure.

The $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ structure was then subject to energy minimization under constant pressure conditions from the experimental monoclinic structure using all the three potential sets both with and without shells. Similar properties were calculated and compared with the available experimental results in Table 5.4 (monoclinic structure). The predicted monoclinic structure remained the monoclinic structure and generally agreed with the experimental monoclinic structure. There was only one exception, the predicted structure using potential C without shells, which showed an imaginary phonon mode, and a large deviation from the experimental data. Thus potential C without shell was not useful for simulation of monoclinic structure.

Simulations starting with the experimental orthorhombic structure were more interesting, as a phase transformation occurred, as shown in Table 5.5. The structure simulated using potential A with and without shells showed a stable structure, with all phonon frequencies being positive (no imaginary phonon modes). The relaxed structure with shells was monoclinic with space group B1a1 and the value for β was in agreement with the available experimental data. The simulation with-

out shells exhibited an orthorhombic structure with space group number 29. This structure had lost some symmetry elements compared to the initial orthorhombic structure. However, when a larger tolerance was allowed (1 Å), the orthorhombic structure (space group number 41) was identified.

After energy minimisation, using potential B with shells included, the structure remained orthorhombic. All the phonon frequencies were found to be positive (no imaginary phonon modes), suggesting a stable structure was achieved by this potential. When the shells were removed, the structure transformed to a lower symmetry and energetically favourable monoclinic structure. However, the distorted cell angle (88.59°) was much smaller than the experimental value (90°) [22].

For potential C both with and without shells, imaginary phonon modes were found. The structure simulated with the shell model was found to be an unstable orthorhombic structure, which was reasonable because it may transform to a lower symmetry monoclinic structure. The structure simulated without shell parameters were found to be an unstable monoclinic structure. However, no lower symmetry structure has ever been observed experimentally for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The only conclusion that can be drawn was that this potential set cannot accurately replicate the forces present in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

The presence of imaginary phonon modes predicted using potential C suggested that this potential is not appropriate for further use on $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Similarly potential B predicted a significant change to one of the angles when the shell was removed. As the MD simulation will be performed without dipole polarisability this potential is also not appropriate. The relaxed structure obtained from energy minimisation of the orthorhombic structure using potential A with the shell model was biased to the monoclinic structure (B1a1 space group). The agreement with experimental lattice parameters from experiment was excellent as shown in Table 5.5. This implied that the pair potential models favoured the monoclinic

structure over the orthorhombic structure. Unfortunately this behaviour was not replicated when shells were removed. Nevertheless the orthorhombic and monoclinic structures were very similar. Potential A has been the most reliable and will be used from now on.

Further energy minimisation simulations were performed on the orthorhombic and the monoclinic structures using the first principles: code CASTEP. A brief overview of the underlying principles of quantum mechanical simulation is given in Sec. 2.7.

Simulations employed ultra-soft pseudo-potentials for Bi, Ti and O and the exchange correlation was described using the GGA function. The plane-wave kinetic energy cut-off was set to 380 eV. Reciprocal space sampling of $4 \times 4 \times 1$ with 8 k-points was used. The structure was geometry optimized using the BFGS (Broyden-Fletcher-Goldfarb-Shanno) method [53] with the following convergence criteria: energy change per ion = 5×10^{-5} eV/ion, maximum force = $0.1 \text{ eV}/\text{\AA}$, maximum displacement = $5 \times 10^{-3} \text{\AA}$ and maximum pressure = 0.2 GPa.

Crystal symmetry can be used to significantly speed up computationally arduous DFT simulations, however, these constraints may also prevent the structures relaxing completely if this breaks the imposed symmetry. Therefore, the energy minimisation simulations were performed both with and without symmetry and the resulting simulated lattice properties, energy per formula unit and space group are shown in Table 5.6.

For the structures with symmetry imposed, the energy difference between the orthorhombic and monoclinic structures were very small and indistinguishable up to two decimal places. For the structures without symmetry, the monoclinic structure had a slightly lower energy state; 0.05 eV lower per formula unit. This agreed with the previous pair potential simulations; that the monoclinic structure had a lower energy, and also in agreement with other first principle simulation [129]. Table 5.6 shows that for the first principles simulation of the orthorhombic

structures, the forces on the atoms were not significantly strong to undergo a phase transition to the monoclinic structure despite the latter structure being slightly lower in energy.

In summary, the low temperature orthorhombic and monoclinic structures were predicted to be very similar although the monoclinic structure had slightly lower energy. Potential A with shells can overcome the energy barrier to find the global minimum energy state, monoclinic structure. Comparatively, potential B can't simulate the correct distorted monoclinic angle and potential C showed an unstable monoclinic structure, which meant that these two potential sets were not ideal for further simulation. The first principles simulations were unable to relax the orthorhombic structure to the monoclinic structure, however, it confirmed that the monoclinic phase has a lower energy.

Table 5.3: Tetragonal $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was simulated using potential sets A, B and C. The lattice parameters, cell angles, energy per formula unit, space group are compared with available experimental data. Negative means that imaginary phonon mode found and phonon has negative energy.

	Exp tetragonal structure [122]	Without shell parameters			With shell parameters		
		A	B	C	A	B	C
$a(\text{\AA})$	3.86	3.86	3.82	3.87	3.76	3.72	3.76
$b(\text{\AA})$	3.86	3.86	3.82	3.87	3.76	3.72	3.76
$c(\text{\AA})$	32.29	33.67	34.36	34.56	33.57	33.23	33.60
$\alpha(^{\circ})$	90.00	90.00	90.00	90.00	89.99	90.00	89.99
$\beta(^{\circ})$	90.00	90.00	90.00	89.81	89.97	90.00	90.13
$\gamma(^{\circ})$	90.00	90.00	88.59	90.00	89.97	90.00	89.96
Energy (eV)	-	-630.48	-635.87	-608.95	-638.04	-643.89	-616.19
Space group	139	139	139	139	139	139	139
Phonon frequency	-	Negative	Negative	Negative	Negative	Negative	Negative

Table 5.4: Monoclinic $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ simulated using potential sets A, B and C. The lattice parameters, cell angles, energy per formula unit, space group, sign of phonon frequency are compared with available experimental data. Negative means that imaginary phonon mode and phonon has negative energy.

	Experimental structure		Without shell parameters			With shell parameters		
	Orthorhombic[120]	Monoclinic[22]	A	B	C	A	B	C
$a(\text{\AA})$	5.45	5.45	5.57	5.52	5.64	5.38	5.45	5.45
$b(\text{\AA})$	5.41	5.41	5.51	5.45	5.56	5.37	5.41	5.58
$c(\text{\AA})$	33.17	33.07	33.07	33.50	33.07	32.81	33.22	32.46
$\alpha(^{\circ})$	90.00	90.00	90.00	90.00	90.00	89.99	90.00	90.48
$\beta(^{\circ})$	90.00	89.96	89.99	89.92	90.18	90.03	89.96	90.90
$\gamma(^{\circ})$	90.00	90.00	90.00	90.00	90.18	90.02	90.00	89.90
Energy fu(eV)	-	-	-633.73	-638.47	-612.27	-638.59	-644.12	-669.93
Space group	7	7	7	7	7	7	7	7
Phonon frequency	-	-	positive	positive	negative	positive	positive	negative

Table 5.5: Orthorhombic $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ are simulated using potential sets A, B and C. The lattice parameters, cell angles, energy per formula unit, space group, sign of phonon frequency values are compared with available experimental data. Negative means that imaginary phonon mode was found and that phonon has negative energy.

	Experimental structure		Without shell parameters			With shell parameters		
	Orthorhombic[120]	Monoclinic[22]	A	B	C	A	B	C
$a(\text{\AA})$	5.45	5.45	5.57	5.49	5.64	5.38	5.32	5.59
$b(\text{\AA})$	5.41	5.41	5.51	5.46	5.56	5.37	5.29	5.58
$c(\text{\AA})$	32.86	32.81	33.17	33.73	33.07	33.50	33.22	31.26
$\alpha(^{\circ})$	90.00	90.00	90.00	90.00	90.00	89.99	90.00	89.99
$\beta(^{\circ})$	90.00	89.96	90.00	90.00	89.81	89.97	90.00	90.13
$\gamma(^{\circ})$	90.00	90.00	90.00	88.59	90.00	89.99	90.00	89.96
Energy fu(eV)	-	-	-633.73	-639.05	-612.27	-638.59	-644.12	-636.74
Space group	41	7	29	7	7	7	41	41
Phonon frequency	-	-	positive	positive	negative	positive	positive	negative

Table 5.6: Comparison of the first principle simulated and low temperature experimental structure.

	With symmetry		Without symmetry	
	Simulated monoclinic	Simulated orthorhombic	Simulated monoclinic	Simulated orthorhombic
$a(\text{\AA})$	5.48	5.50	5.51	5.50
$b(\text{\AA})$	5.43	5.46	5.44	5.46
$c(\text{\AA})$	33.25	33.14	33.34	33.09
$\alpha(^{\circ})$	90.00	90.00	90.00	90.00
$\beta(^{\circ})$	89.94	90.00	89.97	90.00
$\gamma(^{\circ})$	90.00	90.00	90.00	90.00
Energy fu(eV)	-10671.35	-10671.35	-10671.40	-10671.35
Space group	41	7	41	7

5.5.2 Enthalpy of formation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

The enthalpy of formation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was calculated using first principles simulations. In order to determine the enthalpy of formation and to provide further validation of the methodology, it is necessary to model the constituent elemental systems, $\text{Ti}_{(\text{s})}$, $\text{Bi}_{(\text{s})}$ and $\text{O}_{2(\text{g})}$, $\text{TiO}_{2(\text{s})}$, $\text{Bi}_2\text{O}_{3(\text{s})}$ and gaseous state atoms $\text{Ti}_{(\text{g})}$, $\text{Bi}_{(\text{g})}$ and $\text{O}_{(\text{g})}$. The same pseudo potentials, exchange correlation function, energy minimizer and convergence criteria were used. The k point spacing for $\text{TiO}_{2(\text{s})}$, $\text{Bi}_2\text{O}_{3(\text{s})}$ are the same as for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. One k point is used for gaseous state elements and much more dense k points used for Bi and Ti solids (with k point spacing around $0.5\text{\AA}$).

The energy of gaseous Bi was calculated via a single point energy calculation when one Bi atom was placed in a monoclinic box. The gaseous state O and Ti values were obtained in the same way. The simulated gaseous state energies of Bi, Ti and O were -148.81 eV, -1597.71 eV and -431.79 eV respectively. The energy of O_2 was calculated via geometry optimization when two polarized oxygen ions were relaxed in a monoclinic box. The energy of O_2 was 2.81 eV, comparable with an experimental atomization energy of 2.56 eV [12].

The most stable room temperature structure of Bi and Ti solid were geometry optimized [18, 19]. TiO_2 occurs naturally as three phases, rutile, anatase and brookite from which the rutile structure was selected [20] for optimization. Bi_2O_3 has four phase, α , β , γ and δ , of which the β phase was chosen as the starting structure [21] for optimization because it was the lowest temperature phase (200 – 300°C) of the four [148]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was geometry optimized from its experimental monoclinic structure [127]. These solids and related oxides were simulated and compared with experimental lattice parameters, cell angles and available atomization energies in Table 5.7. As shown in Table 5.7, the simulations adequately replicate the lattice parameters and atomisation energies. This provided confidence that further calculation would be reliable.

The enthalpy of formation and atomization energy of Bi_2O_3 , TiO_2 and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ were calculated and compared with experimental data [12] in Fig. 5.2-5.4. Only the enthalpy of formation of Bi_2O_3 at 298 K was available for comparison while the enthalpy of formation of TiO_2 was extrapolated to 0 K from experimental data. All the enthalpies of formation for oxides were exothermic; the oxides were more energetically favourable. The enthalpy of formation of Bi_2O_3 and TiO_2 were generally in good agreement with their respective experimental enthalpies of formation. Because the formation mechanism of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ via a mechanochemical process is complex and not yet clear, the enthalpy of formation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has been computed for the first time and is a slightly exothermic with a value of -1.33 eV per formula unit.

Table 5.7: The simulated lattice parameters and cell angles of Bi solid, Ti solid, Bi_2O_3 and TiO_2 , $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ compared with experimental structure [18, 19, 20, 21, 22]. Calculated atomization energies of these solids and oxides are compared with available experimental values shown in the brackets [12]. No correction to 0 K vibrational energies have been applied for the atomisation energies determined by DFT.

	Bi solid	Ti solid	Bi_2O_3	TiO_2	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$
$a(\text{\AA})$	4.51 (4.53)	2.94 (2.95)	7.86 (7.75)	4.65 (4.60)	5.51 (5.45)
$b(\text{\AA})$	4.51 (4.53)	2.94 (2.95)	7.86 (7.75)	4.65 (4.60)	5.44 (5.41)
$c(\text{\AA})$	11.90 (11.80)	4.66 (4.68)	5.56 (5.70)	2.97 (2.90)	33.84 (32.86)
$\alpha(^{\circ})$	90.11 (90.00)	90.00 (90.00)	90.00 (90.00)	90.00 (90.00)	90.00 (90.00)
$\beta(^{\circ})$	89.99 (90.00)	90.00 (90.00)	90.00 (90.00)	90.00 (90.00)	89.87 (89.96)
$\gamma(^{\circ})$	119.93 (120.00)	120.00 (120.00)	90.00 (90.00)	90.00 (90.00)	90.00 (90.00)
Atomization energy(eV)	2.44 (2.15)	5.41 (4.84)	19.82 (17.93)	20.17 (19.73)	101.47

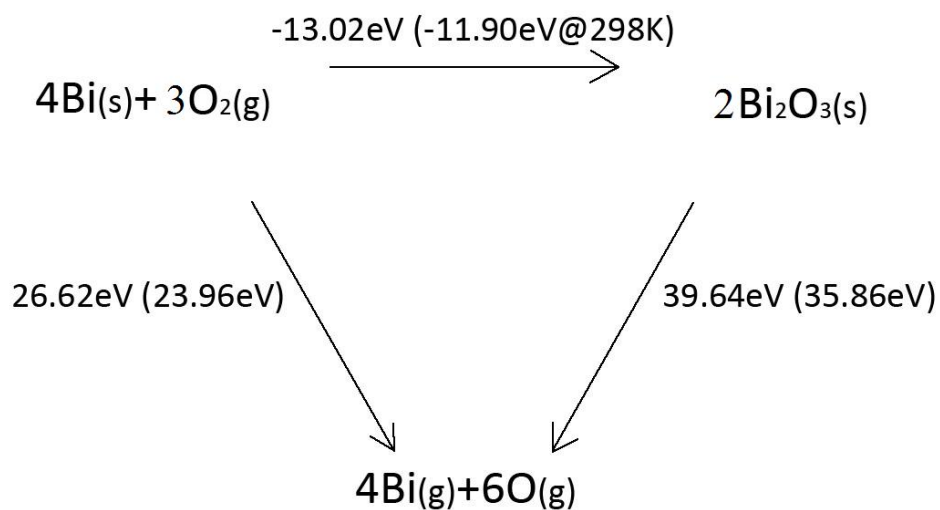


Figure 5.2: Hess cycle showing the enthalpy of formation of $\text{Bi}_2\text{O}_3(\text{s})$ at 0 K, compared with the experimental value at 298 K [12].

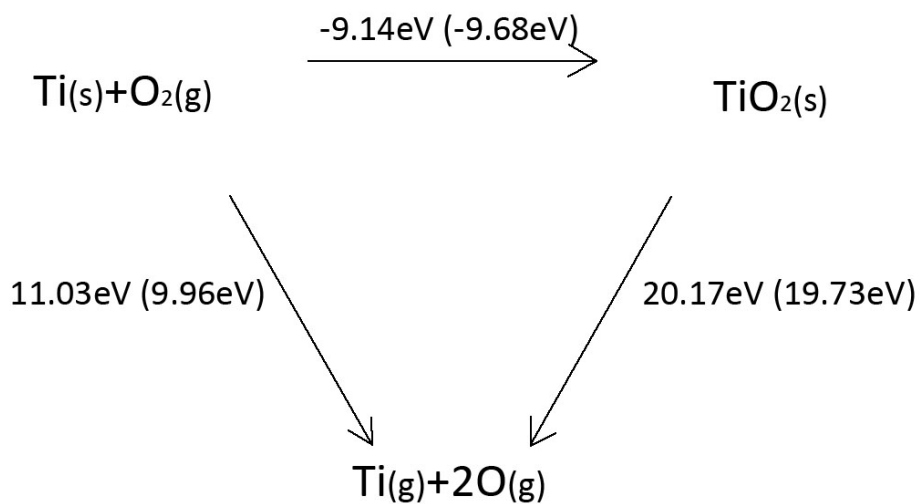


Figure 5.3: Hess cycle showing the enthalpy of formation of $\text{Ti}_2\text{O}_3(\text{s})$ at 0 K, compared with the experimental value at 0 K [12].

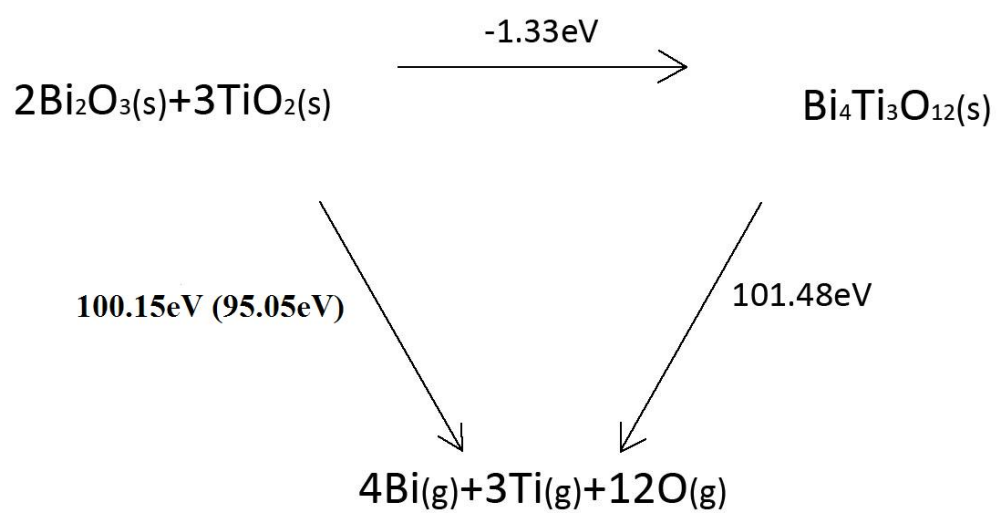


Figure 5.4: Hess cycle showing the enthalpy of formation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}(\text{s})$.

5.5.3 Vacancy defects in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

The lowest energy state monoclinic structure (B1a1) was used for defect calculations, with the same pseudo potential, k point spacing and exchange correlation function as employed in the previous $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ simulations. The formation of a defect can be considered as an exchange between the host material and some atomic/or electronic reservoir. The formation energy of one defect E_F is given by:

$$E_F = E(D) - E(P) + \mu + q\epsilon_F \quad (5.1)$$

where, $E(D)$ and $E(P)$ are the total energies calculated from first principles of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with and without the defect type D (e.g. Bi, Ti or O); q is the charge of a defect and ϵ_F is the Fermi energy. This thesis is limited to the consideration of charge neutral defects (i.e. $q = 0$), therefore final term is omitted. μ is chemical potential of the atom removed, a measure of the reactivity of the component in the solid solution (i.e the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ structure), with unit energy/particle.

The chemical potentials of the constituent elements in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ cannot be in excess of the chemical potential of the atom in its elemental state otherwise the elemental solid (or gas) would precipitate out. Therefore, the chemical potential of the elements in their natural state are the upper limit of the chemical potential and represent the growth conditions that were rich in that element as shown in Eq's. 5.2-5.4.

$$\mu_{\text{Bi}}^{\text{rich}} \leq E(\text{Bi solid}) \quad (5.2)$$

$$\mu_{\text{Ti}}^{\text{rich}} \leq E(\text{Ti solid}) \quad (5.3)$$

$$\mu_{\text{O}}^{\text{rich}} \leq \frac{1}{2}E(\text{O}_2) \quad (5.4)$$

Conversely, poor conditions of Bi, Ti and O were defined as being rich in the other two constituents, as shown in Eq's. 5.5 - 5.7.

$$\mu_{\text{Bi}}^{\text{poor}} \geq \frac{E(\text{Bi}_4\text{Ti}_3\text{O}_{12}) - 3\mu_{\text{Ti}}^{\text{rich}} - 12\mu_{\text{O}}^{\text{rich}}}{4} \quad (5.5)$$

$$\mu_{\text{Ti}}^{\text{poor}} \geq \frac{E(\text{Bi}_4\text{Ti}_3\text{O}_{12}) - 4\mu_{\text{Bi}}^{\text{rich}} - 12\mu_{\text{O}}^{\text{rich}}}{3} \quad (5.6)$$

$$\mu_{\text{O}}^{\text{poor}} \geq \frac{E(\text{Bi}_4\text{Ti}_3\text{O}_{12}) - 4\mu_{\text{Bi}}^{\text{rich}} - 3\mu_{\text{Ti}}^{\text{rich}}}{12} \quad (5.7)$$

Therefore, the following constraints can be obtained as shown in Eq's.5.8 - 5.10,

$$-161.56 \text{ eV} \leq \mu_{\text{Bi}} \leq -151.26 \text{ eV} \quad (5.8)$$

$$-1619.53 \text{ eV} \leq \mu_{\text{Ti}} \leq -1603.1 \text{ eV} \quad (5.9)$$

$$-438.08 \text{ eV} \leq \mu_{\text{O}} \leq -434.60 \text{ eV} \quad (5.10)$$

A diagram of the monoclinic structure showing each of the symmetrically distinct lattice sites is given in Fig. 5.5. Defect formation energies were determined for the creation of a vacancy on each of the unique lattice sites. The calculated formation energies and associate defect volumes are given in Table 5.8.

Vacancies were more energetically favourable in the poor growth condition and relatively energetically unfavourable in the rich condition. This is consistent with

the suppression of oxygen vacancy formation at high O₂ pressure (i.e. O rich condition).

In the poor conditions, the O type defects were least energetically favourable and Bi type defects were most energetically favourable. In the rich conditions, the O type defects were most energetically favourable and Ti type defects were the least energetically favourable.

For all the vacant defects considered, energies of some defects are close: Bi1 $\approx$ Bi2, Bi3 $\approx$ Bi4, O1 $\approx$ O2, O3 $\approx$ O4, O5 $\approx$ O6, O7 $\approx$ O8, O9 $\approx$ O10, O11 $\approx$ O12, Ti2 $\approx$ Ti3. Given the similarity of the monoclinic and orthorhombic structure, this is not surprising because these sites are symmetrically equivalent in the orthorhombic structure, for which these relationships would be exactly equal. The largest disagreement of symmetrical sites were O7 and O8, with a difference 15% for the poor condition and 4% for the rich condition. This suggested that the defect energies should ideally be calculated using monoclinic structure despite the extra computational cost.

All the oxygen defects energies of O3 and O4 in the Bi₂O₂ layer were considerably lower, than all the other oxygen defects especially under the poor condition. This agrees with previous experimental observations and theoretical calculations [132, 134]. O3 had lowest defect energy of all the oxygen defects. The O7 and O8 defects in the TiO₆ octahedra, close to the Bi₂O₂ layer, had higher defect energy than the other oxygen defects and O8 was the least energetically favourable. For bismuth defects energies, Bi3 and Bi4 in the Bi₂O₂ layer were more energetically favourable than Bi1 and Bi2 which are situated between TiO₆ octahedra. The relative instability of vacancy on the Bi1/Bi2 sites, may account for the major driving force between phase transition. The Ti1 site in the central TiO₆ octahedron has the lowest defect energy and this is the most stable Ti vacancy defect. The least stable, highest energy Ti vacancy defect is Ti3.

Removing Ti1 in the central TiO₆ octahedra had the largest influence on cell

Table 5.8: The vacancy defect formation energies and defect volume are represented as % of perfect cell volume. The two values in the bracket correspond to the poor and rich conditions respectively.

Defect species	Energy (eV)	change of cell volume %
Bi1	[-4.59 5.85]	1.69
Bi2	[-4.80 5.64]	0.68
Bi3	[-3.39 7.05]	-0.67
Bi4	[-3.30 7.14]	-0.77
O1	[1.24 4.72]	0.56
O2	[1.21 4.68]	0.10
O3	[0.01 3.49]	0.30
O4	[0.08 3.56]	0.53
O5	[0.83 4.31]	0.30
O6	[0.71 4.19]	0.29
O7	[1.36 4.84]	0.92
O8	[1.57 5.05]	0.62
O9	[0.95 4.43]	0.11
O10	[0.98 4.46]	0.03
O11	[1.31 4.78]	0.04
O12	[1.26 4.74]	0.22
Ti1	[-2.27 11.65]	1.99
Ti2	[-1.65 12.27]	1.29
Ti3	[-1.62 12.29]	0.47

volume, while removing O ions in the TiO_6 was generally less influential. This is because there are 6 oxygen ions in TiO_6 , removing one of them should not greatly change the whole structure and therefore has less influence on the whole structure. Removing Bi in the Bi_2O_2 resulted in contraction of the cell volume. This is because the Bi and its four oxygen neighbours formed a 3D pyramid, removing the Bi ion made the pyramid structure into a flat 2D base consisting of just the four oxygen ions, therefore the whole cell contracts, particularly in z direction.

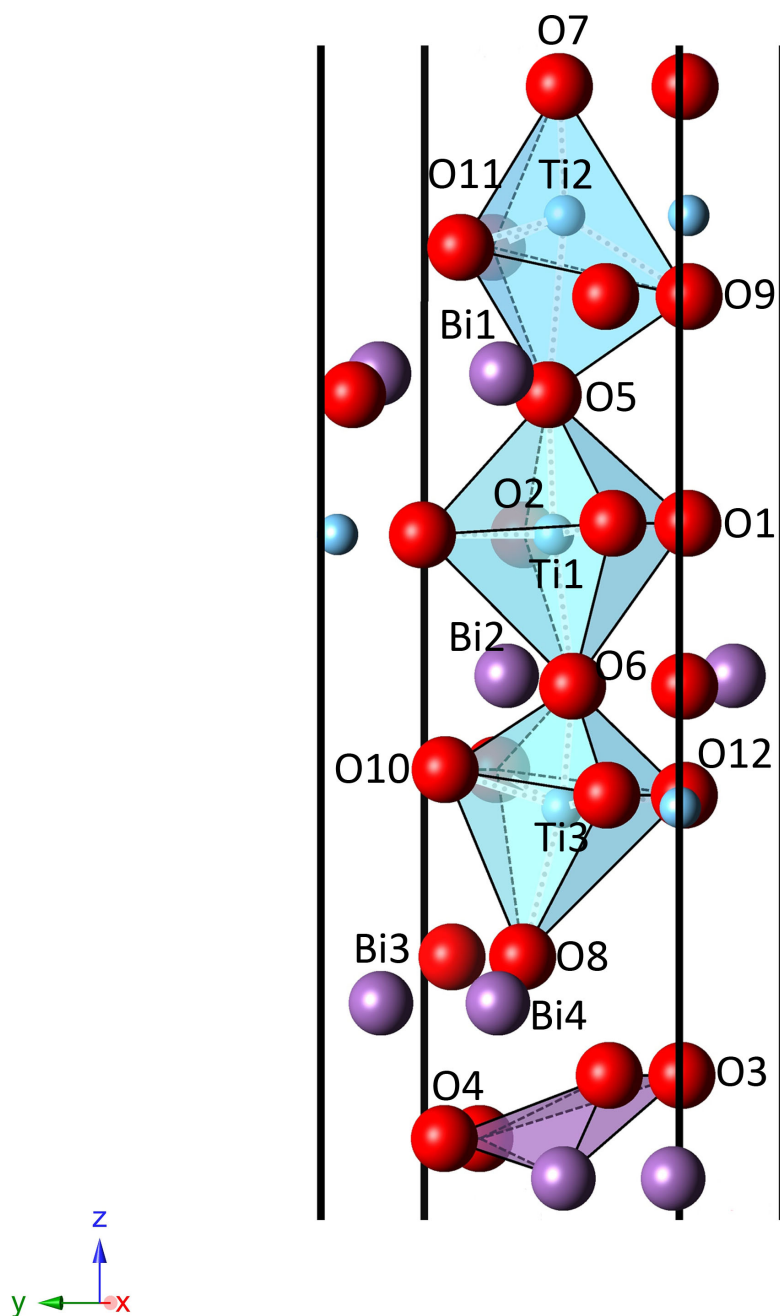


Figure 5.5: The monoclinic structure after energy minimization using first principle theory with atom labels.

5.6 Conclusion

The three sets of pair potentials A, B and C with Bi-O adopted from Bi_2WO_6 but with different Ti-O potentials were compared. All the three potential sets can generally reproduce the high temperature tetragonal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. However, only potential A with the shell mode could replicate the monoclinic structure. Potential B cannot reproduce the correct distorted angle and potential C showed an unstable monoclinic structure. Therefore, potential A will be employed for further investigation of thermal properties in the next chapter. The first principle simulation suggested that the monoclinic structure had a slightly lower energy than the orthorhombic structure. The monoclinic structure was the global energy minimum and the orthorhombic structure was a local minimum energy state. Although the orthorhombic and monoclinic structures were very similar, the energy barrier may not be overcome in all simulations. The orthorhombic-monoclinic transition may be dependent on the pair potential, inclusion of the shell model and the pseudo potential used in DFT simulations.

First principles simulations accordingly replicate the atomization energy of Bi solid, Ti solid and O_2 gas. The oxides TiO_2 and Bi_2O_3 also yielded satisfactory enthalpy of formation. The enthalpies of formation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was calculated for the first time using first principles simulations. This process yielded a slightly exothermic energy of -1.33 eV.

Formation energies and defect volumes for the introduction of vacancies into monoclinic $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ were investigated. Some vacancy energies were similar because they are the symmetrically identical sites in the orthorhombic structure. The vacancies were easier to form in poor conditions (deficiency). The oxygen vacancies were more energetically favourable in the Bi_2O_2 layer, where O3 had the lowest defect energy. The less energetically stable oxygen vacancies were in the TiO_6 layer adjacent to the Bi_2O_2 layer. The volume expanded when removing O and Ti but for Bi in Bi_2O_2 layer, the value decreased. This is because removing

this type of Bi changed the 3D pyramid structure to a flat 2D base consisting of 4 oxygens. Removing Ti in the central TiO_6 resulted in the largest volume change.

Chapter 6

Anisotropic thermal conductivity of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

6.1 Introduction

The thermal conductivity of a material can be reduced by introducing porosity. This is a very efficient method and the resulting thermal conductivity can be as low as $0.1 \text{ Wm}^{-1}\text{K}^{-1}$, in low density xerogel films [149]. A low thermal conductivity is also found in amorphous materials due to their high atomic disorder, which decreases the effective mean free path for travelling phonons. However, increasing porosities and amorphization undermine the mechanical properties and electrical conductivity required for many applications.

Certain types of crystals are able to exhibit low thermal conductivities without degrading their other properties. Low thermal conductivity crystals are widely acknowledged to display the following properties:

1. High atomic weight: the heavy atoms vibrate with smaller amplitude than light atoms with the same heat energy input.

2. Weak bonding: Van der Waals forces between atoms. Weak bonds attenuate the vibrational waves more quickly, which is a very efficient process for decreasing thermal conductivity.
3. Complex layered structure: the inter layers may have a similar effect to defects in the system. The details of the mechanism awaits further investigation.

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ satisfies most of these criteria. It can therefore potentially be used as a thermal barrier coating for some high temperature applications such as gas turbine blades. It has a strong anisotropic thermal conductivity so that heat can be dissipated through high thermal conductivity in the xy plane but reduced along the low thermal conductivity z direction. This particular aspect provides a useful method of heat management.

Other than low thermal conductivity, a thermal barrier coating material is usually required to have properties such as: large thermal expansion (i.e. close to metals), high thermal stability, low density and strong mechanical properties.

The typical single grain size of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is around 15-50 nm [119], and is possible to grow up to a few micrometer. The grains tend to agglomerate when the size is below 20nm [118]. Large single crystals of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ can not be obtained by current methods. Therefore, many experimental properties such as the bulk modulus, Young's modulus and thermal conductivity are measured using polycrystalline materials or the property values are not available. Atomistic simulation provides an excellent method for studying these properties. In this chapter, the Young's modulus, bulk modulus and thermal conductivities are calculated. The origin of the observed anisotropic thermal conductivity was investigated by determining the velocity of sound and the phonon mean free path in x , y and z directions.

6.2 Previous study

6.2.1 Pressure induced phase change

Kourouklis *et al.* [150] investigated the structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ using high pressure Raman spectroscopy up to 17 GPa. They found a phase transition at 3 GPa and a second phase transition that occurs at 11 GPa since a Raman peak at 31cm^{-1} split. Sun *et al.* [151] employed molecular dynamic methods to investigate the orthorhombic structure (B2cb) and reported two stress induced phase transitions at 6 GPa and 20 GPa, as the calculated spontaneous polarization showed a discontinuous change. Therefore, they regarded the pressure induced phase transitions as similar to the ferroelectric to paraelectric transition observed at ambient pressure and elevated temperature.

6.2.2 Thermal conductivity

Shen *et al.* [152] measured the thermal diffusivity up to 1000 °C. The standard relation $k = \rho CD$ was employed to obtain the thermal conductivity k , where D is the thermal diffusivity in the direction of the heat propagation; ρ is the density and C is the specific heat. The polycrystalline of a texture with z axis aligned (achieved by hot forging) and the polycrystalline of a random oriented texture were measured respectively. Assuming that the thermal conductivities along the x and y directions are the same, $k_x = k_y = k_{xy}$, the thermal conductivity in the xy plane. They then used the equation $k_p = \frac{1}{3}(2k_{xy} + k_z)$, where k_p is the value with random oriented polycrystalline material, and k_z is for polycrystalline material forged along the z axis. Their thermal conductivity results are shown in Fig. 6.1. The k_z is almost temperature independent and is much lower than k_{xy} . This anisotropic thermal conductivity persisted up to 1000 °C. Shen *et al.* asserted that the difference in the density of the $(\text{Bi}_2\text{Ti}_3\text{O}_2)^{2-}$ and $(\text{Bi}_2\text{O}_2)^{2+}$ layers was the major

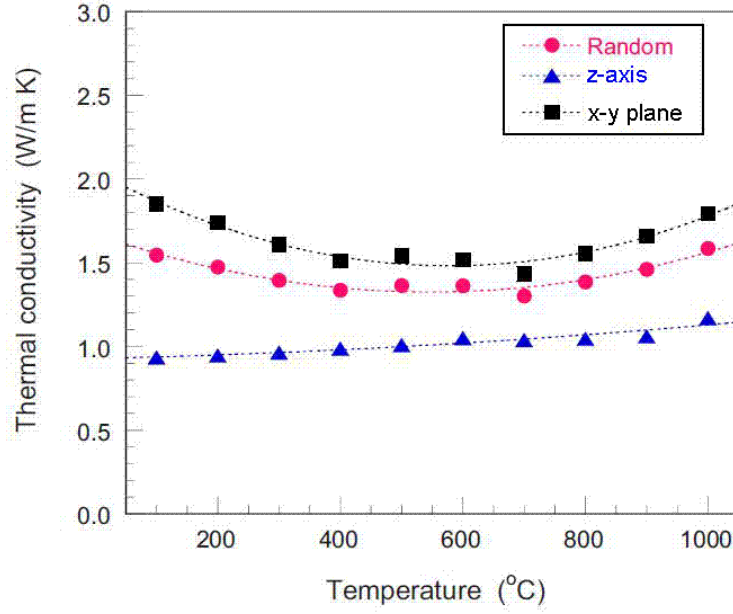


Figure 6.1: Thermal conductivity of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ in the xy plane and the z direction in a sample which exhibits grains of z axis texture compared with a material composed of grains of random axis texture.

contribution to the anisotropic thermal conductivity.

6.3 Results

6.3.1 Temperature induced phase transition validation

A detailed discussion of the complex crystal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is given in the previous chapter. For convenience the orthorhombic structure of Lightfoot *et al.* [120] is used for the simulations of thermal conductivity in this chapter. Due to similarities between the orthorhombic and monoclinic system, the thermal conductivities of the phases are expected to be similar.

A $10 \times 10 \times 2$ supercell (15200 atoms) was equilibrated at zero pressure and at a series of temperatures (200 K to 2000 K) for 15 ps. The lattice parameters, cell angles and volumes were averaged over the last 5 ps of each simulation and plotted as a function of temperature and compared with available experimental data [13, 14], as shown in Fig. 6.2-6.5

In Fig. 6.2, the predicted a and b lattice parameters became almost equal but this occurred at a higher temperature than observed experimentally. In Figs. 6.3 and 6.4, the predicted lattice parameter c and volume show clear discontinuities (at 1500 K). Experimentally these discontinuities in lattice parameter a , b , c and volume provide evidence of a direct orthorhombic-tetragonal transition or a transition via some possible intermediate phase [13, 14]. From the MD simulation data, a phase transition can be identified, however, careful analysis of the Fig. 6.5 revealed the failure of the potential A at high temperature. In Fig. 6.5, all the cell angles were 90° below the transition temperature, in agreement with literature. However, the γ angle was far from 90° above the transition temperature which indicated a non-tetragonal structure, in disagreement with the existing literatures. Possible explanations are:

1. The pair potential A was not derived explicitly to reproduce the phase transition.
2. In MD simulation, the omission of the polarization (shells) resulted in the failure of the model.

Potential A can generally reproduce the trend and the values of the lattice parameters, cell angles and volume at low temperature, but not at high temperatures, this suggests that further calculation should be limited to below the predicted transition temperature of 1400 K, where the structure investigated remains orthorhombic.

The experimental and simulated volume thermal expansion coefficients are mea-

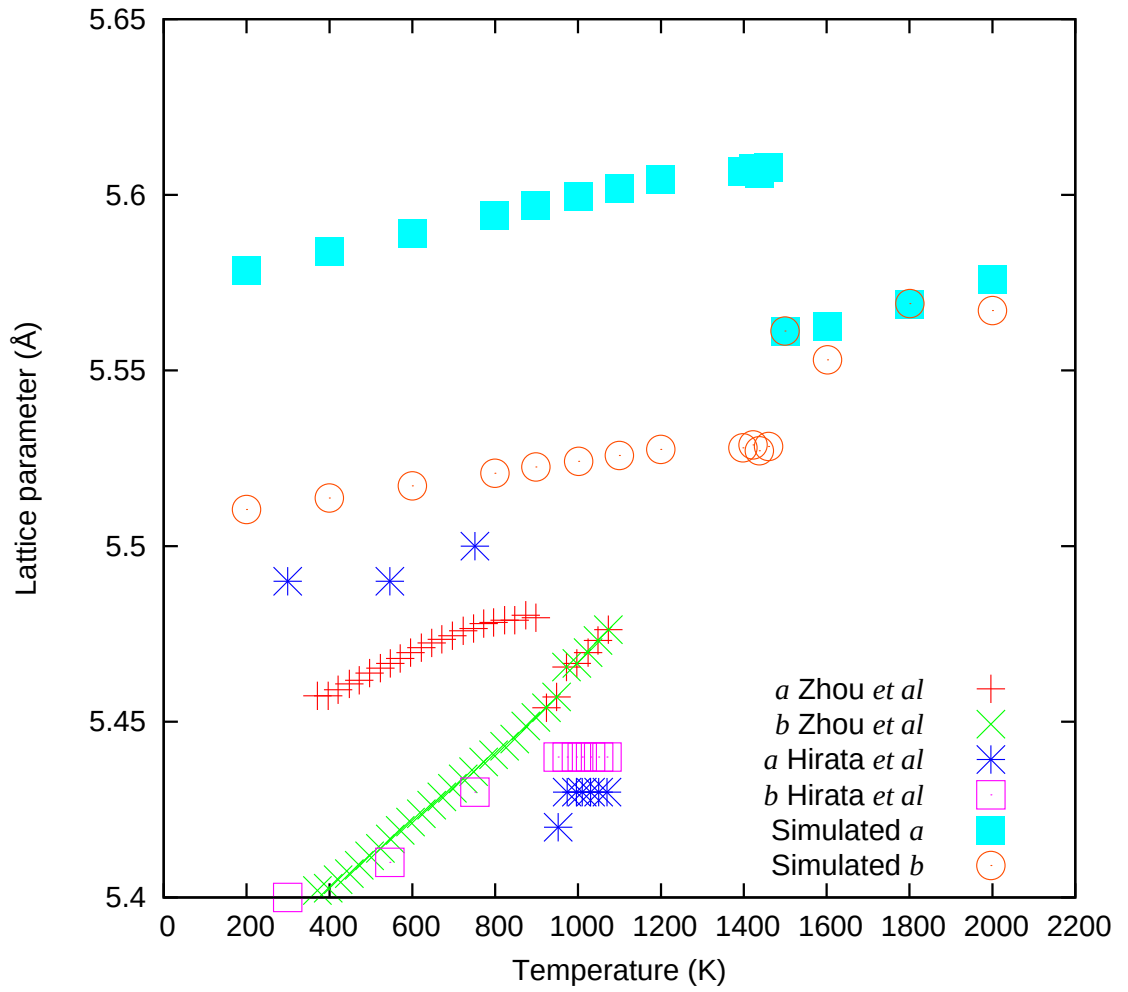


Figure 6.2: The comparison of lattice parameters a and b simulated using potential A and experimental results [13, 14].

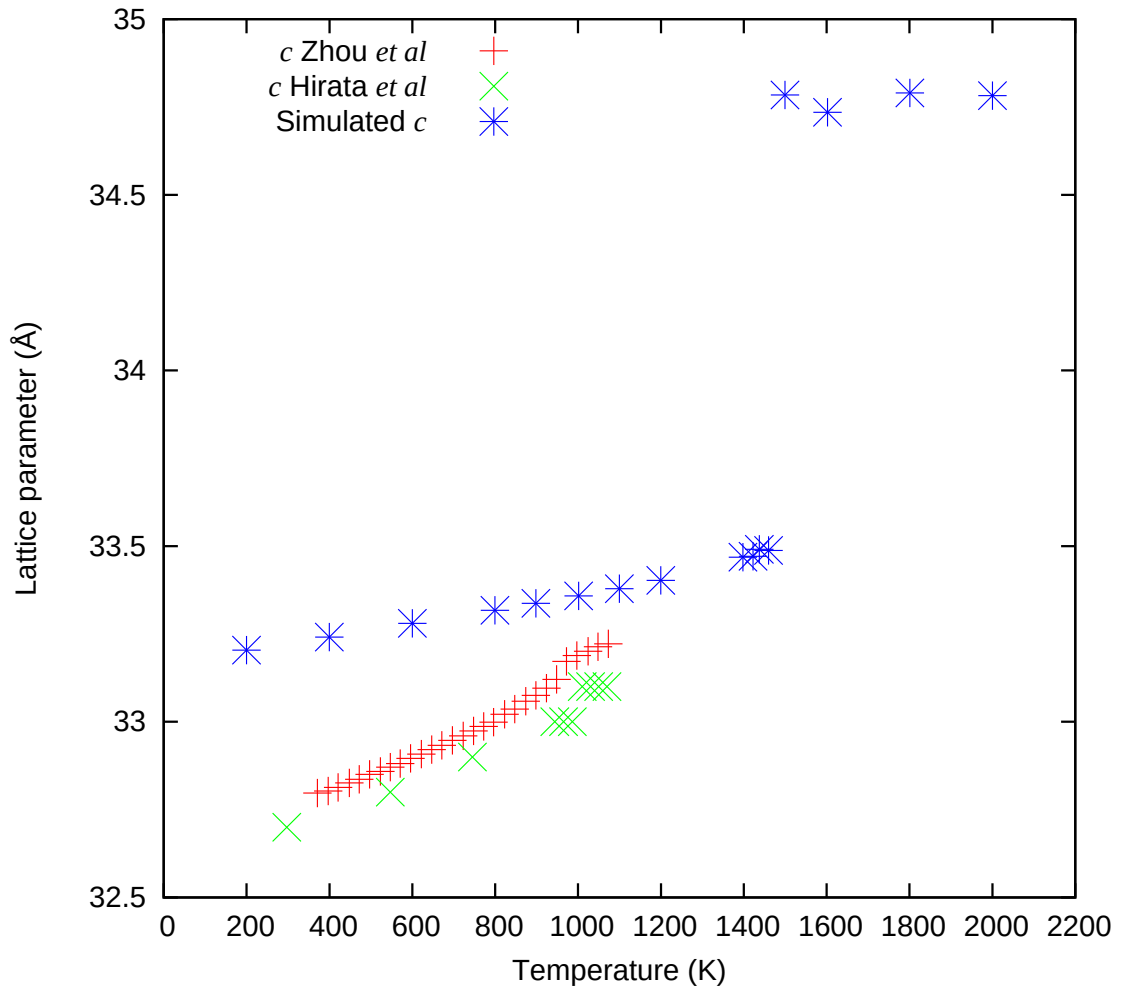


Figure 6.3: The comparison of lattice parameter c simulated using potential A and experimental results [13, 14].

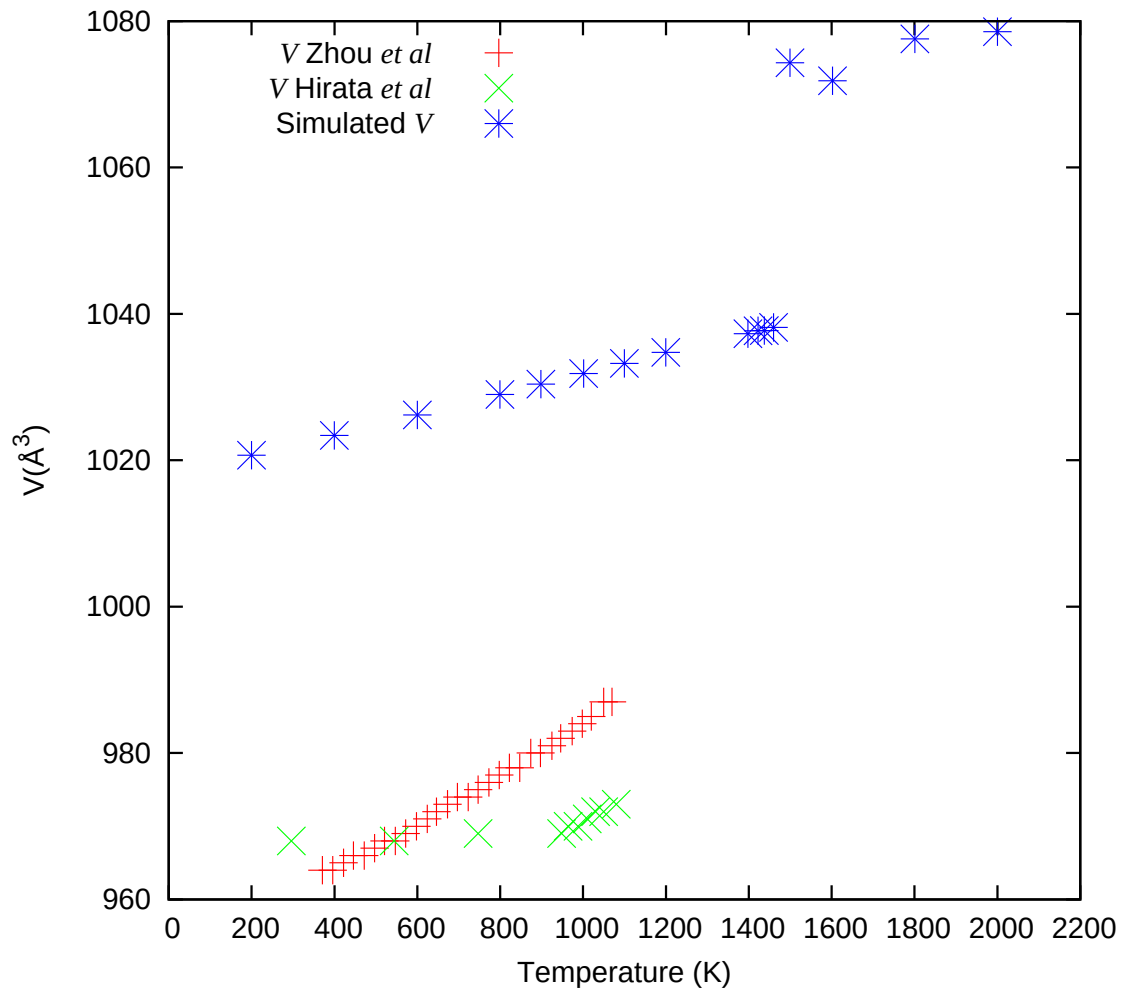


Figure 6.4: The comparison of volume simulated using potential A and experimental results [13, 14].

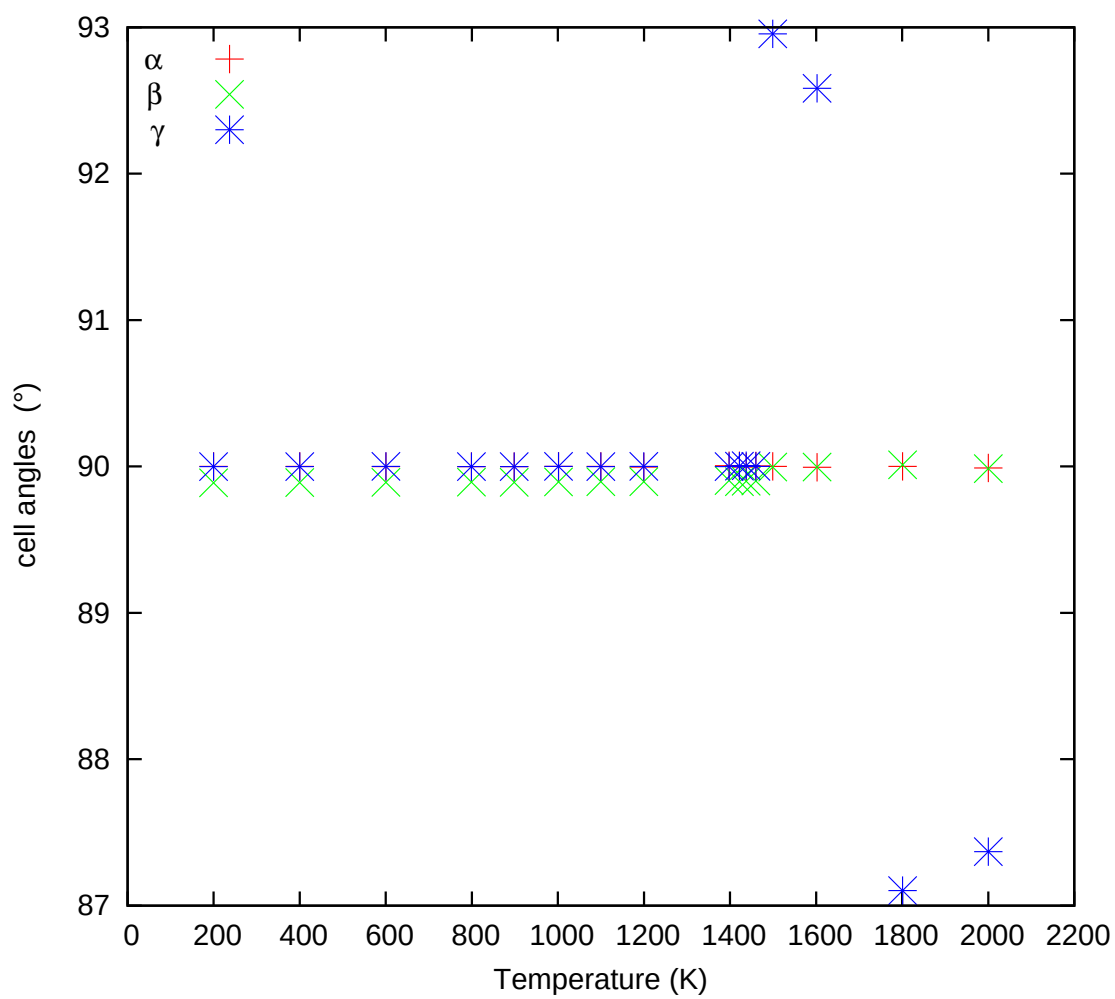


Figure 6.5: The cell angles simulated using potential A.

sured below the transition temperatures from Fig. 6.4 and are compared with experimental data in Table 6.1. The experimental thermal expansion coefficients display considerable variation. The MD simulation provided a theoretical volume thermal expansion coefficient, which was in the range of experimental thermal expansion, shown in Table 6.1.

Table 6.1: Comparison of the thermal expansion coefficient using potential A and experimental data.

	Zhou <i>et al.</i> [13]	Hirata <i>et al.</i> [14]	Potential A
α (K^{-1})	3.28×10^{-5}	3.00×10^{-6}	1.37×10^{-5}

The experimental crystal data were obtained from the same method, X-ray diffraction. Therefore, the possible contributions to the difference could be:

- Slight non-stoichiometric $Bi_4Ti_3O_{12}$ crystal formed in the solid state reaction or defect clusters formed during the heat treatment.
- The data of Hirata *et al.* [14] has only 3 points in the lower temperature region.

6.3.2 Bulk modulus and Young's modulus

The purpose of this section was to report on calculations of the Young's modulus as a function of temperature. Calculations of the Young's modulus in x , y and z is difficult to achieve using dynamical simulation at a finite temperature therefore it is necessary to calculate these values using lattice statics. To verify the feasibility of this approach, the bulk modulus of $Bi_4Ti_3O_{12}$ was calculated in both MD and lattice statics and then compared.

The method of calculating bulk modulus using MD simulation was the same as that employed for Li_2O . The $10 \times 10 \times 2$ supercell of $Bi_4Ti_3O_{12}$ was simulated under different pressures (0 Kbar, 5 Kbar, 10 Kbar and 25 kbar) at a series of temperatures

(400 K, 600 K, 800 K, 1000 K and 1200 K) . The pressures and temperatures were chosen to avoid the possible phase change resulting from increases of temperature and pressure, see Sec. 6.2.1 and Sec. 6.3.1. The bulk modulus obtained was calculated as a function of temperature.

The lattice statics method was carried out as follows: the lattice parameters and cell angles were obtained at finite temperatures from MD simulations. Then this cell information and experimental atomic coordinates were used as the starting configuration for static energy minimization under constant volume conditions. The assumption was that the modified cell information should include the temperature effect while the correct atomic configuration should be obtained by static energy relaxation. This should be valid if the atoms do not move significantly away from their original lattice site, that is no diffusion occurs. Statics simulations were performed using the GULP package. In the simulation, the static elastic constant matrix is computed from which bulk modulus and Young's modulus are obtained [153].

The bulk modulus from the MD and static methods are compared in Fig. 6.6. The difference of bulk modulus from two methods was around 1.5 % and the slopes were almost identical. This demonstrated that the lattice statics approach provided an adequate model of the bulk modulus, therefore it is expected that other elastic properties such as Young's modulus, which can also be computed from the elastic constant matrix will also be adequately reproduced.

The Young's moduli (E) using the static method were then calculated and plotted as a function of temperature in Fig. 6.7. This led to the following observations:

- E_x , E_y and E_z decreases linearly with increasing temperature.
- E_z decreases fastest with increasing temperature.

The atoms in a crystal may be regarded as connected by springs (bonds), the Young's modulus is a measure of the stiffness of the springs (bonds). Therefore,

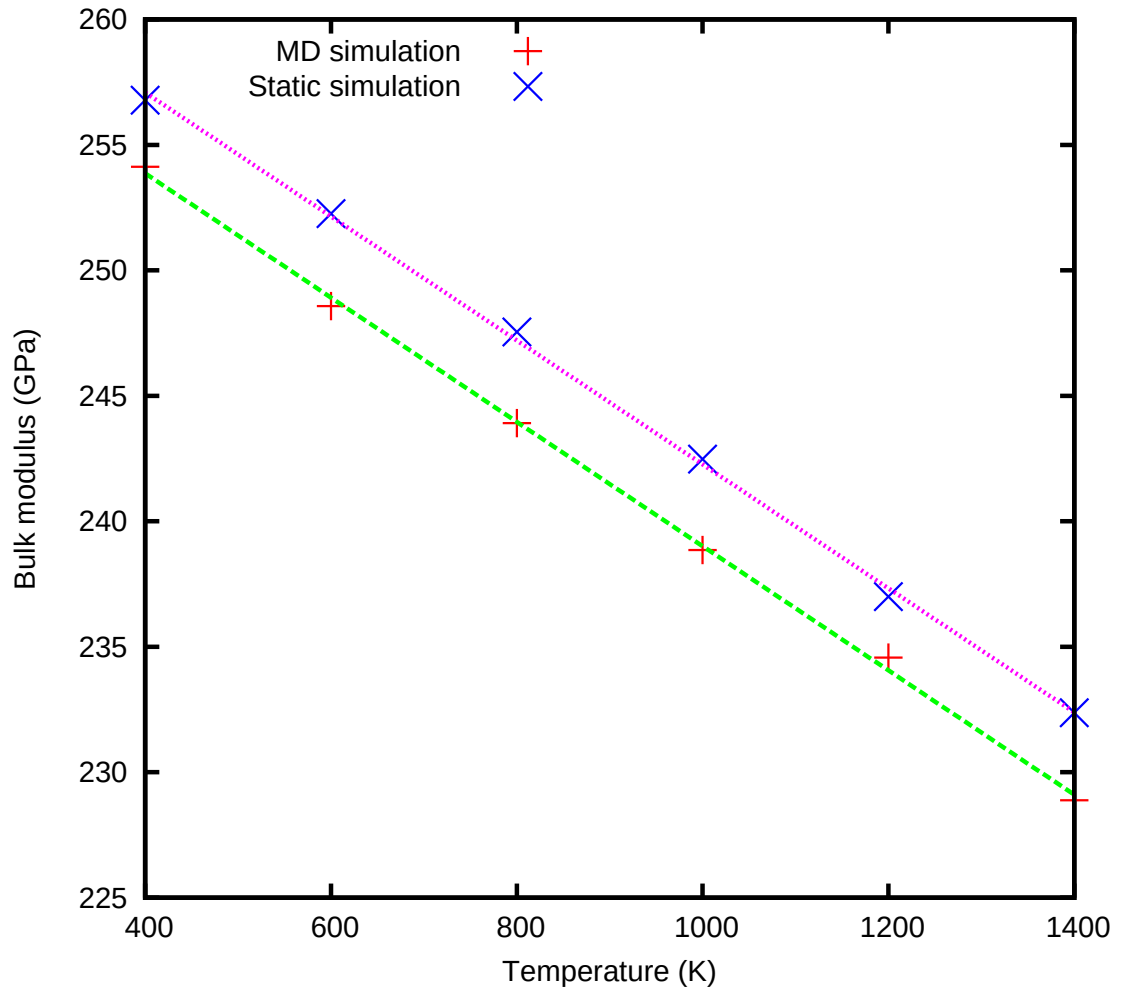


Figure 6.6: Comparison of bulk modulus using MD and lattice dynamic methods.

Fig. 6.7 suggests that the bonds in the x and y directions are stiffer than in the z direction. Furthermore, the bond stiffness decreases with temperature, however, the effect is relatively small. Temperature had a larger effect on bond stiffness in the z direction than that in the x and y directions.

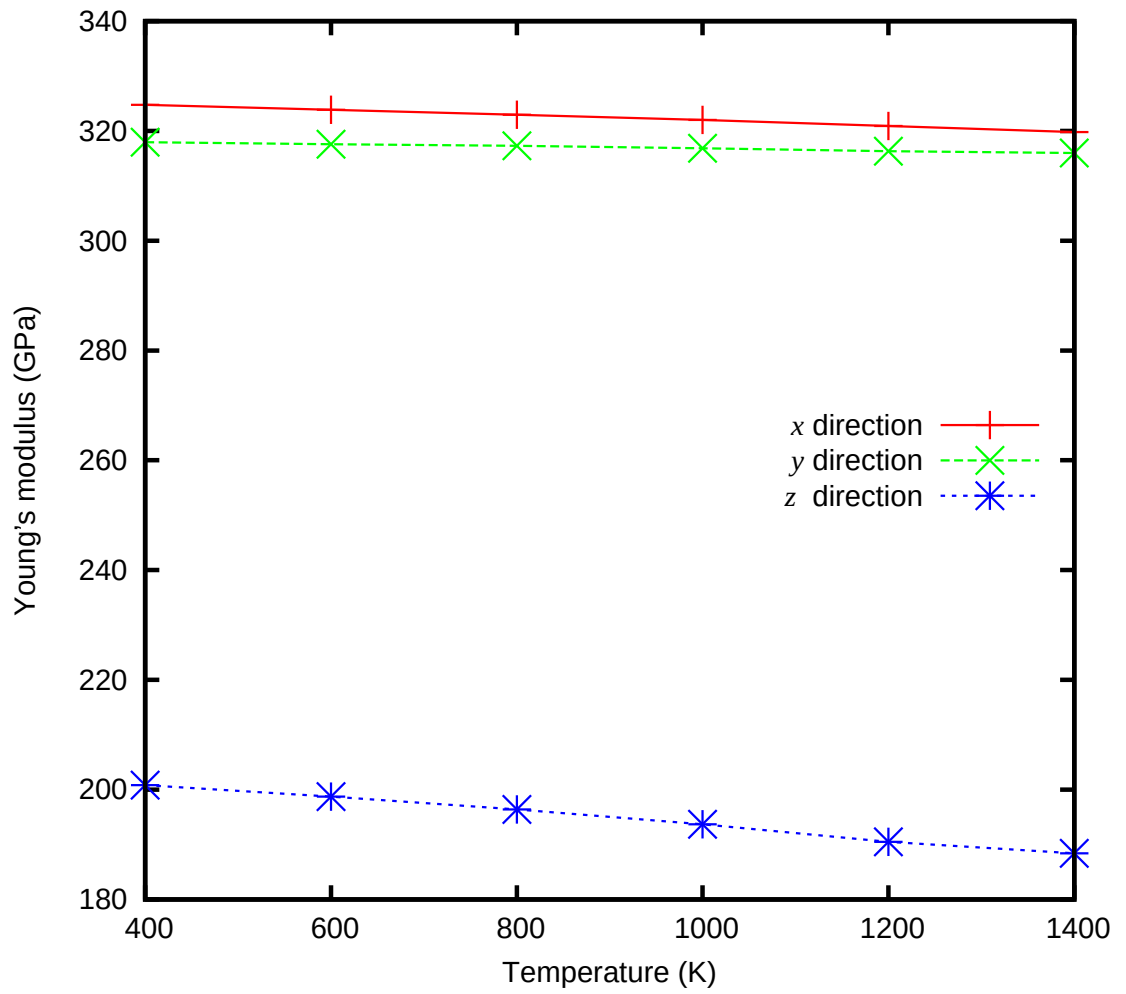


Figure 6.7: Comparison of Young's modulus in x , y and z direction using lattice dynamic method.

6.3.3 Velocity of sound

The velocities of sound in three orthogonal directions, v_x , v_y and v_z were estimated from Y_x , Y_y and Y_z using,

$$v = 0.87 \sqrt{\frac{E}{\rho}} \quad (6.1)$$

where, ρ is the density, 8041 kg/m³ for Bi₄Ti₃O₁₂. The value 0.87 is a error correction factor [35]. The sound velocities in three directions as a function of temperature were plotted in Fig. 6.8. Similar trends were observed in the velocity of sound as in Young's moduli. Specifically, the sound velocities did not decrease significantly over the temperature range considered. The averaged ratios of $\frac{v_x}{v_z}$ and $\frac{v_y}{v_z}$ were 1.28 and 1.27 respectively, again showing the anisotropy.

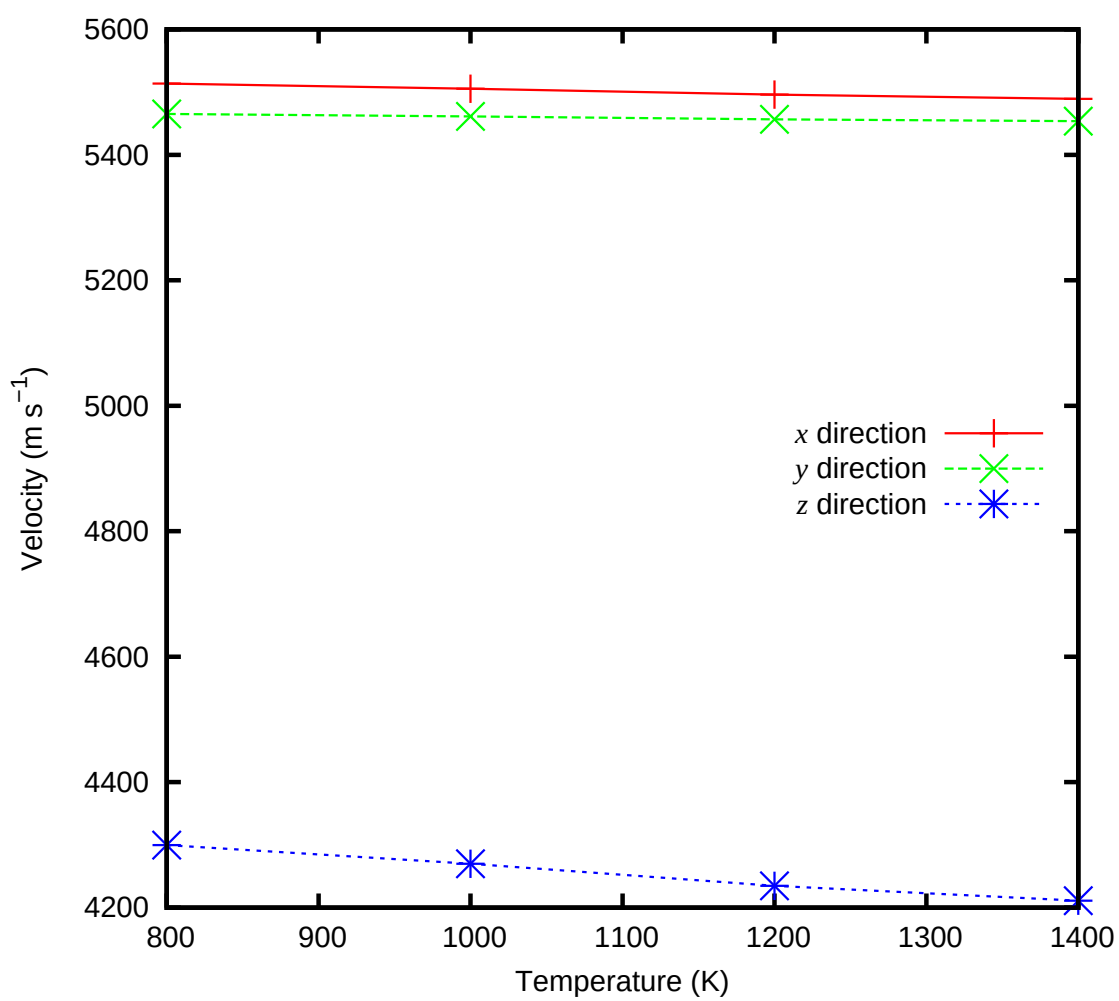


Figure 6.8: The calculated sound velocity in x , y and z directions.

6.3.4 Calculation of Debye temperature

In the Debye theory, the Debye temperature, T_D , is the highest temperature that can be achieved by a single normal mode wave, defined as

$$T_D = h \frac{v_D}{k_B} \quad (6.2)$$

where h is the Plank constant, 6.626×10^{-34} Js and v_D is the Debye frequency which can be written as [154]

$$v_D = \left(\frac{3N}{4\pi V} \right)^{1/3} v_e \quad (6.3)$$

where, $\frac{N}{V}$ is the number density of atoms. There are four formula units in the orthorhombic structure unit cell, therefore the value of $\frac{N}{V}$ is 76 atoms/unit cell volume. $\frac{v_x+v_y+v_z}{3}$ is used as an approximation of effective sound velocity v_e . Therefore, the Debye temperature of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ as a function of temperature can be determined and is plotted in Fig. 6.9.

The Debye temperature decreased linearly with increasing temperature, however, the change is small across the temperature range. Roughly speaking, the Debye temperature can be approximated to be 635 K for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Unfortunately, there are no experimental values with which to compare.

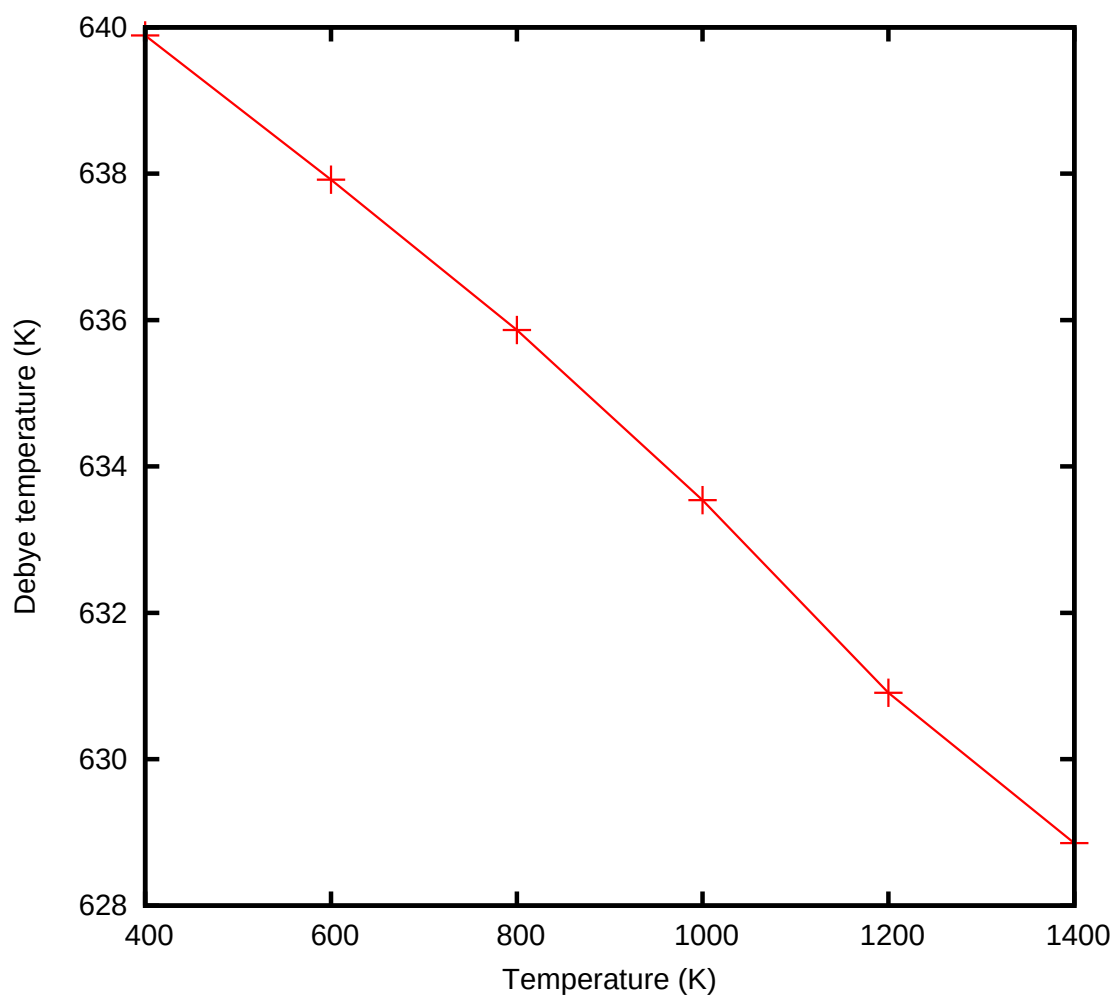


Figure 6.9: The predicted Debye temperature as a function of temperature.

6.3.5 Minimum and anisotropic thermal conductivity

The thermal conductivities of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ in the x , y and z directions were calculated using the velocity exchange method, as described in Sec 2.5.

In order to apply the finite size correction discussed in Chapter 4, thermal conductivities are measured in a number of different sized supercells. The dimensions of the supercells that were longer in x as follows: $10 \times 6 \times 1$ (4560 atoms), $20 \times 6 \times 1$ (9120 atoms), $30 \times 6 \times 1$ (13680 atoms), $35 \times 6 \times 1$ (15960 atoms), $40 \times 6 \times 1$ (18240 atoms). The supercells with long y had the following dimensions : $6 \times 10 \times 1$ (4560 atoms), $6 \times 20 \times 1$ (9120 atom), $6 \times 30 \times 1$ (13680 atoms), $6 \times 35 \times 1$ (15960 atoms), $6 \times 40 \times 1$ (18240 atoms). Those with long z were: $4 \times 4 \times 3$ (3648 atoms), $4 \times 4 \times 4$ (4864 atoms), $4 \times 4 \times 5$ (6080 atoms), $4 \times 4 \times 6$ (7296 atoms), $4 \times 4 \times 7$ (8512 atoms), $4 \times 4 \times 8$ (9728 atoms). Each system was equilibrated under NPT conditions for 15 ps and then NVT conditions for a further 5 ps at a series of temperatures. For a period of 100 ps, temperature profiles along x , y and z directions were induced as discussed in Sec 2.5. The profiles were obtained from many different individual layer temperatures using Eq. 2.26.

The temperature profiles along the x , y and z directions at 773 K for $10 \times 10 \times 1$ supercell are plotted in Fig. 6.10. The temperature profiles along the x and y directions are predicted to be linear. However, the plot in the z direction shows a series of jumps in temperature as a function of the fractional coordinate. This is caused by the alternation of perovskite and Bi_2O_2 like layers, thereby showing the scattering of phonons by such a layered structure.

The phonon-phonon scattering effects (Sec 2.6.2) cannot be separated and identified as for Li_2O due to the lack of an experimental bulk modulus of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ as a function of temperature.

The thermal conductivities in the three directions, however, were extrapolated to an infinite length scale, using the process detailed in Sec 2.6.1. The experimental

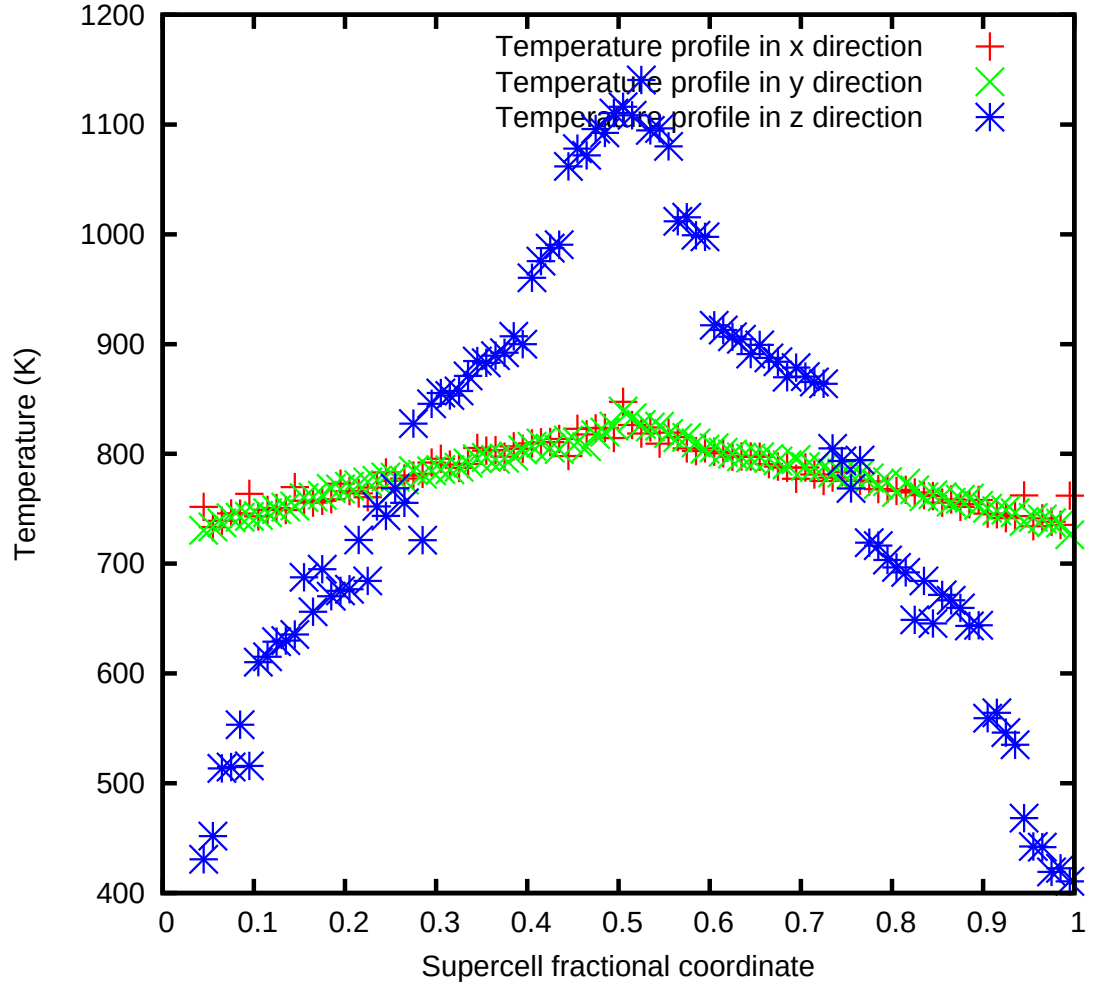


Figure 6.10: The temperature profiles along the x direction of supercell $10 \times 6 \times 1$, along the y direction of supercell $6 \times 10 \times 1$ and along the z direction of supercell $4 \times 4 \times 3$ at 773 K.

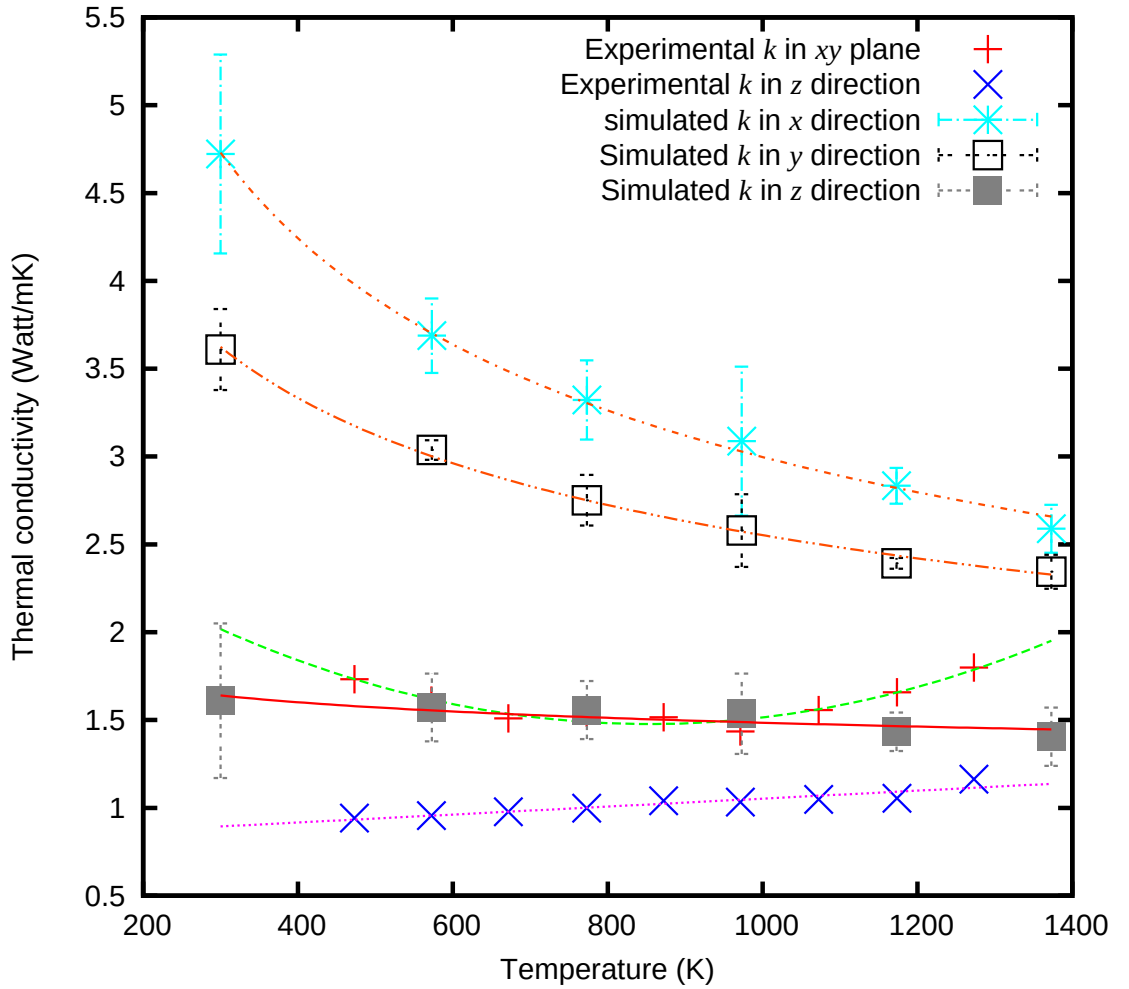


Figure 6.11: The experimental thermal conductivity in the xy plane and the z direction of polycrystalline $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ compared with the simulated thermal conductivity in the x , y and z directions of the infinite length cell extrapolations. The lines were fitted to $k \propto T^n$.

thermal conductivities in the xy plane and the z direction of polycrystalline are compared with the simulated thermal conductivities in all three directions for an infinite length single crystal as a function of temperature in Fig. 6.11.

The simulated values largely overestimates conductivity in comparison with experimental values, the overestimate was particularly large in the x & y directions and closer to experiment in z direction. There are several possible contributions to the error though. i) A formal charge model was used in the simulations. This model replicated a stronger electrical force and therefore overestimates the strength of bonds between oppositely charged species, leading to a larger ther-

mal conductivity. ii) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is spontaneously polarized (ferroelectric) in the orthorhombic/monoclinic structure, there are therefore relatively strong dipoles present in the structure. The removal of shells in MD simulations may have removed the ability of the model to describe such effects iii) The simulated $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ effectively describes a large single crystal. Whilst the experimental samples are a polycrystalline, with a very small grain size (typically 30nm). Consequently, there are many grain boundaries diffracting the phonons and thus reducing the thermal conductivities. This reduction is more prominent in x and y direction because of the concept of minimum thermal conductivity, which will be discussed later.

From Fig. 6.11, some observations are as follows:

- The simulated k_x , k_y and k_z all decrease with increasing temperature.
- The rate of decrease for k_x and k_y are larger in the low temperature than those at high temperatures.
- The rate of decrease for k_z is small across the temperature range. It can be regarded as roughly constant, in agreement with the experimental observations of Shen *et al.* [152].
- The simulated thermal conductivity suggested that the assumption of $k_x = k_y$ is not perfect in the low temperature range, with nearly a 40% difference. In fact, k_x always exhibits the highest thermal conductivity.
- Thermal conductivities k_x and k_y are significantly larger than k_z . The average $\frac{k_x}{k_z}$ and $\frac{k_y}{k_z}$ were 2.18 and 1.8, which is in general agreement with the experimental value of $\frac{k_{xy}}{k_z}$, around 2.0 [152].

Simulated k_x , k_y and k_z values all decreased with increasing temperature because the anharmonic phonon interactions increased with temperature. The phonons collide more frequently and the mean free path is therefore reduced. The Umklapp processes are the dominant phonon process in high temperature.

The thermal conductivity k_z in general is independent of temperature. This is because when the mean free path is reduced to be comparable with the mean interatomic spacing, the thermal conductivity reaches a minimum value [155]. In order to quantitatively verify this concept in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, the mean free paths, l , in all three directions were determined.

The thermal conductivity in terms of specific heat, velocity of sound and mean free path of the phonon is given by,

$$k = \frac{1}{3}Cvl \quad (6.4)$$

In the high temperature region, much larger than the Debye temperature 635 K, the specific heat C has a classical limit $3k_B/V_u$ per atom where V_u is the unit cell volume [34, 156]. The equation is then rewritten as,

$$k = 76K_Bvl/V_u \quad (6.5)$$

where v and k in different directions have been calculated from static and MD simulation and the other terms are constants.

The mean free paths l can be obtained and are plotted as a function of temperature in Fig. 6.12. l_x and l_y are not smaller than the mean atomic spacing (4.6 Å [152]) and therefore decreased with increasing temperature. This explained why k_x and k_y have not reached a minimum, as suggested in Fig. 6.11. Comparatively, l_z is always about 3.5 Å, much smaller than the average atomic spacing. Therefore, the thermal conductivity appeared to be temperature independent.

Another interesting observation is the anisotropic behaviour of the thermal conductivity in different directions. From the MD simulations, the average $\frac{k_x}{k_z}$ and $\frac{k_y}{k_z}$ values are 2.18 and 1.80. From the estimation of Young's modulus, $\frac{v_x}{v_z}$ and $\frac{v_y}{v_z}$ are calculated to be 1.28 and 1.27. This clearly suggests that the differences in

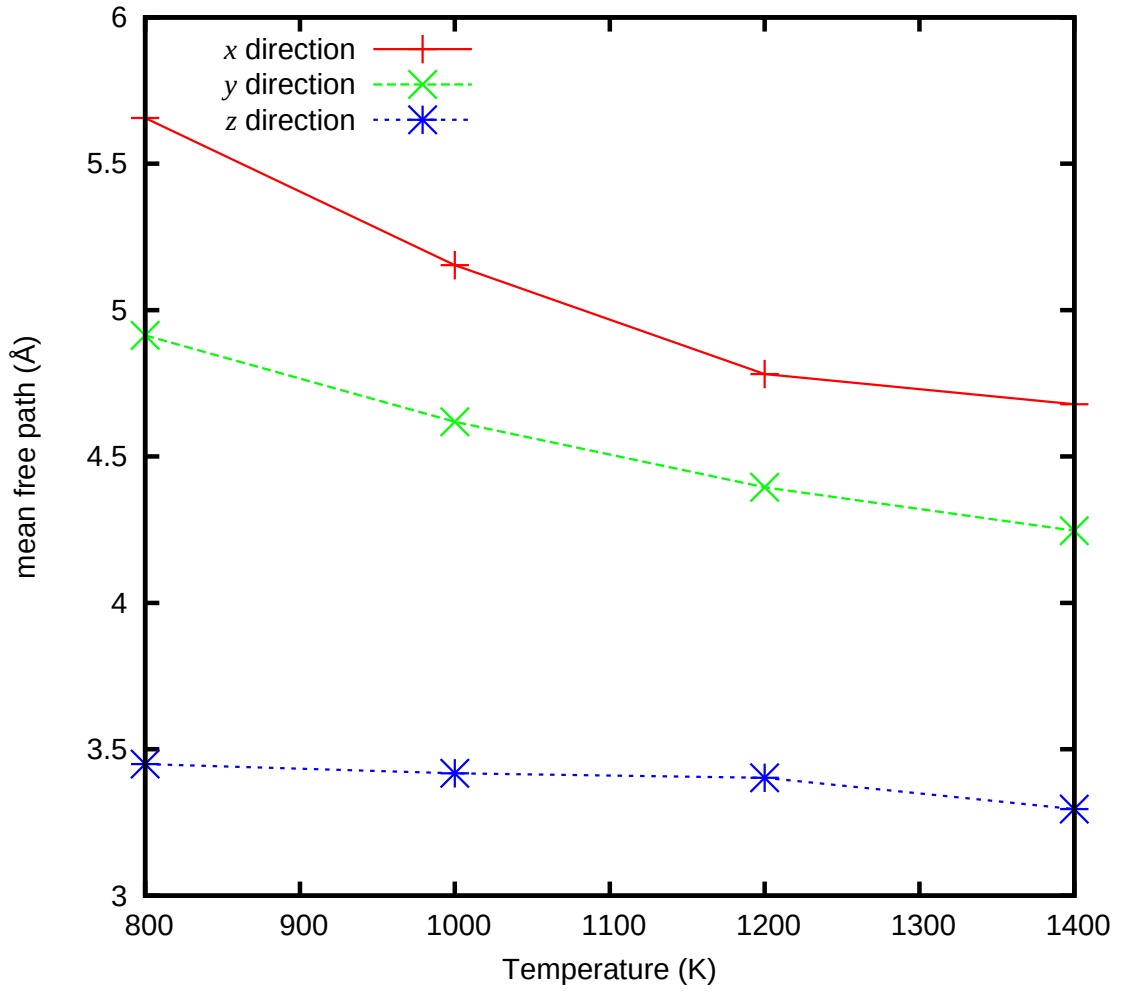


Figure 6.12: The estimated mean free path in x , y and z directions.

bond stiffness in x , y and z direction as only account for a small contribution of the anisotropic thermal conductivity. The major contributor are largely different mean free paths l in the x , y and z directions, as shown in Fig. 6.12. The $\frac{l_x}{l_z}$ and $\frac{l_y}{l_z}$ values are 1.62 and 1.42, account for the major portion of the difference in the thermal conductivity. The fact that l_z is much smaller than l_x and l_y is because of the presence of the layered structure in the z direction. The $(\text{Bi}_2\text{Ti}_3\text{O}_2)^{2-}$ layer and $(\text{Bi}_2\text{O}_2)^{2+}$ layer have largely different densities. This is effectively analogous to two different mediums. Some phonons traveled in the dilute medium $(\text{Bi}_2\text{Ti}_3\text{O}_2)^{2-}$ are reflected or refracted by the dense medium $(\text{Bi}_2\text{O}_2)^{2+}$. The rate of phonon collision will increase, hence reducing the mean free path l , decreasing the thermal conductivity.

6.4 Conclusion

Atomistic simulation have been used to investigate the anisotropic thermal conductivities in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The results showed that the thermal conductivity in the z direction is substantially lower than that in x and y directions, in agreement with previous experimental observation. The absolute values for the thermal conductivities were however, predicted to be larger than the experimental studies. This was at least partly due to the experiments being performed on polycrystalline samples where the grain boundaries diffracted phonons. It may also be due to the removal of shells and the formal charge model used in MD simulations. Effectively this reduced the freedom of ions and increased the strength of bonding.

The MD simulation predicted an almost temperature independent thermal conductivity in z direction. This was explained by the minimum thermal conductivity concept, where the calculated values of l_z is much smaller than the mean atomic spacing. From the simulation, the minimum thermal conductivity in x and y directions should be anticipated at higher temperature when l_x and l_y were further decreased to average interatomic spacing.

The average values of $\frac{v_x}{v_z}$ and $\frac{v_y}{v_z}$ were 1.28 and 1.27, estimated from Young's modulus using static simulations. This was insufficient to fully account for the large anisotropic thermal conductivity ratios $\frac{k_x}{k_z}$ and $\frac{k_y}{k_z}$, 2.0 and 1.6 respectively. The major contribution was due to the large differences in l . l was reduced because of the increased phonon collision rate resulting from the reflection and refraction by the dense $(\text{Bi}_2\text{O}_2)^{2+}$ layer.

The Debye temperature decreased as a function of temperature, however the rate of change with temperature is considered small. It can then be regarded as a material related constant around of 635 K.

Chapter 7

Summary

Atomic scale computer simulation has been used to predict the structural and thermal properties of the oxides Li_2O and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Both static techniques (where equilibrium atoms positions are predicted) and dynamic simulation (that solve Newton's equations of motion) were employed. The dynamic simulations were based on classical pair potential descriptions of the forces between atoms. Some of the static simulations also employed quantum mechanical prediction of the inter-ionic forces.

A number of different pair potentials for Li_2O were evaluated by comparing with experimental properties such as lattice parameters, elastic constants, thermal expansion and bulk modulus. As the thermal conductivity is strongly related to the diffusivity, the Li^+ ion superionic transition temperature, the activation energy and the diffusion coefficient were also computed and compared with experimental data. Of the potentials considered, the potential model of Chroneos *et al.* [1] was particularly good at replicating thermal expansion and bulk modulus as a function of temperature, which was associated with anharmonic phonon interactions. This potential was also able to replicate Li^+ ion diffusivity and its related properties. Therefore, this potential model is considered to be the most reliable and was employed in further simulation of Li_2O .

The superionic diffusion of Li^+ was a complicated process. The Li^+ density contour plot Fig. 3.9-3.10 showed that Li^+ could diffuse via the cubo-octahedral interstitial site or directly between two adjacent sites. Further static defect calculations showed that the lithium Frenkel reaction was the most energetically favourable disorder process.

In chapter 4, the thermal conductivity of Li_2O was investigated using molecular dynamics. The simulated thermal conductivity was systematically higher than available experimental data. The possible reason were that overestimation of forces between ions due to the full charge model, and phonon diffraction due to grain boundaries in the experimental polycrystalline samples. Two corrections were applied to the MD data. The first aimed to reduce the limitation of the small cell sizes used in MD simulations, by determining the thermal conductivity as a function of cell size and then extrapolating to an infinite cell size. The second correction used experimental data such as thermal expansion coefficient and bulk modulus and used this to correct for phonon anharmonicity. As application of these corrections is arduous and does not lead to a significant change in thermal conductivity relative to the uncorrected data (largest super cell), these corrections were not applied in further simulations.

Simulations were performed on the two different Li_2O systems, one in which all Li ions in the system are assigned the same mass and another where the desired isotopic ratio is achieved by randomly allocating the appropriate ratio of ^6Li and ^7Li ions to the cation sublattice. Clearly, the first case is not realistic, however the simulations offer the ability to estimate the magnitude of the isotope effect. The results for the system in which all Li ions were assigned the same mass shows that thermal conductivity decreases linearly as the mass increases from ^6Li to ^7Li . However when ^6Li and ^7Li are distributed randomly on the 8c sublattice, the thermal conductivity at low temperature displays a substantial negative deviation from this linear relationship. The reason is that the randomly distributed point masses create different vibrational modes that interact to reduce

thermal conductivity. At higher temperatures, the isotope effect is reduced and disappears almost completely above the superionic transition temperature. The reason is that the Li ions are able to move so that each lattice site move almost represents a time averaged mass rather than a distinct ^6Li or ^7Li site. These results show that at the operating temperature of the breeder blanket of a fusion reactor, the isotope effect will not have a deleterious effect on the efficiency of the reactor. Furthermore, in addition to being beneficial from a tritium breeding perspective, an increase in ^6Li content may make heat transfer to the coolant more effective and increase the efficiency of the reactor.

Since there was no specially derived pair potential for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, the potential sets adopted from related oxides were validated with high temperature and low temperature structural information (i.e. lattice parameters, angles and space groups). The potential set of Islam *et al.* and Snedden *et al.* [2, 3] were able to replicate the correct crystal structure at low temperature. Pair potential and first principles simulations both predicted that the monoclinic structure was the global energy minimum state, while the orthorhombic structure was a local energy minimum state.

First principles simulations were used to determine atomisation energies of $\text{Bi}_{(\text{s})}$, $\text{Ti}_{(\text{s})}$, $\text{O}_{2(\text{g})}$, TiO_2 , Bi_2O_3 and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The available energies were found to be in excellent agreement with values from the experimental literature. These values were then used to determine the formation energy of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ from Ti_2O and Bi_2O_3 . The reaction was found to be exothermic with a formation energy of -1.33 eV. No comparable experimental data could be found so this data represents the first attempt to calculate this value.

Formation energies and defect volumes associated with the introduction of vacancies into monoclinic $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ were investigated. Some vacancy formation energies were symmetrically identical because they were symmetrically equivalent in the related orthorhombic structure. The O3 vacancy in the $(\text{Bi}_2\text{O}_2)^{2+}$ layer

had the lowest defect formation energy. The less energetically stable oxygen vacancies were in the TiO_6 octahedron near the $(\text{Bi}_2\text{O}_2)^{2+}$ layer. The crystal volume generally expanded when an ion was removed due to like charge repulsion. The exception to this was for Bi in the $(\text{Bi}_2\text{O}_2)^{2+}$ layer, because removing this type of Bi changed the 3D TiO_6 octahedral to a flat 2D base consisting of 4 oxygens.

MD simulations showed the potential without shells was only able to correctly replicate the structure below the transition temperature. The potential used overestimated thermal conductivity in comparison to experiment. This was partly because simulated single crystal data was effectively compared with small grained polycrystalline experimental data. Irrespective of this the potential was able to predict the minimum thermal conductivity in the z direction and the anisotropic thermal conductivity of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. That the mean free path was comparable to the interatomic spacing in the z direction but not in the x and y directions explained the minimum thermal conductivity. The velocity of sound in different directions were estimated from Young's moduli. The sound velocity (a measure of stiffness of the bonds) in different directions was not the major reason for the large anisotropy in thermal conductivity. The major contribution was the mean free path was significantly reduced in the z direction because of the refraction and reflection by the different density $(\text{Bi}_2\text{Ti}_3\text{O}_2)^{2-}$ and $(\text{Bi}_2\text{O}_2)^{2+}$ layers. The Debye temperature decreased slowly with increasing temperature, which can be regarded as a material related constant.

In conclusion, the combination of static and dynamic simulations have resulted in an atomic scale understanding of the thermal properties of these fascinating materials. Both structural anisotropy and distributions of defects have contributed to the different behaviours predicted, which can provide a better understanding and interpretation of the available experimental data and data that can be generated in the future.

Chapter 8

Further Work

8.1 Li_2O

Although the current potential model can replicate the general trend of elastic modulus, it over estimates the value of elastic constants and does not correctly replicate C_{12} . This is probably due to the use of a full charge model (strong electrical force) and the centrosymmetric nature of a purely pair wise interactions. First principles simulation can eliminate these errors by accurately describing the electronic structure. However, these elastic properties are closely related to thermal conductivity, which currently is impossible to measure using first principles simulations due to the large number of atoms required for MD. It would therefore be desirable to derive a new set of interatomic potentials based on a partial ionic charge to avoid the over estimation of the coulombic interaction between ions in Li_2O . The introduction of many body potentials to ensure it is possible for C_{12} to be independent of C_{44} should also be considered. The use of many body potentials or a breathing shell model [157] would be expected to allow the necessary Cauchy violation.

Increasing the thermal conductivity of Li_2O is advantageous for its application as a breeder material in future nuclear fusion reactors. Radiation damage, grain

boundaries and dislocations may influence the thermal conductivity. The degree of influence of these defects should be predicted and investigated using MD simulations.

8.2 $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

A partial charge model with breathing shells [157] should also be specially derived for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ to replicate the monoclinic-orthorhombic-tetragonal phase transition and more accurate thermal properties using MD simulation. The MD simulations presented here omit the shell model. This can be a particular problem for a material that displays spontaneous polarisation, such as $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Therefore, it would be profitable to repeat these simulations with dipole polarisability. The shells can be optimized each time step, the adiabatic method [158] or by assigning a fictitious mass to the shell, analogous to the Car-Parrinello method [159].

The calculated static Young's modulus in the thesis is only an estimation of the velocity of sound in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. A more accurate velocity can be calculated using the longitudinal and transverse wave velocities as $v = 3^{1/3}(\frac{1}{v_p^3} + \frac{2}{v_s^3})^{-1/3}$ [35]. Values of v_p and v_s should be obtained using the full elastic constant matrix at a finite temperature. In MD simulations, the full elastic constant matrix can be obtained by measuring the average stress tensor when a cell equilibrates after a carefully chosen finite deformation to balance statistical and systematic errors under NVT conditions.

Below the Curie temperature, structural disorder was observed in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ such as the tilt of TiO_6 and Bi displacement. It is interesting to investigate the influence of these disorder processes on sound velocity, effective mean free path and thermal conductivity, particularly in the x and y directions (the z direction has already reached minimum thermal conductivity at a relatively low temperature). From first principles simulation, the phonon dispersion curve and density of states for

the monoclinic and tetragonal structure can be obtained to assist the analysis.

In reality, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is a polycrystalline material, consisting of small sized grains. In addition, the Bi ion may be lost during the solid state reaction leading to considerable non-stoichiometry. It may be necessary to predict how the difference in grain size, number of grain boundaries and the Bi non-stoichiometry affects the thermal conductivity in the x and y directions as a function of temperature.

To gain a better understanding of the thermal conductivity mechanism of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, Sound velocity, effective mean free path and thermal conductivity of the individual $(\text{Bi}_2\text{O}_2)^{2+}$ and $(\text{Bi}_2\text{Ti}_3\text{O}_2)^{2-}$ layers should be calculated in the x , y and z directions. Cation and anion disorder can be introduced by doping. It is interesting to establish the effect of the location of doping (in $(\text{Bi}_2\text{O}_2)^{2+}$ or $(\text{Bi}_2\text{Ti}_3\text{O}_2)^{2-}$ layer) and the species of doping, on the thermal conductivity.

The MD techniques for measuring thermal conductivity can be used to investigate more structures in the Aurivillius family, and other complicated perovskite layer like structures such as the Ruddlesden-Popper series of $(\text{Sr}_{n+1}\text{Sn}_n\text{O}_{3n+1})$ structures.

In the current research, a non-equilibrium molecular dynamics (NEMD) method was employed to calculate the thermal conductivity. In future, equilibrium molecular dynamics (EMD) such as Green-Kubo method [160, 161] may be used. It may yield a more accurate thermal conductivity in the layered z direction where the NEMD did not produce a perfect linear temperature gradient, see Fig. 6.10.

The polarization has been investigated in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ recently by Roy *et al.* using first principles simulations [162]. The effect on polarization doping the A site and B site can be investigated as this is important for random non volatile random access memory. For instance, the A site can be doped with elements such as Nd, Pr, Sm, Gd, Yb and the B site can be doped with higher valence cations such as V and finally co-dope ion onto both A & B sites. This should provide direct evidence for how the defects hinder the polarization switching behaviour.

Only neutral vacancy defects were considered for Bi, Ti and O. However, in a real crystal, the defect charge will depend on the Fermi level. Therefore, it would be necessary to investigate the defect formation energies for each unique lattice site for all the available charge states (i.e. 0, +1, +2, +3 +4 for titanium). Clearly, the number of unique lattice positions and available charge states in the monoclinic structure means this would be computationally intensive. However, it would be interesting to establish some relationship such as defect formation energy as a function of charge states. To minimize the self-interaction of charged defects, large super cell size will be beneficial even if this means a very large amount of computer resources would be required. There are a number of corrections that apply to charged defects in DFT simulations and these should be investigated [163].

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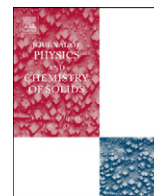
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Appendix



General relationships for isovalent cation substitution into oxides with the rocksalt structure

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ABSTRACT

Isovalent cation substitution into rocksalt oxides, MO, has been investigated using atomistic simulation. A strain related parameter, ε , is established that relates the size of a substitutional cation to the host lattice ion for which it has been substituted. This has allowed us to identify relationships between solution energy, defect volume and a strain parameter, which are general for any rocksalt oxide host lattice and as such are predictive for any combination of a divalent cation and rocksalt host lattice.

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1. Introduction

In a perfect crystal, each ion occupies a defined symmetry site within a unit cell. Substitutional disorder occurs when a lattice ion is replaced by an ion of a different type [1]. An impurity ion can occupy lattice sites with little disturbance to the overall crystal if the substitutional ion is of similar size and the same charge as the ion it replaces. Differences in size between the host ion and the substitutional ion will induce stress in the lattice; in response the ions of the crystal adjust their positions until each ion experiences zero (time averaged) force.

One measure of the relative size of the host and substitutional ion, ε , is described by

$$\varepsilon = \frac{a_{\text{sub}} - a_{\text{host}}}{a_{\text{host}}} \quad (1)$$

where a_{host} and a_{sub} are lattice parameters of the host and substituent oxide lattices so that ε might be described as a lattice “strain” term. The reason for using lattice parameters and their differences as a guide to cation size changes is that it avoids problems associated with defining an artificial measure such as cation radius [2,3]. Consequently, here, when we discuss cation size difference, it implicitly refers to differences in lattice parameter of the rocksalt structures to which the different cations give rise.

We use atomistic simulation, both a parameterised empirical model and a density functional theory (DFT) quantum mechanical approach, to establish relationships between: (i) ε and the internal energy of solution and (ii) ε and the volume change resulting from

the substitution of cations into simple binary, MO, metal oxides. A particular aim is to determine if such relationships can be identified that are independent of the host oxide.

The cations selected for this study are; Ba^{2+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Mg^{2+} , Mn^{2+} and Sr^{2+} , the oxides of which all exhibit the rocksalt structure. A rocksalt unit cell is assigned the $Fm\bar{3}m$ space group where the cation and oxygen sublattices form interpenetrating face centred cubic arrays, such that the cations and anions are octahedrally coordinated. The cations are assigned to the $4a$ Wyckoff sites and the oxygen anions are assigned to the $4b$ sites [4].

Substitution of a divalent cation, S, into a rocksalt oxide, MO, is an isovalent process (i.e. the charge of the substitutional cation and the host cation it replaces are identical) and is illustrated (in Kröger–Vink notation [5])



where $\text{M}_{\text{M}}^{\times}$ represents an M^{2+} cation on its host lattice site, SO contains the substitutional cation in an oxide and $\text{S}_{\text{M}}^{\times}$ shows the substitutional cation, now residing on a host cation lattice site. As this is an isovalent process, there are no charge compensating defects to consider.

2. Methodologies

2.1. Empirical pair potentials

The empirical simulations consider a lattice to be an array of point charges that interact through a combination of a Coulombic contribution and an isotropic short range Buckingham potential [6]. This model is then parameterised by deriving A_{ij} , ρ_{ij} and C_{ij} specific to ion pairs i and j , in order to reproduce experimentally

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observable properties such as the lattice parameter. The total interaction energy of the system can be determined by summing the interactions of each atom with the others in the system, as described in Eq. (3), where $E(r_{ij})$ is the lattice energy:

$$E(r_{ij}) = \sum_{j>n} \sum_{i=1}^n \left[\frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} + A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \right] \quad (3)$$

The pair potential parameters used here are taken from [7] except for the $\text{Mn}^{2+}-\text{O}^{2-}$ potential, which was derived specifically for this work, giving $A_{ij}=697.84$ eV, $\rho_{ij}=0.3252$ Å and $C_{ij}=0.0$ eV Å⁶. This $\text{Mn}^{2+}-\text{O}^{2-}$ potential replicates the MnO lattice parameter to within 0.4%.

Due to the relatively high polarisability of O^{2-} , the shell model of Dick and Overhauser [8] was applied to describe this polarisability. In this model the core was assigned a charge of $0.04|e|$ and the shell $-2.04|e|$ thereby ensuring the overall charge on the ion was equal to the full valence charge. The core and shell interact through a harmonic force constant of $k = 6.3$ eV Å⁻².

Two different methods were adopted for the calculation of the internal energy of solution. In the first instance, the substitutional ion was treated as an isolated defect, therefore, the Mott–Littleton [9] methodology was employed. This approach sees the lattice divided into three concentric regions centred on the defect. Interactions in the innermost region I are treated explicitly and relaxed under energy minimisation. Ions in region IIa are relaxed in one step via the Mott–Littleton approximation, and the interactions between this and the inner region are then determined explicitly. Finally, the outermost region IIb is represented as an array of point charges and is used to generate the Madelung field.

The volume change (i.e. the defect volume, V_{def}) associated with inclusion of an isolated substitutional defect can be determined within the Mott–Littleton [9] framework by solving [10],

$$V_{\text{def}} = -\kappa_T V_C \left(\frac{\delta f_v}{\delta V_C} \right)_T \quad (4)$$

where κ_T is the isothermal compressibility, V_C is the unit cell volume of the perfect lattice, $(\delta f_v / \delta V_C)_T$ is the change, for a given temperature, in the Helmholtz defect formation energy as a function of change in the unit cell volume and f_v is the defect formation energy, determined using the Mott–Littleton approach. In order to compare the relative magnitude of defect volumes between host lattices, each defect volume is divided by the volume of the host primitive unit cell, V_{pMO} (i.e. we introduce a normalisation factor).

To allow direct comparison with the DFT simulations described below (where there is currently no equivalent to the Mott–Littleton methodology), empirical potential based defect energies were also determined using a supercell method. In this approach, the lattice energy of a perfect host supercell that contains x MO formula units, $E_{\text{M}_x\text{O}_x}$, a cell in which one of the cations has been substituted for an extrinsic ion, $E_{\text{M}_{x-1}\text{SO}_x}$, and the primitive cell of the substituted ion oxide E_{SO} are all calculated. The solution energy, E_{sol} , is then the difference between the lattice energies (after they have been fully relaxed subject to energy minimisation) as

$$E_{\text{sol}} = \frac{(x-1)}{x} E_{\text{M}_x\text{O}_x} + E_{\text{SO}} - E_{\text{M}_{x-1}\text{SO}_x} \quad (5)$$

In the supercell approach the cell containing the substitutional defect is tessellated through space, therefore, there is the possibility that if the supercell is not sufficiently large, the strain fields of the defects will overlap significantly. Such defect–defect interactions will not occur for defects in the dilute limit (as determined using the Mott–Littleton methodology [9]). This

problem can be assessed by selecting a range of supercells to establish whether the interactions between defect images are of significance. Here two different supercells were adopted, one constructed of $2 \times 2 \times 2$ full unit cells (i.e. $x=32$) and a $3 \times 3 \times 3$ supercell (i.e. $x=108$).

In the supercell approach the defect volume is calculated by determining the volume of a perfect unit cell, V_{MO} , and subtracting this from the volume of a cell containing a substitutional defect, $V_{\text{M}_{1-x}\text{S}_x\text{O}}$. This volume is again divided by the volume of the relaxed, perfect primitive unit cell of the host lattice, i.e. $(V_{\text{MO}} - V_{\text{M}_{1-x}\text{S}_x\text{O}}) / V_{\text{pMO}}$.

All empirical simulations were conducted using the CASCADE simulation package [11].

2.2. Density functional theory

One limitation of first principles simulation are the high demands they place on the computational resources, therefore, their application is usually limited to smaller systems than empirical potential based simulations. The DFT simulations of isovalent substitution reported here employed a $2 \times 2 \times 2$ cubic supercell.

In the simulations the exchange correlation energy was modelled using the local density approximation (LDA) and a k -point grid with separations of 0.05 Å⁻¹. Ultrasoft pseudopotentials were used and the planewave cutoff energy was converged at a value of 420 eV. The DFT simulations were conducted using the CASTEP [12] software package.

3. Results and discussion

3.1. Solution energy as a function of ϵ

Fig. 1, shows the solution energies for divalent cations (i.e. Mg^{2+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Mn^{2+} , Sr^{2+} and Ba^{2+}) substituted into a series of rocksalt materials (i.e. MgO, CaO, CdO, CoO, MnO, SrO and BaO), as a function of ϵ . The solution energies were determined using all three approaches described previously.

In the case of Mott–Littleton calculations, the solution energy is a balance between the difference in the lattice energies of the host and substituted cation oxides and the defect energy of the substituted ion. Substitution of larger cations results in positive

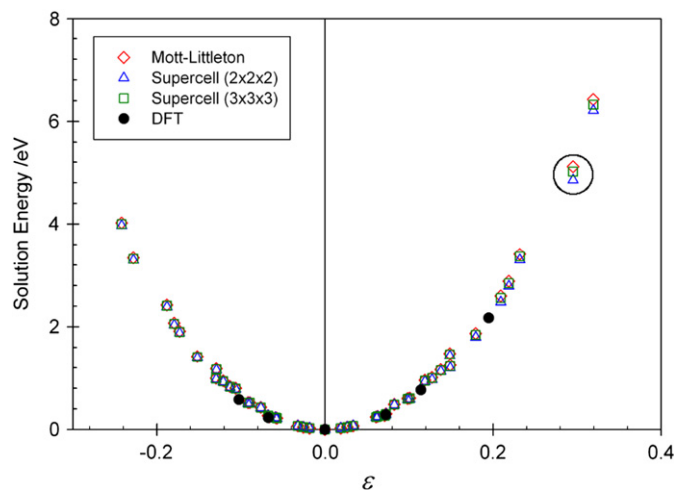


Fig. 1. Plot showing how the solution energy, E_{sol} , for isovalent cation substitution into rocksalt MO oxides, changes as a function of ϵ (Eq. (1)). The hollow points in the plot represent those determined using an empirical technique, whilst the solid points were determined using DFT.

defect energies but the lattice energy differences are negative (i.e. host lattice energy is more negative than that of the substituted cation oxide). Small substitutional cations have negative defect energies but the balance in lattice energies is positive. Fig. 1 shows that the solution energy in both these circumstances, is always positive (i.e. the total process is endothermic). Furthermore, as the magnitude of ε increases (i.e. the difference between the host and substitutional lattice parameters increases), the solution energy increases. Effectively, when a larger cation is substituted onto a host lattice site, the surrounding ions are forced to move away to accommodate the defect. Conversely, when a smaller cation is substituted onto a lattice site the surrounding ions contract around the defect (these processes are illustrated in Fig. 2). The greater the degree of relaxation the lattice must undergo to accommodate the substitutional defect, the greater the solution energy. As the charge on the host and substitutional cation are identical, when $\varepsilon = 0$, the solution energy is, of course, zero.

By fitting a quadratic function (of the form, $E = m\varepsilon^2 + n\varepsilon + o$) to each of the data sets (Mott–Littleton, Supercell $2 \times 2 \times 2$ and $3 \times 3 \times 3$ and DFT) it is possible to: (i) assess to what extent the different approaches are predicting similar results and (ii) allow predictions of the solution energy for divalent cation substitution into rocksalt oxides for other combinations of host and substitute cations, as long as the lattice parameter of the host lattice and the substitutional rocksalt oxide are known.

The quadratic function parameters, reported in Table 1, show that there is excellent agreement between the empirical pair potential data and that obtained using DFT, particularly in the region immediately surrounding the origin. As the difference in the size of the host and substitutional cation increases, the strain field due to the resulting defects increases, therefore the extent to

which the strain fields of the defect images, in neighbouring supercells, will overlap. This is particularly evident for larger separations between the hollow points circled in Fig. 1. The solution energy, E_{sol} , predicted by the Mott–Littleton methodology, represents a defect that is truly at the dilute limit, so it is unsurprising to see that, as the size of the supercell increases (from $2 \times 2 \times 2$ to $3 \times 3 \times 3$), and consequently the separation between defect images increases, the predicted solution energies obtained from the supercell technique converge towards the Mott–Littleton value (similar conclusions have been drawn by Jackson et al. [13]). Nevertheless, the difference is relatively small and thus the $2 \times 2 \times 2$ supercell, used in the DFT simulations, is an adequate approximation to the dilute limit.

The m parameters, reported in Table 1, are all in the range 54–63 which reflects the good agreement between the different techniques as shown in Fig. 1. Furthermore, the n parameters are all much smaller than the m parameters. It also follows that the energy curves are highly symmetric about the y-axis (i.e. $E_{sol}(\varepsilon) \approx E_{sol}(-\varepsilon)$). We next consider the extent to which the defect volumes are also a symmetric function of ε .

3.2. Defect volume as a function of ε

As mentioned above, the larger the mismatch between the size of the host and substituent cations, the greater the relaxation the lattice undergoes to accommodate substitutional disorder. This relationship is highlighted in Fig. 3, where the normalised defect volume is plotted against ε . This shows that when an ion is replaced by a like charged cation with a smaller ionic radius, the lattice contracts around it, that is, the normalised defect volume is negative. Conversely, when the substituent cation is larger, the normalised defect volume is positive and so the crystal expands. Of course, the plot passes through the origin because, in the absence of strain or electronic effects, there is no relaxation required when a cation is substituted by an ion with the same charge and radius.

The data presented in Fig. 3 predicts that the correlation between ε and the normalised defect volume is somewhat non-linear: that is, the substitution of smaller cations leads to a smaller change in the volume of a crystal, for the same change in the magnitude of ε , than substitution of a larger cation (or $V_{NDV}(\varepsilon) < V_{NDV}(-\varepsilon)$). This observation is distinct from the conclusion drawn from Fig. 1, that the change in solution energy is

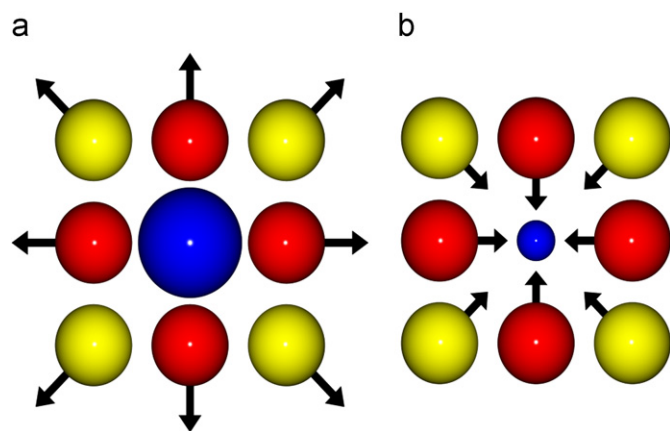


Fig. 2. Diagrams showing the effects of a substitutional cation (blue) with a larger ionic radius (a) and one with a smaller ionic radius (b) on a host binary oxide (red spheres represent oxygen and the yellow spheres represent the host cation). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Coefficients; m and n for quadratic functions fitted to the equation $E = m\varepsilon^2 + n\varepsilon + o$ relating strain, ε , and the solution energy, E_{sol} .

Model	m	n	R^2
Mott–Littleton	62.830	−0.489	0.996
Supercell ($2 \times 2 \times 2$)	61.240	−0.556	0.996
Supercell ($3 \times 3 \times 3$)	62.310	−0.496	
DFT	54.847	0.624	0.794

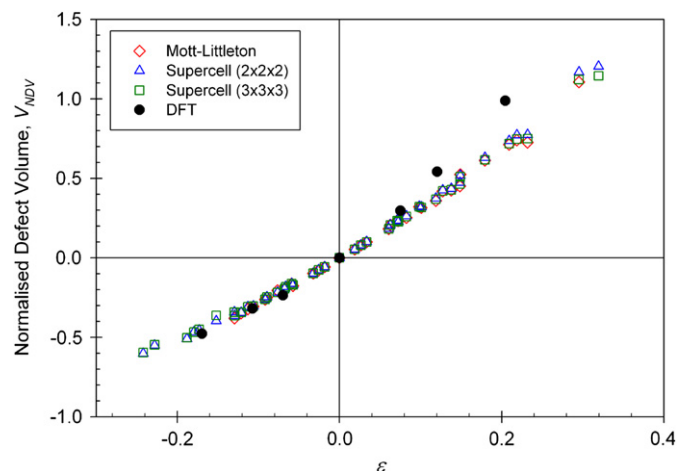


Fig. 3. Plot showing how the normalised defect volume, V_{NDV} , varies as a function of ε . The hollow points in the plot represent those determined using an empirical technique, whilst the solid points were determined using DFT.

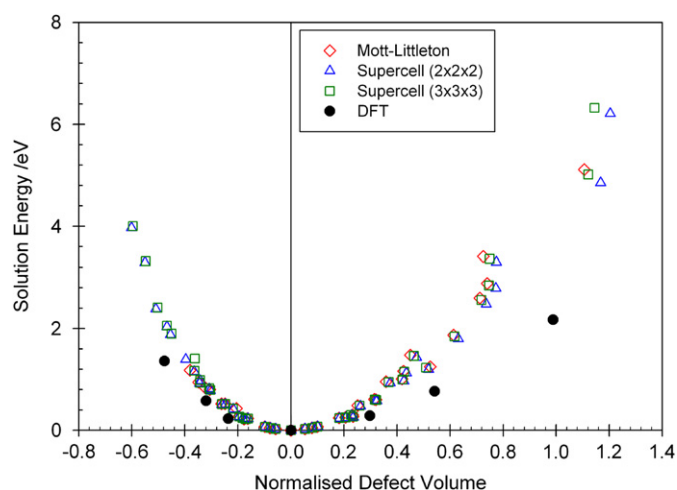


Fig. 4. Plot showing how the solution energy, E_{sol} , varies as a function of the normalised defect volume, V_{NDV} . The hollow points in the plot represent those determined using an empirical technique, whilst the solid points were determined using DFT.

symmetric (i.e. either a positive or negative change in ϵ , of equal magnitude, will require the same energy). To investigate the symmetry issue further, the relationship between solution energy and defect volume is illustrated in Fig. 4. This suggests that the energy penalty associated with a reduction in the lattice volume, due to the substitution of a small cation onto a site previously occupied by a large cation, is greater than for an expansion of the lattice of equal magnitude, due to substitution of a larger cation on a smaller lattice site. This should be expected, due in particular, to the increasing repulsion between the surrounding oxygen anions as they move closer together, when contracting around the smaller substitutional cation.

Fig. 3 shows that there is some divergence between the defect volumes determined using the empirical and DFT simulations, particularly as the strain on the lattice increased. This is due to the limitations of the more simple classical potential based technique, which overestimates elastic constants and as such the simulated lattice is not representatively compliant.

4. Concluding comments

Using both empirical and quantum mechanical approaches we have examined changes in both solution energy and the lattice volume arising from isovalent cation substitution into a range of host materials that exhibit the rocksalt structure. Throughout, we analyse energy and volume changes in terms of a lattice ‘strain’

related term, ϵ , that is defined as the difference in the lattice parameter of the host and substitutional cation oxides divided by the host lattice parameter (see Eq. (1)). The following conclusions can be drawn:

- To a good approximation the solution energy increases proportionally to the square of the strain term. As such, the solution energy is symmetric about $\epsilon = 0$ (see Fig. 1).
- The volume change (defect volume) is less symmetric about $\epsilon = 0$ (see Fig. 3). That is, smaller substitute cations give rise to proportionally smaller lattice contractions than larger substitute cations give rise to lattice expansion. Fig. 4 describes this in terms of the energy penalty, where an incremental defect volume expansion is less energetically costly than the same defect contraction.

Within this group of materials, that assume the rocksalt structure, these relationships are ‘general’ and as such can be used to predict solution energies and volume changes for other combinations of host and substitute cations not simulated here. Equivalent relationships may exist for aliovalent cation substitutions and for other host lattice crystal structures, although these relationships would likely be different from those reported here.

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