A reactive force field for lithium–aluminum silicates with applications to eucryptite phases

Badri Narayanan\(^1\), Adi C T van Duin\(^2\), Branden B Kappes\(^3\), Ivar E Reimanis\(^1\) and Cristian V Ciobanu\(^3\)

\(^1\) Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO 80401, USA
\(^2\) Department of Mechanical Engineering, Pennsylvania State University, University Park, PA 16802, USA
\(^3\) Division of Engineering, Colorado School of Mines, Golden, CO 80401, USA

E-mail: cciobanu@mines.edu

Received 9 May 2011, in final form 25 July 2011
Published 4 November 2011
Online at stacks.iop.org/MSMSE/20/015002

Abstract

We have parameterized a reactive force field (ReaxFF) for lithium–aluminum silicates using density functional theory (DFT) calculations of structural properties of a number of bulk phase oxides, silicates and aluminates, as well as of several representative clusters. The force field parameters optimized in this study were found to predict lattice parameters and heats of formation of selected condensed phases in excellent agreement with previous DFT calculations and with experiments. We have used the newly developed force field to study the eucryptite phases in terms of their thermodynamic stability and their elastic properties. We have found that (a) these ReaxFF parameters predict the correct order of stability of the three crystalline polymorphs of eucryptite, \(\alpha\), \(\beta\) and \(\gamma\), and (b) that upon indentation, a new phase appears at applied pressures \(\geq 7\) GPa. The high-pressure phase obtained upon indentation is amorphous, as illustrated by the radial distribution functions calculated for different pairs of elements.

In terms of elastic properties analysis, we have determined the elements of the stiffness tensor for \(\alpha\)- and \(\beta\)-eucryptite at the level of ReaxFF, and discussed the elastic anisotropy of these two polymorphs. Polycrystalline average properties of these eucryptite phases are also reported to serve as ReaxFF predictions of their elastic moduli (in the case of \(\alpha\)-eucryptite), or as tests against values known from experiments or DFT calculations (\(\beta\)-eucryptite). The ReaxFF potential reported here can also describe well single-species systems (e.g. Li-metal, Al-metal and condensed phases of silicon), which makes it suitable for investigating structure and properties of suboxides, atomic-scale mechanisms responsible for phase transformations, as well as oxidation–reduction reactions.

Online supplementary data available from stacks.iop.org/MSMSE/20/015002/mmedia

(Some figures may appear in colour only in the online journal)
1. Introduction

Lithium–aluminum silicate (LAS) glass ceramics have been investigated extensively over the last few decades owing to their exotic properties, such as small (or slightly negative) coefficient of thermal expansion and exceptional thermal stability [1–3]. Such unique physical properties make LAS ceramics suitable for a variety of applications such as heat exchangers with high thermal shock resistance, high precision optical devices, telescope mirror blanks, and ring laser gyroscopes [1–5]. \(\beta\)-eucryptite (LiAlSiO\(_4\)) is an important LAS glass ceramic material with a hexagonal crystal structure which can be viewed as a stuffed derivative of the high-temperature \(\beta\)-quartz configuration [6–11]. The structure of \(\beta\)-eucryptite confers its superionic conductivity of Li\(^+\) ions along the \(c\)-axis, thus making it a potential electrolyte material for Li ion batteries [12–16].

From a more fundamental perspective, \(\beta\)-eucryptite is known to undergo a reversible order-disorder transformation at \(\sim 755\) K which occurs via spatial disordering of the lithium atoms at high temperatures [13]. Recently, it was reported that \(\beta\)-eucryptite undergoes a reversible pressure-induced transition to a metastable polymorph (called the \(\epsilon\) phase) at \(\sim 0.8\) GPa [17, 18]. Apart from \(\beta\) and the recently discovered high-pressure \(\epsilon\) phases, there are other known polymorphs of eucryptite, i.e. \(\alpha\) and \(\gamma\). Of these, \(\alpha\) is the most stable under ambient conditions and exists over a wide range of temperatures but is typically kinetically hindered [19]. On the other hand, \(\gamma\)-eucryptite is a metastable phase which coexists along with \(\beta\)-eucryptite over a narrow range of temperatures (1038–1103 K) and is, therefore, of lower practical significance [20]. \(\alpha\)-eucryptite has a rhombohedral crystal structure belonging to the \(R3\) space group similar to phenakite and willemite; its thermodynamic, structural and physical properties have been studied [21, 22]. However, its elastic properties, in particular the single-crystal elastic constants, are not yet known. Furthermore, the extent of elastic anisotropy in \(\alpha\)-eucryptite has also not yet been reported. Such a study could provide insight into the structure-property relationship in LAS glass ceramics and assist in designing composites with tailored elastic properties.

The potential development work presented here has emerged from our long term goal of determining the atomic structure of the \(\epsilon\) phase and the atomic-scale mechanism responsible for the \(\beta\)-to-\(\epsilon\) phase transformation. While phase transformations can be directly evidenced in DFT-based Carr–Parrinello molecular dynamics (CPMD) simulations (e.g. [23, 24]), the number of atoms in the unit cell of \(\beta\) eucryptite makes it impractical to undertake such simulations in which usually several unit cells are required along each spatial direction. We have therefore not resorted to CPMD approaches, but turned to molecular-dynamics (MD) simulations based on empirical potentials. To describe the interatomic forces acting during MD simulations, several empirical force fields (EFFs) have been proposed for LAS systems [25–31]. These EFFs reproduce well short-range order, mechanical and transport properties, but may not provide a sufficiently adequate description of phase transformations, medium range order, and vibrational density of states. Recently, van Duin and co-workers [32, 33] developed a reactive force field (ReaxFF) based on a bond-order formalism [34, 35] in conjunction with a charge equilibration scheme [36]. In this study, we have parameterized ReaxFF for LAS by fitting against formation energies, atomic configurations and charge distributions of a number of representative clusters and equations of state of well-known condensed phases of oxides, silicates and aluminates derived from DFT calculations.

This paper is organized as follows. Section 2 describes the methodology we adopted to parameterize the ReaxFF for LAS, the DFT data used to construct the training set for the parametrization of ReaxFF, and the details of these DFT calculations. In order to assist the reader in understanding and using more readily the ReaxFF potential for LAS, an online...
supplementary information section is provided (stacks.iop.org/MSMSE/20/015002/mmedia), which contains all relevant details about the theoretical framework of ReaxFF and the full set of ReaxFF parameters that we determined; these parameters are given in a format compatible with the widely available MD package LAMMPS [37]. Section 3 reports our results for heats of formation and geometric parameters for a number of bulk phases; relative stability of eucryptite phases and amorphization of $\beta$-eucryptite upon indentation; and elastic properties of the two most stable eucryptite polymorphs. We have determined the elements of the stiffness tensor for $\alpha$- and $\beta$-eucryptite at the level of ReaxFF, and discussed the elastic anisotropy of these two polymorphs. Polycrystalline average properties of these eucryptite phases are also reported to serve as ReaxFF predictions of their elastic moduli (in the case of $\alpha$-eucryptite), or as tests against values known from experiments or DFT calculations ($\beta$-eucrypite). Section 4 summarizes the results and discusses the main successes and shortcomings of our ReaxFF parametrization for LAS systems.

2. Methodology

2.1. ReaxFF framework

The energy contributions in ReaxFF are functions of bond orders, which allow for a better description of bond breaking and bond formation during simulations. Furthermore, Coulomb interactions are computed for every atom pair based on charges calculated at every time step using a charge equilibration scheme which allows it to describe covalent, metallic and ionic systems equally well [32, 33]. The ReaxFF framework has been applied successfully to predict the dynamics and reactive processes in hydrocarbons [32, 38], crack propagation in silicon crystals [39], interfacial reactions in Si/Si-oxide [33] and Al/Al-oxide [40], surface reactions in ZnO [41], oxygen-ion transport in Y-stabilized ZrO$_2$ [42], and phase transitions in ferroelectric BaTiO$_3$ [43]. The parameters of the ReaxFF potential are optimized by fitting against density functional theory (DFT) data for various bulk phases and atomic clusters.

The formulation of ReaxFF is based on the concept of bond order [44], which describes the number of electrons shared between two atoms as a continuous function of their spacing. The bond order $BO_{ij}'$ associated with atoms $i$ and $j$ is calculated via

$$BO_{ij}' = BO_{ij}'^{\sigma} + BO_{ij}'^{\pi} + BO_{ij}'^{\pi\pi}$$

$$= \exp \left( p_{bo1} \left( \frac{r_{ij}}{r_0^\sigma} \right)^{p_{bo2}} \right) + \exp \left( p_{bo3} \left( \frac{r_{ij}}{r_0^\pi} \right)^{p_{bo4}} \right)$$

$$+ \exp \left( p_{bo5} \left( \frac{r_{ij}}{r_0^{\pi\pi}} \right)^{p_{bo6}} \right),$$

where $BO_{ij}'^{\sigma}$, $BO_{ij}'^{\pi}$ and $BO_{ij}'^{\pi\pi}$ are the partial contributions of $\sigma$, $\pi$- and double $\pi$-bonds involving the atoms $i$ and $j$, $r_{ij}$ is the distance between $i$ and $j$, $r_0^\sigma$, $r_0^\pi$, $r_0^{\pi\pi}$ are the bond radii of $\sigma$, $\pi$- and double $\pi$-bonds, respectively, and $p_{bo}$ are the bond-order parameters. The bond orders $BO_{ij}$ obtained from equation (1) are corrected to account for local overcoordination and residual 1–3 interactions by employing a scheme [45] detailed in the online supplementary information.

The total energy $E$ of the system is expressed as the sum of partial energy contributions corresponding to bonded and unbonded interactions [32, 33, 38]:

$$E = \sum_{i<j} E_{b_{ij}} + \sum_i E_{ov,i} + \sum_i E_{un,i} + \sum_i E_{lp,i} + \sum_{i<j<k} E_{v_{ijk}} + \sum_{i<j} E_{vdW_{ij}} + \sum_i E_{C_{i}},$$

where $E_{b_{ij}}$, $E_{ov,i}$, $E_{un,i}$, $E_{lp,i}$, $E_{v_{ijk}}$, $E_{vdW_{ij}}$, and $E_{C_{i}}$ represent the bonded, overcoordinated, undercoordinated, lone pair, van der Waals, and cohesive energy contributions, respectively.
where $E_{b,ij}$ is the energy of the $i-j$ bond, $E_{ov,i}$ and $E_{un,i}$ are penalties for over- and undercoordination of atom $i$, $E_{lp,i}$ is the energy associated with lone-pair electrons around an atom $i$, $E_{v,ijk}$ is the energy associated with the deviation of the angle subtended at $j$ by atoms $i$ and $k$ from its equilibrium value, $E_{vdW,ij}$ and $E_{C,ij}$ are the contributions from van der Waals and Coulomb interactions between $i$ and $j$. The terms on the right side of equation (2) are defined in the following paragraphs; for more details, the reader is referred to the online supplementary information (stacks.iop.org/MSMSE/20/015002/mmedia).

The energy of the $i-j$ bond is calculated using the corrected bond orders $BO_{ij}$ as

$$E_{b,ij} = -D^\sigma_e BO_{ij}^\sigma \exp\left(p_{b1}(1 - (BO_{ij}^\sigma)^{p_{b2}})\right) - D^\pi_e BO_{ij}^\pi - D^\pi_e BO_{ij}^{\pi\pi},$$

(3)

where $D^\sigma_e$, $D^\pi_e$ and $D^\pi_e$ are the dissociation energies of $\sigma$, $\pi$- and double $\pi$-bonds, while $p_{b1,2}$ are the bond energy parameters. The contribution associated with lone-pair electrons is calculated as

$$E_{lp,i} = \frac{p_{lp2}(n_{lp,\text{opt}} - n_{lp,i})}{1 + \exp\left(-7S(n_{lp,\text{opt}} - n_{lp,i})\right)},$$

(4)

where $n_{lp,\text{opt}}$ is the optimum number of lone pairs for a given atom $i$ and $n_{lp,i}$ is the number of lone pairs around $i$ calculated using the relation $n_{lp,i} = \left[\frac{\Delta_i^l}{\Delta_i^l}\right] + \exp(-p_{lp1}(2 + \Delta_i^l - 2\left[\frac{\Delta_i^l}{\Delta_i^l}\right]))$ where $\Delta_i^l$ is the difference between the number of outer shell electrons and the sum of bond orders around atom $i$ and $\left[\cdot\right]$ is the greatest integer smaller than $x$. The penalty terms for overcoordination ($E_{ov,i}$) and undercoordination ($E_{un,i}$) of atom $i$ can be written as

$$E_{ov,i} = \frac{\Delta_i^{lp} \sum_{j=1}^{n_{\text{bond}}} p_1 D^\sigma_e BO_{ij}}{\left(\Delta_i^{lp} + \upsilon_i\right) \left(1 + \exp\left(p_2 \Delta_i^{lp}\right)\right)},$$

(5a)

$$E_{un,i} = \frac{-p_S F_{un1}(\Delta_i^{lp})}{1 + p_T \exp\left(p_S F_{un2}(BO_{ij})\right)},$$

(5b)

$$F_{un1}(\Delta_i^{lp}) \equiv \frac{1 - \exp\left(p_0 \Delta_i^{lp}\right)}{1 + \exp\left(-p_2 \Delta_i^{lp}\right)},$$

(5c)

$$F_{un2}(BO_{ij}) \equiv \sum_{j=1}^{n_{\text{gb}(i)}} \left(\Delta_j - \Delta_i^{lp}\right) \left(BO^{\sigma}_{ij} + BO^{\pi\pi}_{ij}\right),$$

(5d)

where $\Delta_i^{lp} = n_{lp,\text{opt}} - n_{lp,i}$, $\upsilon_i$ is the valence of atom $i$, $\Delta_i$ is the degree of overcoordination around the atom $i$ which is corrected for the effect of broken electron pairs (online supplementary information) to obtain $\Delta_i^{lp}$, and $p$’s are over/under coordination parameters.

The energy contribution from the valence angles is written as

$$E_{v,ijk} = f_7\left(BO_{ij}\right) f_7\left(BO_{jk}\right) f_8\left(\Delta_j\right) F_v\left(\Theta_{ijk}\right)$$

(6a)

$$F_v(\Theta_{ijk}) = p_{v1}\left\{1 - \exp\left(-p_{v2}((\Theta_0 - \Theta_{ijk})^2)\right)\right\}$$

(6b)

where $\Theta_{ijk}$ is the angle subtended at central atom $j$ by the atoms $i$ and $k$, $\Theta_0$ is the equilibrium value for $\Theta_{ijk}$ which depends on the sum of $\pi$-bond orders (i.e. $BO^\pi$ and $BO^{\pi\pi}$) around the atom $j$, $f_7$ and $f_8$ are functions of bond order and degree of overcoordination (online
supplementary information (stacks.iop.org/MSMSE/20/015002/mmedia), respectively, and \( p_i \)'s are valence angle parameters.

All the terms on the right side of equation (2) except the van der Waals and Coulomb interactions depend on bond order through equations (3)–(6). The bond orders are updated after every time step in a MD simulation; such a formalism allows for a realistic simulation of dissociation and formation of bonds during a chemical reaction and also provides a good description of the bulk phases \[32, 33, 38\]. The pairwise non-bonded interaction terms, i.e., Coulomb and van der Waals interactions are evaluated for every atom pair irrespective of the geometry and instantaneous connectivity. The van der Waals interaction of atoms \( i \) and \( j \) is evaluated as

\[
E_{vdW,ij} = T(r_{ij})D_{ij} \left\{ \exp \left( \alpha_{ij} \left( 1 - \frac{f_{13}(r_{ij})}{r_{vdW}} \right) \right) - 2 \exp \left( \frac{\alpha_{ij}}{2} \left( 1 - \frac{f_{13}(r_{ij})}{r_{vdW}} \right) \right) \right\}
\]

where \( f_{13}(r_{ij}) = (r_{ij}^{vdW} + \gamma_{vdW})^{-1/2} \) is a shielding term included to avoid excessive repulsive interactions between bonded atoms and atoms containing a valence angle (1–3 interactions), \( D_{ij} \) is the depth of the potential well, \( r_{vdW} \) is the van der Waal radius, \( p_{vdW} \) and \( \gamma_{vdW} \) are the van der Waals shielding parameters and \( T(r_{ij}) \) is the Taper correction (online supplementary information). The Coulomb interaction between atoms \( i \) and \( j \) is

\[
E_{C,ij} = T(r_{ij})C \frac{q_i q_j}{r_{ij}^3 + \gamma_{ij}^{-3}},
\]

where \( q_i \) and \( q_j \) are instantaneous charges of atoms \( i \) and \( j \), \( C \) is the Coulomb constant and \( \gamma_{ij} \) is a shielding parameter included to avoid excessive repulsions due to overlap of orbitals at short distances.

The atomic charges are calculated at every iteration (time step) during minimization (MD) run using the electronegativity equalization method (EEM) \[36\]. This bond-order formalism coupled with the redistribution of charges through EEM enables the ReaxFF model to describe ionic, metallic and covalent systems on equal footing \[32, 33, 38–41, 43, 46–49\]. With one unified (albeit complicated) formalism, ReaxFF has several advantages over other EFFs \[45\]:

(i) The bond-order formalism provides a continuous description of formation and dissociation of bonds during a MD simulation.
(ii) Other interatomic potentials based on bond-order formalism like Tersoff \[34\] and Brenner \[35\] do not account for redistribution of charges. The EEM \[36\] employed in ReaxFF allows the atomic charges to vary continuously with changes in coordination and bond order.
(iii) The evaluation of individual contributions of \( \sigma \)-, \( \pi \)- and double \( \pi \)-bonds to the bond order allows ReaxFF to identify the hybridization state and the coordination of an atom based on the instantaneous geometry around that atom.
(iv) The bond-order correction scheme (online supplementary information) enables ReaxFF to capture more accurately transition states during a reaction, provides a continuous transition between these intermediate states, and in turn describes reaction kinetics better than the other EFFs.

2.2. ReaxFF development

The choice of specific partial energy contributions depends largely on the system of interest. For example, for ionic solids the angle bending and torsion terms have been set to zero \[43, 46–48\]; however, for covalent crystals these contributions cannot be neglected as shown,
e.g. for the case of Si/SiO$_2$ [33]. The partial energy contributions used in the development of ReaxFF for Si/SiO$_2$ system [33] have been found adequate in this study of Li/Al/Si/O as well (equation (2)). We optimized all ReaxFF parameters for the Li/Al/Si/O system by fitting against DFT-computed data. We emphasize that this optimization was done from scratch on all ReaxFF parameters using a larger database of DFT calculations (described in detail below); as such, this new fitting on a larger database yielded parameter values which are different than those published earlier [33], but which give similar descriptions of the material properties. The parameters related to oxygen described here were taken from the ReaxFF water-force field [50, 51]. Once the oxygen parameters were changed, then Si/SiO parameters also required modifications; the potential form used here follows that in [38], which also enforced a revision of the parameters. The parameters related to aluminum have also changed and they perform very well, as indicated, for example, by the andalusite properties listed in section 3. The new parameters for Al, Si, O and their interactions do not bring significant changes in the properties of Al/AlO and Si/SiO systems with respect to previous parameterizations, but they provide a superior description of the Li–Al–Si–O systems under study.

To ensure good transferability of the resulting Li/Al/Si/O parameters, we have included in the training set DFT-calculated data for a wide variety of well-known condensed phases and clusters, as listed below:

(i) Equations of state (i.e. total energy versus volume) for pure Al (fcc, hcp, bcc, sc and diamond) and for corundum ($\alpha$-Al$_2$O$_3$), surface energy of the fcc Al (111), charge distribution and dissociation energies of a number of Al–O–H clusters; data from [40].

(ii) Equations of state of Li (bcc, fcc, hcp, diamond, sc), LiH with sodium-chloride structure, dissociation energies and charge distributions in Li$_2$, LiH and LiH$_2$ clusters; data from [46].

(iii) Equations of state of Si (sc, diamond, $\beta$-Sn), SiO$_2$ ($\alpha$-quartz, trydimite, coesite, $\alpha$-crystobalite, stishovite), dissociation energies of single and double bonds of Si–Si and Si–O in Si/O/H clusters, energies of various Si/O/H clusters as a function of valence angles Si–O–Si, O–Si–O and Si–Si–Si and distortion energies of rings of Si/O/H clusters; data from [33].

(iv) Equations of state of Li-silicates: (a) Li$_2$SiO$_3$ (orthorhombic), (b) stable Li$_2$Si$_2$O$_5$ (monoclinic) and (c) metastable Li$_2$Si$_2$O$_5$ (orthorhombic); data from [52].

It is worth emphasizing that ReaxFF is applicable to pure metals, such as lithium. As mentioned in item (ii) above, the parameters for Li were obtained using the equations of state for Li-fcc, Li-bcc, Li-simple cubic and Li-diamond. These equations of state were computed for volume changes ranging from 50% (volumetric) compression to 20% expansion. The Li-metal parameters were trained against the experimental cohesive energy of the lithium metal (37.7 kcal mol$^{-1}$; ReaxFF gives 36.9 kcal mol$^{-1}$). We have used the ReaxFF Li parametrized in this study to compute the lattice parameter of bcc-Li, most stable phase of Li at room temperature. ReaxFF predicts a lattice parameter of 3.322 Å which is close to the DFT value of 3.390 Å [46].

In addition to using DFT data sets from earlier works, we calculated the equations of state of the following condensed phases within the framework of DFT using the computational details listed in section 2.3:

(v) Li oxides: $\alpha$-Li$_2$O (cubic) [53] and Li$_2$O$_2$ (hexagonal) [54].

(vi) Li aluminates: three polymorphs of LiAlO$_2$ namely (a) $\alpha$ (rhombohedral) [55], (b) $\beta$ (orthorhombic) [56] and (c) $\gamma$ (tетragonal) [57].

(vii) Al silicates: three polymorphs of Al$_2$SiO$_5$ namely (a) andalusite (orthorhombic) [58, 59], (b) sillimanite (orthorhombic) [58, 60] and (c) kyanite (triclinic) [58, 61].
In order to account for the anisotropy of Li–Al silicates, computational supercells of these phases were subjected to different types of strain (depending on the crystal symmetry) when computing their energy as a function of cell volume. The lattice of a crystal is described by three lattice vectors \( a_i \) \((i = 1, 2, 3)\) whose magnitudes are the lattice parameters \( a_i \). The cubic phases \((a_1 = a_2 = a_3)\) were strained triaxially, i.e. all the three lattice vectors \( a_i \) were all equally strained. The tetragonal and hexagonal phases \((a_1 = a_2 \neq a_3)\) were deformed by two types of strains, namely (a) biaxial: \( a_1 \) and \( a_2 \) were strained simultaneously by the same amount while keeping \( a_3 \) fixed at its experimental value, and (b) uniaxial: \( a_3 \) was strained while keeping \( a_1 \) and \( a_2 \) fixed. The lattice vectors of phases with orthorhombic symmetry or lower \((a_1 \neq a_2 \neq a_3)\) were strained individually keeping the other two unstrained, which leads to three distinct uniaxial strains corresponding to three lattice vector directions \( a_i \). In all the cases, the limits of strains range from \(-40\%\) (compressive) to \(+20\%\) (tensile).

For all the phases listed above (items (i)–(vii)), we computed the heats of formation \( \Delta H_f \) as functions of volume for the different types of strains. The heat of formation of a general compound of unit formula \((u.f.) Li^k Al^l Si^m O^n (k, l, m, n \text{ integers } \geq 0)\) at a volume \( V \) for a particular type and value of strain can be evaluated from DFT total energy calculations as

\[
\Delta H_f(V, \epsilon) = E_{Li^k Al^l Si^m O^n}(V, \epsilon) - kE_{Li} - lE_{Al} - mE_{Si} - \frac{n}{2}E_{O_2} \quad (9)
\]

where \( E_{Li^k Al^l Si^m O^n} \) is the total energy of a given volume \( V \) of the phase Li\(_k\) Al\(_l\) Si\(_m\) O\(_n\) subjected to a particular strain \( \epsilon \). The energies of the constituent elements Li, Al, Si and O in equation (9), i.e. \( E_{Li}, E_{Al}, E_{Si} \) and \( E_{O_2} \) are those of the most stable phases at equilibrium calculated by DFT.

The training set data were used to parameterize the ReaxFF using the successive one-parameter search technique described by van Duin et al [62] These parameters are tabulated in appendix A, and are also made available as a data file (online supplementary information (stacks.iop.org/MSMSE/20/015002/mmedia)).

2.3. Details of the DFT calculations

The computational supercell for each phase in the training set described in section 2.2 consisted of one primitive unit cell. The total energy DFT calculations were performed within the framework of the generalized gradient approximation (GGA), using the projector-augmented wave (PAW) formalism [63] as implemented in the ab initio simulation package VASP [64, 65]. The atomic coordinates were relaxed using a conjugate gradient algorithm until the force components on any atom were smaller than 0.01 eV Å\(^{-1}\). The exchange-correlation was described by the Perdew–Wang functional [66], which is a typical choice for ceramics oxide systems (e.g. [52, 57]). The plane wave energy cutoff was set to 500 eV, which performs satisfactorily for similar ceramic systems [52]. The Brillouin zone (BZ) was sampled with a \( \Gamma \)-centered Monkhorst–Pack grid. For the oxides and aluminates of lithium, we used \( 8 \times 8 \times 8 \) \( k \)-point grids which amount to 1024 irreducible \( k \)-points for oxides and 256 irreducible \( k \)-points for aluminates. A \( 4 \times 4 \times 4 \) \( k \)-point grid was found sufficient for the aluminum silicate phases (32 irreducible \( k \)-points), and a \( 3 \times 3 \times 3 \) \( k \)-point grid was selected for the eucryptite phases (14 irreducible \( k \)-points). These grids were chosen on the basis of convergence tests conducted for different BZ samplings for different phases.

3. Results

3.1. Heats of formation

The set of parameters obtained by the technique described in section 2 was validated by comparing the structures and the heats of formations for various phases calculated by ReaxFF
Figure 1. Equations of state of various phases of (a), (b) Li oxides, (c), (d) Li aluminates, (e), (f) Al silicates, and (g), (h) Li silicates as calculated using DFT (a), (c), (e), (g) and ReaxFF (b), (d), (f), (h).
Table 1. Heats of formation at equilibrium ($\Delta H^\circ_f$) of selected phases calculated using DFT and ReaxFF at 0 K. For comparison, experimental values at 298 K are also provided wherever available.

| Phase              | DFT      | ReaxFF   | Exp       |
|--------------------|----------|----------|-----------|
| $\alpha$-Li$_2$O   | $-147.67$| $-145.82$| $-143.10$ [67] |
| $\gamma$-LiAlO$_2$ | $-292.19$| $-299.29$| $-284.37$ [68] |
| Andalusite         | $-635.90$| $-635.35$| $-619.42$ [69] |
| Li$_2$SiO$_3$      | $-406.04$| $-387.31$| $-395.77$ [70] |
| $\alpha$-LiAlSiO$_4$ | $-529.25$| $-526.48$| $-512.53$ [22] |
| $\beta$-LiAlSiO$_4$ | $-528.01$| $-525.51$| $-506.18$ [71] |
| $\gamma$-LiAlSiO$_4$ | $-524.93$| $-517.66$|            |

with those known from experiments or from DFT calculations. As a preliminary test, the heats of formation as functions of volume for the various phases used in the training set calculated by ReaxFF were compared in figure 1 with their DFT counterparts. Figure 1 shows a generally good qualitative agreement between the ReaxFF and the DFT curves in terms of equilibrium volumes and the relative phase stabilities at these volumes. Furthermore, table 1 shows that the ReaxFF heat of formation results are also in good agreement with experimental data on selected oxides, aluminates and silicates at equilibrium. However, in the deformation regimes lying outside equilibrium (particularly in tension) the energetic ordering of Li oxides (figures 1(a) and (b)), Li aluminates (figures 1(c) and (d)), and Al silicates (figures 1(e), (f)) at the ReaxFF level does not preserve so well the DFT ordering. This is most likely due to the choice of deformation range (section 2.2), which contains more data points in compression than in tension. The following subsections contain more tests of the performance of ReaxFF concerning the structure, stability and elastic properties of LAS ceramics.

3.2. Structural parameters

Table 2 compares the lattice parameters for a number of selected phases calculated using ReaxFF with those from DFT calculations and from experiments. With the exception of $\alpha$-eucryptite (for which the supercell energy was optimized as a function of volume) the lattice constants were calculated by optimizing the computational supercell of each phase with respect to all independent lattice parameters that describe its crystal structure. Table 2 shows that the lattice parameters calculated using ReaxFF are all within $\sim 5\%$ of the values reported in literature using DFT or experiments. In order to establish that the structures of bulk phases are faithfully described by ReaxFF, we have also checked the independent fractional coordinates of the atoms in the optimized supercells. For example, tables 3 and 4 show these fractional coordinates for $\alpha$- and $\beta$-eucryptite, respectively. As shown in these tables, the agreement between the ReaxFF-predicted values for fractional coordinates and the experimental ones is very good, which illustrates that ReaxFF predicts the structure of bulk phases accurately.

3.3. Stability of eucryptite phases

There are three well-known crystalline polymorphs of eucryptite, $\alpha$, $\beta$, $\gamma$; of these, $\alpha$ is the most stable phase under ambient conditions but is kinetically hindered [19]. Figure 2 shows the equations of state (energy versus volume curves) for these polymorphs calculated using ReaxFF and DFT at 0 K. The minimum of a calculated energy versus volume curve for a
Table 2. Comparison of calculated lattice parameters of selected phases using ReaxFF with those available in the literature determined from DFT calculations and from experiments. The numbers of unit formulae per unit cell are provided in brackets.

| Phase          | Structure     | Space group | Formula   | Lattice parameter (Å) | DFT  | ReaxFF | Exp  |
|----------------|---------------|-------------|-----------|-----------------------|------|--------|------|
| α-Li₂O        | Cubic         | Fm\overline{3}m | Li₂O (4)  | a                     | 4.631 [53] | 4.738 | 4.622 [72] |
| γ-LiAlO₂      | Tetragonal    | P4\_\text{1}2\_12 | LiAlO₂ (4) | a                     | 5.223 [57] | 5.359 | 5.169 [73] |
| Andalusite     | Orthorhombic  | Pn\text{nn}m | Al₂SiO₅ (4) | a,b,c                 | 7.753 [74] | 7.632 | 7.798 [58] |
| Li₂SiO₃       | Orthorhombic  | Cm\text{mc}2\_1 | Li₂SiO₃ (4) | a,b,c                 | 9.487 [75] | 9.335 | 9.392 [76] |
| α-eucryptite  | Trigonal      | R3          | LiAlSiO₄ (18) | a,c                     | 13.656 | 13.448 | 13.532 [21] |
| β-eucryptite  | Hexagonal     | P6\_\text{3}2\_2 | LiAlSiO₄ (12) | a                       | 10.594 | 10.568 | 10.497 [11] |

Table 3. Fractional coordinates of atoms in a unit cell of α-eucryptite calculated using ReaxFF at 0 K. The experimental values from [21] at 298 K are provided for comparison.

| Atom | ReaxFF | Experiment |
|------|--------|------------|
|      | x      | y          | z         |
| Li(1) | -0.016 | -0.806   | -0.752   | -0.017 | -0.811 | -0.749 |
| Li(2) | 0.022  | 0.814    | 0.749    | 0.021  | 0.812  | 0.754 |
| Si(1) | 0.531  | 0.876    | 0.753    | 0.530  | 0.880  | 0.750 |
| Si(2) | 0.876  | 0.348    | 0.918    | 0.876  | 0.344  | 0.916 |
| Al(1) | -0.533 | -0.883  | 0.754    | -0.530 | -0.882 | -0.749 |
| Al(2) | -0.878 | -0.342  | -0.914   | -0.875 | -0.345 | -0.916 |
| O(1)  | -0.748 | -0.208  | -0.897   | -0.753 | -0.210 | -0.890 |
| O(2)  | 0.764  | 0.211   | 0.903    | 0.766  | 0.216  | 0.898 |
| O(3)  | -0.741 | -0.202  | -0.594   | -0.733 | -0.199 | -0.593 |
| O(4)  | 0.734  | 0.198   | 0.571    | 0.733  | 0.199  | 0.576 |
| O(5)  | -0.097 | -0.886  | -0.931   | -0.105 | -0.888 | -0.937 |
| O(6)  | 0.090  | 0.879   | 0.947    | 0.096  | 0.881  | 0.946 |
| O(7)  | -0.669 | -0.009  | -0.751   | -0.664 | -0.009 | -0.749 |
| O(8)  | 0.656  | -0.004  | 0.753    | 0.655  | -0.004 | 0.750 |

given phase represents its equilibrium state. For convenience, all the energies reported in figure 2 are given relative to the energy of the most stable phase at its equilibrium volume for DFT and ReaxFF. Figure 2 shows that ReaxFF predicts the same order of stability for the three polymorphs of eucryptite as do our DFT calculations. This order is consistent with experimental observations [3, 11, 17, 21].

β-eucryptite, the most technologically relevant of the three polymorphs, has an open structure which collapses at sufficiently high applied pressures [1, 2, 18]. Recently, it was observed that β-eucryptite begins to amorphize at pressures above ∼5 GPa [20]. To test the ability of ReaxFF to capture phase transitions, we have studied the evolution of β-eucryptite under a rigid spherical indenter using MD simulations [37]. An orthorhombic simulation box of dimensions 41.99 Å × 72.73 Å × 56 Å containing 13440 atoms was used to simulate
Table 4. Fractional coordinates of atoms in a unit cell of \(\beta\)-eucryptite calculated using ReaxFF at 0 K. The experimental values from [3] at 298 K are provided for comparison.

| Atom  | ReaxFF x   | ReaxFF y   | ReaxFF z   | Experiment x | Experiment y | Experiment z |
|-------|------------|------------|------------|--------------|--------------|--------------|
| Li(1) | 0.000      | 0.000      | 0.500      | 0.000        | 0.000        | 0.500        |
| Li(2) | 0.500      | 0.000      | 0.000      | 0.500        | 0.000        | 0.000        |
| Li(3) | 0.500      | 0.000      | 0.327      | 0.500        | 0.000        | 0.328        |
| Si(1) | 0.248      | 0.000      | 0.000      | 0.248        | 0.000        | 0.000        |
| Si(2) | 0.251      | 0.502      | 0.000      | 0.247        | 0.494        | 0.000        |
| Al(1) | 0.258      | 0.000      | 0.500      | 0.250        | 0.000        | 0.500        |
| Al(2) | 0.250      | 0.499      | 0.500      | 0.251        | 0.501        | 0.500        |
| O(1)  | 0.115      | 0.201      | 0.248      | 0.112        | 0.199        | 0.242        |
| O(2)  | 0.101      | 0.696      | 0.263      | 0.097        | 0.699        | 0.259        |
| O(3)  | 0.604      | 0.704      | 0.262      | 0.597        | 0.705        | 0.264        |
| O(4)  | 0.605      | 0.202      | 0.258      | 0.608        | 0.201        | 0.249        |

Figure 2. Equations of state of various phases of eucryptite calculated using (a) DFT and (b) ReaxFF. Both the techniques predict the same order of stability of the three polymorphs with \(\alpha\) being the most stable phase in each case.

the crystal, which was indented down the \(z\)-axis (i.e. the \([0 0 1]\) crystal direction). Periodic boundary conditions were applied in the directions perpendicular to the indentation force. The atoms that have \(z\) coordinates within 12 Å of the lowest \(z\) value (of all atoms) were kept fixed during MD runs in order to simulate the underlying bulk. The initial structure was relaxed at
0 K, and then thermalized at 300 K for 30 ps; the time step used in the MD runs was 1 fs. After thermalization, the top face was indented at a rate of 0.065 Å ps$^{-1}$ by a rigid spherical indenter of radius $R = 14$ Å which applies a radial force $F_i$ on atom $i$ given by

$$F_i = \begin{cases} 
-k(r_i - R)^2 & \text{if } r_i \leq R \\
0 & \text{if } r_i > R 
\end{cases}$$

(10)

where $k$ is a force constant ($k = 76.32$ kcal mol$^{-1}$ Å$^{-3}$), and $r_i$ is the distance between the center of the atom $i$ and that of the indenter.

During indentation simulations, we have not found any new phase at indent pressures smaller than 7 GPa even though the $\epsilon$ phase has been reported [17] to occur at $\sim$0.8 GPa. Using hydrostatic pressure on single-crystalline $\beta$-eucryptite does not lead to any room-temperature phase transitions for pressures up to 10 GPa. We have observed the formation of a denser but disordered phase in the vicinity of the indenter. Zhang et al [20] carried out in situ x-ray experiments on polycrystalline samples of $\beta$-eucryptite and reported that amorphization begins at a pressure $\sim$5 GPa and completes at a pressure of 17 GPa. Our indentation MD simulations predict a higher onset pressure for amorphization, $\sim$7 GPa. However, it should be noted that the simulations were carried out on single-crystal $\beta$-eucryptite; this eliminates the defects, porosity, or grain boundaries from our starting phase which would have acted as nucleation sites for the formation of the amorphous phase. Consequently, in the case of our simulations, there is an increased barrier toward amorphization, which is reflected in the increased onset pressure. At the ReaxFF onset pressure of 7 GPa, only regions near the indent amorphize, while those far away from it remain crystalline. As the indent pressure is increased, the amorphized region grows and there is a range of pressures over which amorphization proceeds: this finding is similar to what of Zhang et al have found for polycrystalline samples [20].

We have analyzed the amorphous phase by studying radial distribution functions (RDF) for pairs of different types of atoms in the disordered region. Specifically, the RDFs $g_{A-B}(r)$ were evaluated for Si–O, Al–O, Li–O and Li–Li pairs after indentation proceeded to different depths $h$. Figure 3 shows RDFs evaluated prior to the indentation, compared with those calculated after indentation to $h = 12$ Å; at this depth, we evaluated the contact pressure at $\sim$10 GPa. The RDFs for all the type pairs considered show, prior to indentation, well-defined peaks at characteristic distances of $\beta$-eucryptite. Under pressure, the first peak ($r = 1.6$ Å) of $g_{Si-O}(r)$ (see figure 3(a)) broadens somewhat and decreases in intensity compared with that of the crystalline $\beta$ phase. The peak corresponding to the second-nearest neighbor ($r = 4.1$ Å) is very broad, while peaks at higher distances are not defined. A similar behavior of the RDF was observed in the amorphous phase obtained from high-pressure MD simulations of $\beta$-cristobalite (SiO$_2$) [78]. Figure 3(b) shows the RDF for Al–O, which also exhibits the tell-tale signs of a disordered phase under pressure; the broadening of the first peak, along with the disappearance of the higher order peaks, has also been observed during amorphization of SiC [79] and $\alpha$-quartz [80]. Significant changes in the RDFs occur at contact pressures $\geq$7 GPa and indicate amorphization, which is also apparent from direct visualization of the structure. The pressure necessary for the onset of amorphization is consistent with empirical observations [20].

Interestingly, an additional feature is exhibited by the RDFs of Li–O and Li–Li pairs (figure 3(c) and (d)). The first peaks for the Li–Li and Li–O pairs are shifted significantly to lower distances in the high-pressure phase as compared with the initial crystal (figures 3(c) and (d)). For the Li–O pairs, the first peak shifts from 2 Å to 1.67 Å under pressure (figure 3(c)), which is close to the typical Li–O bond length of 1.606 Å [81]. Figure 3(d) shows that the smallest most probable Li–Li spacing at high pressure is $\sim$2.88 Å which is closer to the experimental value of the bond length (3.04 Å) in Li-metal [82] than it is to the lowest Li–Li
Figure 3. Pair distribution functions ($g_{A-B}(r)$) for (a) Si–O, (b) Al–O, (c) Li–O and (d) Li–Li pairs in $\beta$-eucryptite (black lines) and in the phase obtained under a spherical indent (red lines) at an applied contact pressure $\sim 10$ GPa. The broadening of the peaks corresponding to higher order neighbors and lowering of the nearest-neighbor distances in Li–O and Li–Li pairs at high pressures indicates that the new phase formed under the indent is amorphous.

distance (3.8 Å) in $\beta$-eucryptite. This suggests the existence of Li–Li bonds in the high-pressure phase, which were not present in the crystalline phase. In the crystalline phase, the smallest distance between Li atoms is 3.8 Å; at this distance there is no bond formed between the Li atoms, which simply reside in the spaces between Si–O$_4$ and Al–O$_4$ tetrahedra without bonding.
Table 5. Predicted stiffness constants $C_{ij}$ (in GPa) of $\alpha$-eucryptite using ReaxFF at 0 K.

|       | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{24}$ | $C_{15}$ | $C_{33}$ | $C_{44}$ |
|-------|----------|----------|----------|----------|----------|----------|----------|
| ReaxFF| 131.86   | 67.92    | 25.18    | 1.96     | 1.28     | 175.24   | 37.29    |

Table 6. Comparison of the calculated stiffness constants $C_{ij}$ (in GPa) of $\beta$-eucryptite at 0 K with the experimental data from [84] extrapolated to 0 K using the thermoelastic constants $T_{ij} = \frac{d \log C_{ij}}{dT}$. The uncertainty in any of the experimental values (exp) is smaller than 2.5 GPa.

|       | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{33}$ | $C_{44}$ |
|-------|----------|----------|----------|----------|----------|
| DFT   | 165.64   | 70.98    | 78.59    | 132.83   | 58.68    |
| ReaxFF| 178.92   | 102.77   | 118.28   | 181.26   | 47.37    |
| Exp   | 176.3    | 68.5     | 89.8     | 139.9    | 61.2     |
| $T_{ij}$ ($10^{-3}$/K) | −0.14 | 0.13 | −0.27 | −0.42 | −0.24 |

to any of the atoms of these tetrahedra. When indentation is applied, the tetrahedra are broken, leaving the Li atoms open to move. Often Li atoms find themselves in the vicinity of other Li atoms and create Li–Li bonds of 2.88 Å (figure 3(d)): this value is very close to the bond length in metallic Li-bcc [46]. Segregation of Li was not observed in the vicinity of the indenter, but densification of each of the four atomic species was. This densification is not likely to be an artifact of our potential, but it is the physical consequence of locally increasing the pressure.

3.4. Elastic properties of eucryptite phases

To assess the performance of ReaxFF in predicting elastic properties, we computed the elements of elastic stiffness tensor $C_{ij}$ for two polymorphs of eucryptite, $\alpha$ and $\beta$, by employing the technique outlined in appendix B. We have found that the stiffness tensors for both eucryptite phases are positive definite, which means that at the ReaxFF level the Born stability criterion [83] is met. The seven independent elastic constants of $\alpha$-eucryptite (rhombohedral structure) were calculated using ReaxFF at 0 K and are listed in table 5; to the best of our knowledge, so far there are no reports of elastic constants in the literature for this phase.

We have also calculated the five independent elastic constants of $\beta$-eucryptite (hexagonal structure) at 0 K predicted by ReaxFF and listed them in table 6. Haussühl et al [84] have measured these elastic constants using an ultrasonic technique at ambient temperature, 293 K. To compare the elastic constants predicted by ReaxFF in our study and those predicted by DFT (also at 0 K) [77] with the experimental values, we have extrapolated the measured values of $C_{ij}$ to 0 K using thermoelastic constants $T_{ij} = \frac{d \log C_{ij}}{dT}$ [84]. As shown in table 6, the ReaxFF elastic constants are in good agreement with experiment; with the exception of $C_{12}$, all the calculated constants are within $\sim$30% of experimental values extrapolated to 0 K. These ReaxFF values are also consistent with those predicted by DFT and reported in an earlier work [77].

The $\alpha$ and $\beta$ polymorphs of eucryptite are known to possess highly anisotropic physical properties. The overall elastic anisotropy of hexagonal and rhombohedral crystals is usually assessed through three ratios, $C_{11}/C_{33}$, $C_{12}/C_{13}$ and $2C_{44}/(C_{11} - C_{12})$, whose deviations from unity serve as measures of the anisotropy in the crystals being studied. Table 7 lists the anisotropy ratios for rhombohedral $\alpha$ and hexagonal $\beta$-eucryptite using the $C_{ij}$ predicted by ReaxFF.

The anisotropy of eucryptite polymorphs manifests, expectedly, in Young’s modulus $E$ as well as in other elastic properties. The direction-dependence of Young’s modulus can be
Table 7. Anisotropic factor ratios for α and β eucryptite (LiAlSiO₄) evaluated using single-crystal elastic constants \( (C_{ij}) \) predicted by ReaxFF in this study. For β-eucryptite, these ratios are also calculated using \( C_{ij} \) known by DFT and experiments for comparison.

| Phase          | Technique  | \( C_{11} \) | \( C_{33} \) | \( C_{12} \) | \( C_{13} \) | \( 2C_{44} \) | \( C_{11} - C_{12} \) |
|----------------|------------|--------------|--------------|--------------|--------------|--------------|---------------------|
| α-LiAlSiO₄    | ReaxFF     | 0.7525       | 2.6974       | 1.1664       |              |              |                     |
|                | DFT⁹       | 1.2470       | 0.9032       | 1.2398       |              |              |                     |
| β-LiAlSiO₄    | ReaxFF     | 0.9871       | 0.8688       | 1.2441       |              |              |                     |
|                | Exp⁸       | 1.2602       | 0.7628       | 1.1354       |              |              |                     |

Derived from the elastic constants, and we show it here as a way to directly visualize the anisotropic character of Young’s modulus (figure 4). Young’s modulus for a rhombohedral crystal in the \( R3 \) space group along a crystallographic direction of direction cosines \( l_1, l_2, l_3 \) can be expressed in terms of elastic compliance constants as [85]

\[
\frac{1}{E} = (1 - l_3^2)S_{11} + l_2^2S_{33} + l_1^2(1 - l_3^2)S_{13} + 2l_1l_2(3l_1^2 - l_2^2)S_{14} + 2l_1l_3(3l_2^2 - l_1^2)S_{25},
\]

(11)

where \( S_{ij} \) are the elements of elastic compliance matrix, \( S \) given by the inverse of the elastic stiffness matrix, \( C \), i.e. \( S = C^{-1} \). For hexagonal crystals, the directional dependence of \( E \) is given by [85]

\[
\frac{1}{E} = (1 - l_3^2)S_{11} + l_2^2S_{33} + l_1^2(1 - l_3^2)(2S_{13} + S_{44}).
\]

(12)

Figure 4(a) shows the variation of Young’s modulus of α-eucryptite with the angle \( \theta \) between a given crystallographic direction and the \( z \)-axis, for three different planes containing the \( z \)-axis; these planes are \( yz \) \( (l_1 = 0) \), \( xz \) \( (l_2 = 0) \) and the plane containing the first bisector of the \( xy \) plane, \( l_1 = l_2 = \sin \theta / \sqrt{2} \). The three polar plots in figure 4(a) were generated using equation (11) and the ReaxFF elastic constants in table 5.

Young’s modulus of β-eucryptite depends only on the angle \( \theta \) between a given direction and the \( z \)-axis (crystallographic \( c \)-axis), owing to the symmetry of a hexagonal crystal. Figure 4 shows the dependence of Young’s modulus of β-eucryptite on \( \theta \) calculated using the ReaxFF elastic constants and those known from DFT and experiments (table 6). The variation with \( \theta \) of the Young’s modulus of β-eucryptite calculated using elastic constants predicted by ReaxFF follows the same trends as the \( E \) calculated using the elastic constants known by DFT or experiments. We now focus on elastic properties corresponding to polycrystalline eucryptite phases.

The theoretical average bulk \( (B) \) and shear \( (G) \) elastic moduli of polycrystalline α- and β-eucryptite can be derived from their single-crystal elastic constants. There are two well-known approximations typically used to evaluate the polycrystalline elastic moduli, namely the Voigt [86] and Reuss [87] methods, which provide upper bounds (identified by the subscript \( V \)) and lower bounds (subscript \( R \)), respectively, for the bulk and shear moduli. For rhombohedral and hexagonal crystal systems, the polycrystalline bulk and shear moduli can be expressed in terms of the single-crystal elastic constants as

\[
B_V = \frac{1}{9} (2C_{11} + C_{33} + 2C_{12} + 4C_{13})
\]

(13)

\[
\frac{1}{B_R} = 2S_{11} + 2S_{12} + 4S_{13} + S_{33}
\]

(14)
Figure 4. Polar plots illustrating the directional dependence of Young’s Modulus $E$ for (a) $\alpha$-eucryptite using the elastic constants predicted by ReaxFF in three different crystallographic planes containing the $z$-axis and (b) $\beta$-eucryptite using the elastic constants predicted by ReaxFF and those known by DFT and experiments.

$$G_V = \frac{1}{30} (7C_{11} + 2C_{33} - 5C_{12} - 4C_{13} + 12C_{44})$$

(15)

$$\frac{1}{G_R} = \frac{1}{15} (14S_{11} - 10S_{12} - 8S_{13} + 4S_{33} + 6S_{44})$$

(16)

The Hill values ($B_H$, $G_H$) of the bulk and shear moduli are the arithmetic averages of the corresponding Voigt and Reuss bounds, and are considered the best estimates of these polycrystalline moduli [88]. The polycrystalline Young’s modulus $E_{\text{poly}}$ and Poisson’s ratio ($\nu_{\text{poly}}$) can be obtained through the relations applicable to isotropic materials [89].

$$E_{\text{poly}} = \frac{9B_H G_H}{3B_H + G_H}; \quad \nu_{\text{poly}} = \frac{3B_H - 2G_H}{2(3B_H + G_H)}.$$  (17)

Table 8 lists the average elastic moduli of polycrystalline $\alpha$ and $\beta$ eucryptite derived from the single-crystal constants $C_{ij}$ (tables 5 and 6) through the relationships in equations (13)–(17). For $\alpha$-eucryptite, the polycrystalline bulk modulus evaluated using the single-crystal elastic constants predicted by ReaxFF (75.06 GPa) is in excellent agreement with an earlier measurement (74 GPa) of Fasshauer et al [22]. Furthermore, the polycrystalline elastic
Table 8. Average values of bulk moduli ($B$, in GPa) and shear moduli ($G$, in GPa) using the Voigt, Ruess and Hill’s approximations for polycrystalline eucryptite phases derived from their single-crystal elastic constants $C_{ij}$. Young’s moduli ($E_{\text{poly}}$, in GPa) and Poisson ratios ($\nu_{\text{poly}}$) are evaluated using equations (17).

|            | $\alpha$-LiAlSiO$_4$ | $\beta$-LiAlSiO$_4$ |
|------------|----------------------|---------------------|
|            | ReaxFF | DFT$^a$ | ReaxFF | Exp$^b$ |
| $B_V$      | 75.06  | 102.27 | 135.31 | 109.85 |
| $B_R$      | 75.06  | 101.55 | 134.88 | 109.55 |
| $B_H$      | 75.06  | 101.91 | 134.88 | 109.70 |
| $G_V$      | 42.69  | 48.67  | 39.88  | 51.55  |
| $G_R$      | 38.44  | 46.08  | 38.48  | 47.10  |
| $G_H$      | 40.56  | 47.37  | 39.18  | 49.32  |
| $E_{\text{poly}}$ | 103.12 | 123.05 | 107.18 | 128.69 |
| $\nu_{\text{poly}}$ | 0.27   | 0.30   | 0.37   | 0.31   |

$^a$ From $C_{ij}$ in [77].
$^b$ From $C_{ij}$ in [84], extrapolated to 0 K.

constants of $\beta$-eucryptite calculated from the single-crystal elastic constants predicted by ReaxFF are in good agreement with those calculated using the elastic constants known by DFT and experiments (refer to table 8).

4. Summary and conclusion

In conclusion, we have developed a reactive force field for lithium–aluminum silicates and used it to describe (i) the atomic structure and heats of formation of several oxides, silicates and aluminates, (ii) the relative stability of three crystalline eucryptite polymorphs and the response of $\beta$-eucryptite under indentation, and (iii) the anisotropic and polycrystalline-averaged elastic properties of eucryptite phases.

**Successes.** We have found that structural properties and heats of formation for selected condensed phases agree well with the results of DFT calculations and with experimental reports. In terms of applications to the stability of eucryptite phases, we have verified that the order of the stability of three well-known polymorphs predicted by ReaxFF is the same as that obtained from DFT calculations and that known from experiments. The response of $\beta$-eucryptite to pressure is the formation of a denser and disordered phase which we characterized by a set of radial distribution functions and comparisons with condensed phases. In terms of elastic properties analysis, we have determined the elements of the stiffness tensor for $\alpha$- and $\beta$-eucryptite at the level of ReaxFF, and discussed the elastic anisotropy of these two polymorphs. Polycrystalline average properties of these eucryptite phases are also reported to serve as ReaxFF predictions of their elastic moduli (in the case of $\alpha$-eucryptite), or as tests against values known from experiments or DFT calculations ($\beta$-eucryptite). In addition to the elaborate but physically motivated description of the bond-order formalism coupled with the EEM scheme, the novel aspects/results of this work include the ability of ReaxFF to predict the formation of an amorphous phase under pressures exceeding 7 GPa, and the prediction of all elastic properties of $\alpha$-eucryptite—which is the most stable LiAlSiO$_4$ phase at room temperature and ambient pressure.

**Shortcomings.** We noted in section 3.1 that in the deformation regimes far outside equilibrium, the ReaxFF-predicted order of phase stability may not match the DFT predictions, especially in the tensile regimes. This problem is likely to manifest during reaction calculations.
at the level of several atoms, molecules, or small clusters, but may not easily manifest in large-scale MD simulations because fracture in tensile regimes will probably occur before any phase transformation. The values of the ReaxFF elastic constants $C_{ij}$ for $\beta$-eucryptite compare reasonably well with those predicted by other empirical force fields [27–31]. These values are not of superior accuracy, as they deviate by about 30% from the experimental values. The reasoning for such discrepancy can be understood as follows. The heat of formation curves (figure 1) include a few points in the low strain regimes because the emphasis for this potential is to describe reactions, formation of compounds, phase transitions, etc. As such, the potential is trained for very wide large ranges of strain (from 50% volumetric compression to 20% volumetric expansion). So when such large ranges of deformations are used, then during the fitting process there is very little weight given to the region of linear elastic strain (2% linear strain). Since this is the region that is directly and solely responsible for the elastic constants, then it comes as no surprise that some of the elastic constants are not of superior accuracy. Still, the values of $C_{ij}$ predicted by ReaxFF (table 6) deviate from experiments by amounts that are similar to the deviations made by the Pedone force field in predicting the elastic constants for spodumene (LiAlSi2O6) [31]. However, we found that PFF [31] and a core–shell model potential developed by Winkler et al (THB) [28] describe the elastic properties of aluminum silicate phases (especially those of andalusite, Al2SiO5) much better than ReaxFF. While this observation seems to place ReaxFF at a disadvantage, it should be noted that the PFF and other models were obtained by fitting against experimental values of the elastic properties of binary oxides and silicates [28, 31], while these properties were not a part of the training set used to determine the ReaxFF parameters in our study.

Concluding remark. The ReaxFF potential reported here can also describe well single-species systems (e.g. Li-metal, Al-metal and condensed phases of silicon), which makes it suitable for investigating structure and properties of suboxides, atomic-scale mechanisms responsible for phase transformations, as well as oxidation–reduction reactions. Based on the results of indentation on $\beta$-eucryptite and elastic properties of $\alpha$-eucryptite reported here, we believe that the parametrization of ReaxFF for Li–Al silicates will help provide fundamental understanding of other interesting phenomena in LAS glass ceramics, especially in regard to the atomic-scale mechanisms underlying the pressure-induced $\beta$-to-$\epsilon$ phase transformation where direct dynamic simulations at the level of DFT are currently intractable.

Acknowledgments

The work at the Colorado School of Mines was performed with support from the Department of Energy’s Office of Basic Energy Sciences through Grant No DE-FG02-07ER46397 and from the National Science Foundation (NSF) through Grant No CMMI-0846858. ACTvD acknowledges funding from KISK startup grant C000032472. We thank Professor Jincheng Du from the University of North Texas for providing the lithium-silicates DFT data that was published in [52]. Supercomputer time for the DFT calculations was provided by the Golden Energy Computing Organization at Colorado School of Mines.

Appendix A. ReaxFF parameters for Li–Al–Si–O systems

The mathematical formulation of the ReaxFF with details about the individual parameters can be found in (online supplementary information (stacks.iop.org/MSMSE/20/015002/mmedia)). The ReaxFF parameters for the Li–Al–Si–O systems determined in this study are listed in tables A1–A8.
Table A1. General parameters.

| Parameter | Value      | Description       |
|-----------|------------|-------------------|
| $p_{\text{boc}1}$ | 50.0000    | Bond-order correction |
| $p_{\text{boc}2}$ | 9.5469     | Bond-order correction |
| $p_3$      | 50.0000    | Overcoordination   |
| $p_4$      | 0.6991     | Overcoordination   |
| $p_6$      | 1.0588     | Undercoordination  |
| $p_7$      | 12.1176    | Undercoordination  |
| $p_8$      | 13.3056    | Undercoordination  |
| $p_{\text{lp}1}$ | 6.0891    | Lone-pair parameter |
| $p_{\text{v}7}$ | 33.8667   | Valence undercoordination |
| $p_{\text{v}8}$ | 1.8512     | Valence angle      |
| $p_{\text{v}9}$ | 1.0563     | Valence angle      |
| $p_{\text{v}10}$ | 2.0384    | Valence angle      |
| $p_{\text{vdW}1}$ | 1.5591    | van der Waals shielding |
| BOcut     | 0.0010     | Bond-order cutoff  |

Table A2. Atom parameters. All the parameters except $p_{\text{lp}2}$ (kcal mol$^{-1}$) are unitless.

| Atom | $V_i$ | $V_e^0$ | $V_a^0$ | $V_{\text{boc}}^0$ | $p_2$ | $p_5$ |
|------|-------|---------|---------|--------------------|-------|-------|
| Li   | 1.0000| 1.0000  | 1.0000  | 1.0000             | −24.7916| 0.0000 |
| Al   | 3.0000| 3.0000  | 3.0000  | 8.0000             | −23.1826| 0.0076 |
| Si   | 4.0000| 4.0000  | 4.0000  | 4.0000             | −4.1684 | 21.7115 |
| O    | 2.0000| 6.0000  | 4.0000  | 4.0000             | −3.5500 | 37.5000 |

| $p_{\text{v}3}$ | $p_{\text{v}5}$ | $p_{\text{lp}2}$ | $p_{\text{boc}3}$ | $p_{\text{boc}4}$ | $p_{\text{boc}5}$ |
|-----------------|-----------------|-----------------|-------------------|-------------------|-------------------|
| Li              | 2.2989          | 2.8103          | 0.0000            | 6.9107            | 5.4409            | 0.1973            |
| Al              | 1.5000          | 2.5791          | 0.0000            | 0.2500            | 20.0000           | 0.0000            |
| Si              | 2.0754          | 2.5791          | 0.0000            | 23.8188           | 9.0751            | 0.8381            |
| O               | 2.9000          | 2.9225          | 0.4056            | 0.7640            | 3.5027            | 0.0021            |

Table A3. Covalent radii ($r_0$, $r_0^\pi$, $r_0^{\pi\pi}$ in Å) and Coulomb interaction parameters ($\eta$ (eV), $\chi$ (eV) and $\gamma$ (Å)).

| Atom | $r_0$ | $r_0^\pi$ | $r_0^{\pi\pi}$ | $\eta$ | $\chi$ | $\gamma$ |
|------|-------|-----------|-----------------|--------|--------|---------|
| Li   | 1.6908| −0.1000   | −1.0000         | 11.0234| −3.2182| 1.0000  |
| Al   | 2.1967| −1.6836   | −1.0000         | 6.5000 | −0.3343| 0.4961  |
| Si   | 2.1932| 1.2962    | −1.0000         | 5.5558 | 4.2033 | 0.5947  |
| O    | 1.2450| 1.0548    | 0.9049          | 8.3122 | 8.5000 | 1.0898  |

Table A4. Van der Waals interaction parameters.

| Atom | $r_{\text{vdW}}$ (Å) | $D_{ij}$ (kcal mol$^{-1}$) | $\alpha$ | $r_{\text{vdW}}$ (Å) |
|------|----------------------|-----------------------------|----------|----------------------|
| Li   | 1.6121               | 0.2459                       | 10.8333  | 1.4649               |
| Al   | 2.3738               | 0.2328                       | 9.4002   | 1.6831               |
| Si   | 1.8951               | 0.1737                       | 11.3429  | 5.2054               |
| O    | 2.3890               | 0.1000                       | 9.7300   | 13.8449              |
Table A5. Bond parameters. The bond dissociation energies $D^\sigma_e$, $D^\pi_e$ and $D^{\pi\pi}_e$ are in kcal mol$^{-1}$ while $p_{be1}$, $p_{be2}$ and $p_1$ are unitless.

| Bond          | $D^\sigma_e$ | $D^\pi_e$ | $D^{\pi\pi}_e$ | $p_{be1}$ | $p_{be2}$ | $p_1$ |
|---------------|--------------|-----------|----------------|-----------|-----------|-------|
| O–O           | 142.2858     | 145.0000  | 50.8293        | 0.2506    | −0.1055   | 0.3451 |
| Si–O          | 274.8339     | 5.0000    | 0.0000         | −0.5884   | −0.2572   | 9.9772 |
| Si–Si         | 70.9120      | 54.0531   | 30.0000        | 0.4931    | −0.8055   | 0.2476 |
| Al–O          | 181.1998     | 0.0000    | 0.0000         | −0.2276   | −0.3500   | 0.2086 |
| Al–Si         | 0.0000       | 0.0000    | 0.0000         | 1.0000    | 0.0000    | 0.5000 |
| Al–Al         | 34.0777      | 0.0000    | 0.0000         | 0.4832    | −0.4197   | 6.4631 |
| Li–O          | 78.3666      | −0.0200   | 0.0000         | −1.0000   | −0.2500   | 0.2022 |
| Li–Si         | 0.0000       | 0.0000    | 0.0000         | 1.0000    | 0.0000    | 0.5000 |
| Al–Li         | 0.0000       | 0.0000    | 0.0000         | 1.0000    | 0.0000    | 0.5000 |
| Li–Li         | 42.9780      | 0.0000    | 0.0000         | 0.3228    | 0.2022    | 1.7161 |

Table A6. Bond-order parameters.

| Bond          | $p_{bo,1}$ | $p_{bo,2}$ | $p_{bo,3}$ | $p_{bo,4}$ | $p_{bo,5}$ | $p_{bo,6}$ |
|---------------|------------|------------|------------|------------|------------|------------|
| O–O           | 5.5000     | 1.0000     | 9.0000     | 1.0000     | −0.1000    | 0.6051     |
| Si–O          | 8.4790     | 6.0658     | 28.8153    | 1.0000     | −0.3000    | 0.2131     |
| Si–Si         | 8.7229     | 0.0000     | 7.1248     | 1.0000     | −0.3000    | 0.0392     |
| Al–O          | 6.1462     | 0.0000     | 25.0000    | 1.0000     | −0.3000    | 0.1925     |
| Al–Si         | 10.0000    | 0.0000     | 12.0000    | 1.0000     | 0.3000     | 1.0000     |
| Al–Al         | 6.1608     | 0.0000     | 14.3085    | 1.0000     | −0.3000    | 0.5154     |
| Li–O          | 7.8656     | 0.0000     | 11.9965    | 1.0000     | 0.3000     | 0.3228     |
| Li–Si         | 10.0000    | 0.0000     | 12.0000    | 1.0000     | 0.3000     | 1.0000     |
| Al–Li         | 10.0000    | 0.0000     | 12.0000    | 1.0000     | 0.3000     | 1.0000     |
| Li–Li         | 4.0000     | 0.0000     | 12.0000    | 1.0000     | 0.3000     | 0.6003     |

Table A7. Off-diagonal bond parameters ($D_{ij}$ (kcal mol$^{-1}$), $\alpha$ (unitless)) and bond radii ($R_{vdW}$, $r^\sigma_0$, $r^\pi_0$ and $r^{\pi\pi}_0$ (Å)).

| Bond          | $D_{ij}$  | $R_{vdW}$ | $\alpha$ | $r^\sigma_0$ | $r^\pi_0$ | $r^{\pi\pi}_0$ |
|---------------|-----------|-----------|----------|--------------|-----------|--------------|
| Si–O          | 0.1836    | 1.9157    | 10.9070  | 1.7073       | 1.2375    | −1.0000      |
| Al–O          | 0.2017    | 1.8458    | 11.0700  | 1.6009       | −1.0000   | −1.0000      |
| Al–Si         | 0.1000    | 1.8500    | 10.3237  | −1.0000      | −1.0000   | −1.0000      |
| Li–O          | 0.0790    | 2.2000    | 9.0491   | 1.8165       | −1.0000   | 1.0000       |
| Li–Si         | 0.0200    | 1.5000    | 10.0529  | −1.0000      | 1.0000    | 1.0000       |
| Al–Li         | 0.1146    | 2.2000    | 9.7537   | −1.0000      | 1.0000    | 1.0000       |

Appendix B. Calculation of elastic constants

The elements of the elastic stiffness tensor $C_{ijkl}$ for $\alpha$ and $\beta$ eucryptite were computed within the framework of ReaxFF by calculating the second derivatives of strain energy density with respect to the strain components [90]

$$C_{ijkl} = \frac{\partial^2 (E/V)}{\partial \epsilon_{ij} \partial \epsilon_{kl}}, \quad (B1)$$

where $E$ is the elastic energy stored in a domain of volume $V$ of the crystal subjected to homogeneous deformations. A similar approach has been employed earlier for computing the elastic constants of $\beta$-eucryptite using DFT calculations (see [77]). For sufficiently small strains, the total energy $E$ of a crystal subjected to a general strain can be expressed as a Taylor
Table A8. Valence angle parameters.

| Θ_{θ_{0,0}} (°) | \( p_{v1} \) (kcal mol\(^{-1}\)) | \( p_{v2} \) | \( p_{v4} \) | \( p_{v7} \) |
|-----------------|-------------------------------|----------|----------|----------|
| O–O–O           | 80.7324                       | 30.4554  | 0.9953   | 1.0783   |
| Si–Si–Si        | 78.5339                       | 36.4328  | 1.0067   | 1.6608   | 0.1694   |
| O–Si–Si         | 86.3294                       | 18.3879  | 5.8529   | 1.2310   | 1.7361   |
| O–Si–O          | 79.5581                       | 34.9140  | 1.0801   | 2.2206   | 0.1632   |
| Si–O–Si         | 82.3364                       | 4.7350   | 1.3544   | 1.0400   | 1.4627   |
| O–O–Si          | 59.5433                       | 20.0000  | 4.0000   | 2.0988   | 3.0000   |
| Si–O–Al         | 20.7204                       | 13.4875  | 4.0000   | 1.4098   | 0.6619   |
| Al–O–Al         | 50.9423                       | 7.0901   | 3.9271   | 2.5544   | 1.0000   |
| Si–O–Li         | 18.0953                       | 5.3220   | 4.0000   | 1.0139   | 1.0000   |
| Si–O–Li         | 18.0953                       | 5.3220   | 4.0000   | 1.0139   | 1.0000   |
| O–O–Al          | 20.7204                       | 13.4875  | 4.0000   | 1.4098   | 0.6619   |
| O–Si–O          | 79.5581                       | 34.9140  | 1.0801   | 2.2206   | 0.1632   |
| O–Si–Si         | 86.3294                       | 18.3879  | 5.8529   | 1.2310   | 1.7361   |
| O–Si–Si         | 86.3294                       | 18.3879  | 5.8529   | 1.2310   | 1.7361   |

Table B1. The strains used to calculate the five independent elastic constants of hexagonal \( \beta \)-eucryptite (also used in [91] and [77]). The relationship between \( A_2 \) in equation (B3) and \( C_{ij} \) is also provided.

| Strain parameters (unlisted \( \epsilon_i = 0 \)) | Second-order coefficient \( A_2 \) in equation (B3) |
|-----------------------------------------------|-----------------------------------------------|
| \( \epsilon_1 = \epsilon_2 = \delta \)       | \( C_{11} + C_{12} \)                           |
| \( \epsilon_1 = -\epsilon_2 = \delta \)      | \( C_{11} - C_{12} \)                           |
| \( \epsilon_1 = \epsilon_2 = \epsilon_3 = \delta \) | \( C_{11} + C_{12} + 2C_{13} + C_{33}/2 \) |
| \( \epsilon_3 = \delta \)                     | \( C_{33}/2 \)                                  |
| \( \epsilon_5 = \delta \)                     | \( 2C_{44} \)                                   |

series expansion truncated at the second order [90]

\[
E(V, \epsilon) = E_0 + V_0 \left( \sum_i \sigma_{ij} \eta_i \epsilon_i + \sum_{i,j} \frac{1}{2} C_{ij} \eta_i \epsilon_i \eta_j \epsilon_j \right),
\]

(B2)

where the subscripts are cast in the Voigt notation (\( 11 = 1 \), \( 22 = 2 \), \( 33 = 3 \), \( 23 = 4 \), \( 31 = 5 \) and \( 12 = 6 \)), \( \eta_i = 1 \) if \( i = 1 \), \( 2 \) or \( 3 \) and \( \eta_i = 2 \) if \( i = 4 \), \( 5 \) or \( 6 \), \( E_0 \) is the energy of the crystal volume \( V_0 \) at equilibrium, \( \sigma_{ij} \) are the elements of the stress tensor, and \( \delta_{ij} \) is the Kronecker symbol. For the strains listed in tables B1 and B2, equation (B2) reduces to

\[
E(V, \delta) = E_0 + V_0 (A_1 \delta + A_2 \delta^2),
\]

(B3)

where \( A_1 \) is related to stress components \( \sigma_{ij} \), and \( A_2 \) is a linear combination of the elastic constants \( C_{ij} \) expressed in the Voigt notation.

\( \beta \)-eucryptite has five independent elastic constants, namely \( C_{11}, C_{12}, C_{13}, C_{33} \) and \( C_{44} \) due to the hexagonal symmetry associated with its structure [85]. Table B1 lists the five different strains that we utilized to compute the elastic constants of \( \beta \)-eucryptite along with the relationship between the second-order coefficient \( A_2 \) and the elastic constants \( C_{ij} \) for each type of strain.

On the other hand, \( \alpha \)-eucryptite has a rhombohedral crystal structure and thereby, has seven independent elastic constants, namely, \( C_{11}, C_{12}, C_{13}, C_{14}, C_{15}, C_{33} \) and \( C_{44} \) [85].
different strains used to compute these seven elastic constants and the relationships between $A_2$ and $C_{ij}$ for each type of strain have been summarized in Table B2.

For a given crystal, the total energy was computed for different values of $\delta$ ranging from $-2\%$ to $2\%$ using the LAMMPS [37] implementation of ReaxFF. The calculated data were then fit to equation (B3) to extract the second-order coefficients $A_2$ which were then used to evaluate the elastic constants through the relationships given in Tables B1 and B2.

### Table B2

| Strain parameters (unlisted $\epsilon_i = 0$) | Second-order coefficient $A_2$ in equation (B3) |
|------------------------------------------|----------------------------------|
| $\epsilon_1 = \delta$                   | $C_{11}/2$                      |
| $\epsilon_3 = \delta$                   | $C_{33}/2$                      |
| $\epsilon_1 = \epsilon_2 = \epsilon_3 = \delta$ | $C_{11} + C_{12} + 2C_{33} + C_{33}/2$ |
| $\epsilon_1 = -\epsilon_2 = \epsilon_3 = \delta$ | $C_{11} - C_{12} + C_{33}/2$    |
| $\epsilon_1 = \epsilon_4 = \delta$     | $C_{11}/2 + 2C_{14} + 2C_{44}$ |
| $\epsilon_1 = \epsilon_5 = \delta$     | $C_{11}/2 + 2C_{15} + 2C_{44}$ |
| $\epsilon_4 = \delta$                   | $2C_{44}$                       |

### References

[1] Bach H and Krause D (ed) 1995 *Low Thermal Expansion Glass Ceramics (Schott Series on Glass and Glass Ceramics)* (Berlin: Springer)

[2] Palmer D C 1994 *Reviews in Mineralogy* ed P J Heaney *et al* (Mineralogical Society of America, Washington DC, 1994) vol 29, p 83

[3] Xu H, Heaney P J, Yates D M, von Dreеле R B and Bourke M A 1999 *J. Mater. Res.* **14** 3138

[4] Lichtenstein A I, Jones R O, Xu H and Heaney P J 1998 *Phys. Rev. B* **58** 6219

[5] Lichtenstein A I, Jones R O, de Gironcoli S and Baroni S 2000 *Phys. Rev. B* **62** 11487

[6] Winkler H G F 1948 *Acta Crystallogr.* **1** 27

[7] Buerger M J 1954 *Am. Mineral.* **39** 600

[8] Schulz H and Tscherry V 1972 *Acta Crystallogr.* **28** 2174

[9] Tscherry V, Schulz H and Laves F 1972 Z. Kristallogr. **135** 161

[10] Tscherry V, Schulz H and Laves F 1972 Z. Kristallogr. **135** 175

[11] Pillars W W and Peacor D R 1973 *Am. Mineral.* **58** 681

[12] Alpen U V, Schulz H, Talat G H and Böhm H 1977 *Solid State Commun.* **23** 911

[13] Press W, Renker B, Schulz H and Böhm H 1980 *Phys. Rev. B* **21** 1250

[14] Nagel W and Böhm H 1982 *Solid State Commun.* **42** 625

[15] Renker B, Bernotat H, Heger G, Lehner N and Press W 1983 *Solid State Ion.* **9** 1341

[16] Sarlbaeva A, Wels S A and Redfern S A T 2004 *J. Phys.: Condens. Mater.* **16** 8173

[17] Zhang J, Celestian A, Praise J B, Xu H and Heaney P J 2002 *Am. Mineral.* **87** 566

[18] Jochum T, Reimanns I E, Lance M J and Fuller E R Jr 2009 *J. Am. Ceram. Soc.* **92** 857

[19] Beall G H 1994 *Reviews in Mineralogy* ed P J Heaney *et al* (Mineralogical Society of America, Washington DC, 1994) vol 29 p 469

[20] Zhang J, Zhao Y, Xu H, Zelinskas M V, Wang L, Wang Y and Uchida T 2005 *Chem. Mater.* **17** 2817

[21] Daniels P and Fylde C A 2001 *Am. Mineral.* **86** 279

[22] Fasshauer D W, Chatterjee N D and Cemick L 1998 *Constr. Mineral. Petrol.* **133** 186

[23] Martoňák R, Laio A and Parrinello M 2003 *Phys. Rev. Lett.* **90** 075503

[24] Donadio D, Martoňák R, Raiteri P and Parrinello M 2008 *Phys. Rev. Lett.* **100** 165502

[25] Lewis G V and Caltow C R A 1985 *J. Phys. C: Solid State Phys.* **18** 1149

[26] Huang C 1990 *PhD Thesis* Alfred University

[27] van Beest B W H, Kramer G J and van Santen R A 1999 *Phys. Rev. Lett.* **84** 1955

[28] Winkler B, Dove M T and Leslie M 1991 *Am. Mineral.* **76** 313

[29] Cormack A N and Cao Y 1996 *Mol. Eng.* **6** 183
[82] Weast R C (ed) 1987 Handbook of Chemistry and Physics 68th Edn (Boca Raton FL: CRC Press)
[83] Born M and Huang K 1956 Dynamical Theory of Crystal Lattices (Oxford: Clarendon)
[84] Haussühl S, Nagel W and Böhm H 1984 Z. Kristallogr. 169 299
[85] Nye J F 1985 Physical Properties of Crystals (Oxford: Oxford University Press)
[86] Voigt W 1928 Lehrbuch der kristallphysik (Leipzig: Teubner)
[87] Reuss A Z 1929 Angew. Math. Mech. 9 49
[88] Hill R 1952 Proc. Phys. Soc. Lond. A 65 349
[89] Simmons G and Wang H 1971 Single Crystal Elastic Constants and Calculated Aggregate Properties 2nd edn (Cambridge, MA: MIT)
[90] Wallace D C 1972 Thermodynamics of Crystals (New York: Wiley)
[91] Fast L, Wills J M, Johansson B and Eriksson O 1995 Phys. Rev. B 51 17431