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Structural properties and mechanical stability of lithium-ion based materials. A theoretical study

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ABSTRACT

An extension of the existing force field for classical simulations was derived, and applied to Li_2TiO_3, Li_2SnO_3, Li_2SiO_3 and other oxides such as SiO_2 and SnO_2. Using density functional theory, bulk properties such as elastic constant tensor components, Bulk, Shear and Young's modulus were computed. This force field was subsequently applied to calculate the bulk properties of some lithium-based materials (Li_2MO_3 where M = Sn^{4+}, Si^{4+} and Ti^{4+}), as well as to explore their elastic stability and isotropy. The doped Li_2MO_3 materials reveals the improvements-deteriorations effect of their mechanical properties as well as ductile/stiffness character. The capability of the force fields parameters is verified by testing the structural and mechanical properties of monoclinic $Li_2Si_2O_5$, $Li_2Ti_6O_{13}$ and the unreported monoclinic $Li_2Sn_6O_{13}$. The results in general are in good agreement with previous experimental and theoretical studies. We propose that monoclinic $Li_2Sn_6O_{13}$ can also be obtained experimentally via Sn/Ti ion exchange.

1. Introduction

Lithium-containing ceramics have been considered as possible solid breeder materials in the blanket fusion reactors [1–3]. The use of a breeder material is to produce tritium atoms from Li-transmutation, performing as fuel components of the reactor. Bearing in mind that some key properties should be satisfied for the materials to be used as breeder, many researchers focused on the exploration of physical properties of materials such as Li_2SiO_3, Li_2SnO_3 and more recently Li_2TiO_3 [1–5]. Other important technological applications of such lithium oxide Li_2MO_3 (M = Ti, Si, Sn) materials include the lithium rechargeable batteries in electric and hybrid vehicles, portable electronic devices as well as in large-scale energy packing systems for solar energy [3–12]. Lithium atom content, low electrical conductivity and activation energy, lithium release performance and chemical stability are the main physical properties that permit these materials to be used as solid blanket materials in nuclear reactors, as well as in lithium ion batteries [13,14]. Of the materials currently considered, Li_2TiO_3 emerges as one of the best candidates as breeder materials. Atomistic simulations are a powerful tool to explore the bulk properties, even transport of charge and mass and surface properties of materials in general. Studies based on density functional theory (DFT) showed that structural and thermodynamic properties, as well as the lithium diffusion pathway and elastic properties of Li-based materials can also accurately be achieved [15–17]. Classical simulations based on empirical potential (force field) revealed the most probable Li-diffusion pathway in Li_2TiO_3 [17–19]. It is well known that lattice parameters, mechanical, thermal and transport properties of any material are modified by a substitution of a foreign ion in the host structure (action known as doping) [20–23].

Although the effects of doping can be studied using atomistic molecular dynamics (MD) simulations, but as far as we are aware, the doped materials have rarely been investigated theoretically [21–23]. The fact that the formal charges of the host ions in Li_2TiO_3 are fractional, inhibits the research of the defects formation for its use in classical MD in other materials [24–28] making use of the existing empirical potentials [18]. Indeed, the actually available force fields are limited to the undoped compounds such as Li_2TiO_3 [17–19].

In this context, the aim of the present work is to determine a new set of potential parameters (or force field) to model the Li^+ ion based materials. For this purpose, ternary oxides such as Li_2MO_3 where M = Sn^{4+}, Si^{4+} and Ti^{4+}, are analyzed. The compounds Li_2TiO_3, Li_2SnO_3 and Li_2SiO_3 are thus used as the basic

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compounds for the development of an appropriate set of force field parameters. This provides us with an additional reliable toolbox to examine the mechanical properties and stability of Li_2MO_3, without the computational high costs that are normally required for *ab initio* quantum chemical calculations in solid state compounds, including an accurate prediction of many properties without experiment examination.

2. Methodologies

2.1. Quantum based calculations

The procedure to obtain a set of potential parameters for simulations is rather standard. To develop a new force field, it is necessary to decide upon the data that will be used for the fitting procedure. For crystal systems, the lattice parameters of the unit cell and cohesive energy are of the most commonly used along with known properties such as the Young's modulus, elastic constant tensor components and high-frequency dielectric permittivity [25,27–30].

These quantities can be determined by using two different approaches, namely by using experimental values, if determined and reported in the literature, or by carrying out DFT calculations (geometry optimizations and elastic constant calculations). Thus, by using the available values, the potential parameters can be fitted in order to reproduce not only the cohesive energies but also all the aforementioned bulk properties. A comparison with the experimental values allows the accuracy of the obtained force field to be calibrated, and its capabilities to reproduce and to predict the crystal structures of the desired materials to be established.

In the present work we start the process by carrying out full DFT calculations. Geometry optimizations using the CASTEP computer code [31] were performed. The convergence thresholds-between optimization cycles- are used with total energy change of 5×10^{-6} eV/atom, maximum force, stress and atomic displacements of 10^{-2} eV/Å, 2×10^{-2} GPa and 5×10^{-4} Å, respectively. The exchange-correlation is designated by the use of the generalized gradient approximation of Perdew, Burke and Ernzerhof (GGA-PBE) [32]. A Γ-centered Monkhorst-Pack scheme [33] was used to sample the Brillouin zone with the separation of points maintained as close as possible to 0.05 along each axis. Pseudo atomic functions for Li-$2s^1$, O-$2s^2$ $2p^4$, Ti-$3d^2$ $4s^2$, Si-$3d^2$ $4s^2$ and Sn-$3d^2$ $4s^2$ in the reciprocal representation are employed. The plane-wave energy cut-off, adopted for the standard norm-conserving pseudopotentials, is 550 eV, which is chosen considering the larger value of the energy cut-offs in the pseudopotentials. This setup is used to obtain structural parameters, and for elastic constant calculations (seven cycles are performed for the elastic constant calculations). The selected structures include Li_2TiO_3 (space group C2/c) [17,18], SiO_2 cristobalite high (Fd-3m) [34,35], SnO_2 ($P4_2/Mnm$) [36], Li_2SiO_3 ($Cmc2_1$) [16,37,38], and Li_2SnO_3 (C2/c) [39,40] taken for the literature.

2.2. Fitting procedure

To model the structures, we adopt a potential model based on the Born model which consists of both short-range and long-range interactions. A standard Buckingham potential is used for short-range interactions (Eq. (1)), with a 20 Å cut-off:

$$U(r_{ij}) = A\exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^6} \quad (1)$$

where A, ρ and C are fitted parameters for a pair of ions i and j and r_{ij} is the interatomic distance between them. The r^{-6} term takes the attractive dispersion or van der Waals interaction into account, whereas the exponential term describes the Pauli repulsion. Long-distance interactions are considered as purely Coulombic for each ion, and the ion's polarization is explicitly involved by using the shell model [41], where the charge of each ion is represented as core and shell charge (joined by a spring with a spring constant k), F and Y respectively, in such a way that F + Y = Z, where Z is the charge of the ion considered. This method was used in many similar studies and gave good agreement with experiments [24–28].

The General Utility Lattice Program (GULP) is used for the derivation of the force field [29]. Based on the force field previously reported in Ref. [18] we set the charges of Li to be +0.55 electron, Ti (+2.2 electron) and O (shell charge −1.60 electron). The A, ρ, and C parameters (of Eq. (1)) are kept fixed for the Li-Li, Li-O, O-O, Ti-O and Ti-Li pairs, while the A, ρ and C parameters for Si-O, Si-Si, Si-Li, Sn-Sn, Sn-Li and Sn-O are obtained by assigning the Ti charge to the Sn and Si dopants. Firstly, the potential parameters of Si-O, Si-Si, Sn-Sn and Sn-O are fitted to reproduce the cell parameters, as well as mechanical properties of SnO_2 and SiO_2 cristobalite high. Secondly, the potential parameters for Si-Li and Sn-Li pairs are obtained by considering the mechanical properties as the main quantities to be reproduced for Li_2SnO_3 and Li_2SiO_3 structures.

A schematic representation of the fitting procedure is shown in Fig. 1. In order to perform a derivation of any potential parameter, the accuracy criteria for the obtained results is expressed by the sum of squares (Eq. (2)):

$$S = \sum_{j=1}^{N} w_j (s_j^{obs} - s_j^{cal})^2 \quad (2)$$

where N is the number of observable parameters which corresponds to the magnitudes of elastic constant tensor components, Bulk, Shear and Young's modulus. These observable parameters are obtained from previous DFT calculations. The amounts of s_j^{obs} and s_j^{cal} represent the fitted and calculated values of the observable parameters, respectively. The w_j represents a weight factor for a given observable parameter [29], which is assigned automatically by the GULP code. The use of the observable parameters obtained by DFT computations give the advantage that one can get many properties for solid state materials where no experimental data exist, or for geometries that are significantly perturbed from the structure of interest.

The fitting procedure includes a minimization of the S function in the same manner as used in classical optimization procedures. The potential parameters are determined by a least-squares procedure, minimizing the S function. The relaxed fitting at constant pressure has been employed, as encoded in the GULP program, which has also been used for all atomistic calculations of the present work. The structures are relaxed to zero strain for each evaluation of the sum of squares, and the difference between the observed and calculated structural parameters is used as accuracy criteria of fitting.

3. Results and discussion

3.1. Validation of the potential (force field) parameters

The new set of potential parameters defining the force field is listed in Table 1. Using these potential parameters, we start to obtain the bulk properties of the materials considered by means of structural optimization using the Newton-Rapson procedure under constant pressure optimizations and the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm to update the Hessian [42]. During the geometry optimization, the convergence thresholds criteria are selected as: 10^{-2} eV/Å, 5×10^{-4} Å and 2×10^{-2} GPa for maximum force, atomic displacement and stress, respectively.