Development of a machine learning potential model of Li_2TiO_3 for radiation damages and effects

Donggyu Lee, Takuji Oda
Department of Nuclear Engineering, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826
**Corresponding author: oda@snu.ac.kr*

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1. Introduction

Li_2TiO_3 is a promising candidate material for the tritium breeder in nuclear fusion reactors. The helium-cooled ceramic reflector (HCCR) blanket of K-DEMO plans to adopt Li_2TiO_3 as the breeder material. However, radiation effects on the material properties of Li_2TiO_3 are yet to be understood and quantified.

To investigate the radiation damage and effects of materials by computational simulations, molecular dynamics (MD) simulations have been widely used. To accurately evaluate the radiation effects by MD, an interatomic potential model that can accurately calculate material properties and defect energies is needed. In this study, to simulate radiation damage and effects of Li_2TiO_3 by MD in the future, we develop a machine learning potential model, which is trained using density functional theory (DFT) calculations, in the framework of moment tensor potential (MTP) [1]. The accuracy of the MLP is evaluated in comparison with available DFT and experimental data for material properties and defect formation energies.

2. Methods

The training set of MTP, which is composed of energy, force, and stress values for structures relevant to Li_2TiO_3 properties, was prepared by DFT calculations using the Vienna Ab-initio Simulation Package (VASP). We used supervised learning and active learning to train an MTP efficiently.

2.1. Moment tensor potentials (MTPs)

MTPs are linearly parameterized machine learning potentials. The energy of a system is described by the sum of per-atom energy functions V, as

$$E^{mtp}(cfg) = \sum_{i=1}^{N} V(n_i) = \sum_{i=1}^{N} \sum_{\alpha=1}^{m} \xi_\alpha B_\alpha(n_i) \quad (1)$$

where N is the number of atoms in the system, m is the number of basis functions B_α, ξ_α is the coefficient of each basis function, and n_i denotes the neighborhood of the i-th atom. The name of moment tensor potentials comes from the way its basis function is formulated: the descriptor tensors, which look like moment tensors in mechanics, are contracted to form basis functions. A set of ξ_α values are optimized to accurately reproduce the training set prepared by DFT calculations.

2.2. Preparation of dataset for supervised learning

We performed static calculations and first-principles molecular dynamics (FPMD) calculations by DFT to prepare the training set.

The static data consists of elastic deformation and point defects. As for point defects, (i) Frenkel pairs for Li, Ti, and O, (ii) Li-Ti antisite defects, and (iii) Schottky defects of a unit of Li_2O, TiO_2, or Li_2TiO_3 were prepared in a 2×1×1 supercell composed of $Li_{32}Ti_{16}O_{48}$. For all cases, the charge neutrality was satisfied.

For FPMD calculations, 2000 steps each for 600 K (solid) and 2600 K (liquid) were performed.

2.3. Active learning

By evaluating the similarity between data, a machine can actively decide whether certain data needs to be incorporated into the training set without human judgment. This method is called active learning, and it can be utilized to efficiently broaden the configurational space on which a model is trained when building machine learning potentials. We used the MLIP package for active learning [1].

Active-learning MD simulations of heating up to 2600 K were performed. Subsequently, the system was cooled down until it reached 1200 K. This active learning step was expected to make an MTP accurate not only for solid crystals but also for liquid and amorphous phases, improving MTP accuracy in irradiation damage simulations.

3. Results

We validated the developed MTP by comparing several material properties to DFT or experimental values. In addition to the fundamental material properties of perfect Li_2TiO_3 crystals, defect formation energies obtained by the MTP were compared to the ones by DFT. The experiment using single-crystal Li_2TiO_3 showed that the fundamental space group for triclinic β-Li_2TiO_3 is C2/c [2]. We, therefore, dealt with C2/c Li_2TiO_3.

We also present properties computed by using a conventional Buckingham potential developed by Vijayakumar *et al.* [3], which has been widely used for MD studies on Li_2TiO_3 to evaluate the performance of MTP compared to the existing potential model.

3.1. Elastic constants

Table I: Elastic constants of Li_2TiO_3 determined using MD and DFT.

(GPa)	MTP	Buck [4]	DFT
C_{11}	267 (-2%)	228 (-16%)	272 (276)
C_{22}	274 (+2%)	224 (-16%)	268 (270)
C_{33}	223 (+10%)	123 (-39%)	202 (210)
C_{12}	73.7 (-5%)	83.9 (+8%)	77.9 (74.2)
C_{13}	29.6 (+20%)	41.2 (+67%)	24.7 (23.9)
C_{23}	32.0 (+20%)	40.9 (+54%)	26.6 (24.2)
C_{44}	53.0 (+16%)	37.4 (-18%)	45.8 (57.5)
C_{55}	52.1 (+16%)	37.0 (-18%)	44.9 (56.8)
C_{66}	97.4 (+2%)	71.8 (-25%)	95.3 (104)

Selected elastic constants of C2/c β-Li_2TiO_3 for the MTP (this work), Buckingham potential (Buck), and DFT (this work) are compared in Table 1. The parentheses on the MTP and Buck columns denote relative errors to the DFT. The parentheses on the DFT columns are the values reported in a previous DFT study by Murphy *et al.* [4]. Our DFT results coincide with Murphy's results with less than 12 GPa differences.

The MTP generally shows good correspondence to the DFT-evaluated elastic constants and outperforms the Buckingham potential, particularly on *c*-axis-related constants (C_{33}, C_{13}, C_{23}). As indicated by Murphy *et al.*'s work [4], the Buckingham potential fails to correctly evaluate *c*-directional information by underestimating the distance between the cation (Li, $LiTi_2$) layer and an oxygen layer compared to both DFT and experiments, which resulted in a notable contraction in the *c* lattice parameter and large errors in C_{33}, C_{13}, and C_{23}.

3.2. Thermal expansion

MD simulation of heating was performed with an NPT ensemble. The equilibrium lattice constants were obtained at every 100 K and compared with available experimental data.

Linear thermal expansion coefficients for the lattice constants *a* and *b* agreed with experimental data. Those equilibrium lattice constants obtained using the MTP were similar to those using the empirical Buckingham potential.

A difference between MTP and the Buckingham potential appears in linear thermal expansion for the lattice constant *c*. As shown in Fig. 1, the Buckingham potential significantly underestimated the optimized value at 0 K and overestimated the thermal expansion coefficients at high temperatures.

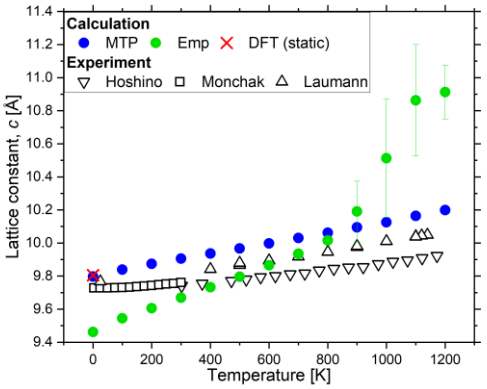

Fig. 1. The equilibrium lattice constant *c* from 0 K to 1200 K determined by MD simulations using the developed MTP and the Buckingham potential. Three experimental data are presented for comparison

3.3. Thermal conductivity

We computed the lattice thermal conductivity using the Green-Kubo relations in the framework of equilibrium molecular dynamics.

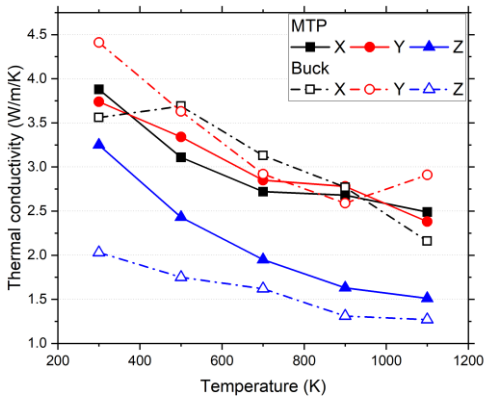

Fig. 2. Directional thermal conductivity by MTP and empirical Buckingham potential measured using Green-Kubo methods.

Li_2TiO_3 is known to have anisotropy in thermal conductivity both by experiment [2] and MD calculation using the Buckingham potential [5]. Fig. 2 shows the evaluated directional thermal conductivities. While x-directional and y-directional thermal conductivities are comparable, z-directional thermal conductivity is significantly lower, which means that our potential model can successfully capture the anisotropy in the thermal conductivity of Li_2TiO_3. The only experimental measurement asserts that the z-directional thermal conductivity is ~0.9 W/m/K at 294 K [2], which is much lower than our calculation result. The cause of this disagreement is unclear at this moment. The effective thermal conductivities evaluated by the MTP and Buckingham potential, which are the average values over

the three directions, show good agreement with the experimental values.

3.4. Defect formation energy

In a multi-component system, a point defect may be locally charged. In this study, we only dealt with charge-neutral systems for simplicity. The charge neutrality was regarded by supposing the charge state of Li, Ti, and O as +1, +4, and -2 and confirming the charges of constituent atoms summing up to zero. As described in section 2.2, the defect formation energy of each Frenkel pair, Li-Ti antisite defect, and Schottky defect was calculated.

The defect formation energy E_f is defined as

$$E_f = E_{def} - E_{ref} \quad (2)$$

Here, E_{def} is the energy of a defective system, and the reference energy E_{ref} depends on the type of defect. We herein used 2×1×1 supercell. For Frenkel pairs and antisite defects, the composition of the system is unchanged, so

$$E_{ref} = 2 \times E_{Li_2TiO_3} \quad (3)$$

where $E_{Li_2TiO_3}$ is the system energy of Li_2TiO_3 unit cell ($Li_{16}Ti_8O_{24}$).

The composition is changed in a system with a Schottky defect. If *m* units of Li_2O-type Schottky defect are introduced, the reference energy is

$$E_{ref} = 2 \times E_{Li_2TiO_3} - \frac{m}{4} \times E_{Li_2O}. \quad (4)$$

For TiO_2-type and Li_2TiO_3-type Schottky defects, the reference energy is respectively defined as

$$E_{ref} = 2 \times E_{Li_2TiO_3} - \frac{1}{2} \times E_{TiO_2} \quad (5)$$

and

$$E_{ref} = 2 \times E_{Li_2TiO_3} - \frac{1}{8} \times E_{Li_2TiO_3}. \quad (6)$$

Here, E_{Li_2O} is the system energy of Li_2O unit cell (Li_8O_4) and E_{TiO_2} is the system energy of rutile TiO_2 unit cell (Ti_3O_6).

Table II: Formation energy (in eV) of each defect for the most stable configuration.

Defect type	MTP	Buck	DFT
Li Frenkel	1.583	0.468	1.631
Ti Frenkel	0.766	2.528	0.793
O Frenkel	0.785	7.500	0.699
Li-Ti antisite	0.737	1.641	0.751
1 Li_2O Schottky	2.808	3.514	2.625
2 Li_2O Schottky	5.380	7.470	5.073
3 Li_2O Schottky	7.433	10.51	7.210
4 Li_2O Schottky	9.379	17.42	9.083
TiO_2 Schottky	12.149	3.363	12.004
Li_2TiO_3 Schottky	4.366	6.465	4.164

The defect formation energies are compared between DFT and MTP in Table II for the most stable defect configuration identified by DFT for each defect type. MTP shows not more than 0.2 eV error and up to 12% difference from DFT. The Buckingham potential, however, largely failed to estimate the defect formation energy.

4. Conclusions

We developed the MTP trained on the DFT dataset for Li_2TiO_3. The validation tests confirmed that the MTP can accurately simulate basic material properties such as lattice constants, elastic constants, thermal expansion, and thermal conductivity, outperforming the empirical Buckingham potential. Moreover, the formation energies of charge-neutral defects were well estimated compared to DFT. The confirmed ability of the present MTP to describe both material properties and defect formation energies indicates that this MTP can be used in investigating the radiation damage and effects in Li_2TiO_3 in future studies.

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