

Molecular dynamics simulation on Yttria-doped Zirconia: solid-state diffusion and other physical properties

1. Introduction

1.1 YSZ ionic conductor

Yttria stabilized zirconia (YSZ) is well known as a good ionic conductor at high temperature (>800°C). Doping with sufficient amount of trivalent or divalent metal ions, the cubic phase of zirconia can be fully stabilized even to the room temperature, and extra oxygen vacancies are introduced into zirconium oxide, enhancing its oxygen diffusion in lattice. In the recent 10-15 years, much attention had been paid on the trivalent atoms doped ZrO_2 as a popular candidate for the electrolyte of solid oxide fuel cell (SOFC). Dopants as Sc_2O_3 , Y_2O_3 , Er_2O_3 , Yb_2O_3 dopants had been well studied, and Y_2O_3 is found to be the best choice when both cost and performance are taken into account. The YSZ also exhibits many advantages over the other candidates for SOFC electrolyte, including phase stability, highly ionic conduction ($t_o \sim 1$ to very wide range of oxygen chemical potential)[1], high mechanical strength and low cost...etc.

1.2 Simulation on ionic transportation in YSZ: literature review

1.2.1 Potential models

Much simulation work had been found in literatures to discover the nature of oxygen transportation in YSZ (or other Ln_2O_3 - ZrO_2 systems). In the past 10~15 years, the most popular work is taken with classical molecular dynamics simulation and static lattice calculation. In recent years many interest had been paid on first principle total energy calculations for defect (or defect complex) energy and oxygen migration energy profile had also been reported. The ion – ion Interaction is described with Columbic electric potential and Buckingham short range potential model:

$$V_{ij} = \frac{Z_i Z_j}{4\pi\epsilon_0 r_{ij}} + A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$

The first term is Columbic potential, the second and third term are the short-range interaction potential in Buckingham (or also Born-Meyer-Huggins) form. The model parameter for $O^{2-} - O^{2-}$, $Zr^{4+}-O^{2-}$ interaction was first given by the work of Catlow and Lewis [2, 3]. The parameter for $Y^{3+} - O^{2-}$ interaction is first given by Bush *et al.* [4]. Also other potential parameters are given by Minervini *et al.* [5], including the $O^{2-} - O^{2-}$, $Zr^{4+}-O^{2-}$ and $Y^{3+} - O^{2-}$. The potential parameters are listed below:

a. Catlow's potential [2, 3]

	A(eV)	$\rho(\text{\AA})$	C(eV \AA^6)
O ²⁻ - O ²⁻	22764.0	0.149	27.89
Zr ⁴⁺ - O ²⁻	1024.6	0.376	0
Y ³⁺ - O ²⁻	1325.6	0.3461	0

b. Minervini's potential [5]

	A(eV)	$\rho(\text{\AA})$	C(eV \AA^6)
O ²⁻ - O ²⁻	9547.96	0.2192	32.0
Zr ⁴⁺ - O ²⁻	1502.11	0.3477	5.1
Y ³⁺ - O ²⁻	1766.40	0.33849	19.43

Most researchers used these two potential parameters directly applying in their molecular dynamic simulation, or slightly alter the values of these parameters.

1.2.2 Diffusivity and conductivity

In our best knowledge, the earliest molecular dynamics study on YSZ was taken by Shimojo *et al* [6] with NVE ensemble. They gave a simulated D_0 value of 10 mol% Y₂O₃ doped ZrO₂ at 2073K, and the value only deviated from the experimental value by a factor of 3~4. The subsequent simulation studies took the same analysis for diffusivity in either NVE or NVT ensemble, but only conducted at temperatures above 1500K.

In the recent 10 years, as the advance on the performance of computers and simulation techniques, more different conditions had been tested. The results with NPT ensembles had been reported by Yamamura *et al.*[8] Sawaguchi *et al.*[9] and Devanathan *et al.*[10], all of them had given a series of diffusivity test under different Y₂O₃ contents and different temperatures, and the oxygen migration enthalpy at given content was calculated from Arrhenius plot. The simulated conductivity at 1000°C~800°C was close to the experimental reported values and the trend of oxygen migration enthalpy to the Y₂O₃ content was consistent with most experimental data.

Other than molecular dynamics simulation, ionic transportation properties have been simulated by first principle calculations. Even ab-initio molecular dynamics (AIMD) method can obtain some time-relating properties; diffusivity is hard to be obtained with AIMD simulation due to the restriction to the equipment-affordable time scale (usually only to ~ 1 ps). Instead, researchers had combined the energy barrier calculation with first principle simulation and kinetic Monte Carlo method to observe the ionic transport phenomena [11, 12]. But one of the common problems among these data is the calculated oxygen migration enthalpy (~0.6 eV with Classical MD and ~0.7 eV with ab-initio DFT+kMC calculation [22]) is lower than most experimental reported (~1.0 eV). Besides, of our best knowledge there was no

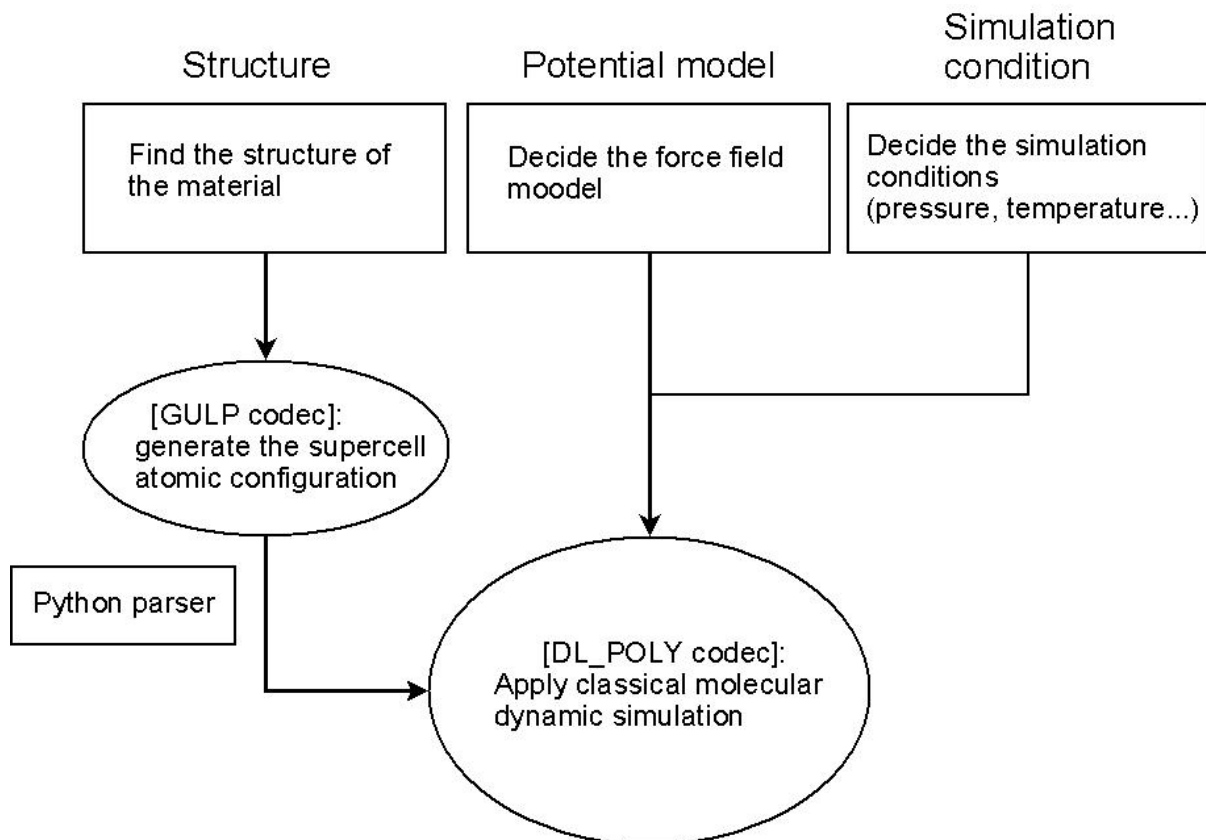
experiment-supported simulated coefficient of diffusion reported at temperatures below 600°C. This problem had not been solved even in the newest simulation studies.

1.3 Objectives

The aim of this study is to observe the ionic transport phenomena and some other physical properties from room temperature to high temperature (300 K to 1800 K). The phase stability is also investigated by observing the evolution of static lattice energy and lattice parameters with time.

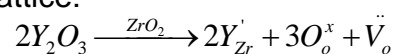
2. Simulation Conditions

2.1 Flow chart of simulation work



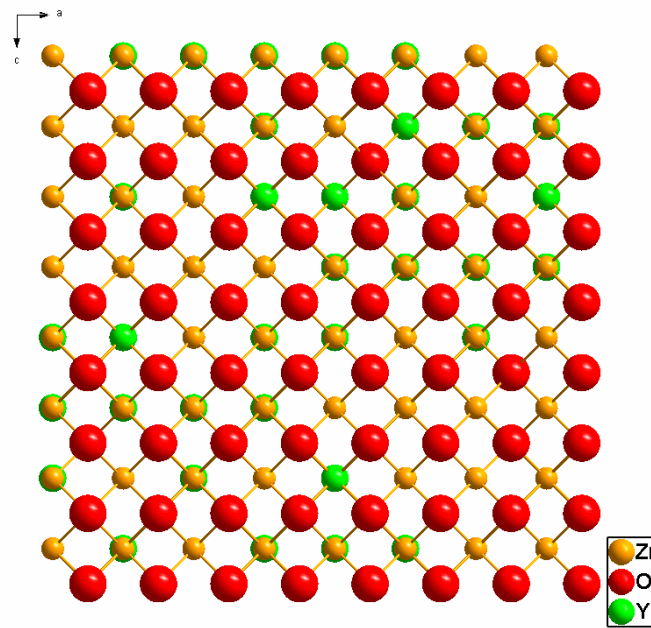
2.2 Simulation details

Present work focuses on the 8 mol%Y₂O₃ doped ZrO₂ (8YSZ) system. The periodic boundary condition is used, and the cell consists of 4x4x4 unit cells, with 256 Zr atoms and 512 O atoms (19 oxygen vacancies). By the defect reaction enhanced by Y₂O₃ doping into ZrO₂ lattice:



Consequently, one oxygen vacancy is produced when two zirconium atoms are substituted with yttrium atoms. The yttrium atoms and oxygen vacancies randomly substitute the sites of zirconium atoms and oxygen atoms. The simulation cell is

visualized and given as the following picture (viewed from [0 1 0] direction):



The potential used in this study followed the values given by Schelling *et al.* [13], which were developed from Minervini's potential [5]. The potential parameters are shown below:

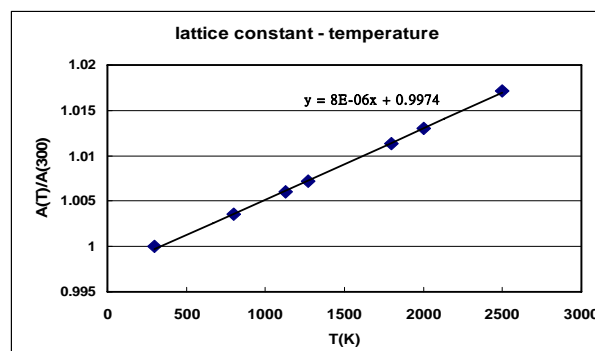
	A(eV)	$\rho(\text{\AA})$	C(eV \AA^6)
O ²⁻ - O ²⁻	9547.96	0.224	32
Zr ⁴⁺ - O ²⁻	1502.11	0.345	5.1
Y ³⁺ - O ²⁻	1366.35	0.348	19.6

The long-range potential was calculated by Ewald Summation with Verlet neighbor list, and the potential cut-off is set to 9 \AA . The position and velocity is calculated with leapfrog algorithm with the time step of 0.5 ps. and the total simulation time is 1 ns.

3. Results and Discussion

3.1 The Thermal expansion

First, in order to understand the reliability of the potential model we use, we start from testing the thermal expansion coefficient of 8YSZ. We calculate the CTE by determining the linear relation of lattice constant to temperature with Nose-Hoover NPT ensemble:



As shown above, the specific lattice constant varies linearly with temperature, and the calculated CTE is 8.0×10^{-6} , which is consistent with the experimental result measured by Kisi *et al.* [20]: 9.6×10^{-6} . This result shows a basic reliability of the potential model we use.

3.2 The diffusivity measurement

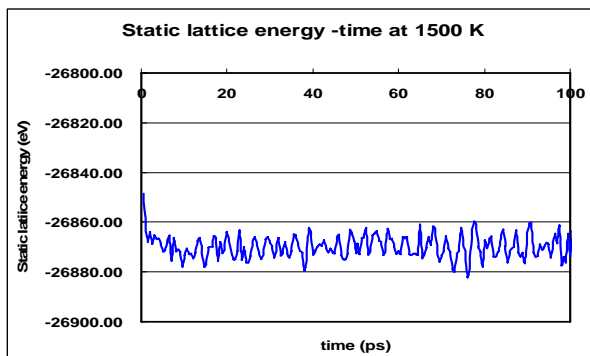
The diffusivity of oxygen is calculated from the mean-square displacement of oxygen after the time period of simulation. This gives:

$$D_{\alpha} = \frac{1}{6\tau N_{\alpha}} \sum_{\alpha} \langle [\mathbf{r}_i(t+\tau) - \mathbf{r}_i(t)]^2 \rangle$$

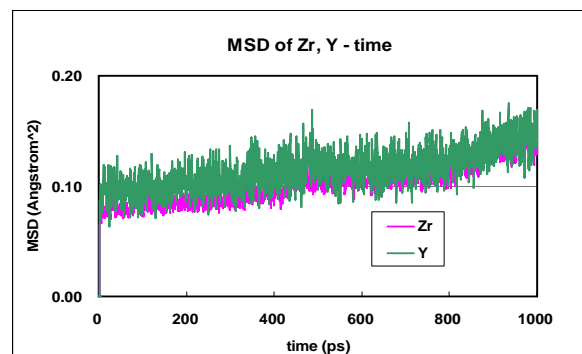
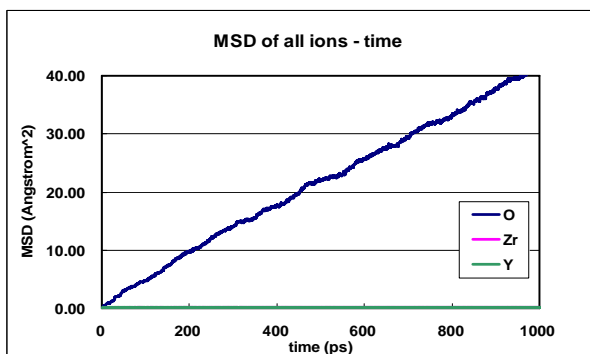
D is defined as self diffusivity. The α subscript represents the species of atom, i subscript is the label of individual atom of that species in the cell, the square brackets means the average over all the atoms of that species. \mathbf{r} means the position vector and τ represents the simulation time, more precisely saying, the simulation time period for which the MSD increase linearly with time. This is also the basic premise for any global physical properties to be observed: The system must reach an equilibrium state.

So before the diffusivity test, we need to find out the equilibrium time. We can do this by testing the evolution of static lattice energy with simulation time. This work had been taken under each temperature we wanted to simulate with $N\sigma T$ ensemble, in which the volume of the system was anisotropic changeable; Below is an example given at 1500 K. (for other temperatures similar behavior was observed)

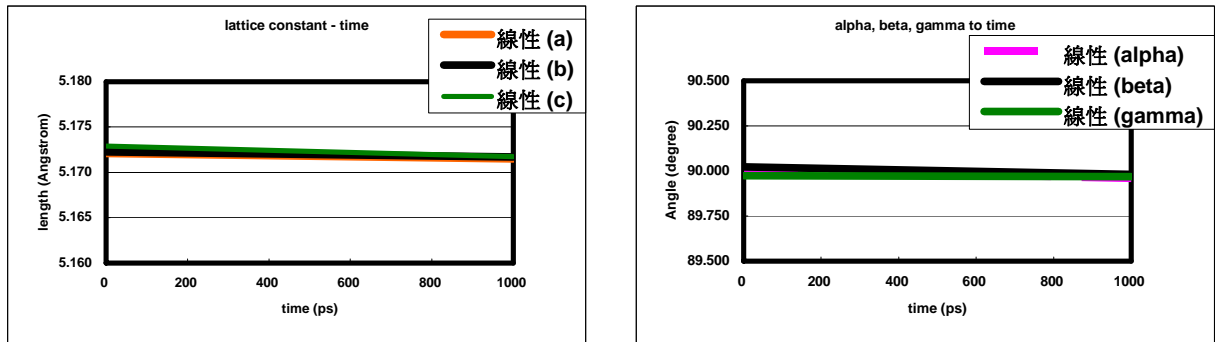
The static lattice energy:



Then the MSD of all ions are observed:



Furthermore, the lattice parameter evolution with time is also checked to ensure the fluorite structure is stable. Only the linear fittings of the data points were shown because of enormous amounts of data points:



From the above data we can see :

- (1) The system is almost energetic stable after 5 ps, so 5 ps (10000 time steps) is chosen as equilibrium time.
- (2) The MSD of O is much greater than that of Zr and Y, which is very consistent with the experimental observation [14, 15].
- (3) The cell parameters are very consistent with cubic structure and seem stable with time.

In the MD simulation works the conductivity is often calculated in order to compare with the conductivity values measured by either d.c. method or a.c. impedance method, also we include this job here.

The conductivity can be estimated with Nernst-Einstein relation:

$$\sigma_{\alpha} = \frac{N_{\alpha} q_{\alpha}^2 D_{\sigma\alpha}}{k_B T}$$

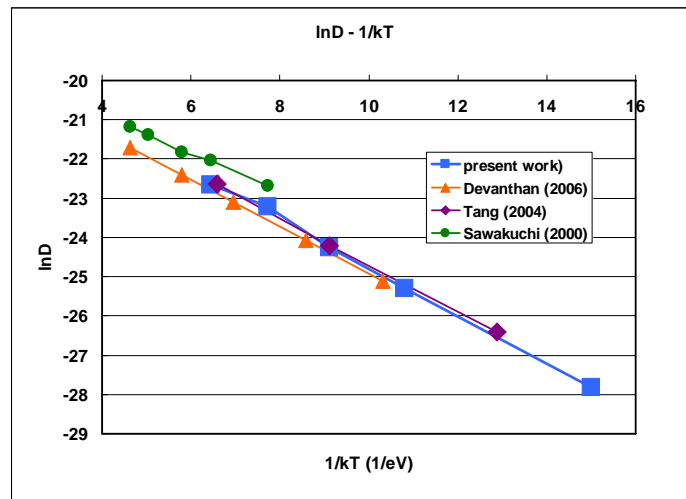
where D_{σ} is defined as conductive diffusivity, and is believed to be a “self diffusivity” when no external electric field is applied [7]. The Nose-Hoover NVT ensemble was used in this system, and the lattice constant was estimated by the following equation:

$$a(T) = a_0(1 + \alpha(T - T_0))$$

where $a(T)$ is lattice constant at temperature T , T_0 is set to room temperature (300K) and a_0 is consulted from the ICSD database[19]. α is the linear coefficient of thermal expansion (CTE) of 8-YSZ, we take the value 9.6×10^{-6} measured by Kisi *et al.* [20]. The simulated diffusivity and conductivity values are listed below:

T(K)	Lattice const. (Å) (predict by CTE = 9.6×10^{-6})	Self diffusivity of oxygen ions and S.T.D ($10^{-11} \text{ m}^2/\text{s}$)	Conductivity (S/cm)
773	5.1621	0.083622 ± 0.084989	0.00455
1073	5.1775	1.0347 ± 0.10672	0.0312
1273	5.1878	2.9255 ± 1.0836	0.0777
1500	5.1995	8.1861 ± 0.19532	0.173
1800	5.2118	14.506 ± 0.59775	0.254

The results, simulation conditions and Arrhenius plot are shown below, along with the simulation results by Devanathan *et al.* [10] and Tang *et al.* [16].



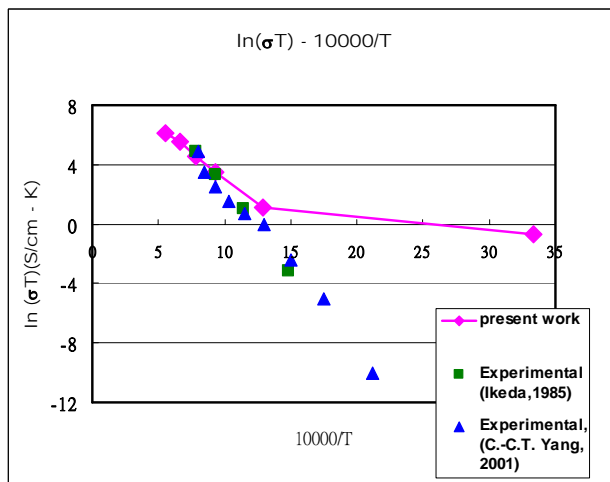
	Present work (2007)	Devanathan <i>et al.</i> (2006)	Tang * <i>et al.</i> (2004)	Sawakuchi <i>et al.</i> (2000)
Ensemble	NVT	NPT	NVT	NPT
Potential model	Schelling's potential	Schelling's potential	Minervini's potential	Minervini's potential
Cell size	4 x 4 x 4	5 x 5 x 5	3 x 3 x 3	5 x 5 x 5
Simulation temperature	773~1800K	1125~2500K	900~1759K	1500~2500K
Activation energy (eV)	0.61	0.60	~0.6	0.48
External electric field	N/A	N/A	Constant external electric field	N/A

*The study of Tang *et al.* performed a non-equilibrate MD simulation by applying an external electric field on the system, in which the conductivity is calculated with alternative way to the other studies:

$$J = \frac{\sigma}{E_x} = \frac{1}{V} \sum_i^n q_i v_{ix}$$

Where J denotes conductivity, E_x denotes electric field (which is applied at +x direction), V is the volume of the cell, q is the charge of the ions and v_x is the x- component velocity of ion i. Summation is taken over all the ions, and diffusivity is converted from Nernst-Einstein relation shown above.

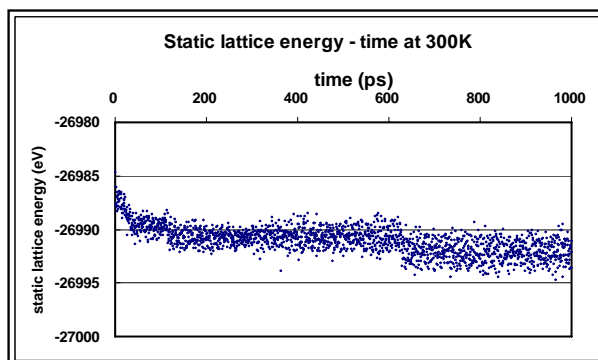
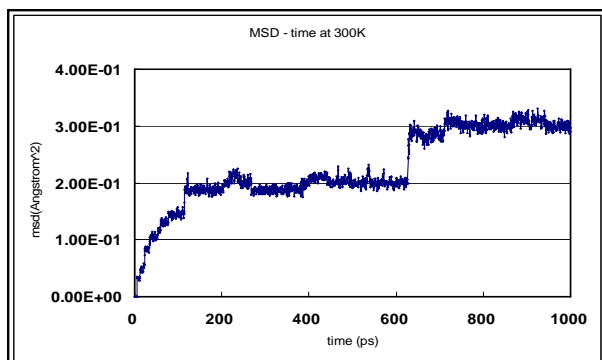
Further we simulated the conductivity at the temperatures lower than any other simulation studies ever reported, e.g. 300K, and then compare our results with the experimental data:



	Present Work	Ikeda <i>et al.</i> [17]	C.-C. T. Yang [18]
Measuring method		4 – pt a.c. method	d. c. measurement
Sample conditions		Single Crystal	Polycrystalline
Conductivity at 1000oC(S/cm)	~0.084	~0.1	0.067
Activation energy	0.61 eV	0.97 eV (above 540°C) 1.09 eV (below 540°C)	0.97 eV (above 550°C) 1.07 eV (below 550°C)

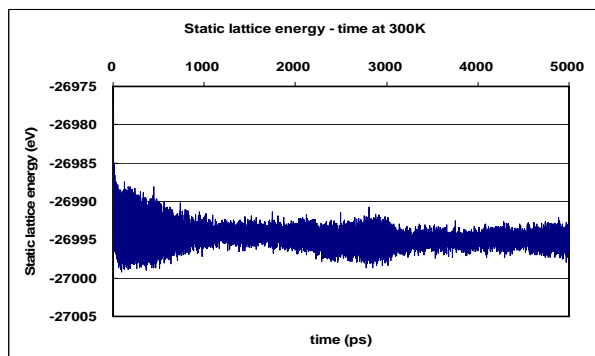
We can find that the simulated conductivity at 500°C, 800°C and 1000°C are in well agreement with experimental measured values. However, the calculated activation energy is deviated from the experimental values with a factor about 30%.

Furthermore, the simulated diffusivity at 300K is higher than the estimated experimental value. To find what account for this phenomenon, we re-examined the energetic stability and oxygen MSD-t plot:

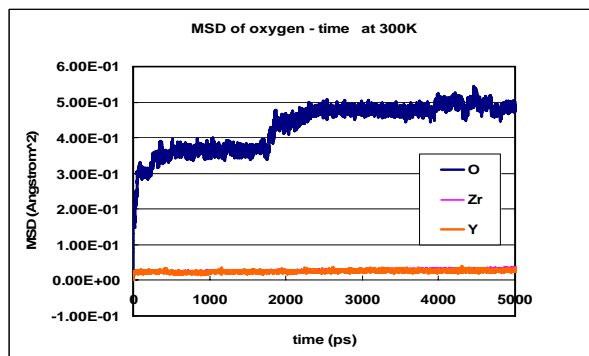


We found that the static lattice was hard to be concluded “in equilibrium” after 5 ps, which was the equilibrium time we set for this system. More confusing, the MSD of oxygen behaved rather monotonic linear, but as step-halt-step movement with time. For deciding the new equilibrium time, we took 5 times the original simulation time to do the same equilibrium test:

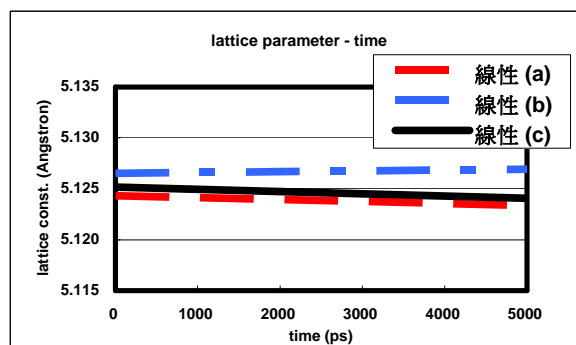
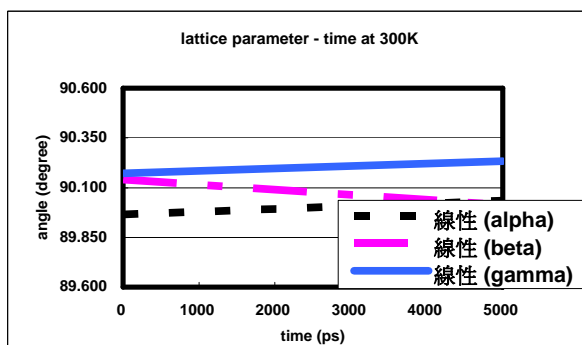
Static lattice energy



Mean square displacement:

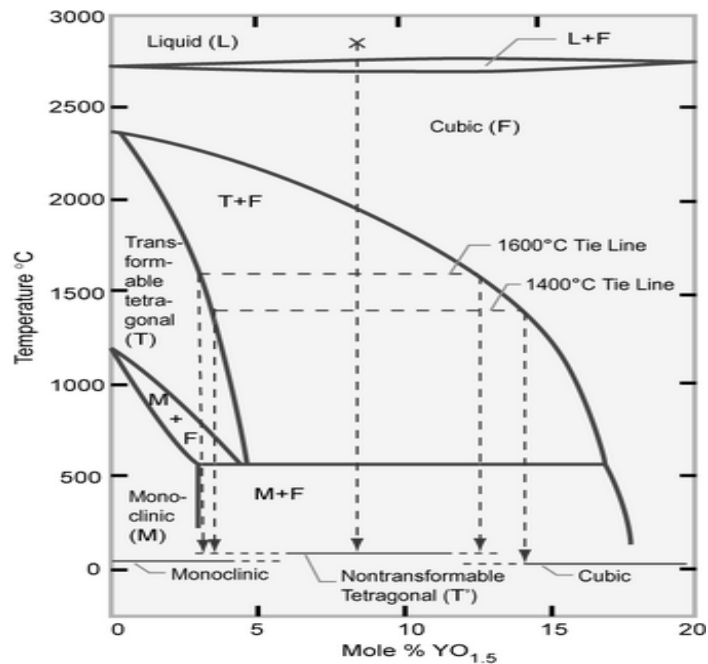


Lattice parameters:



From the static lattice energy and MSD plot, we can see we got an analogous result despite the simulation time is changed to 5 ns. It seems hard to find a good equilibrium period after which the MSD increases linearly within acceptable simulation time of MD simulation.

The lattice parameters exhibit poorer phase stability in cubic structure, which is in consistent with the equilibrium phase diagram [21]:



At 300K the stable state is monoclinic + cubic phases, so the cubic phase 8-YSZ is in metastable, while at 1500K the point is more close to the cubic phase region, so the structure reaches its equilibrium state soon (also they are both metastable, but from the viewpoint of free energy, single cubic phase is surely more stable at 1500K than 300K).

4. Conclusion

In our simulation system, we model $8\text{Y}_2\text{O}_3\text{-ZrO}_2$ system to investigate its energetic stability and ionic transportation properties. The simulated oxygen diffusivity is close to the experimental results at 500~1000 °C, but the calculated activation energy, although be consistent with other simulation studies, is of 30% lower than the experimental results. Besides, the diffusivity at 300K is abnormally high, this may be interpreted with the facts that (1) the oxygen migration mechanism may be different at low temperature to high temperature. (2) From the phase diagram the cubic fluorite structure is for 8YSZ at 300K is less stable than at higher temperature from the thermodynamic point of view. So the equilibrium condition may hard to reach under the time scale of molecular dynamic simulation.

5. Reference

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