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A STUDY OF THERMAL PROPERTIES OF PEROVSKITE CERAMIC MATERIALS VIA MOLECULAR DYNAMICS SIMULATION

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ABSTRACT

Molecular dynamics simulation has been performed on strontium titanate and barium zirconate ceramic materials to investigate their thermal-physical and thermal transport properties. The intricate interatomic potentials can be reduced to pairwise interactions, which consist of Ionic interaction, short-range repulsion, Van der Waals attraction and Morse covalent bonding. The potential parameters were parameterized to explain the thermal properties. Using these empirical potential parameters, the thermal expansion and thermal conductivity of the perovskite ceramic materials have been evaluated in the temperature range of 298 K – 2000 K. Comparison between the two ceramic materials suggests that strontium titanate is slightly more expansible and possess a higher thermal conductivity than barium zirconate. The simulation results show good agreement with the experimental findings.

Keyword: molecular dynamics simulation; strontium titanate; barium zirconate; thermal conductivity; thermal expansion;

INTRODUCTION

Perovskite ceramic materials attract many research opportunities due to their interesting and intriguing properties, such as superconductivity, ferroelectricity and thermodynamics. Furthermore, the perovskite materials are useful in a wide range of applications such as thermal barrier coating [1], electrical applications [2], fuel cell applications [3,4], and thermoelectric applications [5,6]. In this work, we are particularly interested in strontium titanate ($SrTiO_3$) and barium zirconate ($BaZrO_3$) ceramic materials; we wish to understand their thermal-physical and thermal transport properties.

In order to gain quantitative knowledge of physical properties of a material, experimental measurements are usually carried out. In some cases, performing experiments can be costly or difficult due to some pragmatic reasons, such as the limitations of instruments. On the other hand, computer simulation offers an alternative way to understand the material behavior. It provides a route to investigate the material behavior at extreme temperature and pressure, without actually carrying out in the lab. In this paper, we present a molecular dynamics (MD) simulation on $SrTiO_3$ and $BaZrO_3$ to study their thermal expansion and thermal conductivity at high temperatures.

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METHOD

Potential Model

Obtaining a reliable potential is a first step in MD simulation. This step is of primal importance because the correctness of the simulation results depends on the accuracy of the potential used. In this work, we used a simple pairwise interaction to represent the intricate interatomic potential. The pairwise potential, which consists of ionic interaction, short-range repulsion, Van der Waals attraction and Morse covalent bonding, is shown below:

$$U(r_{ij}) = \frac{q_i q_j}{r_{ij}} + f_0(\rho_{ij}) Exp\left[\frac{\sigma_{ij} - r_{ij}}{\rho_{ij}}\right] - \frac{c_{ij}}{r_{ij}^6} + D_{ij}\left\{Exp\left[-2\omega_{ij}\left(r_{ij} - r_{0_{ij}}\right)\right] - 2Exp\left[-\omega_{ij}\left(r_{ij} - r_{0_{ij}}\right)\right]\right\} \quad (1)$$

where i,j = {Sr,Ba,Ti,Zr,O}, q_{ij} is the effective ionic charge, σ_{ij} is the ionic radii, ρ_{ij} is the ionic softness, c_{ij} is the Van der Waals attraction parameter, f_0 = 1.0 kcal/Åmol is the force constant and r_{ij} is the distance between the ions. D_{ij}, ω_{ij} and r_{oij} typify the depth, steepness and equilibrium distance of the Morse potential. The potential parameters were parameterized to explained the thermal properties. The potential parameters used in this work are shown in Table 1. The values of $SrTiO_3$ are taken from our previous work [7], whereas the values of $BaZrO_3$ are obtained by trail-and-error. Note that the parameters of O ion are transferable between $SrTiO_3$ and $BaZrO_3$. The materials' interatomic potentials are plotted in Figure 1.

Table 1: Potential parameters of the potential model

Ion	q_i (e)	σ_i (Å)	ρ_i (Å)	c_i (Kcal$^{1/2}$Å^{3}mol$^{-1/2}$)
Sr	2.00	1.846	0.130	0
Ba	2.00	2.020	0.157	0
Ti	2.20	1.385	0.100	0
Zr	2.20	1.490	0.0862	0
O	-1.40	1.850	0.180	25.04
Pair	D_{ij} (Kcal mol^{-1})		ω_{ij} (Å^{-1})	r_{0ij} (Å)
Ti-O	26.0		2.00	1.60
Zr-O	24.4		2.05	1.79

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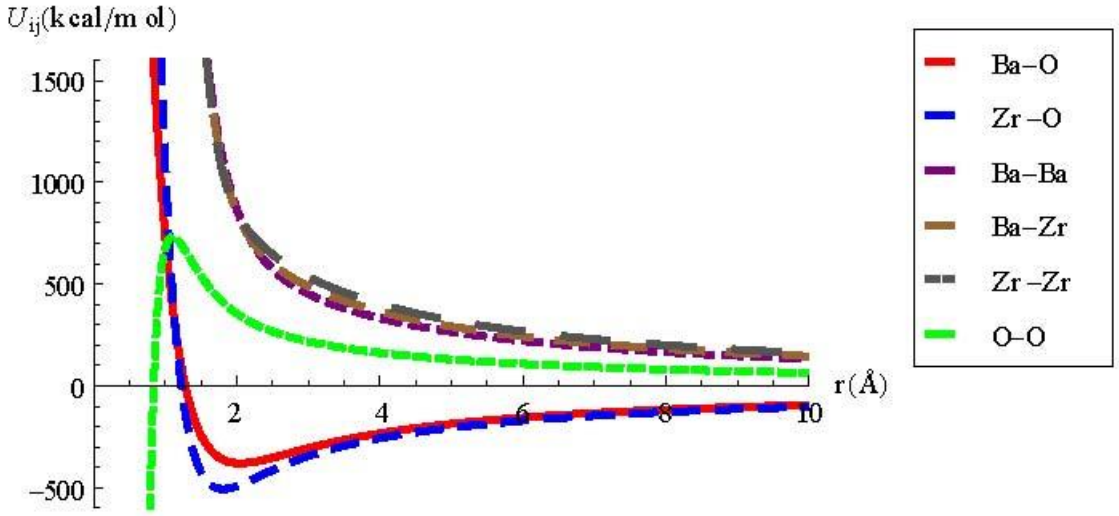

(b)

Figure 1: Interatomic potential of (a) $SrTiO_3$ and (b) $BaZrO_3$

Simulation Procedure

At first, the simulation system of $SrTiO_3$ and $BaZrO_3$ were created according to the experimental perovskite structure. Each simulation cell consists of 2560 atoms. After that, the particles' velocities were generated according to the Maxwell-Boltzman velocity distribution. While Verlet algorithm with a time step of 1.0 fs was used to solve the equation of motion, simulations in canonical ensemble and isothermal-isobaric ensemble were performed using Nose-Hoover algorithm with a time constant of 0.1 ps for thermostat and 1.0 ps for barostat. In order to expedite the computations, a global cut-off distance of 11.0 Å was used. For long-range ionic interaction, Ewald summation with a precision of 10-4 was used. Periodic boundary condition was imposed. This simulation was performed using LAMMPS [8]. Simulation systems were equilibrated for about 20,000 time steps before extractions of the results, which were performed by a time averaging of about 100,000 time steps.

RESULTS AND DISCUSSION

Crystal Structure and Structural Parameters

Using the potential parameters presented in Table 1, physical properties of the perovskite materials were evaluated. Table 2 shows the structural parameters of $SrTiO_3$ and $BaZrO_3$, together with the experimental data [9,10]. It can be seen from the table that barium zirconate has larger lattice constants and volume compared with strontium titanate. Since their interatomic interaction are quite similar as shown in Figure 1, one of the reasons why barium zirconate has a larger volume is that the barium and zirconium ions have a larger atomic diameter compared with strontium and titanium ions, and this makes the atomic separation in $BaZrO_3$ larger. Compared to the experimental findings [9,10], our results show excellent agreement.

Table 2: Structural parameters of $SrTiO_3$ and $BaZrO_3$ at 298K and 1 atm. a, b, c are the lattice constants, A, B, Γ are the angles and ρ is the density

Structural parameters	Simulation		Experiment [9,10]	
	$SrTiO_3$	$BaZrO_3$	$SrTiO_3$	$BaZrO_3$
a (Å)	3.90516	4.19167	3.9051	4.1918
b (Å)	3.90509	4.19148	3.9051	4.1918
c (Å)	3.90516	4.19152	3.9051	4.1918
A (deg)	89.999	90.006	90	90
B (deg)	90.000	89.994	90	90
Γ (deg)	90.001	90.001	90	90
ρ (kg/m3)	5116.09	6235.88	5116.70	6234.80
Molar volume ($\times 10^{-5} m^3 mol^{-1}$)	3.5864	4.4348	3.5863	4.4356

Variation of Crystal Structure with Temperature and Pressure

In order to investigate the material behavior at high temperatures, the simulation has been extended from room temperature up to 2000 K. Thermal variation of lattice parameter is shown in Figure 2. The lattice parameter of $SrTiO_3$ increased from 3.905 Å at 298 K to 3.983 Å at 2000 K, whereas the counterpart of $BaZrO_3$ increased from 4.192 Å at 298 K to 4.268 Å at 2000 K. A crude estimation of the thermal expansion coefficient gives a value of $10.1 \times {}^{10\text{-}6}\ K^{-1}$ for $SrTiO_3$ and $8.16 \times {}^{10\text{-}6}\ K^{-1}$ for $BaZrO_3$. This infers that $SrTiO^3$ is slightly more expansible than $BaZrO_3$. Our simulated results agree very well with the experimental findings [1,11,12,13].

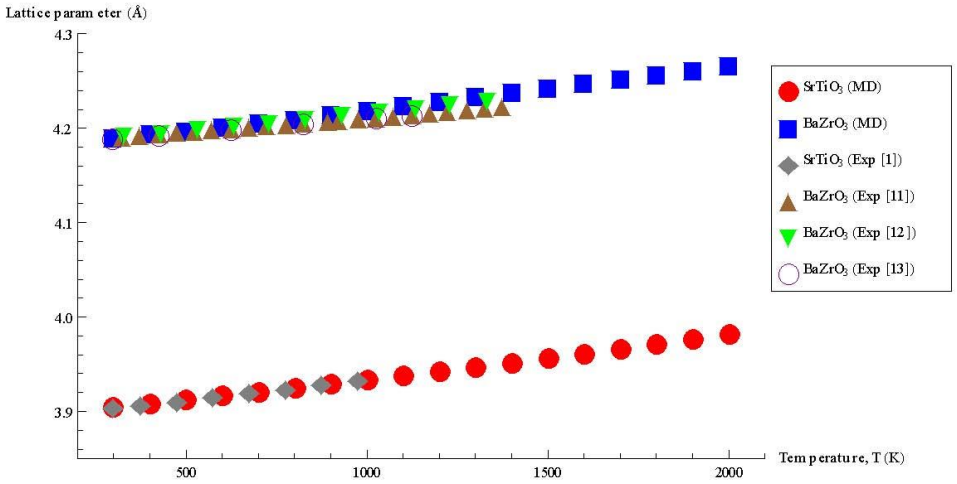

Figure 2: Thermal variation of lattice parameter of $SrTiO_3$ and $BaZrO_3$

Thermal Conductivity

Thermal conductivity is one of the most important characteristics of perovskite ceramic materials. It is of particularly interest because of their applicability in thermal barrier

coating and thermoelectric application. In this work, thermal conductivity calculation was carried out in canonical ensemble using non-equilibrium molecular dynamics (NEMD) method, which is implemented in LAMMPS [8]. In this method, kinetic energy swaps are conducted between the first bin and the middle bin of the simulation cell. The temperature gradient, which is generated as a result of these energy swaps are measured. The thermal conductivity, κ is calculated as the ratio of the total heat flux transferred, Jz and the temperature gradient, dT/dz :

$$\kappa = \frac{J_z}{dT/dz} \quad (2)$$

Details can be found elsewhere [7,14].

Figure 3 shows the thermal conductivity of $SrTiO_3$ and $BaZrO_3$ as a function of temperature. $SrTiO_3$ has higher values of thermal conductivity than $BaZrO_3$, this infers that the former has a higher Debye temperature than the latter, and thus, $SrTiO_3$ is stiffer than $BaZrO_3$. In other words, $SrTiO_3$ should possess a lower isothermal compressibility value. In fact, the Debye temperature of $SrTiO_3$ and $BaZrO_3$ are 694 K [15] and 544 K [16] respectively, and the isothermal compressibility of $SrTiO_3$ and $BaZrO_3$ are 5.75×10^{-12} Pa^{-1} [17] and 7.86×10^{-12} Pa^{-1} [12] respectively, where our affirmation has been confirmed. If we were to select a material among the two to be used in the applications of thermal barrier coating or thermal insulation, barium zirconate would be a suitable material due to its low thermal conductivity. Compared with the experimental results, our simulation results are in good agreement with the experimental results from Muta et al. [6], Vassen et al. [1] and Yamanaka et al. [18].

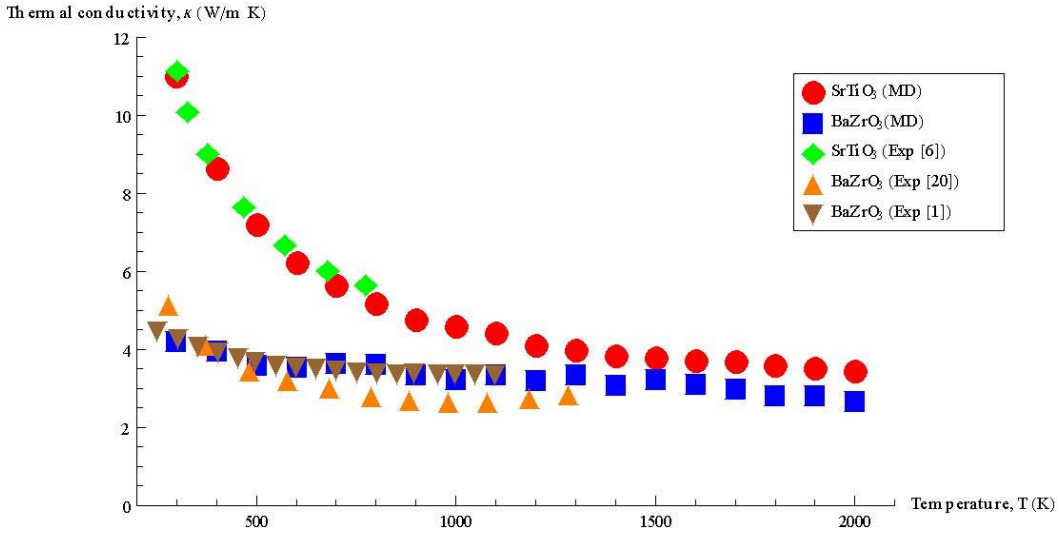

Figure 3: Thermal conductivity of $SrTiO_3$ and $BaZrO_3$

CONCLUSION

Molecular dynamics simulation has been performed on strontium titanate and barium zirconate in the temperature range of 298 K – 2000 K. Using our own derived potential parameters, the structural parameters, thermal expansion and thermal conductivity have been investigated. We found that $SrTiO_3$ has a smaller volume compared with $BaZrO_3$, which is due to the smaller atomic size of Sr and Ti ions than Ba and Zr ions. The results of thermal expansion of $SrTiO_3$ and $BaZrO_3$ are in good agreement with the experimental known values. It also suggests that $SrTiO_3$ is slightly more expansible than $BaZrO_3$. Thermal conductivities of the materials have been calculated based on the NEMD method. $SrTiO_3$ has been found to possess a higher thermal conductivity than $BaZrO_3$; as a result, $SrTiO_3$ has a higher Debye temperature and stiffness than $BaZrO_3$. Our simulation results show good agreement with the experimental findings.

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