Theoretical approaches for studying anisotropic negative thermal expansion: A case of cordierite

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1. Introduction

First-principles simulation is a powerful tool to understand electronic structure and thermal properties of solids. Applications of the density functional theory (DFT) to compute free-energy for thermal expansion of solid states were demonstrated. In order to reproduce the thermal expansion, precise calculation of free-energy of solid state under finite temperature is necessary. The practical ways of free-energy calculations are 1) calculating entropy by phonon to compute Helmholtz free-energy and 2) performing ab-initio molecular dynamics (MD) simulation under constant-temperature and pressure allowing change of lattice vectors. Within the quasi-harmonic approximation, the Helmholtz free-energy is given by

\[ U + \frac{1}{2} \sum_q \hbar \omega_q + k_B T \sum_q \ln \left[ 1 - \exp \left( - \frac{\hbar \omega_q}{k_B T} \right) \right]. \]  

where \( U \) is the total energy at absolute zero, \( q \) is the wave vector, \( \omega \) is the phonon frequency, \( T \) is the temperature, \( k_B \) and \( \hbar \) are the Boltzmann constant and the reduced Planck constant, respectively.

For the first-principles calculation, we employed the plane-wave basis set method and performed DFT calculations within the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional. The electronic charge density was expanded using a plane-wave basis set of energy cutoff 40 Ry for the solid-state DFT calculations. The wave vector was sampled on the Brillouin zone using the Monkhorst–Pack scheme.

2. Computational method

2.1 The Helmholtz free-energy derived from the first-principles phonon calculation

Within the quasi-harmonic approximation, the Helmholtz free-energy at finite temperature is given by

\[ E = U + \frac{1}{2} \sum_q \hbar \omega_q + k_B T \sum_q \ln \left[ 1 - \exp \left( - \frac{\hbar \omega_q}{k_B T} \right) \right] \]  

where \( U \) is the total energy at absolute zero, \( q \) is the wave vector, \( \omega \) is the phonon frequency, \( T \) is the temperature, \( k_B \) and \( \hbar \) are the Boltzmann constant and the reduced Planck constant, respectively.

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wave band-structure scheme with use of pseudopotentials\(^\text{(10)}\) in the framework of the density functional theory\(^\text{(11),\text{(12)}}\) as implemented in the CASTEP code.\(^\text{(13)}\) The local density approximation (LDA) in CA-PZ (Ceperley and Alder\(^\text{(14)}\)) as parameterized by Perdew and Zunger\(^\text{(15)}\)) was used for exchange–correlation functional. Norm-conserving pseudopotentials\(^\text{(16),\text{(17)}}\) were employed with the maximum cutoff energy of the plane wave basis set of 380 eV. The Brillouin zones of the unit cells were sampled by a \(2 \times 2 \times 2\) q-vector mesh. Electronic energy minimization was performed with a self-consistent field tolerance of \(5.0 \times 10^{-3}\) eV/atom. The total energy \(U\) at absolute zero and the zero point energy [second term of Eq. (1)] were calculated with primitive cell model of orthorhombic cordierite (space group 66, \(\text{Ccmm}\), 58 atoms) and converted to \(P1\).

Phonon calculations were performed by the linear response method.\(^\text{(18)}\) Helmholtz free energies \(F\) were calculated with \(3 \times 3 \times 3\) q-vector mesh and 0.1 Å\(^{-1}\) q-vector grid spacing. In Fig. 1, the phonon band structure of cordierite is shown. There is no soft mode in the phonon band structure. In Fig. 2, total energies at finite temperature with each volume at 0 to 1000 K are shown. To vary the volume, hydrostatic pressure was applied to the model. Solid state equation of Birch-Murnaghan\(^\text{(19),\text{(20)}}\) was used to determine the minimum energy at each temperature and that of volumes. By plotting the relationship between the temperature and volume obtained here, we obtained the thermal expansion curve.

2.2 First-principles MD simulation

For the first-principles MD simulation, we employed the plane-wave basis pseudopotential approach using CASTEP code, and the PAW (Projector Augmented Wave method) method using VASP code\(^\text{(21),\text{(22)}}\) in the framework of the density functional theory as implemented. The MD simulations were performed twice with different initial conditions under each temperature of 0, 200, 400, 600, 800, 1000, 1200°C.

In using the CASTEP code, Parrinello–Rahman NPT ensemble was employed\(^\text{(23),\text{(24)}}\) being combined with Nose–Hoover thermostat.\(^\text{(25)}\) An external pressure was set to 0 GPa. The generalized gradient approximation (GGA)\(^\text{(26)}\) of Perdew-Burke-Ernzerhof (PBE) was used for exchange–correlation functional.\(^\text{(27)}\) A plane-wave energy cutoff of 500 eV was used. The Brillouin zones of the unit cells were sampled by a \(\Gamma\) point. The supercell model of orthorhombic cordierite (space group 66, \(\text{Ccmm}\), 116 atoms), which was converted to \(P1\), was used. For the MD simulations, the interval of the time step 2 fs and the total time period of 1 ps (500 steps) were taken. For the values of lengths of \(a\), \(b\), and \(c\) axes and cell volume, we took a time-average from 0.4 to 0.9 ps.

The robustness in the results of the MD simulation was confirmed by using the VASP code. In the calculations using VASP, the numerical schemes are different from those employed in using the CASTEP code. Parrinello–Rahman NPT ensemble was employed being combined with Langevin thermostat.\(^\text{(25)}\) An external pressure was set to 0 GPa. The generalized gradient approximation (GGA)\(^\text{(26)}\) of Perdew-Burke-Ernzerhof (PBE) was used for exchange–correlation functional.\(^\text{(27)}\) A plane-wave energy cutoff of 500 eV was used. The Brillouin zones of the unit cells were sampled by a \(\Gamma\) point. The supercell model of orthorhombic cordierite (space group 66, \(\text{Ccmm}\), 116 atoms), which was converted to \(P1\), was used. For the MD simulations, the interval of the time step 2 fs and the total time period of 60 ps (30,000 steps) were taken. For the values of lengths of \(a\), \(b\), and \(c\) axes and cell volume, we took a time-average from 2 to 60 ps.

2.3 Classical MD simulation

For the classical MD simulation, we employed Berendsen NPT ensemble\(^\text{(28)}\) in the LAMMPS.\(^\text{(29)}\) The \(4 \times 4 \times 4\) supercell model of orthorhombic cordierite (\(\text{Mg}_{512}\text{Al}_{1024}\text{Si}_{1280}\text{O}_{4608}\)) was used. The potentials of the Miyake\(^\text{(30)}\) was employed. The potential equation is given by

\[
\phi(r) = \frac{Z_i e^2}{r_i j} + f_{\beta}(B_i + B_j) \exp\left(\frac{A_i + A_j - r_{ij}}{B_i + B_j}\right) - \frac{C_i C_j}{r_{ij}^6} + D_i \exp[-2\tilde{\varepsilon}_{ij}(r_{ij} - \tilde{r}_{ij})] - 2 \exp[-\tilde{\varepsilon}_{ij}(r_{ij} - \tilde{r}_{ij})],
\]

where \(r\) is the distance between two atoms, \(e\) is the electronic
charge, $f_0 = 6.9511 \times 10^{-1} N = 4.1861 \text{ kJ/(mol}\cdot\text{Å})$ is the constant. $A$, $B$, $C$, and $z$ are parameters of each atom, $D$, $\xi$, and $r^8$ are parameters of each pair of cation-anion. These parameters are shown in Table 1. The cutoff distance of 12 Å was used. The interval of the time step 1 fs and the total time period of 6.15 ns (6,150,000 steps) were taken. To make the initial structure, the supercell model was equilibrated at 300 K in the first 50 ps and cooled to 50 K in the next 100 ps. The temperature was elevated 50 K every 200 ps from 50 to 1500 K. The first 100 ps was used for equilibration and a time-average of the last 100 ps was used for the values of lengths of $a$, $b$, and $c$ axes and cell volume.

3. Results and discussion

3.1 Negative volume expansion by quasi harmonic approach

Volume thermal expansion curves of cordierite are shown in Fig. 3. Volume thermal expansion of cordierite is defined by \( V/V_0 = \alpha_x + \alpha_y + \alpha_z \), where $\alpha_x$, $\alpha_y$, $\alpha_z$ are the linear expansion coefficient of each axis. Differences between the experimental works are probably due to the limit of experimental precision in measuring the small thermal expansion of cordierite or by due to the fact that samples were not single crystals as assumed in current simulations. In view of this dispersion, our calculation was generally consistent with the experiments.

The linear expansion curve is shown in Fig. 4. The thermal expansion anisotropy ($a$, $b$-axes are positive, but $c$ axis is negative) was seen in the experiments, but not in the calculation. The reason for this was considered as following. The anisotropy did not appear in the structure optimization applied hydrostatic pressure in the 0 K. This anisotropy might be obtained if we searched the most stable axial length independently changing the $a$-, $b$-, and $c$-axes respectively, like Ogata et al.\(^{11}\) To reproduce the anisotropy, we tried the first-principles MD simulation as presented in the next subsection.

Table 1. Parameters of Miyake potential

| Ion | $z$ | $a$ | $b$ | $c$ | $D$ | $\xi$ | $r^8$ |
|-----|-----|-----|-----|-----|-----|------|------|
| O   | 0.96| 1.7700 | 0.138 | 51.23 |
| Si  | 1.92| 0.5983 | 0.025 | 63.0  |
| Al  | 1.44| 0.6758 | 0.030 | 50.4  |
| Mg  | 0.96| 0.9400 | 0.040 | 20.49 |
| Ca  | 0.96| 1.4255 | 0.042 | 30.74 |

Table 2. The target temperature and the average temperature at the first-principles molecular dynamics simulation by using CASTEP and VASP

| Target temp. [°C] | CASTEP [°C] | VASP [°C] |
|-------------------|--------------|-----------|
| 200               | 199.0        | 399.5     |
| 400               | 589.8        | 795.4     |
| 600               | 796.1        | 986.1     |
| 800               | 987.4        | 1187.4    |
| 1000              | 1183.3       |           |
| 1200              |              |           |

Average temp. by using CASTEP [°C]: 194.1, 393.2, 589.8, 795.4, 986.1, 1187.4

Average temp. by using VASP [°C]: 1.6, 199.0, 399.5, 599.5, 796.4, 997.4, 1183.3

3.2 Constant pressure MD simulation showing anisotropy

To consider anisotropy, the first-principles MD simulation of constant pressure was performed. The first-principles MD was performed by using CASTEP and VASP codes. CASTEP code, which was used for the phonon calculation, was again used to confirm that the first-principles MD simulation was able to reproduce the anisotropy. VASP code was used to perform the long scale (60 ps) calculation which was necessary to add credibility. The reason to use VASP code for long-time MD simulations is the authors' computational resources and we believe there should no essential difference in results obtained by these codes except for details originating from difference in numerical conditions. Table 2 shows the target temperature and the average temperature in the first-principles MD simulation. The target temperature from 0 to 1000°C was well controlled, because the difference between the target temperature and the average temperature was several degrees. At 1200°C, the average temperatures were lower 12.6°C (CASTEP) or 16.7°C (VASP) than the target, but they were sufficiently controlled because the errors were only about 0.9% (CASTEP) or 1.1% (VASP) at the absolute temperature.
Figure 5 shows the temperature dependence of the volume thermal expansion obtained by the first-principles MD simulation. Unlike the phonon calculation, the volume increased against temperature monotonically. Figure 6 shows the temperature dependence of the length of $a$-, $b$-, $c$-axes. Besides detailed difference between results by CASTEP and VASP due to different time-constant for the MD-simulation, both codes derived a common trend; The $a$- and $b$-axes increased monotonically, but the $c$-axis was found to exhibit negative. (VASP code shows minimum of thermal expansion of $c$-axis at 600°C.) This is the reproduction of the tendency of the anisotropy of the thermal expansion of cordierite in the experiment. On the other hand, unlike experiments, the volume expansion increased monotonic. This is probably because of limited numerical precision in describing small proportion of the negative expansion of $c$-axis.

The correlation of the bond length and axis thermal expansion was investigated. Table 3 shows Al–O, Mg–O, Si–O bond lengths and $a$, $b$, $c$-axes lengths of the 0 and 600°C, and the difference between them. These were obtained by performing the structural optimization at 0 K for the location of the atom at 0 and 600°C. The different binding distances of the Mg–O and Al–O mean the different binding ways. The bond lengths with temperature of Al–O and Si–O were small, which were 0.1% or less, but that of Mg–O was about 0.2 to 0.5%. The change of $a$, $b$-axes were about 0.4%, so the thermal expansion of $a$, $b$-axes were caused by a change in bond length of Mg–O, and these results suggested that the anisotropic thermal expansion was caused by different temperature-dependence of each bond.

![Figure 5](image_url)  
**Fig. 5.** Correlation of the temperature with the ratio of the volume thermal expansion of the cordierite using first-principles molecular dynamics simulation: Experimental result from Fischer et al. (dashed curve), Predecki et al. (dashed-dotted curve), Lee et al. (dotted curve), and Ikawa et al. (solid curve), calculated by using CASTEP (▲), by using VASP (□).

![Figure 6](image_url)  
**Fig. 6.** Correlation of the temperature with the axis ratio of the cordierite using first-principles molecular dynamics by using CASTEP (dashed curve) and VASP (solid curve). The axis ratio was calculated by the axis length at each temperature divided by the length at 0°C.

![Figure 7](image_url)  
**Fig. 7.** Correlation of the M–O distance with the ratio of the lattice length ($a$-axis: ◆, $b$-axis: ■, $c$-axis: ▲) and the volume: ●.

![Figure 8](image_url)  
**Fig. 8.** Correlation of the temperature with volume thermal expansion of the Mg-cordierite and Ca-cordierite by using classical MD (Mg-cordierite: ▲, Ca-cordierite: □).

| Table 3. Correlation of the axes length with the bond lengths of Mg–O, Al–O, and Si–O at the temperature of 0 and 600°C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CASTEP | Mg–O | Mg–O | Mg–O | Al–O | Al–O | Si–O | $a$-axis | $b$-axis | $c$-axis |
| Bond length at 0°C [Å] | 2.0895 | 2.0963 | 2.0979 | 1.7053 | 1.7362 | 1.6004 | 16.9210 | 9.6197 | 9.2233 |
| Bond length at 600°C [Å] | 2.0939 | 2.1018 | 2.1036 | 1.7068 | 1.7380 | 1.6017 | 16.9475 | 9.6479 | 9.2153 |
| Difference | 0.21% | 0.27% | 0.27% | 0.09% | 0.10% | 0.08% | 0.16% | 0.29% | −0.09% |
| VASP | Mg–O | Mg–O | Mg–O | Al–O | Al–O | Si–O | $a$-axis | $b$-axis | $c$-axis |
| Bond length at 0°C [Å] | 2.1246 | 2.1298 | 2.1360 | 1.7724 | 1.7731 | 1.6478 | 17.2665 | 9.8353 | 9.4473 |
| Bond length at 600°C [Å] | 2.1307 | 2.1384 | 2.1466 | 1.7733 | 1.7743 | 1.6498 | 17.3121 | 9.8794 | 9.4328 |
| Difference | 0.29% | 0.40% | 0.50% | 0.05% | 0.07% | 0.12% | 0.26% | 0.45% | −0.15% |
By using CASTEP, the effect of the substitution Mg with other alkali earth metal (Be, Ca, Sr, Ba) on the thermal expansion was investigated. When the M-O distance increased, a, b-axes extended and c-axis shrank, but the volume increased (See Fig. 7). Similar tendency was obtained in GGA. Thus, it was revealed Mg–O bond length was affecting the thermal expansion anisotropy.

3.3 Classical MD simulation for Mg substitution

In performing classical MD simulation, the effect of substituting Mg with Ca on the anisotropy was investigated. Figures 8 and 9 show temperature dependence of the volume and the lattice constant of Mg-cordierite and Ca-cordierite respectively. The simulated change of the lattice constants could reproduce the anisotropy agreeing with the results by first-principles MD simulations. The volume thermal expansions of both cordierites increased monotonically with temperature, and these were overestimated the experimental result. However, the anisotropy of Ca-cordierite was less than Mg-cordierite. This suggests the anisotropy is affected to the existence of Mg in the cordierite. In order to examine the dependence of the inter-atomic potentials, we also tested the Matsui’s potential,34 and obtained the same tendency.

4. Conclusions

We have demonstrated usefulness of the computational approaches to simulate anisotropic and negative thermal expansion of cordierite. By performing the first-principles phonon calculation to derive the Helmholtz free-energy, the negative thermal expansion at a certain temperature region was reproduced. First-principles MD simulations allowing lattice motion could reproduce anisotropy in positive and negative thermal expansions appeared in a, b-axes and c-axis, respectively, which was attributed as the temperature dependence of the Mg–O bond lengths. Moreover, classical force-field MD performed by checking size-effect of the unit cell also could reproduce anisotropic thermal expansion, which was found to be suppressed by substituting an Mg atom to a Ca atom. This finding suggests the role of Mg atoms in triggering the anisotropy in thermal expansion. We conclude that reproduction of experimental results by combination of several computational schemes for materials with anisotropic thermal expansion having complex structures like as cordierite is promising. Further intensive comparison, for example, between measured data of the single crystal and corresponding theoretical computations is expected to derive guiding principles for designing novel materials that satisfies industrial requirements.

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