Abstract Molecular dynamics (MD) simulations of the influence of the Al-O-Al linkage on the P1-I1 phase transition of pure anorthite (An) were carried out using two different types of structures with fully ordered (FO) and partially disordered (PD) arrangements of Al/Si in tetrahedral sites. Discontinuous changes in unit cell volumes and structure factors at the transition temperature were observed in FO-An but not in PD-An. These results show that the orders of the transitions of FO-An and PD-An are first and non-first, respectively. In both structures, the motions of the Ca atoms and the framework are strongly correlated with each other during the transition and Ca atoms dominate the system. Since high-temperature X-ray studies have shown that the transition of natural anorthite is non-first order, it is suggested that the natural anorthite has a partially disordered arrangement of Al and Si atoms.

Key words Molecular dynamics simulation · anorthite · Al-O-Al linkage · P1-I1 phase transition · Ca position

Introduction

The fundamental structure of anorthite, CaAl$_2$Si$_2$O$_8$, consists of an aluminosilicate tetrahedral framework within which Ca cations occupy large interstitial sites (Kempster et al. 1962). Brown et al. (1963) first discovered a reversible phase transition of anorthite from the P1 structure at room temperature to the I1 structure at high temperature by showing that the c type reflections ($h + k = \text{even}, l = \text{odd}$, as defined by Bown and Gay 1958) decreased continuously with increasing temperature and disappeared above around 515 K. Czank (1973) found that the anorthite structure at 513 K has body-centred framework atoms and whereas the Ca atoms are in multiple positions (Ca ‘split’ position). This phase transition and Ca ‘split’ positions have been subsequently studied by high temperature X-ray and neutron diffraction methods (Foit and Peacor 1973; Frey et al. 1977; Adlhart et al. 1980; Ghose et al. 1993), $^{27}$Al nuclear magnetic resonance (NMR) (Staehli and Brinkmann 1974), $^{29}$Si MAS NMR (Phillips et al. 1992; Phillips and Kirkpatrick 1995), electron microscopy (Czank et al. 1973; Van Tendeloo et al. 1989), the order parameter treatment in terms of Landau theory (Salje 1987; Redfern and Salje 1987; Hatch and Ghose 1989) and hard mode infrared spectroscopy (Redfern and Salje 1992). Various hypotheses of the mechanism of this phase transition and Ca ‘split’ position, e.g. space average model, Ca-jumping model, and soft-mode model, have been proposed (for a historical review, see Redfern and Salje 1992). The detailed nature of the phase transition is not fully understood and remains enigmatic.

Al and Si atoms occupy tetrahedral sites in the crystal structure of pure anorthite. The arrangement of Al and Si atoms must be in a fully ordered state as far as it obeys the Al-avoidance rule. An NMR study (Phillips and Kirkpatrick 1995) has suggested that natural specimens are not in the fully ordered state but have partial Al/Si disordering violating the Al-avoidance rule and/or that they have a small quantity of albite component (Na + Si substituted for Ca + Al). Since the degree of the Al/Si ordering cannot be controlled in experiments using actual specimens because of the extremely sluggish exchange of Al and Si atoms below 1000 K, the effect of the partial Al/Si disorder on the transition has not been elucidated.

Molecular dynamics (MD) simulations using appropriate interatomic potentials between atoms have been
Molecular dynamics simulations

In the present study, MD simulations of anorthite were carried out, between temperature ranges of 300–1000 K at atmospheric pressure, to clarify the correlation between Ca motions and lattice distortion of framework through the P1-I2 phase transition. To investigate the influence of the Al/Si disorder on the phase transition, MD simulations of two structures with fully ordered and partially disordered arrangements of Al/Si in tetrahedral sites were carried out.

\[ \phi_{ij}(r_{ij}) = \frac{z_iz_j\varepsilon}{r_{ij}} + f_0(b_i + b_j)\exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r_{ij}^6} + D_{ij}\exp\left(-2\beta_{ij}(r_{ij} - r_{ij}^0)\right) - 2\exp\left[-\beta_{ij}(r_{ij} - r_{ij}^0)\right], \]

where \( r_{ij} \) is an interatomic distance, \( f_0 = (6.9511 \times 10^{-11}) \) a constant, \( \varepsilon \) the electronic charge, \( z, a, b, c \) are parameters for each atomic species, and \( D_{ij}, \beta_{ij} \) and \( r_{ij}^0 \) parameters for cation-anion pairs. The parameters used in the present study (Table 1) were newly evaluated by Miyake (1998) to reproduce the thermal behaviour of plagioclase feldspar.

MD simulations of two types of crystal structures of anorthite with fully ordered and partially disordered arrangement of Al/Si were carried out using an MD program, MXDTRICL (Kawamura 1997). The Ewald method was applied for the summations of Coulombic interactions. Integration of motions of ions was carried out by using the Verlet’s algorithm (\( \Delta t = 2.0 \) fs). Every MD simulation was carried out by an NPT ensemble, where \( N \) is number of particles, \( P \) pressure and \( T \) temperature in the system. Temperature and pressure were controlled by scaling particle velocities and cell lengths, respectively. In the present study, pressure was controlled around atmospheric pressure throughout every run of the MD simulation. The unit cell used in the present MD simulation (MD cell) was a parallelepiped and the number of atoms in the system was 1248 (containing 12 crystallographic unit cells of P1-anorthite; \( a_{MD} = 3a_{an}, b_{MD} = 2a_{an}, c_{MD} = 2c_{an}\)). Taking an initial structure of each MD experiment, the MD calculation was carried out by increasing the temperature of the system to a required level and the system was ‘annealed’ for at least 10 000 steps which is long enough for the cell parameters and energies to settle around constant values. After attaining equilibration, equilibrium structures and energies of all MD calculations were calculated from time-averages taken over a sufficiently long time interval (at least 10 000 steps = 20 ps).

### Results

**Fully ordered anorthite (FO-An)**

#### Heating experiments

The initial structure with the fully ordered arrangement of Al/Si and Ca positions (FO-An) for MD-simulations is the P1 structure of natural anorthite determined experimentally by Wainwright and Starkey (1971). The temperature of MD simulations was varied in the range of 300–1000 K.

Cell parameters and cation-oxygen distances obtained from the MD-simulated structure of FO-An at 300 K show a good agreement with those of natural P1 anorthite determined by the X-ray diffraction method (Wainwright and Starkey 1971) (Table 2). The temperature dependence of the cell parameters and the volume of FO-An are shown in Fig. 1a. The lengths of the a, b, and c-axes of FO-An increase gradually with temperature up to 1000 K, with small discontinuities around 500 K. The \( \alpha \) angle decreases gradually with temperature up to 500 K and then decrease gradually with temperature above 500 K. The unit cell volume of FO-An increases gradually with temperature up to 1000 K, but jumps to the larger value around 500 K. While these temperature dependences seem to be similar to those of natural anorthite measured by the X-ray method (Fig. 1 in Redfern and Salje 1987), the significant discontinuities of the cell parameters and the unit cell volume around 500 K were recognised in the present MD simulation study. Since the discontinuities are related to the phase transition from P1 to I2 phases, the transition temperatures (\( T_c \)) of FO-An are then estimated to 500 K.

Space groups of low and high temperature phases of natural anorthite are P1 and I2, respectively. The conditions for possible reflections for \( hkl \) reflections are all for P1 and \( h + k + l = 2n \) for I2. Structure factors of the MD simulated FO-An determined by using a program to calculate structure factors, \( F_{MD}(hkl) \), (Miyake et al. 1998) show that every \( |F_{MD}(hkl)| \), where

<table>
<thead>
<tr>
<th>Ion</th>
<th>( z ) (e)</th>
<th>( a ) (Å)</th>
<th>( b ) (Å)</th>
<th>( c ) (kJ1/2Å3/mol1/2)</th>
<th>Ion pair</th>
<th>( D ) (kJ/mol)</th>
<th>( \beta ) (Å⁻¹)</th>
<th>( \tau ) (Å)</th>
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<tr>
<td>O</td>
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<tr>
<td>Al</td>
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<td>0.030</td>
<td>0.00</td>
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<td>2.0</td>
<td>2.20</td>
</tr>
<tr>
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<td>0.042</td>
<td>30.74</td>
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