



## Elastic anomalies of anorthite: Molecular dynamics simulations



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### ARTICLE INFO

#### Article history:

Received 10 March 2015

Accepted 8 May 2015

Available online 14 May 2015

#### Keywords:

Anorthite

High-pressure

High-temperature

Molecular dynamics

### ABSTRACT

We investigated the elastic anomalies of anorthite using molecular dynamics simulations in which the temperature and pressure induced  $P\bar{1}/I\bar{1}$  phase transitions were reproduced. The resulting changes in structure were investigated as functions of pressure and temperature. It was found that the temperature-induced elastic anomaly is caused by two different thermal expansion behaviors of atomic motion, that is, increased distance between nearest neighbor atoms and increased Si–O–Al angle. Furthermore, the pressure-induced elastic anomaly was found to be caused by a decrease in the Si–O–Al angle in six-membered rings, which is similar to the cases of vitreous silica or acidic silicate liquids.

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### 1. Introduction

With the recent improvements in seismic wave tomography techniques (Nakajima and Hasegawa, 2003), the variation in seismic wave velocity in the crust can be clearly observed. To reproduce these geophysical observations theoretically, we need to know the properties of minerals. Matsukage et al. (2015) investigated the elastic properties of anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) using *in situ* experiments under high pressure and high temperature. Anorthite is a calcium end-member of plagioclase that is the one of the major rock-forming minerals in the crust. It has a  $P\bar{1}$  space group under standard conditions. A three-dimensional network structure composed of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra is present in the anorthite crystal. Three polymorphs may exist in the anorthite system. One is high-temperature  $I\bar{1}$  (Foit and Peacor, 1973) and the other is high-pressure  $I\bar{1}$  (Angel et al., 1989). The former is a stable phase, and the latter is a meta-stable phase (Hariya and Kennedy, 1968). These three polymorphs have the same topology, that is, there is no breaking and reconnection of bonds and the network topology is preserved throughout the phase transition, while there are pressure and temperature induced anomalies in elastic wave velocity (Matsukage et al., 2015). At the lower pressure, S wave and P wave velocities decrease at temperatures up to 510 K, increase between 510 K and 900 K, and then decrease above 900 K. Under high pressure, both velocities decrease above 3 GPa.

To understand the mechanism of these anomalies of anorthite, we need to establish the changes that occur in atomic structure

with pressure and temperature and the relationship between the structural and physical properties of anorthite. In addition, it may be possible to extend the knowledge of anorthite to other crustal minerals that have similar network structure. It should be noted that structural detail is difficult to investigate through experiments.

Molecular dynamics simulations are widely used for investigating the physical properties and structures of crystals, liquids and gases. In molecular dynamics simulations, we define the initial positions and velocities of all atoms, and then the atoms are forced to move according to given force fields under a proper ensemble. The properties of anorthite, including the temperature-induced phase transition and the Si/Al ordering and nature of the phase transition, have previously been investigated using molecular dynamics simulations (Miyake et al., 1999). The behavior of silicate under high pressure has also been studied using molecular dynamics simulations. For example, high-pressure polymorphs of  $\text{SiO}_2$  crystal have been reproduced, and a new pressure-induced phase transition of  $\text{SiO}_2$  was predicted (Tsuneyuki et al., 1989). In this investigation, we will explore the crystal structure and physical properties of anorthite under high pressure and temperature using molecular dynamics simulations.

### 2. Simulation method

The molecular dynamics simulations were performed under NPT ensembles with  $N_{\text{atom}} = 3774$  ( $4 \times 3 \times 3$  unit cells of anorthite). The MXDTRICL code (Miyake et al., 1999) was used. The calculated pressure ranged from 0.1 MPa to 7 GPa (with an interval of every 1 GPa) and the temperature from 300 K to 1073 K. We imposed periodic boundary conditions in all directions. The

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**Table 1**  
Inter-atomic potential parameters.

Atomic parameters	$q$	$a$ (Å)	$b$ (Å)	$c$ (kJ/mol Å <sup>3</sup> )
Si	2.1000	0.987	0.083	0.0000
Al	1.9500	1.089	0.088	0.0000
O	-1.2625	1.868	0.151	27.4000
Ca	2.0000	1.494	0.094	6.0000
Pair parameters	$D_1$ (kJ/mol)	$\beta_1$ (1/Å)	$D_2$ (kJ/mol)	$\beta_2$ (1/Å)
Si–O	49200.0	5.0	-3281.0	2.24
Al–O	36200.0	5.0	-1946.0	2.24
3-body parameters	$f$ (kJ/mol)	$\theta_0$ (degree)	$r_m$ (Å)	$g_r$ (1/Å)
Si–O–Si	0.00061	120.0	1.77	16.8

Ewald summation was applied to evaluate the long-range Coulomb interactions. The pressure and temperature were kept constant at given values through a scaling procedure. Starting with a given experimental crystal structure that was obtained by an experiment (Wainwright and Starkey, 1971) and with randomly generated velocities of atoms, all of the atoms were moved using the Verlet algorithm under a time interval of 0.5 fs. Under constant isobaric and isothermal conditions, we performed the relaxation up to 50 ps. Then the statistical averages of the structural and physical properties were obtained from the velocities and coordinates of each atom in the simulations through 50 ps. Elastic stiffness was obtained by constant strain NVT ensemble simulations. We performed relaxations and production runs for NVT ensemble simulations as for NPT simulations. The function of inter-atomic potential model was the same one used in our previous work (Noritake et al., 2012):

$$U_{ij(r_{ij})} = \frac{1}{4\pi\epsilon_0} \frac{Z_i Z_j e^2}{r_{ij}} + f_0 (b_i + b_j) \exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) + \frac{c_i c_j}{r_{ij}^6} + D_{1ij} \exp(-B_{1ij} r_{ij}) + D_{2ij} \exp(-B_{2ij} r_{ij})$$

where  $U_{ij}(r_{ij})$  is the potential energy,  $\epsilon_0$  is the vacuum permittivity,  $Z_i$  is the partial charge of the  $i$ -th atom,  $e$  is the elementary charge,  $r_{ij}$  is the distance between the  $i$ -th and  $j$ -th atoms, and  $f_0$  is the constant (4.1865 kJ Å<sup>-1</sup> mol<sup>-1</sup>). The variables  $a_i$ ,  $b_i$  and  $c_i$  are the repulsion diameter, the softness coefficient and the van der Waals coefficient of the  $i$ -th atom, respectively.  $D_{1ij}$ ,  $\beta_{1ij}$ ,  $D_{2ij}$  and  $\beta_{2ij}$  are the parameters for the radial covalent bonds. Note that the first term of this model gives the Coulomb potential, the second one the short-range repulsion, the third one the van der Waals force, and the fourth and fifth ones the radial part of the covalent effect. Three-body interactions between  $i$ ,  $j$ , and  $k$  are represented as follows:

$$U_{kij} = -f[\cos\{2(\theta_{kij} - \theta_0)\} - 1] \sqrt{k_{ij} k_{ik}}$$

$$K_{ij} = \frac{1}{\exp[g_r(r_{ij} - r_m)] - 1}$$

where  $f$  is the force constant,  $\theta_{kij}$  is the angle among the atoms  $k$ ,  $i$ , and  $j$ , and  $\theta_0$ ,  $g_r$  and  $r_m$  are parameters for adjusting the angular part of the covalent bonds. Atomic and pair parameters are given in Table 1. The parameters are taken from Nakano et al. (2003) and modified slightly for this study. We verified the potential parameters by calculating lattice constants and compressibility of some silica polymorph, calcium silicate, aluminosilicate, and calcium aluminate crystals containing SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra (Table 2).  $K_0$ , the bulk modulus, and  $K'$ , the pressure derivative of the bulk modulus, are obtained by fitting the simulated

**Table 2**  
Comparison of lattice constants between MD simulations and experiments.

	Quartz		Coesite		Wollastonite		Krotite	
	MD	Exp <sup>a</sup>	MD	Exp <sup>c</sup>	MD	Exp <sup>e</sup>	MD	Exp <sup>f</sup>
$a$ (Å)	4.8178	4.9134	7.1926	7.135	7.98	7.94	8.9365	8.6996
$b$ (Å)	4.8178	4.9134	12.5343	12.371	7.38	7.32	8.3684	8.0994
$c$ (Å)	5.3563	5.4205	7.2805	7.174	7.03	7.07	15.7628	15.217
$\alpha$ (degree)	90.00	90.00	90.00	90.00	90.187	90.033	90.00	90.00
$\beta$ (degree)	90.00	90.00	120.18	120.36	96.509	95.367	90.046	90.188
$\gamma$ (degree)	120.00	120.00	90.00	90.00	103.558	103.433	90.00	90.00
$K_0$ (GPa)	64.70	37.12 <sup>b</sup>	136.61	96 <sup>d</sup>	-	-	-	-
$K'$	6	5.99 <sup>b</sup>	7.4	8.4 <sup>d</sup>	-	-	-	-
	Sillimanite		Calcio-Olivine		Anorthite			
	MD	Exp <sup>g</sup>	MD	Exp <sup>i</sup>	MD	Exp <sup>j</sup>		
$a$ (Å)	7.5056	7.4883	5.311	5.073	8.273	8.173		
$b$ (Å)	7.6120	7.6808	11.775	11.211	12.835	12.869		
$c$ (Å)	5.8079	5.7774	7.201	6.753	14.144	14.165		
$\alpha$ (degree)	90.00	90.00	90.00	90.00	92.685	93.113		
$\beta$ (degree)	90.00	90.00	90.00	90.00	115.466	115.913		
$\gamma$ (degree)	90.00	90.00	90.00	90.00	91.472	91.261		
$K_0$ (GPa)	195.79	164 <sup>h</sup>	-	-	-	-		
$K'$	5	5 <sup>h</sup>	-	-	-	-		

<sup>a</sup> Wright and Lehmann (1981).<sup>b</sup> Angel et al. (1997).<sup>c</sup> Gibbs et al. (1977).<sup>d</sup> Levien and Prewitt (1981).<sup>e</sup> Peacor and Prewitt (1963).<sup>f</sup> Ma et al. (2011).<sup>g</sup> Winter and Ghose (1979).<sup>h</sup> Burt et al. (2006).<sup>i</sup> Gobechiya et al. (2008).<sup>j</sup> Wainwright and Starkey (1971).

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