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Anisotropic thermal expansion of calcium dialuminate ($CaAl_4O_7$) simulated by molecular dynamics

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Abstract

The anisotropic thermal expansion behavior of $CaAl_4O_7$ was studied by molecular dynamics (MD) simulation in the temperature range from 298 to 700 K. The monoclinic crystal structure (space group C2/c) has been successfully reproduced by using a simple 2-body potential. The principal distortions (λ_1, λ_2, λ_3) and the coefficients of linear thermal expansion (α_1, α_2, α_3) along with the principal axes have been calculated from the temperature dependence of the unit-cell parameters, a, b, c, and β. The distortion λ_3 was much smaller than the other two distortions for all the temperature range, which was partially consistent with the experimental work performed by Fukuda et al. The anisotropic thermal expansion behavior can be explained by the crystallographic geometry, i.e. directional difference in the packing density.

Keywords: C. Thermal expansion; $CaAl_4O_7$; Grossite; Lattice constants; MD simulation

1. Introduction

Calcium dialuminate, $CaAl_4O_7$, is a refractory compound (melting point: 1765±25 °C) in the CaO–Al_2O_3 binary system [1,2]. $CaAl_4O_7$ is a component phase of high-alumina cements, and often denoted as 'CA_2' in the cement industry. $CaAl_4O_7$ is also found in natural terrestrial rocks and meteorites; it was termed 'grossite' in the mineralogical field in 1994 [3]. Currently, $CaAl_4O_7$ is of interest because of its unique crystallographical characteristics, particularly on the coordination states of O and Al atoms (i.e. 'tricluster' O atom, shared by three Al tetrahedra [4]). They are eagerly studied by solid state NMR spectroscopy [5–7].

Another renovated interest in $CaAl_4O_7$ is its low coefficient of thermal expansion (CTE). Following the earlier work by Criado and De Aza [8], Jonas et al. [9–11] recently reported that $CaAl_4O_7$ is a promising refractory ceramic with high-thermal shock resistance, because of its low thermal expansion among aluminates ($\alpha = 4.1 \times 10^{-6}$/°C up to 900 °C [9]). Stimulated by the Jonas's work in 1998 [9], Temuujin et al. [12] prepared $CaAl_4O_7$ powders from mechanochemical treated mixtures of $Al(OH)_3$ (gibbsite) + $Ca(OH)_2$ (portlandite) and $Al(OH)_3$ + $CaCO_3$ (calcite). Suzuki et al. [13,14] synthesized porous and dense $CaAl_4O_7$ and $CaAl_4O_7$/$CaZrO_3$ bodies via reactive sintering technique, and studied the in situ reactions by high-temperature X-ray diffractometry (HT-XRD).

Recently, Fukuda and Yamauchi [15] have investigated the anisotropic thermal expansion behavior of $CaAl_4O_7$ by HT-XRD and matrix algebra analysis, and they have concluded that the low CTE of $CaAl_4O_7$ is attributable to negative thermal expansion along with one principal axis ($\boldsymbol{\lambda}_3$, nearly [207]–$[50\,\underline{16}]$ direction).

In this study, we attempted to examine the anisotropic thermal expansion behavior of $CaAl_4O_7$ by using a molecular dynamics (MD) simulation method, in order to understand the anisotropy in atomic scale. Simulated unit-cell parameters were evaluated by the matrix algebra analysis to determine the principal distortions, similarly to the Fukuda's study [15], and compared with the experimental ones.

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Table 1
Reported unit cell parameters of $CaAl_4O_7$ (monoclinic, C2/c)

Reference	a (nm)	b (nm)	c (nm)	β (deg)	Remarks
Boyko and Wisnyi (1958) [4]	1.289	0.888	0.545	107.1	Single crystal
Goodwin and Lindop (1970)[16]	1.2840 (6)	0.8862 (3)	0.5431 (2)	106.8 (0)	Single crystal
Baldock et al. (1970) [17]	1.2888 (1)	0.8888 (1)	0.5443 (1)	106.93 (1)	Synthetic powder
Fukuda and Yamauchi [15]	1.28947 (8)	0.88894 (4)	0.54419 (3)	107.019 (3)	Synthetic powder
Weber and Bischoff (1994) [3]	1.294 (1)	0.8910 (8)	0.5446 (4)	107.0 (1)	Grossite in meteorite

2. Computational methods

2.1. Crystal structure of $CaAl_4O_7$

$CaAl_4O_7$ has the monoclinic structure with a space group C2/c. Table 1 summarizes reported cell parameters of $CaAl_4O_7$ [3,4,15–17]. Fig. 1 illustrates a $CaAl_4O_7$ unit cell projected on **a**–**c** plane; the unit cell contains 4 Ca, 16 Al and 28 O ions (four formula units). Unit cell parameters and atomic positions reported by Goodwin and Lindop [16] were used for preparing the initial arrangement of MD simulations.

2.2. MD simulations

A basic crystal consisting of 84 unit cells (3**a**×4**b**×7**c**, containing 4032 ions, ca. 3.5–3.8 nm for each axis) was used for the MD simulations (Fig. 2). Three-dimensional periodic boundary condition was employed for the calculation. A pairwise interatomic potential [18] was used to describe the interactions in the $CaAl_4O_7$ crystal,

$$V(r_{ij}) = q_i q_j r_{ij}^{-1} - C_i C_j r_{ij}^{-6} + f(B_i + B_j)\exp[(A_i + A_j - r_{ij})/(B_i + B_j)] \quad (1)$$

where the terms represent Coulomb, van der Waals, and repulsion interactions, respectively. Here, r_{ij} is the interatomic distance between atoms i and j, f is a standard force of 41.84 kJ mol^{-1} nm^{-1}, and q_i, A_i, B_i, and C_i are the net charges, repulsive radii, softness parameters and van der Waars coefficients of the ion i. Table 2 shows the potential parameters used in this study, which is a subset of the CMAS94 parameters reported by Matsui [18]. The CMAS94 set was designed for reproducing various compounds and glasses in the CaO–MgO–Al_2O_3–SiO_2 system.

MD simulations were performed in the constant-temperature, constant-pressure (NTP) mode, by using MASPHYC program (Fujitsu Co. Ltd.). The system was first equilibrated for 10,000 time steps (10 ps) at each temperature, and then, the cell parameters were statistically determined from time averages of 10,000 time steps after the equilibration period.

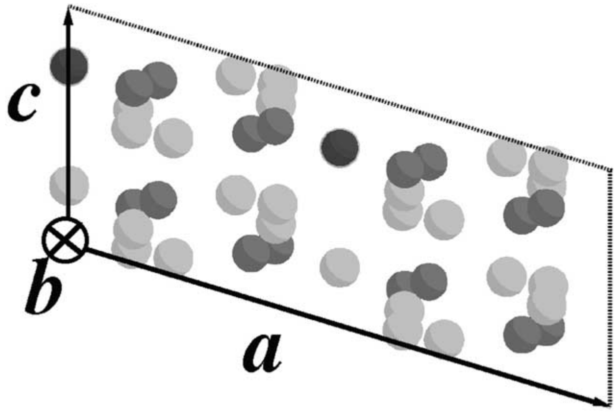

Fig. 1. Crystal structure of $CaAl_4O_7$ (projection on the **a**–**c** plane).

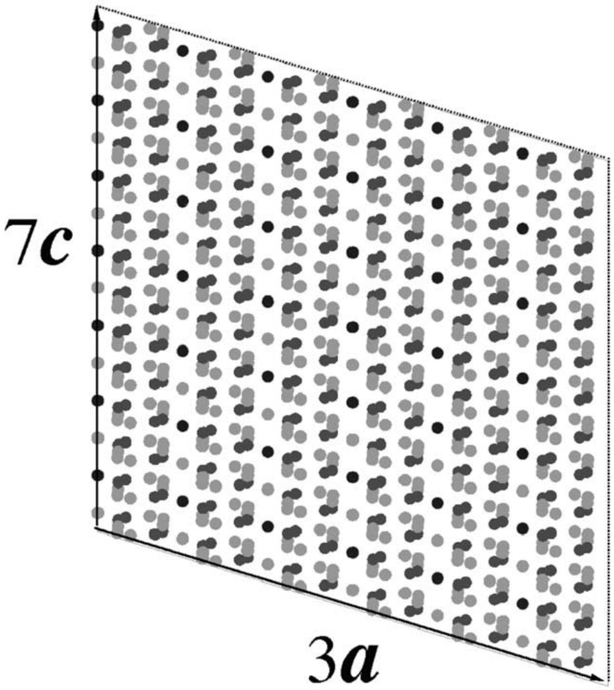

Fig. 2. Basic crystal consisting of 84 unit cells (3**a**×4**b**×7**c**, containing 4032 ions, ca. 3.5–3.8 nm for each axis) for the MD simulations (projection on the **a**–**c** plane).

3. Results and discussion

3.1. Simulated unit cell parameters

Simulated unit cell parameters of $CaAl_4O_7$ are summarized in Table 3. Those at 298 K were a = 1.2791(1) nm, b = 0.87665(4) nm, c = 0.54533(3) nm, and β = 106.74 (1)°. Although the simulated a, b were slightly smaller than the reported ones, they were in good agreement (<1.5%) with those of pure $CaAl_4O_7$. The ***a***-, ***b***- and ***c***-axes as well as the β-angle gently increased with increasing temperature. Although the negative expansion in ***c***-axis as reported by Fukuda et al. [15] was not observed in this simulation, the increase rate in ***c***-axis was rather smaller than the other two axes.

3.2. Anisotropic thermal expansion analysis

Simulated cell parameters at each temperature in Table 3 were analyzed by a matrix algebra analysis, as reported by Fukuda et al. [15,19,20], to determine the magnitude of the principal distortions and coefficients of thermal expansion (CTE). According to the theory on crystallographic deformation by Bowles and Mackenzie [21–23], a homogeneous strain (i.e. thermal expansion in this case) is characterized by the three mutually orthogonal directions, called the principal axes. The directions of the principal distortions upon heating from 298 K to T K are determined by the non-zero solution for $\boldsymbol{\lambda}_i$ (i = 1–3, eigenvectors, in the monoclinic basis at 298 K) of the equation,

$$(\mathbf{G}_T - \lambda_i^2 \mathbf{G}_{298})\boldsymbol{\lambda}_i = 0 \tag{2}$$

and the magnitude of the principal distortions, λ_i (eigenvalues), must satisfy the determinantial equation,

$$\left|\mathbf{G}_T - \lambda_i^2 \mathbf{G}_{298}\right| = 0 \tag{3}$$

where **G** is so-called "metric." A matrix notation of the metric tensor can be written as,

$$\mathbf{G} = \begin{pmatrix} a\bullet a & a\bullet b & a\bullet c \\ b\bullet a & b\bullet b & b\bullet c \\ c\bullet a & c\bullet b & c\bullet c \end{pmatrix} = \begin{pmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{pmatrix} \tag{4}$$

Its determinant, |**G**|, is the square of the unit cell volume. For the monoclinic system, since α and λ are 90°, the metric **G** is given as follows.

$$\mathbf{G} = \begin{pmatrix} a^2 & 0 & ac\cos\beta \\ 0 & b^2 & 0 \\ ac\cos\beta & 0 & c^2 \end{pmatrix} \tag{5}$$

The coefficients of linear thermal expansion (α_i) along with the principal axes are derived from the principal strains (λ_i–1) as follows:

$$\alpha_i = (\lambda_i - 1)/\Delta T, \quad (\Delta T = T - 298(K)) \tag{6}$$

Table 2
Potential parameters: the net charges (q), repulsive radii (A), softness parameters (B) and van der Waals coefficients (C) after Matsui [18]

Ion	q (|e|)	A (nm)	B (nm)	C [nm^3 (kJ/mol)$^{1/2}$]
Ca	0.945	0.11720	0.0040	0.04500
Al	1.4175	0.07852	0.0034	0.03682
O	−0.945	0.18215	0.0138	0.09061

Table 3
Cell dimensions of $CaAl_4O_7$ obtained from MD simulation as a function of temperature

Temperature (K)	a (nm)	b (nm)	c (nm)	β (deg)	Volume (nm^3)
298	1.2791 (1)	0.87665 (4)	0.54533 (3)	106.74 (1)	0.58558 (3)
400	1.2804 (1)	0.87750 (5)	0.54583 (3)	106.77 (1)	0.58719 (3)
500	1.2817 (1)	0.87854 (4)	0.54631 (3)	106.77 (1)	0.58893 (3)
600	1.2827 (1)	0.87937 (4)	0.54683 (5)	106.78 (1)	0.59054 (3)
700	1.2840 (2)	0.8804 (1)	0.5470 (1)	106.78 (1)	0.5920 (2)

Table 4
Principal distortions and the coefficients of thermal expansion of $CaAl_4O_7$ obtained from MD simulation as a function of temperature

Temperature (K)	λ_1	λ_2[a]	λ_3	α_1 ($\times 10^{-6}$)	α_2 ($\times 10^{-6}$)	α_3 ($\times 10^{-6}$)
298	1.00000	1.00000	1.00000	–	–	–
400	1.00117	1.00097	1.00061	11.5	9.51	5.98
500	1.00219	1.00216	1.00142	10.8	10.7	7.03
600	1.00304	1.00310	1.00231	10.1	10.3	7.65
700	1.00388	1.00428	1.00280	9.65	10.6	6.97

[a] The direction of $\boldsymbol{\lambda}_2$ is parallel to ***b***-axis.

From the Eqs. (3) and (6), the principal distortions and the CTE are calculated in Table 4. Note that the $\boldsymbol{\lambda}_2$ direction is parallel to ***b***-axis [15]. It is obvious that a principal distortion λ_3 shows smaller values than the others. At 700 K, for example, $\boldsymbol{\lambda}_1$ and $\boldsymbol{\lambda}_3$ are calculated [from Eq. (2) and $\lambda_3 = 1.00388$, $\lambda_3 = 1.00280$] to be,

$$\begin{aligned} \boldsymbol{\lambda}_1 &\propto \begin{pmatrix} 1 \\ 0 \\ -0.5975 \end{pmatrix} = \boldsymbol{a}\text{-}0.5975\boldsymbol{c}, \\ \boldsymbol{\lambda}_3 &\propto \begin{pmatrix} 1 \\ 0 \\ 4.639 \end{pmatrix} = \boldsymbol{a} + 4.639\boldsymbol{c} \end{aligned} \tag{7}$$

When these vectors are overlapped to the atomic arrangement (Fig. 3), we can immediately understand the reason why the principal distortion λ_1 became larger and the λ_3 became smaller. As can be seen from Fig. 3, the packing density of ions is higher along with the $\boldsymbol{\lambda}_1$ direction, while it is rather smaller along with the $\boldsymbol{\lambda}_3$ direction. Such a directional difference in the packing density caused the anisotropic thermal expansion of $CaAl_4O_7$ crystal. To reproduce λ_i and α_i values more quantitatively, further optimization of the interatomic potentials will be required. Analyses of the local atomic displacement and the change in bond angles would be the next targets in a future work.

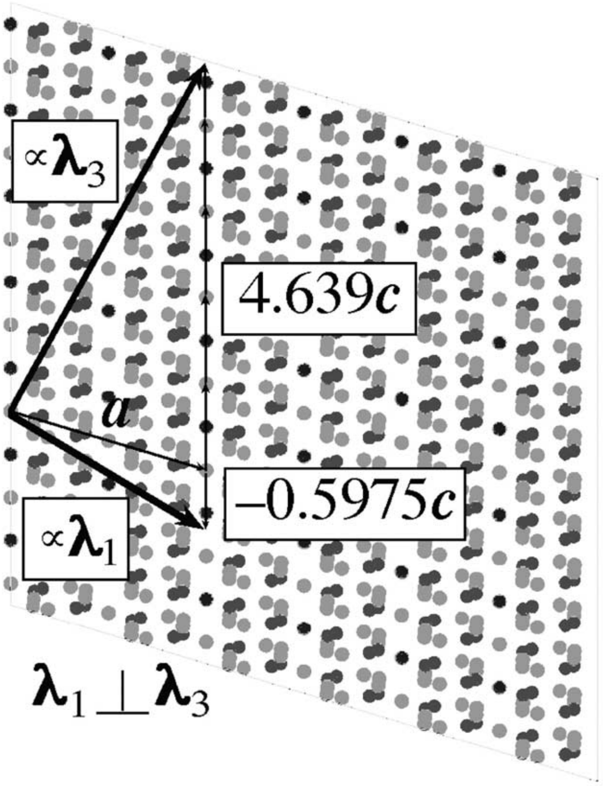

Fig. 3. Directions of principal distortions ($\boldsymbol{\lambda}_1$ and $\boldsymbol{\lambda}_3$) at 700 K, superimposed on the basic crystal.

4. Conclusions

In this paper, the anisotropic thermal expansion behavior of $CaAl_4O_7$ was studied by MD simulation. Qualitatively speaking, the anisotropic thermal expansion behavior was successfully reproduced by the MD calculation using a simple 2-dody potential. The anisotropy was well-explained by the directional difference in the packing density.

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