Computational Modeling of the Liquid Structure of Grossular Ca$_3$Al$_2$Si$_3$O$_{12}$ Glass-Ceramics

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In this work, we present an atomistic model to simulate the structural and some thermodynamic properties of biomaterials as a test case of grossular glass-ceramics. The potential model used in our simulations included short range Born–Mayer type forces and long-range Coulomb interactions. We modelled the atomistic structure of grossular using the different structural optimization methods in conjunction with molecular dynamics simulations. The calculated values of the lattice constant, bulk modulus, elastic constants and cohesive energy are in reasonable agreement with experimental measurements and previous data. The melting point of grossular produced from a volume of the heating process is in a good agreement with literature. Comparison of the predictions of partial pair distribution functions and available experimental data shows that this model has simulated the liquid structure of grossular reasonably well.

1. Introduction

Grossular glass-ceramics use various applications e.g., biomaterials and environmentally friendly materials through calcium and silicon elements with large Clarke numbers [1]. Among the calcium silicate based glass-ceramics, grossular has interesting properties like high degradability and biocompatibility [2, 3]. Grossular is a member of the garnet group which shows a wide compositional range [4]. One class of silica garnet, calcium silicate glass-ceramics occur commonly in nature and thermodynamically stable over very large pressure and temperature regimes and show phase transitions or instability as a function of pressure and temperature. The aluminosilicate garnets of the general formula X$_3$Al$_2$Si$_3$O$_{12}$, where X = Ca^{2+} (grossular), X = Mg^{+2} (pyrope), X = Fe^{2+} (almandine), X = Mn^{2+} (spessartine) are a good example for such phase stability [5]. Grossular was classified as a calcium-aluminium garnet with the formula Ca$_3$Al$_2$(SiO$_4$)$_3$.

Understanding of magmatic processes such as magma generation and transport and evolution of igneous rocks are important for the determination of thermodynamic properties of glass-ceramics melts. A knowledge of properties such as bulk modulus and density are important because these properties provide to explain upward ascent or downward descent of magmas and determine the densification of magmatic liquids at depth [6, 7]. In this work, the Born–Mayer type interatomic interaction potential containing all two-body interactions are used for Ca$_3$Al$_2$Si$_3$O$_{12}$ grossular and the structural properties; lattice constant, bulk modulus, elastic constants of the examined system are obtained by molecular dynamics (MD) simulation calculations. The structural,

atomic-dynamic, thermodynamic properties and some physical properties of grossular glass during their melting processes are discussed in detail using the interatomic interaction potential with MD simulations. Melting points of bulk materials were determined using the structural and thermodynamics properties such as pair distribution functions and volume–temperature dependence. The calculated melting point is found to be compatible with literature. We use the open source code LAMMPS MD Simulator, which can be run in massively parallel environments and provide efficient simulation on metal atomic scale systems [8] and GULP (General Utility Lattice Program) [9].

2. Materials and method

Potential sets have been used for grossular in recent studies [10]. One of these are metal–oxygen (M–O) based Buckingham potentials and others involve three-body O–M–O angle-bending terms, the core-shell model for the oxygen and the Born–Mayer type interatomic interaction potential containing all two-body interactions. Two-body ionic short range interaction Born–Mayer potentials formed combination of the Buckingham type with a long-range Coulombic interaction term [11] and is given by

$$E_{ij} = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{r_{ij}}, \qquad (1)$$

where r_{ij} is the distance between ions i and j, with charges q_i and q_j, and A_{ij}, ρ_{ij} and C_{ij} are fitted parameters. Lattice energy minimization was performed using both GULP and LAMMPS simulation codes at 0 K and 0 GPa. However, all molecular dynamic simulations during heating of grossular were performed with the only LAMMPS. The grossular glass-ceramics simulations adopted three-dimensional (3D) periodic boundary conditions using the Ewald sum method for long distance interactions and processed the integration of motion equations by velocity Verlet algorithm. The constant pressure ensemble as NPT and Nose–Hoover barostat was

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used to control the pressure and temperature. The integration step was 0.0005 ps with the velocity given by the Maxwell distribution and the value of Born–Mayer type potential cutoff radius as 5.5 Å. Grossular crystallize in the *Ia3d* space group which is one of the most symmetric space groups of the cubic system, their structural formula is $Ca_3Al_2Si_3O_{12}$, where the Ca, Al, Si and O atoms were containing 24c, 16a, 24d, and 96h ions, respectively, according to the Wyckoff notation [12] and the cubic simulation cells, $3 \times 3 \times 3$ repeated periodically in space group. The initial structure was given by random functions followed by a heating process ranging from 0 to 3500 K with the temperature interval of 100 K and a relaxation time of 250 ps at each interval.

3. Results and discussion

The potential parameters used in the MD simulations were obtained from the garafolini.lib force field libraries from GULP [13]. The potential parameters of grossular are listed in Table I. The values of ρ_{ij} are taken as 0.29 Å for all type of interactions. For atoms of Ca, Al, Si and O the q values are $+2$, $+3$, $+4$ and -2, respectively.

TABLE I

Potential parameters for grossular.

Buckingham	A_{ij} [eV]
Ca–Ca	4369.0100
Ca–Al	1359.3878
Ca–Si	1382.4811
Ca–O	3557.6200
Al–Al	312.0700
Al–Si	1574.7178
Al–O	1554.1210
Si–Si	1171.5201
Si–O	1848.7174
O–O	452.5051

The reliabilities of the values for interatomic potentials were determined with computer simulations study using interaction potentials. Understanding the anisotropic elastic behaviour of tissues is important for the calculating of accurate elastic constants of grossular. Table II shows the calculated values of lattice constant, elastic constants (C_{11}, C_{12}, C_{44}) and bulk modulus for grossular with the experimental data. The reason for the high value of C_{11} and low values of C_{44} is owned by anisotropic elastic constants.

TABLE II

Structure optimization results of grossular.

Constant	GULP	LAMMPS	Experimental
lattice constant [Å]	12.11	12.10	11.85 [14]
bulk modulus [GPa]	214		173 [15]
C_{11} [GPa]	391		321.7 [16]
C_{12} [GPa]	126		98.3 [15]
C_{44} [GPa]	113		104.6 [16]

Radial distribution functions, $g(r)$, are an important physical quantity to determine various characteristics of liquids and amorphous state. We define the melting temperature T_m, at the maximum volume corresponding to the melting point. Figure 1a shows that volume increases linearly with the temperature and linear behaviour during the heating process shows that no solid–solid phase transition occurs at any temperature. At the melting point, the system passes to a liquid state to have lost the ionic bonds and this is indicated by a sudden increase in the energy curve. It is observed a sharp increase in volume near the temperatures of 3000 K. The melting temperature is obtained as $T_m = 3000$ K. Figure 1b shows the calculated $g(r)$ curves at 300 K where it behaves like a solid. First peak position of $g(r)$ is around ≈ 1.63 Å which is not sensitive to temperature as well as other peaks. It has been observed that as the temperature increases, the $g(r)$ peaks become wider. As the temperature is increasing to 2900 K, which corresponds that grossular is not completely melted, an amorphous phase identified because of the hump in the second peak. However, grossular has lost the other peaks and then became liquid at 3000 K. The $g(r)$ of liquid grossular shows an obvious first peak, visible second peak and featureless tail at 3000 K which corresponds to melting temperature obtained by MD simulations.
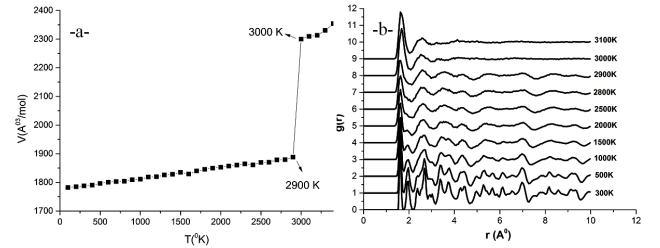

Fig. 1. (a) Temperature dependence of the volume for grossular, (b) total radial distribution functions of grossular at different temperatures.
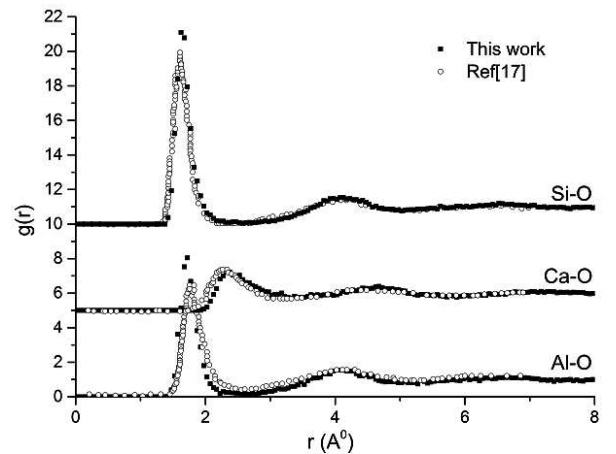

Fig. 2. Comparison of pair distribution functions for grossular at 3000 K along with data taken from Volker Haigis et al. [17].
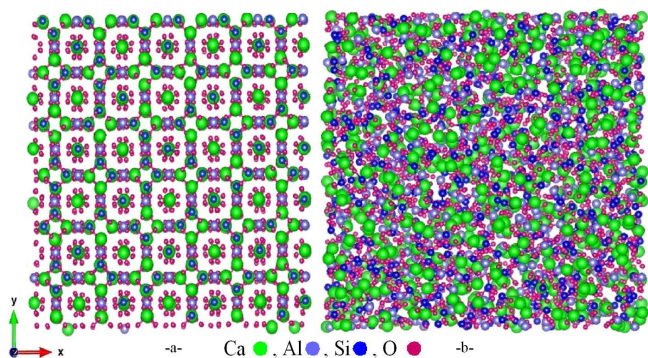
Fig. 3. Snapshots of the grossular at (a) 300 K, (b) 3000 K.

The Al and Si atoms in grossular have been essentially in fourfold coordination. The bonding distance of Si–O and Al–O in grossular glass are 1.63 Å, 1.95 Å, respectively, which are estimated from the peak position of radial distribution function curve at 300 K. These T–O distances (T = Al and Si) are consistent with the common average T–O distance in AlO_4, SiO_4. The Ca–O distance in the grossular glass is 2.37 Å at 300 K. The calculated partial pair distribution functions of Si–O, Ca–O, Al–O are shown in Fig. 2 along with the data are taken from Haigis et al. [17]. Open circles represent data taken from [17]. There were obtained the partial pair distribution functions between Si–O and Al–O active short-range interaction, Ca–O active medium range interaction. The first peak position of Si–O and Al–O is almost equal but the values for Ca–O is greater, ≈ 1.7 Å, than for Si–O and Al–O.

MD simulation images have been observed at different temperature in order to define the atomic structure of grossular through the melting process. When temperature increases, bonds between atoms become weak, convert to an irregular structure from regular structure and phase transition occurs. Figure 3a shows a structure of complete grossular crystal ($3 \times 3 \times 3$) at 300 K, part (b) shows it becomes the liquid structure at 3000 K; MD simulation results show that, when grossular at 300 K is in the solid phase and stable structure, it is completely melted and in the liquid phase at 3000 K.

4. Conclusion

The melting evolution of grossular possessing large unit cell (160 atoms/cell), complex structure and high symmetry space group $Ia3d$ is investigated by MD simulations using the Born–Mayer type interaction potential. We modelled the atomistic structure of grossular with different structural optimization methods using both GULP and LAMMPS. The calculated values of the lattice constant, bulk modulus, elastic constants and cohesive energy are in reasonable agreement with experimental measurements and previous data. We have determined that the volume of the system is linearly related with the temperature during heating. The melting point obtained from the MD simulations is $T_\mathrm{m} = 3000$ K. We conclude from the comparison of produced partial pair distribution functions with available data that the Born–Mayer type potentials are capable for understanding the liquid structure of grossular. This work will be extended in order to define the atomic structure of amorphous grossular and determine the glass transition temperature.

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