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Molecular dynamics simulation of thermodynamic properties of YAG*

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In this paper we study the thermodynamic properties of $Y_3Al_5O_{12}$ (YAG) by using molecular dynamic method combined with two- and three-body potentials. The dependences of melting process, elastic constant and diffusion coefficient on temperature of crystal YAG are simulated and compared with the experimental results. Our results show that anion O has the biggest self-diffusivity and cation Y has the smallest self-diffusivity in a crystal YAG. The calculated diffusion activation energies of ions O, Al and Y are 282.55, 439.46, 469.71kJ/mol, respectively. Comparing with experimental creep activation energy of YAG confirms that cation Y can restrict the diffusional creep rate of crystal YAG.

Keywords: YAG, diffusion, elastic constant, molecular dynamics
PACC: 6630H, 6220D

1. Introduction

Yttrium aluminium garnet ($Y_3Al_5O_{12}$, or YAG) is an important material which is widely used as a solid laser material[1,2] and high temperature structure material.[3−6] YAG has a high melting temperature ($T_m = 2213.15$ K)[7] and is highly stable in oxidizing and reducing environments. The coefficient of thermal expansion is $8.7 \times 10^{-6}\,^{\circ}C^{-1}$,[8] making YAG a good match for many potential oxide matrices. What is more, YAG has a relatively high creep resistance[5,6] and very little elastic anisotropy. It has been universally received that YAG is a more attractive candidate for high temperature structure applications than any other garnet material.

As most of oxides, the diffusional creep is an important deformation mechanism of YAG. Some creep experiments[9−12] have focused on this subject. Parthasarathy *et al*[9] have compressed the YAG crystal at temperatures from 1643.15 K to 1853.15 K and their results show that cation diffusivity (Y or Al) restricts the creep rate in YAG. Further, the reported creep activation energy varies between 596 kJ/mol and 678 kJ/mol[5,10,11] for single crystal YAG, and is 584 kJ/mol[12] for a polycrystal YAG, which are almost twice the oxygen diffusion energy (325 kJ/mol).[13] It is also indicated that the cations rather than oxygen ions govern the diffusional creep in a crystal or polycrystal YAG. But in a recent creep test,[14] Peters and Reimanis have observed different behaviours of the diffusion in YAG. Based on grain boundary grooving, they have obtained a creep activation energy of 375 kJ/mol. And comparing with the activation energy of O ion in YAG, they have found that oxygen is a diffusion-restricting species in boundary grooving in YAG. To understand the rate-restricting species in diffusional creep of YAG, direct diffusivity measurement is necessary. The oxygen self-diffusion coefficient has been reported both in crystal YAG and grain boundary in YAG in Refs.[13,15]. But for cation Al or Y, as radioactive-trace experiments are required to measure the diffusivity, which are very expensive and need dedicated instrument, the diffusion data have been unavailable up to now.[16] However, Jimenez *et al*[16] have determined the Yb diffusivity in polycrystal YAG by substituting Yb for Y ion.

A detailed knowledge of the melting behaviour, elastic properties, and diffusion coefficients of YAG at high temperatures certainly are beneficial to an understanding of the creep mechanism of YAG. But few theoretical publications on this subject are available. In this paper, we report on the results of molecular dynamic (MD) simulations of the melting process,

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temperature-dependent elastic constants, and diffusivity in crystal YAG. The MD method is a suitable tool to study the melting process, and to estimate the diffusion coefficients and elastic constants based on statistical fluctuations.[17−20] In our simulation, the melting process is carried out from 300 K to 2500 K using the constant number, constant pressure and constant temperature (NPT) ensemble. After the stable structure at a given high temperature has been obtained, the elastic constants and the self-diffusion coefficients of YAG are calculated by using the constant number, constant volume and constant temperature (NVT) ensemble. The rest of this paper is organized as fellows. In Section 2, we briefly describe the computational method used and the simulation process. In Section 3, our results are presented and analysed in detail. A brief summary is given in Section 4.

2. Computational method and initial model

2.1. Potential

In molecular dynamics, a key issue is the accuracy of the interatomic potential. Some researchers have used pair potentials whose parameters are fixed by simulating the property of crystalline YAG.[21,22] However, the pair potentials cannot properly represent the angular effect of bonding. In the present work, we use a modified Born–Mayer–Huggins (BMH) pair potential plus a three-body term. This type of multiatom potential has been extensively used by Blonski and Garofalini[23] to study surface and bulk properties of α-Al_2O_3. The BMH potential is given by

$$V_{ij}^{(2)} = \frac{q_i q_j}{r_{ij}} + A_{ij}\exp\Big(-\frac{r_{ij}}{B_{ij}}\Big), \tag{1}$$

where r_{ij} is the separation between ions i and j; q_i and q_j are the ionic charges; A_{ij} and B_{ij} are the potential parameters. The three-body interactions[23] are described by the following terms:

$$\begin{aligned} &V_{jik}^{(3)} = \Big[\lambda_{jk}\exp\Big(\frac{\gamma_{ij}}{r_{ij}-r_{ij}^0} + \frac{\gamma_{ik}}{r_{ik}-r_{ik}^0}\Big)\Omega_{jik}\Big], \\ &\text{if} \quad r_{ij} < r_{ij}^0 \quad \text{and} \quad r_{ik} < r_{ik}^0, \\ &V_{jik}^{(3)} = 0, \\ &\text{if} \quad r_{ij} \geq r_{ij}^0 \quad \text{or} \quad r_{ik} \geq r_{ik}^0, \end{aligned} \tag{2}$$

where r_{ij}^0 is the cutoff of atomic bonding of atoms i and j; r_{ij} is the distance between atoms i and j; $\lambda_{jik} = \gamma_{ij}^{1/2}\gamma_{jk}^{1/2}$. The angular factor Ω_{jik} is given by

$$\begin{aligned} &\Omega_{jik} = [(\cos\theta_{jik} - \cos\theta_{jik}^0)\sin\theta_{jik}\cos\theta_{jik}]^2, \\ &\text{for} \quad \text{O} - \text{Al/Y} - \text{O}. \\ &\Omega_{jik} = (\cos\theta_{jik} - \cos\theta_{jik}^0)^2, \\ &\text{for} \quad \text{Al/Y} - \text{O} - \text{Al/Y}, \end{aligned} \tag{3}$$

where θ_{jik} is the angle formed by the ions j, i, and k with the ion i located at the vertex. θ_{jik}^0 is the fitting angle parameter between atomic bonds.

We have obtained the necessary potential parameters of interactions between ions by fitting the experimental lattice constant and elastic moduli[24,25] of crystal YAG by using the 'GULP' program.[26] The fitted potential parameters are listed in Table 1.

Table 1. The potential parameters used for the Y–Al–O system.

Two-body potential			Three-body term				
Atoms			Atoms				
ij	A_{ij}/eV	B_{ij}/Å^{-1}	ijk	λ_{ij}/eV	γ_{ij}/Å	r_{ij}^0/Å	θ_{jik}^0/(°)
O–O	2449.44	3.44	Al/Y–O–Al/Y	6.242	2.0	2.6	109.5
Al–O	1740.31	3.44	O–Al–O	149.324	2.8	3.0	109.5
Y–O	1250.85	2.86	O–Y–O	168.250	2.8	3.0	109.5
Al–Al	312.11	14.06					
Y–Y	245.14	14.06					
Y–Al	256.55	14.06					

*Ion charge q_i: O (−2); Al (+3); Y (+3).

And then the potential parameters are used in MD simulation in program 'MOLDY'.[27] The simulated model is extended to $2 \times 2 \times 2$ as a unit cell of YAG, which will be discussed late. In Table 2 listed are the lattice constant and elastic constants for YAG crystal at $T = 300$ K and pressure $P = 1$ MPa ob-

tained from the MD simulation by using these fitted potential parameters. The deviation of the lattice constant from the experimental value is about 2.9%. And the elastic constants C_{11}, C_{12} and C_{44} are reasonably consistent with the experiment values in Ref.[25]. The atomic coordinates of YAG from the MD simulation are Al1: (0.00, 0.00, 0.00), Al2: (0.375, 0.00, 0.25), O:(0.0298, 0.045, 0.653) and Y: (0.125,0.00,0.25) which are consistent with the experimental values in Ref.[27]. The pair correlation function (PCF)[28] of crystal YAG at $T = 300$ K and $P = 1$ MPa are also shown in Fig.2(a). It is clear that the first peak is Al–O peak which is at 1.87 Å, and the second peak is Y–O peak which is at 2.40 Å. The positions of Al–O and Y–O peaks calculated here are in agreement with the average bond lengths 1.85Å and 2.36Å calculated by the *ab initio* theory in Ref.[29], respectively. These results show that our potential parameters are suitable to study the properties of crystal YAG.

Table 2. The MD calculated equilibrium lattice constants and elastic constants of supercell models of YAG at $T = 300$ K and $P = 1$ MPa.

	lattice constant a/Å	C_{11}/GPa	C_{12}/GPa	C_{44}/GPa
Theory	12.35	308.8	133.9	140.2
Exp.	12.004[27]	339[23]	114[23]	116[23]
Error	2.9%	8.9%	17.4%	20.8%

2.2. Initial model and simulation process

The crystal YAG has a complicated garnet structure, which contains 80(160) atoms in a primitive (cubic) cell.[29] And the space group is O_h^{10}. In our simulation, the initial model is extended to $2 \times 2 \times 2$ as a unit cell, which comprises 1280 atoms (320 Al, 192 Y and 768 O ions in total). All simulations are carried by using program "MOLDY". The simulated temperatures range from 300 K to 2500 K. Two simulation ensembles, NVT and NPT ($P = 1$ MPa), are chosen for two different processes. The NPT ensemble is used to simulate the melting process so that we can obtain stable structures at different temperatures. We use 100000 MD steps with time steps of $\Delta t = 0.002$ ps so that the total simulation time is 200 ps for each temperature. The heating is considered in a step-by-step procedure. At a given temperature T and after 100000 MD steps, the temperature increases by 100 K and then the next 100000 MD steps are carried out.

After the stable structures for YAG supercell at different temperatures have been obtained, we calculate the temperature-dependent elastic constants by using the NVT ensemble. For the NVT ensemble simulation, the MD parameters are chosen to be $\Delta t = 0.002$ ps and $N = 50000$ with a total simulation time of 100 ps. Due to the fact that the NVT ensemble converges much faster than the NPT ensemble, the simulation time of 100 ps is quite sufficient for our purpose. The elastic constants $C_{\rm pqrs}$ are obtained from the statistical fluctuation formula[17,18] as follows:

$$\begin{aligned} & V_0 {h_{0ip}}^{-1} {h_{0jq}}^{-1} {j_{0ms}}^{-1} C_{\rm pqrs} \\ = & -\frac{4}{k_{\rm B}T}\delta(M_{ij}M_{lm}) \\ & + 2Nk_{\rm B}T(G^{-1}_{mi}G^{-1}_{jl} + G^{-1}_{li}G^{-1}_{jm}) \\ & + \Big\langle \sum_{a,b} g(r_{ab}) s_{abi} s_{abj} s_{abl} s_{abm} \Big\rangle, \end{aligned} \tag{4}$$

where the first term is the fluctuation term (pressure), the second term is the kinetic term (thermal), and the third term is the Born term (static). V_0 is the volume containing the N particles, h_0 is a 3×3 cell matrix, $k_{\rm B}$ is the Boltzmann constant, T is the temperature, G^{-1} is the inverse of the metric $G = h'h$, $s_{\rm ab}$ is the vector joining atoms a and b with a length of $r_{\rm ab}$, and $g(r_{\rm ab})$ and M_{ij} are related to momentum and potential, respectively. Detailed descriptions concerning $g(r_{\rm ab})$ and M_{ij} can be found in Ref.[17].

The inclusion of a three-body term in the potential implies that the Born term in Eq.(4) now comprises two parts: the two body part and the three body part, such that

$$\begin{aligned} & V_0 {h_{0ip}}^{-1} {h_{0jq}}^{-1} {h_{0lr}}^{-1} {h_{0ms}}^{-1} C_{\rm pqrs} \\ = & -\frac{4}{k_{\rm B}T}\delta(M_{ij}M_{lm}) \\ & + 2Nk_{\rm B}T(G^{-1}_{mi}G^{-1}_{jl} + G^{-1}_{li}G^{-1}_{jm}) \\ & + \langle (\text{two-body-Born})_{ijlm} \rangle \\ & + \langle (\text{three-body-Born})_{ijlm} \rangle. \end{aligned} \tag{5}$$

In accordance with the classical diffusion theory, the diffusion coefficient D is obtained from the mean-

square displacement (MSD) data as a function of time, or the Einstein relation as follows:

$$\sum_i \langle |r_i(t_i) - r_i(t_0)| \rangle = 6DNt, \tag{6}$$

where $r_i(t_i)$ is the position of atom i at a given time t_i, and $r_i(t_0)$ is the initial position. D is obtained from the slope of an MSD curve vs time. The activation energy, Q, for grain boundary (GB) diffusion is obtained by running MD simulations at different values of temperature T and fitting the results to the Arrhenius relation as follows:

$$D = D_0 \exp(-Q/k_B T), \tag{7}$$

where D_0 is a pre-exponential factor, and Q is the activation energy. From the Arrhenius plot of D vs $1/T$, the slope yields the activation energy Q and the intersection with the vertical axis gives D_0.

3. Results and discussion

3.1. Melting temperature and elastic constant

To test the potential parameter at high temperatures, we first study the melting process of YAG. The data for volume change during the MD simulations of YAG at $P = 1$ MPa and values of temperature T from 300 K to 2500 K are shown in Fig.1. For YAG, the volume increases linearly with temperature until $T_m = 2131$ K. At $T_m = 2131$ K, the supercell volume shows a sudden upward jump, indicating the first-order melting of the crystal. Compared with the experimental equilibrium melting temperature of 2213.15 K,[7] our result is 3.7% lower. This also shows that our potential parameters represent a stronger short-range interaction between ions.

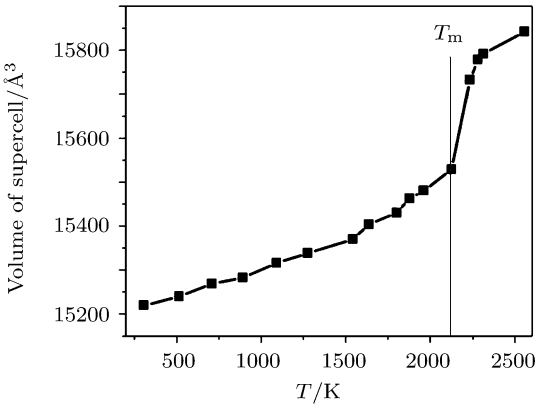


Fig.1. Volume vs temperature in the MD simulations at a pressure of 1 MPa. The volume is for the supercell containing 1280 atoms.

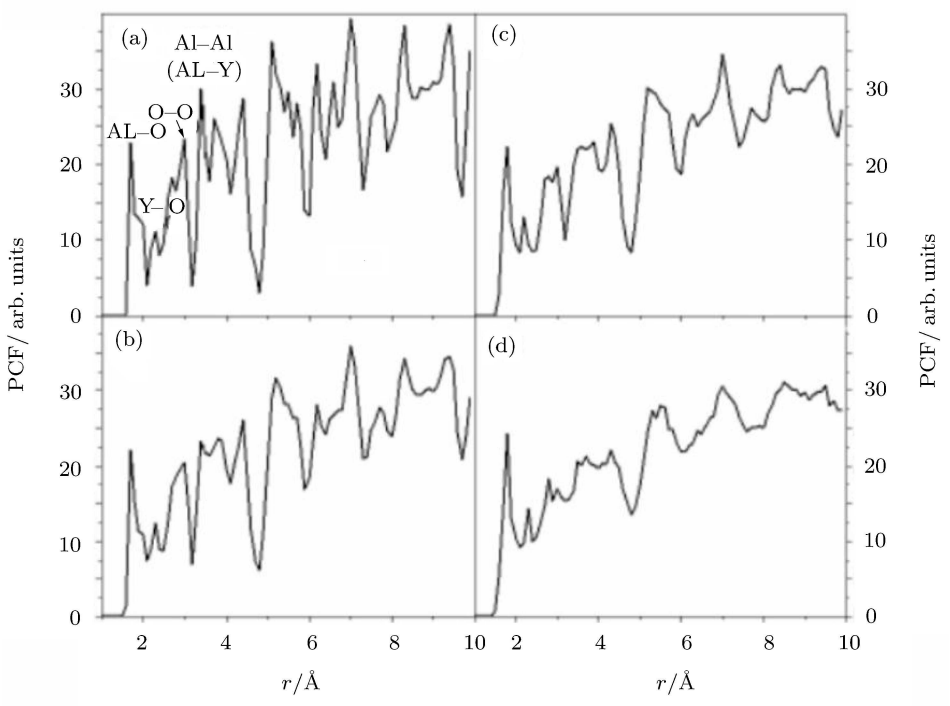


Fig.2. Calculated pair correlation function (PCF) for YAG at different temperatures: (a) 302 K; (b) 890 K; (c) 1802 K; (d) 2234 K.

To better illustrate the melting process, we have calculated the PCF function before and after the melting. The PCF of supercell model of YAG at the values of temperature T: 302 K, 890 K 1802 K and 2234 K, are shown in Fig.2. It can be seen that the nearest neighbours Al–O and Y–O peaks are still there, but, the nearer neighbours Al–Al, Al–Y and the O–O peaks become broader or disappear when the temperature is above a melting temperature of 2131 K. Thus the PCF diagrams fully support the description of melting process described above.

Figure 3 shows the temperature-dependent elastic constants in the supercell model of YAG. The elastic constant is also an important parameter for YAG application at high temperatures. What is more, shear moduli $C' = (C_{11} - C_{12})/2$ and C_{44} are used for monitoring the melting process. In Fig.3, the experimental elastic constants[25] in a temperature range from 300 K to 1400 K are also shown. A linear reduction in C_{11} with temperature increasing from 300 K to 2131 K is observed. Near the melting point of $T_{\rm m} = 2131$ K, the shear moduli $C' = (C_{11} - C_{12})/2$ and C_{44} are still positive but they decrease very rapidly. This signals that the crystal starts to soften and eventually melts. Our results are consistent with the Born instability rule in which melting is preceded by the continuous softening of the lattice with the increase of temperature and volume. The crystal no longer has adequate rigidity to resist melting when its elastic shear modulus is sufficiently small.[30]

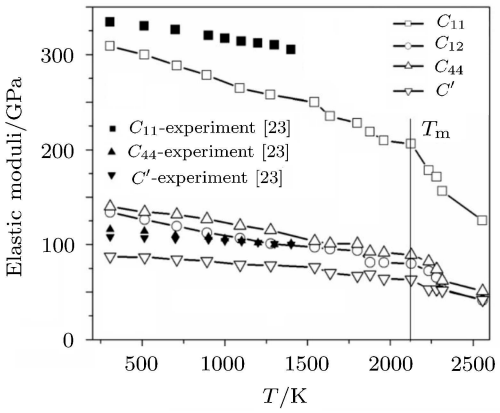


Fig.3. Elastic constants of crystal YAG as a function of temperature from MD simulation.

Compared with experimental elastic constants[25] at temperatures from 300 K to 1400 K, our calculated C_{11} and C' are about 10% to 20% less than experimental results, and C_{44} is about 10% more than experimental results. But the curves of elastic constant of our calculated results and experimental values have a similar tendency to vary with temperature increasing. Overall, our results show that our potential parameters are suitable to study the properties of YAG at high temperatures.

3.2. Diffusion coefficients and activation energy

We also calculate the diffusion coefficients of the ions in the GB for temperatures ranging from 1500 K to 2500 K. The MSD data of atoms as a function of MD simulation steps at temperatures 1543 K, 1962 K for YAG are displayed in Fig.4. The slopes of the curves are proportional to the values of diffusion coefficient D through the Einstein relation of Eq.(6).

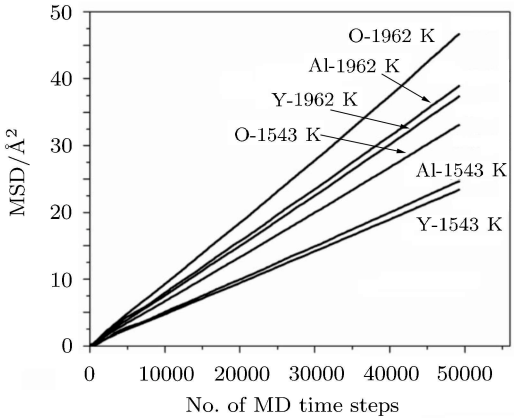


Fig.4. Mean-square displacements vs simulation time for YAG at $T = 1543$ and 1962 K.

The calculated values of diffusion coefficient D as a function of $1/T$ for Al, Y and O are shown in Fig.5, separately. Also shown in Fig.5 are the experimental values for O diffusion[13] in crystal YAG. In general, diffusion coefficients of Al and Y have the same orders of magnitude. However, O ions have a higher value of D. The ion self-diffusivity satisfies the inequality $D_{\rm O} > D_{\rm Al} > D_{\rm Y}$. Comparing with experimental diffusivity of O, our calculated data are larger than experimental data. At a temperature of 1500 K, the calculated data is more than twice the experimental data, which may be due to two reasons. First, our unit cell is 2.9% large than the experiment value, so the ion diffusion will be easy in a bigger volume. Second, our potential has shown a stronger short-range interaction just as analysed in melting process, the ion will obtain a bigger repulsive force to diffuse. Moreover, we also find that experimental diffusion coefficient increases faster with temperature than the calculated diffusion

coefficient. We can explain it according to the role in increasing the diffusion via defects with temperature during experimental process.

Activation energy can be estimated from temperature-dependent curve of D by fitting to the Arrhenius equation. In Table 3, we list the activation energies Q and the values of pre-diffusion parameter D_0 for O, Al, and Y. We find that the activation energies of ions satisfy the inequality $Q_{\rm Y} > Q_{\rm Al} > Q_{\rm O}$. In some creep experiments the activation energy of YAG has been measured. For the creep activation energy of crystal YAG, it varied between 596 kJ/mol[5,10] and 678 kJ/mol[11] which is roughly in agreement with our calculated Y activation energy 469.71 kJ/mol. And, our calculated O diffusion activation energy is also in agreement with the experimental value. Using a trace technical, Haneda *et al* have measured oxygen activation energy to be 325 kJ/mol.[13] This is also in line with our calculated O activation energy 282.55 kJ/mol.

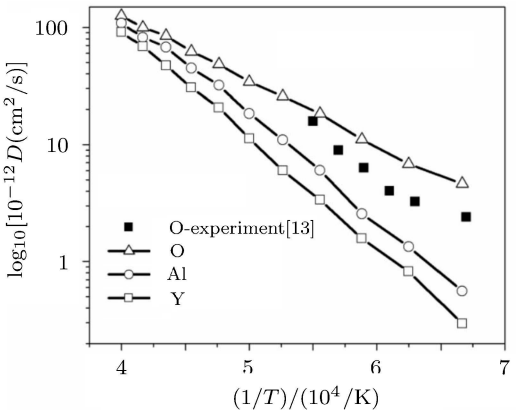


Fig.5. Diffusion coefficients of O, Al, and Y as a function of temperature (> 1500 K). The experimental values for ion O diffusion in crystal YAG are cited from Ref.[13].

Table 3. Calculated activation energies $Q$and pre-diffusion parameters D_0 for O, Al and Y in YAG.

	O	Al	Y
$D_0/(\mathrm{cm}^2/\mathrm{s})$	1.963×10^{-8}	4.114×10^{-7}	5.594×10^{-7}
$Q/(\mathrm{kJ/mol})$	282.55	439.46	469.71

From our results, Y has the smallest ion diffusivity in crystal YAG compared with those of O and Al. So, in the process of diffusional creep of crystal YAG, Y ion will be a creep-restricting rate species. Our conclusion is supported from experimental observations. For experimental creep activation energy 596 kJ/mol[10] or 678 kJ/mol[11] for single crystal, and 584 kJ/mol[12] for polycrystal YAG, they are almost twice the oxygen diffusion activation energy (325 kJ/mol).[13] These results indicate that cations rather than oxygen ions govern the diffusional creep in crystal or polycrystal YAG.

In Ref.[14], Peters and Reimanis have obtained a diffusion activation energy of 330 kJ/mol in grooving grain boundary Σ5 in YAG, which is consistent with the diffusion activation energy of O ion (325 kJ/mol)[13] in crystal YAG. They also have concluded that O is a diffusion-restricting species in boundary grooving in YAG. This implies that there exists a different diffusion mechanism in grain boundary grooving structure from that in perfect crystal, we think. A detailed understanding of the diffusion mechanism in grain boundary in YAG requires building a grain boundary model to study the diffusion mechanism.

4. Conclusions

In this paper, we have reported on the results of MD simulation of crystal YAG at high temperatures. The melting process, the temperature-dependent elastic constants, and the diffusion coefficients and activity energy of ions in crystal YAG are all calculated and compared with experimental data.

The calculated melting temperature $T_{\rm m}$ and elastic constant at temperatures from 300 K to 1400 K are in agreement with experimental results. It shows that our fitting potential parameter is good enough to describe various properties of YAG at high temperatures. Our results also show that ion self-diffusivity in YAG satisfies the inequality $D_{\rm O} > D_{\rm Al} > D_{\rm Y}$. Cation Y has the smallest self-diffusivity in YAG. Based on our present results, we can conclude that the cation Y is a rate-restricting species in diffusional creep mechanism of crystal YAG.

In our future work, we will study the diffusion mechanism in grain boundary in YAG. We think that there will be different diffusion mechanisms between grain boundary and perfect crystal.

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