

Structure and the interactions in the crystal structure of cellulose III_I calculated by using ab initio molecular dynamics simulation

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ABSTRACT

The structure and the interactions existing in the crystal of cellulose III_I was evaluated by using the computational chemical approach. Cellulose is one of the most abundant renewable resources and the application of it to use as a future energy and materials has been progressing. In this study, we performed the optimization and ab initio molecular dynamics simulation of cellulose III_I to investigate the detail information of it. We previously performed the geometry optimization with variable-cell relaxation using the Quantum ESPRESSO program and showed that it is in good agreement with the experimentally obtained crystal structure. However, the cell parameters were slightly smaller than the experimental one which was observed at an ambient temperature. The smaller cell parameter can be considered as an effect of the thermal expansion. That is, the optimized structure with density functional theory corresponds to that at 0K. Therefore, in this work, we performed ab initio molecular dynamics simulation at the temperature from 100K to 500K and investigated the temperature effect of the cell parameters. The results showed that the thermal expansion, especially in the “a” axis direction, was observed during the increment of the temperature.

Keywords: cellulose, crystal structure, ab initio molecular dynamics simulation

1 INTRODUCTION

Cellulose is one of the most abundant renewable resources, with high potential as a future source of energy and chemicals. However, cellulose crystals difficult to dissolve in solvents, and are therefore challenging to use in industrial applications. Fortunately, polymorphs of cellulose crystals can be prepared using different pretreatments. For example, cellulose III_I can be derived from native cellulose I by treatment with liquid ammonia or some amines like ethylenediamine.[1] Compared to native crystals, crystals of cellulose III_I are more solvent-accessible, and are thus more reactive and easier to convert to ethanol, derivatives or other chemicals.[2] Nevertheless, maximum exploitation of these polymorphs requires accurate knowledge of their structure, and of the phase transition mechanism. In this study, we apply the density

functional theory to investigate the crystal structure of cellulose III_I in detail. Especially, we focused on the temperature dependence of the crystal structure how the interaction works between the cellulose molecular chains in the crystal structure during the heating. Recently, Wada et al.[3] examined highly oriented fibers of cellulose III_I by X-ray and neutron diffraction, and proposed a new crystal structure in the monoclinic $P2_1$ space group with cell dimensions $a = 0.445$ nm, $b = 0.785$ nm, c (chain axis) = 1.031 nm and $\gamma = 105.1^\circ$. We used this structure as an initial structure for the calculation in this study. Firstly, we fully optimized the crystal structure *in silico* to evaluate the reproducibility of the experimental crystal structure.[4] However, the cell parameters were slightly smaller than the experimental one which was observed at an ambient temperature. As the optimized structure with density functional theory corresponds to that at 0K, temperature effect of the crystal structure should be investigated. Recently, ab initio molecular dynamics simulation method has greatly progressed and it can be possible to apply on the crystal structure. Therefore, in this work, we performed ab initio molecular dynamics simulation at the temperature from 100K to 500K and investigated the temperature effect of the cell structures.

2 CALCULATION PROCEDURES

All calculations were performed with the Quantum ESPRESSO program package 5.0.1.[5] The calculations were the variable-cell relaxation (abbreviated later as vc-relax), which optimizes both the cell parameters and internal geometry with monoclinic $P1$ space group, and the Car-Parrinello ab initio molecular dynamics calculation at the temperature from 100 K to 500 K with the 100 K intervals. [6]

Interchain interactions in the optimized crystal, such as, hydrogen bond and CH/O interactions, were evaluated by analysing the distance between the atoms involved in the interactions.

We used ultrasoft pseudopotentials and plane-wave basis sets downloaded from the Quantum ESPRESSO homepage. [5] Convergence and total energy were tested at different energy cutoff values of 50, 70, 100 and 150 Ry and 70 Ry was used in all calculations. Monkhorst-Pack $2 \times 2 \times 2$ k -point

grid[7] was used for the geometry optimization. As the Car-Parrinello ab initio molecular dynamics calculation can only use Γ point in this version, super-cell of $2 \times 2 \times 1$ was constructed and used in the calculation instead to increase the number of k -point. A corrected Perdew-Burke-Ernzerhof (PBE) gradient density functional[8] was used; the correction term for long-range van der Waals forces was incorporated into DFT-D calculations (PBE-D).[9] As the Car-Parrinello method in this version did not include the correction term for long-range van der Waals forces (D), the pressure of 20 kbar was applied instead of the correction of it. The pressure value was selected after the test run at ambient temperature condition to reproduce the similar unit cell size of the experiment at the ambient temperature condition. The simulation times are 20 ps at each temperature. Some of other calculation conditions are summarized in Table 1.

Table 1. Some of the conditions and the parameters used in the calculation.

optimization	
software	Quantum Espresso-5.0.1
Energy cut	70Ry
k-point	Monkhorst-Pack $2 \times 2 \times 2$ grid
functional	PBE(Perdew,Burke,Ernzerhof)
Pseudo potential	PBE-RRKJUS
Dispersion correction	PBE-D

Molecular dynamics	
software	Quantum Espresso-5.0.1
Energy cut	70Ry
Energy cutoff for charge density	560Ry
Time step	0.12fs
Effective electron mass	600 a.u.
k-point	Γ -point
Temp. control	Nose
Cell dynamics	Parrinello-Rahman
functional	PBE(Perdew,Burke,Ernzerhof)
Pseudo potential	PBE-RRKJUS

3 RESULTS AND DISCUSSIONS

3.1 Optimization of the Cell structure

The cell parameters obtained by the optimization procedure have been published in our previous paper. [4] Here, we listed again the part of the data in Table 2 for the discussion of the molecular dynamics simulation. The crystal structure of cellulose III_I is shown in Figure 1 with the definition of the crystal parameters of a , b , c and γ . [3] Table 2 shows that the calculated cell parameters of a , b , c and γ are in good agreement with the experimental values.

However the precise investigation of these values, the calculated results are a little smaller than that of the experimentally obtained values. This is reasonable if we take into account the thermal effect of the expansion of the crystal structure. It is because that the optimized crystal structure corresponds to the temperature at 0 K. On the other hand, cell structure obtained in the experiment was measured at room temperature. The temperature effect on the crystal structure of cellulose III_I was observed experimentally by Wada [11] from room temperature to 250 °C. In the next section, we investigated theoretically the temperature dependence of the crystal structure by using the ab initio molecular dynamics simulation. It enables to obtain the molecular level of information about the crystal structure and the interactions in the crystal during the increment of the temperature.

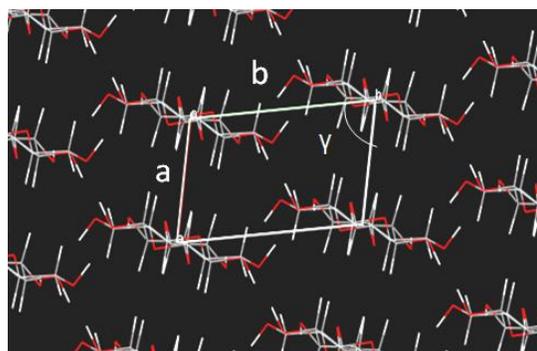


Figure 1. The crystal structure of cellulose III_I. [3] Cellulose chains align to the c -axis, which is orthogonal to the ab -plane.

Table 2. Comparison of the calculated cell parameters with experiment. [4]

	a [Å]	b [Å]	c [Å]	γ [°]
PBE-D	4.29	7.69	10.38	102.1
Exp. [3]	4.45	7.85	10.31	105.1

Before to investigate the behavior of the crystal structure during the change of the temperature, the interaction among cellulose III_I chains in the crystal after the optimization were analyzed. The interacting atom pairs among the cellulose III_I crystal were evaluated from the distance between atom pairs of neighboring chains which were less than 3 Å apart. The positions of these atom pairs found in the crystal structure were shown in Figure 2. Four blue lines from 1 to 4 connect the pair atoms of oxygen and the hydrogen of the CH bond. Two green lines of 5 and 6 connect the pair atoms of oxygen and hydrogen of the OH bond. That is, it suggests the possible existence of four CH/O and two hydrogen bonds interactions among the cellulose chains in the crystal. The existence of these interactions should be proved theoretically by the nature of the electron behaviour using the quantum chemical methods.

Such calculation will be published as an another work in the near future. In this work, the change of the atom distances on these positions during the heating process were investigated by the ab initio molecular dynamics simulation.

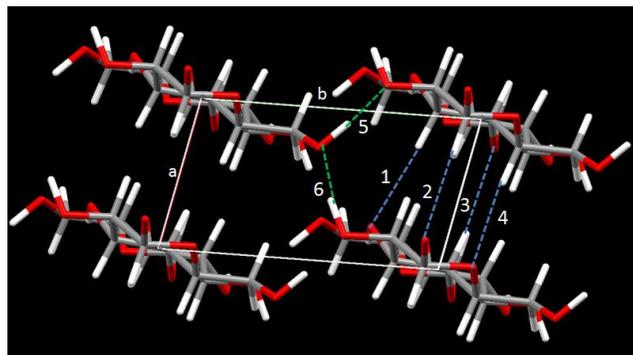


Figure 2. The positions of the interactions existing in the crystal structure of cellulose III_I. Blue dotted lines from 1 to 4 are CH/O interactions and green dotted lines from 5 to 6 are H-bonds.

3.2 Temperature dependence of the cell structure

Ab initio molecular dynamics simulation was performed on the crystal structure of cellulose III_I at the temperature from 100 K to 500 K. As an example, Figure 3 shows the time course of the cell parameter *a* at the temperature from 100 K to 500 K. It can be seen that the *a*-axis gradually increased its cell length according to the increment of the temperature. Especially, the length tends to highly expand at 500 K. These results indicate that the thermal expansion of the crystal can be examined by this method.

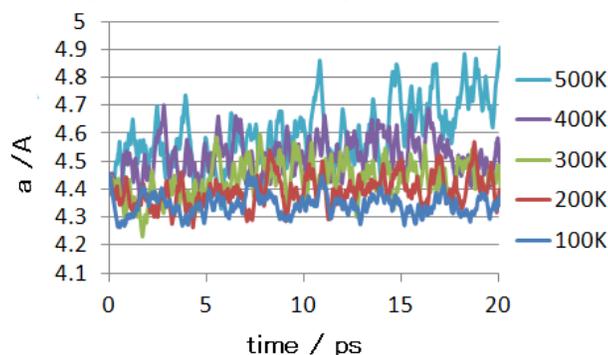


Figure 3. Time course of the length of the *a*-axis simulated at different temperatures.

Temperature dependences of the time averaged unit cell parameters *a*, *b* and *c*, are shown in Figure 4, respectively. It can be seen that the temperature dependence of the cell length of *a* is larger than those of *b* and *c*. Figure 2 shows that the glucose ring of the cellulose chain stacked with each other faced with their hydrophobic sides along to the direction of *a*-axis. That is, there are four CH/O interactions works along the *a*-axis.

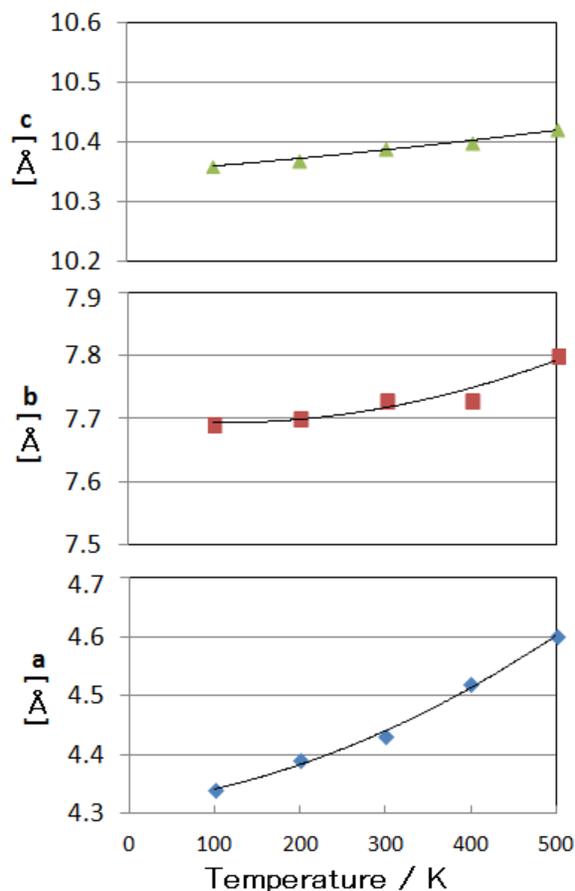


Figure 4. Temperature dependence of the time averaged unit cell parameters *a*, *b* and *c*.

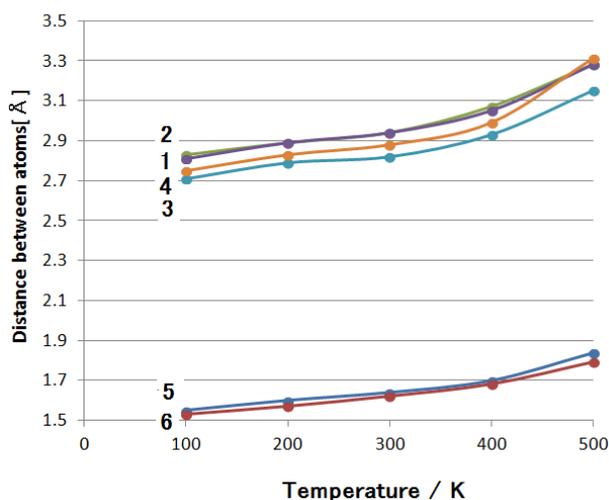


Figure 5. Temperature dependence of the distance between the interacting atom pairs in the cellulose III_I crystal. The numerals indicate the position of the interaction sites, which are defined in Figure 2.

Generally, the CH/O interactions are weak compared to the hydrogen bond. Therefore, thermal expansion of the crystal occurs mainly along to this axis direction.

Figure 5 shows the temperature dependence of the atom distances between the interacting pair atoms in the cellulose III_I crystal. The numerics indicate the position of the interaction sites which are defined in Figure 2. This indicates that the distances in both of the CH/O and hydrogen bond interactions gradually increase according to the increment of the temperature. However, the rate of the increment of the CH/O distance is a little larger than that of hydrogen bond. This indicates that the cell expansion occurs mainly along to this direction. At 500 K, the increment of the CH/O distance tend to become large. These results indicate that the thermal decomposition of the cellulose III_I crystal should occur along to *a*-axis.

4 CONCLUSION

Temperature dependence of the structure and the interactions existing in the crystal of cellulose III_I was evaluated by using the *ab initio* molecular dynamics simulation. This method can well represent the thermal expansion of the crystal structure of cellulose III_I. The results showed that the thermal expansion occurs especially along to the *a*-axis direction, where CH/O interaction works between the glucose residues of the cellulose chain. This would suggest the initial decomposition mechanism of the cellulose III_I crystal during the heating process. That is, the crystal structure would be degraded by the expansion of the *a*-axis direction because of the CH/O interactions along this direction, which may easily disrupted by the thermal fluctuation. The results obtained in this work and the methods of the *ab initio* molecular dynamics simulation used in this work would be an important information and the tool in the research of the cellulose for the use of it as a source of energy and chemicals in industrial applications.

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