Development of a fragment kinetic Monte Carlo method for efficient prediction of ionic diffusion in perovskite crystals

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A massively parallel kinetic Monte Carlo (kMC) approach is proposed for simulating ionic migration in a crystal system by introducing the atomic fragmentation scheme (fragment kMC). The fragment kMC method achieved a reasonable parallel efficiency with 1728 central processing unit (CPU) cores, and the method enables the simulation of ionic diffusion in µm-scale perovskite crystals. To demonstrate the feasibility of the proposed approach, the fragment kMC method was applied to predict the diffusion coefficients of hydrogen and oxygen in SrTiO$_{(3-x)}$H$_x$ and BaTiO$_{(3-x)}$H$_x$ systems. Next, the diffusion coefficient for each hydrogen and oxygen atom was comprehensively predicted at a significantly low computational cost. Finally, the fragment kMC method was customized for µ-scale BaTiO$_3$ simulation under an applied bias voltage, and oxygen diffusion in BaTiO$_3$ model was evaluated. The respective grain sizes are sub-nanometre, and we conclude that the proposed fragment kMC method can be applied to calculate the extent of ionic migration in µ-scale materials with fully atomistic simulation models at a reasonable computational cost.

I. INTRODUCTION

Perovskite material, which is typically composed of an ABO$_3$ type stoichiometry with a cubic crystal structure, draws considerable attention, because of its applicability in many electronic devices that are important for industry. The potential application fields include sensors, random access memory, batteries, capacitors, piezoelectric devices, solid fuel cells, and catalysts for the water-splitting reaction.

In all these applications, the stability and migration of oxygen vacancies are a key factor for determining the utility of the electronic devices. For example, the diffusion of oxygen vacancies through the grain boundaries is assumed to be a main reason for the long-term failure of multilayer ceramic capacitors (MLCCs), and a number of experimental studies of the degradation mechanism have been reported. For these reasons, experimental investigations of oxygen diffusion in per-
ovskite oxides played a central role in designing highly functional materials for industrial devices\textsuperscript{22–28}.

Until recently, ionic migration was empirically predicted according to the ionic radius and size of the unit cell. With the development of computer science, a more detailed analysis of the diffusion mechanisms can be performed for a more sophisticated design towards the development of highly functional materials. Therefore, theoretical simulations are becoming powerful tools for understanding the vacancy-mediated ionic diffusion. In particular, quantum mechanics (QM)-based analysis of vacancy diffusion in perovskite materials has been performed intensively for BaTiO\textsubscript{3}\textsuperscript{29–32}, SrTiO\textsubscript{3}\textsuperscript{33,34}, AZrO\textsubscript{3}\textsuperscript{35,36}, and many other perovskite materials\textsuperscript{37–39}. The above QM approaches were mostly limited to static analysis of phenomena such as formation enthalpy and activation barriers because of the high computational cost. To focus on the kinetics of the ionic migration, the stability of vacancies near the grain boundary, crystal dislocation, or crystal transition, a number of molecular dynamics (MD) simulations were performed for the bulk\textsuperscript{40–44}, surface or interface\textsuperscript{45}, and dislocations\textsuperscript{46}. Although the above MD simulations can cover most ionic migration behaviours, the applications are limited within the ionic diffusion of oxygen in the relatively high-temperature region (more than 1000 K), the system size is within several nm\textsuperscript{3}, and the simulation time scale is several ns. However, for a typical electronic device operating environment, the temperature range is between 300 K and 500 K, and the material sizes are around 1 \(\mu\)m. Thus, it is necessary to develop an alternative approach to simulate the ionic migration in such low-temperature regions with much larger computational models.

The kinetic Monte Carlo (kMC) method\textsuperscript{47} is one of the promising approaches towards such large-scale ionic migration simulation. kMC enables one to calculate long-time scale simulations, in which the vacancy jumps into a different nearest site based on the predefined transition probability. kMC has been applied to predict the kinetics of many problems, such as yttria-stabilized zirconia\textsuperscript{48–50}, chemical reactions\textsuperscript{51–57}, material diffusion\textsuperscript{58–61}, electrochemical impedance\textsuperscript{62}, chemical catalysis\textsuperscript{63–69}, adsorbate–adsorbate interactions\textsuperscript{70,71}, and crystal growth\textsuperscript{72,73}. Despite the success of the kMC approach, there are basically two limitations to applying the method to oxygen migration in perovskite materials. First, the simulation time scale decreases with the increase in system size. Second, the efficient parallel programming of ionic migration for kMC is difficult. The update of the event list
and their selection can be straightforwardly estimated at minor computational cost, but the bottleneck is the communication between the boundary regions of the respective parallelized lattice. Thus, despite the mentioned success of the kMC approach, a more sophisticated approach is necessary towards the simulation of ionic migration in μm-scale ceramic materials.

In this study, we propose a highly efficient approach of ionic migration simulation, in which the kMC simulation is fragmented based on the respective atoms (fragment kMC). Then, the complex event selection and its parallelization can be decomposed into the respective fragments. The fragment kMC approach shows a reasonable parallel efficiency with a large number of central processing unit (CPU) cores. Subsequently, we discuss the effectiveness of the fragment kMC approach by applying the method to predict the diffusion of the hydride ion in the SrTiO$_{3-x}$H$_x$ and BaTiO$_{3-x}$H$_x$ systems. It is experimentally known that diffusion of the hydride ion is vacancy-mediated, and its diffusion coefficient depends significantly on the concentration of hydrogen atoms. The prediction of diffusion coefficients of different types of atoms with the kMC model is a difficult problem, but we demonstrate that the fragment kMC approach can straightforwardly predict the diffusion coefficients in such complex ionic migrations. Second, the oxygen migration in BaTiO$_3$ was evaluated under applied voltage. To make a μ-scale model, the computational model contained 7,680,000,000 atoms, and the simulation time was 5 ms. In this study, the effectiveness of fragment kMC was demonstrated by performing vacancy migration for several specific examples related to energy and electronic devices, and we opened up a new territory of application of atomistic material simulation in large-scale diffusion analysis.

II. THEORETICAL METHOD

A. Summary of the conventional kMC method

In the jump-diffusion kMC approach, the transition rate for the $i$th event, $k_i$, is evaluated based on the rate constant of the chemical reaction as follows:

$$k_i = A \exp \left[ -\frac{E_a}{RT} \right], \quad (1)$$

where $E_a$, $R$, $T$, and $A$ are the activation energy, universal gas constant, temperature, and pre-exponential factor, respectively. Then, the transition probability for the $i$th event $p_i$ is estimated by

$$p_i = \frac{k_i}{\sum_j k_j}. \quad (2)$$

Based on the probability $p_i$, one of the events is chosen, and the geometry is updated ac-
According to the selected event. To select an event, typically, a random number \( r \) is generated, and then one can define the selected event \( l \) so as to satisfy the following equation:

\[
\sum_i^l k_i \leq r \leq \sum_i^{l+1} k_i.
\]  

(3)

The geometry and the transition probability \( p_i \) for respective events are updated according to the selected event \( l \), and the simulation time \( t \) is also updated by another random number, \( r' \), as follows:

\[
t = t - \frac{\ln(r')}{\sum_i k_i}.
\]  

(4)

Despite its simple theory and algorithm, the application of kMC to a large system is sometimes difficult, because there are basically two bottlenecks for practical application of the kMC simulation. First, it is not difficult to see that the time step shown in Eq. (4) becomes smaller and smaller when the number of events in the system increases. Second, the sequential event selection and event update are difficult to parallelize. As a result, the application territory of the standard kMC method is limited within a relatively small size of the computational model and a short simulation time in the case of the jump-diffusion approach.

B. Atomic-based fragment kMC method

Towards the simulation of microscale kinetics of atomic diffusion and its massive parallel algorithm, the rate constant of the chemical reaction in Eq. (11) can be rewritten with atomic-based formulation as follows:

\[
k'_i = A \exp \left[ -\frac{E_a}{RT} \right],
\]  

(5)

where \( I \) is the atomic index. Then, the total rate for each atom \( R_I \) and the maximum rate constant \( R_{\text{max}} \) are

\[
R_I = \sum_{i \in I} k'_i,
\]  

(6)

\[
R_{\text{max}} = \max(R_I).
\]  

(7)

Using the maximum rate constant \( R_{\text{max}} \), the transition probability \( p_i \) is reformulated as

\[
p_i = \frac{R_{\text{max}}}{\sum_J \sum_j k'_j \sum_{i \in I} k_i} \frac{k_i}{R_{\text{max}}},
\]  

(8)

and the probability to select atom \( I \) \( (p^I) \) is

\[
p^I = \sum_{j \in I} p^I_j
\]  

(9)

\[
= \frac{R_{\text{max}}}{\sum_J \sum_j k'_j \sum_{j \in I} k_j} \frac{k_j}{R_{\text{max}}},
\]  

(10)

The first term in Eq. (10) is independent of fragment \( I \), which means that the selection probability only depends on the rate constants related to atom \( I \).

By introducing the auxiliary value \( R_{\text{max}} \), the event selection can be decomposed into
selection of atoms and of events. Then, the kMC algorithm can be reformulated (see Figure 1). First, $N_{\text{frg}}$ atoms in the system are selected randomly (there are three selected atoms in Figure 1 for example). Then, for each selected atom, the events are chosen based on the transition probability $\frac{k_i}{R_{\text{max}}}$. If the total transition rate constant $\sum_{i \in I} k_i$ is less than $R_{\text{max}}$, we introduce a vacancy event region, where no atomic transition and no time integration occur. With the pseudo-event selection, the probability of selecting each event is exactly the same as the original formulation of the transition probability shown in Eq. (2), and each event can be updated independently.

This fragmentation of the event update procedure enables performing an efficient parallel implementation of kMC for atomic diffusion or for a chemical reaction. Then, all the related event lists are gathered, and the rate constant for the next stage of event selection is updated. Simultaneously, the simulation time $t$ is incremented as follows:

$$t = t - \frac{\ln(r')}{\sum_i k_i} N_{\text{updated}}, \quad (11)$$

where $N_{\text{updated}}$ is the event number except that the selected event is null. Thus, if the number of the updated event $N_{\text{updated}}$ is more than one, the event and corresponding atoms are updated independently.

III. COMPUTATIONAL DETAILS

The fragment kMC approach was implemented into the kMC programme (written in C++), and the programme was parallelized with message passing interface (MPI). (the fragment kMC programme is available free of charge at GitHub (https://github.com/hiroyanakata/kMC)).

As for the pilot test of the developed programme, the vacancy diffusion in SrTiO$_3$ and BaTiO$_3$ single perovskite crystals was evaluated (see Figure 2 for the crystal structure). The hydrogen diffusion in SrTiO$_3$ was recently reported by Liu et al.\textsuperscript{74}, but the diffusion coefficient for each hydrogen and oxygen atom separately is not yet clearly understood. Thus, in this study, the hydrogen diffusion in SrTiO$_3(3-x)H_x$ and BaTiO$_3(3-x)H_x$ was also evaluated, where $x = 0.25$, 0.35, and 0.45. The activation energies $E_a$ for the vacancy diffusion of oxygen are 0.6 eV for SrTiO$_3$,\textsuperscript{28,75} and 0.7 eV for BaTiO$_3$,\textsuperscript{76} which were verified by experiment. Because there is no experimental study of the activation barrier of a pure hydrogen atom, the activation energy of hydrogen was estimated from a previous first principle calculation\textsuperscript{74,77}; the activation barrier of hydrogen was chosen as 0.17 and 0.28 eV for SrTiO$_3$ and BaTiO$_3$, respectively. For all the simulation, the pre-exponential factor $A$ is set to 1.0e13 (1/s).
First, the accuracy of the developed fragment kMC was evaluated by comparing with the standard kMC. Then, the parallel efficiency of fragment kMC was evaluated by performing a million-step kMC simulation, and the computational timing was evaluated from a single core to 1728 cores. The system size was $600^3$ unit cells for the performance tests, while we used a relatively large system size ($1200^3$ unit cells) for evaluation of the parallel efficiency from 32 to 1728 cores; 0.1% of oxygen atoms in the crystal were replaced with vacancies.

Second, the hydrogen and oxygen diffusion coefficients were evaluated for the temperature range from 550 to 700 K. Then, the apparent activation barrier was evaluated by the Arrhenius plot. In this study, the diffusion coefficients for hydrogen and oxygen were separately evaluated by tracking the trajectory of the respective atoms.

Finally, to demonstrate the effectiveness of the fragment kMC approach, the oxygen vacancy diffusion in $\mu$ scale BaTiO$_3$ was evaluated under an applied voltage. To consider the effect of the applied voltage, the electrostatic potential was considered by solving the Poisson equation, and the effect of electrostatic potential (ESP) on the rate constant was included as follows:

$$k_i^f = A \exp \left( -\frac{E_a + \Delta E_{pot}}{RT} \right), \quad (12)$$

where $\Delta E_{pot}$ is the ESP difference between product and reactant position. The system size was 641.6 nm $\times$ 160.4 nm $\times$ 962.4 nm, which is nearly the experimental size of a ferroelectric material, and the total number of atoms was 7,680,000,000. To run such a large-scale computational model, the simulation was performed with 1536 CPU cores. The detailed calculation model is shown in the next section.

IV. RESULTS AND DISCUSSION

A. Accuracy and parallel efficiency of the fragment kMC method

To investigate the accuracy of the fragment kMC approach, the simulation results of vacancy diffusion were compared between different numbers of fragments from $N^{frg} = 1$ (conventional kMC) to $N^{frg} = 216$, and the parallel efficiencies of the respective fragment patterns were evaluated to demonstrate the effectiveness of the developed approach. For this purpose, the vacancy diffusion coefficients in SrTiO$_3$ and SrTiO$_{2.75}$H$_{0.25}$ were investigated.

The simulation results for various numbers of fragments $N^{frg}$ are summarized in Figure 3(a) and (b) for SrTiO$_3$ and SrTiO$_{2.75}$H$_{0.25}$, respectively. In Figure 3, the different colours denote the vacancy diffusion
coefficient of the respective fragment number.

As shown in Figure 3(a), the diffusion coefficients in SrTiO$_3$ agree well with each other. The average and standard deviations of the oxygen vacancy diffusion coefficient are shown in Table I. The differences between the respective fragmentation types are only within several nanometres/microseconds, which is less than the value of the standard deviation.

In the SrTiO$_{2.75}$H$_{0.25}$ system, the hydrogen and oxygen atoms have two different transition barriers, with activation barriers of 0.6 and 0.17 eV, respectively. The initial step of vacancy transition was dominated by hydrogen, but the vacancy in transition was trapped by oxygen diffusion. Thus, the initially high diffusion coefficient immediately decreased to a smaller value. Such vacancy diffusion with a mixture of different transition barriers can also be reasonably reproduced by the fragment kMC approach.

Furthermore, the temperature dependence of the vacancy diffusion coefficient was evaluated to demonstrate the accuracy of the fragment kMC method. For this purpose, the vacancy diffusion coefficients in both SrTiO$_3$ and SrTiO$_{2.75}$H$_{0.25}$ were evaluated for the temperatures 500, 550, 600, 650, and 700 K, respectively. A comparison of the results between the conventional kMC and fragment kMC (where the number of fragments is 80) approaches is shown in Figure 4. A perfect agreement is observed between the results with and without fragmentation for both SrTiO$_3$ and SrTiO$_{2.75}$H$_{0.25}$. The agreement between the diffusion coefficients with and without the fragmentation approach also proves that the developed fragment kMC method works for simulation of vacancy diffusion of oxygen and hydrogen atoms.

Finally, the efficiency of the kMC approach was evaluated for vacancy diffusion in the SrTiO$_{2.75}$H$_{0.25}$ system. For this purpose, the parallel efficiency of vacancy diffusion was evaluated with 600$^3$ unit cells from a single core to 216 cores (where the number of fragments ranged from 10 to 2160). The results are shown in Figure 5(a). If the number of fragments and the number of CPUs are small, the calculation requires to update the respective event information for the entire system, and then a large amount of atomic information has to be stored and accessed, operations that take additional computational time. Thus, the simulation with a small number of CPU cores was indeed inefficient. Increasing the number of CPU cores drastically reduced the computational time (Figure 5(a)). In the simulation with more than 32 cores, the computational time showed almost perfect parallel efficiency. The computational time with 1 CPU core is 2850 min, and the computational time is reduced to 3.1
min with 32 CPU cores, and 0.6944 min with 216 CPU cores. (140% parallel efficiency estimated the computational time between 32 CPU and 216 CPU).

For further evaluation of the feasibility of the proposed kMC approach, the parallel efficiency with a relatively large system of $1200^3$ unit cells was evaluated from 32 to 1800 cores (Figure 5(b)). Like with the parallel efficiency shown in Figure 5(a), the computational time could be reduced to 3.61 and 2.6 min with 512 and 1728 CPU cores, and we achieved a reduction in computational time by a factor of 24 and 33 in comparison with 32 CPU cores, and the parallel efficiency of 512 and 1728 CPU cores was 148.6 and 61.1%. Comparison of the parallel efficiency with the other simulation software is also listed in TABLE II. The parallel efficiency in this study shows reasonable performance in comparison with the other previous studies. Thus, the developed fragment kMC approach could be successfully applied to large-scale atomic diffusion by using a high-performance computing system. Note that the parallel efficiency is not main factor for determining the quality of kMC soft, and one of the merit of fragment kMC is the simple structure of the method (See also https://github.com/hiroyanakata/kMC), and it is possible to understand diffusion mechanism of complex perovskite materials (see next sections).

B. Oxygen and hydrogen diffusion coefficients in SrTiO$_3$ and BaTiO$_3$

Another advantage of the fragment kMC programme is the efficient evaluation of the diffusion coefficient for independent hydrogen or oxygen atoms. Because the number of vacancies is significantly lower than the number of oxygen and hydrogen atoms, the standard kMC approach generates an event list based on the vacancy, so the event selection process can be significantly reduced in comparison with the explicit update of oxygen or hydrogen atoms. By contrast, the fragment kMC randomly selects the possible event based on the atoms in the system of interest, and therefore the event selection scheme can be extended not only to vacancy diffusion, but also to the explicit diffusion of oxygen or hydrogen atoms. Thus, we do not need the additional modification of the programme towards the evaluation of the diffusion coefficient for each hydrogen and oxygen atom.

As for the pilot test of the fragment kMC approach, the oxygen and hydrogen diffusion coefficients were evaluated for both SrTiO$_{(3-x)}$H$_x$ and BaTiO$_{(3-x)}$H$_x$, where the hydrogen concentrations were 0.25, 0.35, and 0.45, respectively. To evaluate the apparent
activation barrier for the respective hydrogen and oxygen atoms, the simulations were performed for 550, 600, 650, and 700 K; thus, 24 types of kMC simulations were performed to evaluate the respective activation barriers.

The results for the oxygen diffusion coefficients are shown in Figure 6(a) and (b) for SrTiO$_{(3-x)H_x}$ and BaTiO$_{(3-x)H_x}$, respectively. In both cases, the oxygen diffusion is the rate determining step for vacancy diffusion, and thus the diffusion coefficients of oxygen vacancy do not vary with the concentration of hydrogen.

Likewise, the diffusion coefficient of hydrogen was evaluated, and the results were compared with the diffusion coefficient of oxygen. The results for the hydrogen diffusion coefficient are shown in Figure 6(c) and (d) for SrTiO$_{(3-x)H_x}$ and BaTiO$_{(3-x)H_x}$, respectively. As shown in Figure 6(c) and (d), the diffusion coefficients vary significantly with hydrogen concentration ($x = 0.25, 0.35, 0.45$). The hydrogen diffusion is the vacancy-mediated diffusion, and the diffusion rate of a vacancy is determined by oxygen diffusion. In other words, when the concentration of hydrogen is low, the diffusion rate is low because it is trapped by oxygen. As a result, the magnitude of the hydrogen diffusion coefficient increases with the number of hydrogen atoms, because the vacancy diffusion can go a longer distance through only hydrogen atoms.

To understand the diffusion mechanism in more detail, the apparent activation barrier of hydrogen was evaluated for each hydrogen concentration ($x = 0.25, 0.35, 0.45$). The results for the apparent activation barrier from the kMC simulation are summarized in Table III. The activation barriers were 0.545 and 0.700 eV for SrTiO$_{2.75H_{0.25}}$ and BaTiO$_{0.75H_{0.25}}$, respectively, which are almost the same values as the activation barriers of oxygen diffusion. Thus, the obtained apparent activation barriers also suggest that oxygen migration blocks the diffusion of hydrogen when the concentration of hydrogen is low ($x = 0.25$). Then, the activation barriers decrease with the increase in hydrogen concentration; the apparent activation barriers for $x = 0.45$ were 0.300 and 0.410 eV in SrTiO$_{(3-x)H_x}$ and BaTiO$_{(3-x)H_x}$, respectively. These results are consistent with the experimental study of hydrogen diffusion reported by Liu et al., and the fragment kMC simulation can comprehensively and easily reproduce the respective diffusion coefficient of hydrogen and oxygen atoms.
C. Oxygen diffusion in \( \mu \)-scale BaTiO\(_3\) model

To demonstrate the effectiveness of the fragment kMC approach, the \( \mu \)-scale BaTiO\(_3\) model is constructed, and the oxygen vacancy diffusion is evaluated. The BaTiO\(_3\) is a material that is important for industry, and the oxygen vacancy diffusion under voltage application has a crucial role in insulation deterioration. Thus, the oxygen vacancy diffusion in BaTiO\(_3\) was investigated to demonstrate the effectiveness of the fragment kMC approach.

Likewise with the other ceramic materials, we practically use the polycrystalline BaTiO\(_3\) for MLCC, whose grain boundary structures have not yet been understood in detail. In the simulation perspective, it is also difficult to make such a complex grain boundary structures at current stage of the fragment kMC approach. As for the initial pilot test whether the \( \mu \)-scale oxygen vacancy diffusion can be evaluated or not, the simulation models are separated into respective grains, and we introduce an artificial intermediate BaTiO\(_3\) layer to separate the respective grains, and the transition of oxygen vacancies inside the grain are investigated. The details of the test model are described as follows.

The Voronoi tessellation method was used to make the geometry of BaTiO\(_3\) test model, and the simulation model of this study are shown in Figure 7(a). The test model is constructed in two dimensions (Figure 7) for simplicity, but the actual kMC simulation was performed in three dimensions. The white colour denotes the grain, the black solid line is the grain boundary, and the orange circle is the edge of the grain boundary. The test model was constructed to satisfy the periodic boundary condition (PBC), and the centre region depicted with an open rectangular (blue dotted line) was explicitly treated by kMC, where the size of the simulation model was 641.6 nm \( \times \) 160.4 nm \( \times \) 962.4 nm and the model contained 7,680,000,000 atoms in the system.

In this study, the activation barrier over the respective boundary region was set higher than those in the bulk area, by adding positive electrostatic potential (0.2 eV). The value 0.2 eV was determined from the reported experimental study for oxygen vacancy diffusion\(^{28}\), and thus, the total activation barrier through the boundary was set to 0.9 eV. As noted, the additional intermediate layers are set nearby the grain boundaries to remove the effect of vacancy transition over the grains as shown in Figure 7(b). The analysis concentrated on the oxygen vacancy diffusion within the respective grains, and we define the region between the grains and the additional intermediate layer as the layer boundary region.
In this study, the electrostatic potential was considered by solving the Poisson equation. To apply the bias voltage, the boundary conditions were set to 10.0 eV for the top of the z-axis and −10.0 eV for the bottom of the z-axis, and the PBC was applied for the x- and y-axes to solve the Poisson equation. The electrostatic potential after applying the bias voltage is shown in Figure 7(c). Because we applied the bias voltage along the z-axis, the PBC of the z-axis is broken. Instead of the PBC, the open boundary approximation was applied. If the oxygen vacancy diffuses over the boundary, we consider that the same amount of oxygen vacancies enters from the other side of the boundary region. This approximation maintains the total number of oxygen vacancies.

The distribution of oxygen vacancies obtained by a 5 ms simulation is shown in Figure 8. It can be observed that the oxygen vacancies tend to gather around the bottom of the layer boundary. The highest oxygen vacancy concentration can be found around $x = 138$ and $z = 686$, and the density of oxygen vacancy in the highest region is $1.4 \text{ nm}^{-3}$. The average vacancy concentration in this study was $0.0465 \text{ nm}^{-3}$, and an oxygen vacancy concentration about 30 times larger was observed. It should be noted that we have also found some oxygen vacancy concentration in the bottom of intermediate layers (nearby the top of grain), because of the artificial separation of respective grains. More detail information for the oxygen vacancy concentration in the intermediate layers are shown in supplementary materials, and here we focus on the oxygen vacancy concentration inside the grain.

The highest oxygen vacancy concentration can be found near the triangular layer boundary on the bottom of Figure 8(a), and the detailed distribution of oxygen vacancies is shown in Figure 9(a). As shown in Figure 9(a), the oxygen vacancies diffuse to increasingly low regions, but the layer boundary area prohibits to transfer the vacancy further, and the vacancy migrates to the next lower layer boundary area. As a result, the oxygen vacancies gather to the lowest edge area (See Figure 9(a)).

The grain size is also an important factor to determine the oxygen vacancy density in the edge area. Figure 9(b) and Figure 8(b) show the oxygen vacancy density at the edge area in the case of small grain size. The total number of oxygen vacancies in small grains is lower than in large grains, which also results in a smaller vacancy concentration in the edge area. Compared with the results in Figure 9(a), the edge in a small grain (Figure 9(b)) has a lower oxygen vacancy concentration, and the concentration of oxygen vacancies is about 35.7% lower than the highest.
Another type of oxygen vacancy concentration can be found in the region where the layer boundary is a horizontal line (parallel to the $x$-axis, see Figure 8(c)). The distribution of oxygen vacancies around the horizontal layer boundary is shown in Figure 9(c), where it can be observed that the number of oxygen vacancies is lower than that of the edge area, even for the largest grain size (Figure 8(c)).

In summary, the simulation results indicate that the oxygen vacancy diffusion processes occur as follows. The oxygen vacancies tend to be trapped in the layer boundary area, and going through the boundary region, the vacancies are finally trapped at the edge area. Thus, without the edge area (i.e., the layer boundary is parallel to the $x$-axis), the oxygen vacancy concentration is very low. The oxygen vacancy migration inside the respective grains is considered to be reasonable based on the general behaviour of oxygen vacancy migration in grains $^{14,15,19}$ and the above pilot test suggest that the developed fragment kMC can simulate the oxygen migration in such a large $\mu$ scale BaTiO$_3$ model with a fully atomistic computational model.

V. CONCLUSION

In this study, the fragment kMC method is proposed. This approach introduces the auxiliary value $R^{\text{max}}$, and the event selection can be decomposed into atomic-based fragments. The kMC method can be easily parallelized towards calculation of atomic migrations. The approach does not rigorously satisfy the kinetic theory, because several rare events are neglected. Nevertheless, the diffusion coefficients perfectly agree with the conventional kMC simulation, and the parallel efficiency of fragment kMC was good enough until the number of CPU cores reached 1728.

The method can be straightforwardly extended to analyse the diffusion coefficient for independent atomic types. The respective hydrogen and oxygen diffusion coefficients were evaluated in perovskite SrTiO$_{(3-x)}$H$_x$ and BaTiO$_{(3-x)}$H$_x$ systems. The simulation was performed with various hydrogen compositions ($x = 0.25, 0.35, 0.45$), which were slightly difficult to predict using conventional kMC. Then, the simulation provided good prediction of the diffusion coefficient of hydrogen at reasonable computational cost.

Finally, the fragment kMC was extended to simulate the $\mu$ scale BaTiO$_3$ under bias voltage application. We found that the oxygen vacancy concentration in the edge region was the highest, and the obtained re-
results were reasonable based on the general behaviour of oxygen migration in BaTiO$_3$ materials. Thus, we conclude that the developed fragment kMC programme can be useful for simulating many kinds of atomistic diffusion in crystal systems, and we hope that the proposed method can be widely used to understand the diffusion mechanism in the field of materials and chemistry.

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TABLE captions.

TABLE I. Average and standard deviation (SD) of the oxygen vacancy diffusion coefficient (Å/µs) in SrTiO$_3$ single crystal.

| number of fragment | Average (SD) |
|--------------------|--------------|
| 1                  | 6433 56      |
| 8                  | 6428 75      |
| 32                 | 6433 54      |
| 64                 | 6385 59      |
| 125                | 6412 49      |
| 216                | 6391 66      |

TABLE II. Parallel efficiency comparison with previous studies.

| Software            | CPU cores efficiency |
|---------------------|----------------------|
| LAKIMOCA$^{80}$     | Only Serial          |
| mesokMC$^{50}$      | 32 55                |
| Crystal-KMC$^{81}$  | 800 56               |
| spKMC$^{82}$        | 256 82               |
| this study          | 512 148              |

TABLE III. Apparent activation barrier (eV) estimated by the diffusion coefficient of hydrogen. The simulation results are shown in Figure 6.

| H concentration | SrTiO$_3$ | BaTiO$_3$ |
|-----------------|-----------|-----------|
| 0.45            | 0.300     | 0.410     |
| 0.35            | 0.464     | 0.611     |
| 0.25            | 0.545     | 0.700     |
FIG. 1. Schematic illustration of how the fragment kMC method updates the event selection and the geometry update process.
FIG. 2. Crystal structure of the Ba(Sr)TiO$_3$ system used in this study.
FIG. 3. Comparison between the vacancy diffusion coefficients obtained with different numbers of fragments. The unit of the vacancy diffusion coefficient is Å²/µs. (a) SrTiO₃: The red, blue, and green lines denote the results with 216 and 80 fragments and conventional kMC, respectively. (b) SrTiO₃₋ₓHₓ with x = 0.25: Red, blue, green, magenta, sky blue, and yellow denote the results with conventional kMC and 1, 8, 32, 64, 125, and 216 fragments, respectively.
FIG. 4. The average vacancy diffusion coefficient for different temperatures. Comparison between (blue) standard kMC and (red) fragment kMC for (a) SrTiO$_3$ and (b) SrTiO$_{(3-x)}$H$_x$ with $x = 0.25$. The number of fragments is 80.
FIG. 5. Computational timing and its parallel efficiency of fragment kMC. The black dashed line is the ideal computational time estimated by using the computational time with 32 cores. (a) for $600 \times 600 \times 600$ unit cells from 1 to 216 cores and (b) for $1200 \times 1200 \times 1200$ unit cells from 32 to 1728 cores.
FIG. 6. Oxygen and hydrogen diffusion coefficients from 550 to 700 K for (a) and (c) SrTiO$_{3−x}$H$_x$ and for (b) and (d) BaTiO$_{3−x}$H$_x$. Red closed squares, blue open circles, and green closed circles illustrate the simulation results for $x = 0.25$, 0.35, and 0.45, respectively.
FIG. 7. Simulation model for polycrystalline BaTiO$_3$. (a) Overview of the periodic simulation model used in this study, where the blue dotted line denotes the actual simulated area. (b) Detailed simulation model for oxygen diffusion analysis, where the purple colour denotes the respective grain, and the oxygen vacancy concentration is evaluated for each grain area. The red colour denotes the intermediate layer between the grains. (c) Schematic illustration of applying bias voltage and electrostatic potential.
FIG. 8. The oxygen vacancy concentration of the simulation model in Figure 7(b). Detailed analysis was performed for the orange open square areas (a), (b), and (c). See the main text and Figure 9 for detail.
FIG. 9. Oxygen vacancy concentration of the respective areas shown in Figure S(a), (b), and (c).