Molecular Dynamics Studies of Layered Fluorite Superionic Conductors

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Abstract. A computer simulation by a molecular dynamics method at constant volume has been performed to a model material which is composed of accumulating two different fluorite conductors: \( \ldots \text{BaF}_2\text{-CaF}_2\text{-BaF}_2\text{-CaF}_2\ldots \). CaF\(_2\) region is compressed and BaF\(_2\) region is stretched along the c-axis (z-axis). It is obtained that the diffusion coefficient and ionic conductivity of F ions in the layered fluorite conductors increases with decreasing periods, namely with the number of interfaces.

1. Introduction

Recently Sata et al. [1] have carried out an epoch-making experiment on the mesoscopic fast ion conduction in nanometre-scale planar heterostructures composed of CaF\(_2\) and BaF\(_2\). The conductivity increases progressively with decreasing period in the period range 500 to 16 nm. Here the period means the thickness of CaF\(_2\) plus BaF\(_2\) unit layer.

To get the microscopic information about transport properties of superionic superlattice AgI-AgS system, Kobayashi et al. [3] tried a computer simulation to the layered system by the molecular dynamics (MD) method. The calculated ionic conductivity of the superlattice-system has been larger than that of either case of AgI-system or AgS system. Their calculation suggested the possibility of the existence of the new material which has a larger ionic conductivity.

In the present study, to investigate the experiment by Sata et al. [1] microscopically, we devise a model material which is composed of accumulating two different fluorite conductors: \( \ldots \text{BaF}_2\text{-CaF}_2\text{-BaF}_2\text{-CaF}_2\ldots \). We have performed a computer simulation to the layered fluorite conductors by a MD method at constant volume to get the microscopic information about transport properties of the material. We will discuss our computing results with the experimental data.

2. Method of Computation

Before calculating the layered-system, we perform the MD calculation to each single material, CaF\(_2\) and BaF\(_2\), in order that we may establish the values of parameters in a model potential to get the physical properties of each material.

The lattice constants of CaF\(_2\) and BaF\(_2\) are 5.46 Å and 6.20 Å at the extreme low temperature, respectively. To perform the calculation of a model material which is composed of CaF\(_2\) and BaF\(_2\), we assume the equal lattice-constant for two each material for simplicity. We choose 6.10 Å at 1400 K which is the average value of two materials. We make use of the effective pair potentials used by Kaneko and Ueda [2]. Those are given by

\[
V_{ij}(r) = A_{ij} \left( \frac{\sigma_i + \sigma_j}{r} \right)^7 + \frac{z_i z_j e^2}{r},
\]

where \( i, j \) describe the type of ions, \( A_{ij} \) the repulsive strength, \( \sigma_i, \sigma_j \) the particle radii, \( z_i, z_j \) the effective valence, and \( e \) the elementary charge. The values of \( A_{ij} \) is taken as 0.28 eV. The values of parameters are shown in Table 1.

<table>
<thead>
<tr>
<th>( A_{ij} )</th>
<th>( z_i )</th>
<th>( \sigma_i (\text{Å}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(^{2+})</td>
<td>+2</td>
<td>1.37</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>+2</td>
<td>0.99</td>
</tr>
<tr>
<td>F(^-)</td>
<td>-1</td>
<td>1.36</td>
</tr>
</tbody>
</table>

3. Results and Discussion

When the system has reached an equilibrium state, CaF\(_2\) region is compressed and BaF\(_2\) region is stretched along the c-axis (z-axis). This phenomena may be due to taking the
average value for a lattice constant of a layered superlattice system. The value of a lattice constant of the z-direction is changed as follows:

Table 2. Lattice constants in Å.

<table>
<thead>
<tr>
<th></th>
<th>Value (Å)</th>
<th>Percentage</th>
<th>Part</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>6.41</td>
<td>+5%</td>
<td>for BaF₂ part</td>
</tr>
<tr>
<td>a</td>
<td>5.70</td>
<td>-6.6%</td>
<td>for CaF₂ part</td>
</tr>
</tbody>
</table>

These changes may be caused to remove the pressure difference.

The mean-square displacement (MSD) is defined by

$$\langle |r(t)|^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} \left( |r_i(t) - r_i(0)|^2 \right)$$

where $\langle \ldots \rangle$ is to be understood as an average over time. The linear regions in the functions $\langle |r|^2 \rangle$ may be related to the diffusion coefficients $D$ by the well-known equation

$$\langle |r(t)|^2 \rangle = 6Dt + C,$$

where $C$ is a constant. The diffusion coefficient $D$ is also obtained from the velocity auto-correlation function (VAF) $\varphi(t)$. It is defined by

$$D = \frac{k_BT}{M} \int_0^{\infty} dt \varphi(t).$$

Here the normalized VAF is defined by

$$\varphi(t) = \frac{\sum_{i=1}^{N} \langle v_i(t)v_i(0) \rangle}{\sum_{i=1}^{N} \langle v_i(0)v_i(0) \rangle},$$

where $v_i(t)$ is the velocity of the $i$-th ion at time $t$. The Fourier transform $\Phi(\omega)$ of the function $\varphi(t)$ is given by

$$\Phi(\omega) = \int_0^{\infty} dt \varphi(t) e^{i\omega t}.$$

Using eq.(6), eq.(4) is rewritten as

$$D = \frac{k_BT}{M} \Phi(\omega=0).$$

The ionic conductivity $\sigma$ is given by the Kubo formula using the current-current correlation function by

$$\sigma(\omega) = \frac{1}{3Vk_BT} \int_0^{\infty} dt e^{i\omega t} \langle j_i(t) \cdot j_i(0) \rangle,$$

where $V$ is the volume.

It is obtained that the diffusion coefficient and ionic conductivity of $F^-$ in the layered fluorite conductors increases with decreasing period, which is shown in Tables 3 and 4.

Table 3. Diffusion coefficient of $F^-$ in the layered fluorite conductors at $T = 1400$ K in the unit of $10^{-10}$ cm²/s.

<table>
<thead>
<tr>
<th>Direction</th>
<th>20 period</th>
<th>10 period</th>
<th>4 period</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>0.335</td>
<td>0.939</td>
<td>1.10</td>
</tr>
<tr>
<td>y</td>
<td>0.363</td>
<td>0.945</td>
<td>1.06</td>
</tr>
<tr>
<td>z</td>
<td>0.276</td>
<td>0.784</td>
<td>0.89</td>
</tr>
</tbody>
</table>

Table 4. Ionic conductivity of $F^-$ in the layered fluorite conductors at $T = 1400$ K in the unit of $10^{-2}$ (Ωcm)⁻¹.

<table>
<thead>
<tr>
<th>Conductivity</th>
<th>20 period</th>
<th>10 period</th>
<th>4 period</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$</td>
<td>1.65</td>
<td>3.74</td>
<td>3.87</td>
</tr>
</tbody>
</table>

The period dependence on those transport coefficients is in accord with the experiment [1] approximately. It is shown in Table 3 that the self-diffusion coefficients of x-y plane are larger than that of the c-axis (z direction) direction. These may be due to the appearance of the interface and a slight change of the lattice constant for CaF₂ and BaF₂. Table 3 also shows that the values of the self-diffusion coefficients for both x and y directions are nearly equal. Then the x-y plane is isotropic for mobile ions. Both transport coefficients of a diffusion coefficient and an ionic conductivity increase with decreasing periods and will reach the saturation values. This might mean that the inter-surface effect to the transport coefficients increases with decreasing periods.

Figure 1 shows the integrated distribution of ions in a limited time for a 20 period system at $T = 1400$ K. A vertical and horizontal lines are the c-axis (z-axis) and x-axis, respectively. The numerical values express the length in unit of Å. The area over about $z = 57$ Å is occupied by BaF₂. Gray ellipses which are arranged to form regularly square lattices show Ba ions. Black ellipses are F ions. The area below about $z = 57$ Å is occupied by CaF₂. Gray ellipses which are arranged to form regularly square lattices show Ca ions. Black ellipses are F ions.

We also see that from Fig. 1, that F ions in the CaF₂ region take a zigzag pattern along the c-axis (z-axis). This may signify the occurrence of the double well potential for...