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Short communication

First-principles molecular dynamics investigation on Na_3AlF_6 molten salt

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ABSTRACT

Local structure and transport properties of Na_3AlF_6 molten salt were investigated by First-principles molecular dynamics (FPMD) simulation. For Na_3AlF_6 molten salt, the local ionic structure is governed by five-coordinated $[AlF_5]^{2-}$ and six-coordinated $[AlF_6]^{3-}$. Coulomb force dominates the interionic interactions for Na_3AlF_6 molten salt. The first-shell average coordination number (CN) of Na-F, Al-F in the Na_3AlF_6 molten salt is 6.03, 5.45, respectively and the F-Al-F bond angles are mainly located at 87°, 124° and 171°. The percentage of bridging F_b is small about 1–2%, while the free F_f is up to 26%, suggesting the polymerization degree of local structure is lower. Al-F bonds of the $[AlF_x]^{3-x}$ groups in Na_3AlF_6 molten salt have ionic characters as well as partial covalent characters due to the hybridization of F-2p and Al-3s (3p) orbitals, while the Na-F and F-F bonds are mainly ionic. The order of ion diffusion ability was found as $Na^+ > F^- > Al^{3+}$. Calculated results of viscosity and ionic conductivity are in good agreement with the experimental results, generally within 7%.

1. Introduction

Deep understanding about the structure and transport properties of Na_3AlF_6 molten salt has become an interesting issue, because its physical and chemical properties play key roles on the electro-deposition of Al metal from alumina in the industrial Hall–Heroult process. In addition, a better knowledge of the microscopic structure and transport properties of Na_3AlF_6 molten salt system is required for the correct interpretation of their spectroscopic data. For this reason, Na_3AlF_6 molten salt has been already investigated extensively both by theoretical simulations [1–3] and experiments [4–7]. Gilbert has reproduced the structural properties and Raman spectra of several NaF–AlF_3 crystal compounds by using interatomic potential molecular dynamics (IPMD) simulation based on the rigid ionic (RI) model, and proposed that, only the tetrahedral $[AlF_4]^-$ groups exist in $NaAlF_4$ molten salt [5]. In 2014, Serpil Cikit pointed out the five-coordinated $[AlF_5]^{2-}$ and six-coordinated $[AlF_6]^{3-}$ groups are the dominant roles in Na_3AlF_6 molten salt (cryolite) by the interatomic potential molecular dynamics (IPMD) simulation [3]. Furthermore, high temperature Raman [4,7] and NMR [5,6,8] spectrums give an alternative experimental window to insight the evolution of $[AlF_x]^{3-x}$ groups with different molten salt compositions and temperatures. The predominance of $[AlF_5]^{2-}$ in cryolite melt, proposed by Serpil Cikit is consistent with the NMR data [6]. However, the experimental measurement on molten fluoride salts can be limited by its expensive cost and strong corrosion of fluoride salt. Fortunately, computational simulation assisted with experiment provides a low cost method to explore the molten fluoride salt.

Classical IPMD has been widely applied to predict the structure and dynamic properties of Na_3AlF_6 molten salt [3,9] and other melts [10–18]. However, each new component requires fitting a set of new potential parameters, which is time consuming and limited by the inevitable indeterminacy. In addition, classical interaction potentials lose sight of the interaction between electrons, and therefore cannot be applied to study the relevant electronic property. First-principles molecular dynamics FPMD (also called as *ab initio* molecular dynamics, or AIMD) simulation has several advantages over IPMD, including the accuracy of first-principles calculation of the atomic interactions forces. FPMD therefore is flexible to study any system without needing to aforehand fit to any experimental or computed values and gets access to the full

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electronic structure that is not accessible to the IPMD. Nevertheless FPMD calculation is computationally many orders of magnitude slower than IPMD, therefore it is limited to shorter simulation time and smaller system.

The combination of classical and First-principles simulation represents a very powerful tool and has been successfully applied to study these molten salts such as KCl–LiCl [19], Li_2BeF_4 [20], LiF–NaF–KF [21], $CaAl_2O_4$ [22], $CaMgSi_2O_6$ [23] and $Y_3Al_5O_{12}$ [24]. These studies to date show that FPMD simulation method can be used effectively, and Amelia Bengtson has pointed that the 216 atom unit cells and simulation time of 6–12 ps is sufficient to provide results with acceptable uncertainties and agreement with experimental data of LiCl–KCl molten salt [19]. Due to the rapid growth of computer performance, we have reasons to believe that FPMD simulation can be able to reproduce the structure and predict properties of Na_3AlF_6 molten salt.

In this paper, instead of using IPMD with the interatomic potentials, we firstly employed FPMD directly to enhance our knowledge of local structure and transport properties of Na_3AlF_6 molten salt. Firstly, details of computational method to simulate Na_3AlF_6 molten salt by FPMD are illustrated. In the results and discussions section, the basic structure-transport properties were addressed and compared with the experimental measurements to verify our FPMD model of Na_3AlF_6 melt.

2. Computational methods

2.1. Details of first-principles molecular dynamics

In this work, we employed the combination of IPMD and FPMD to improve the calculation efficiency. Initial configuration of ions system for molecular dynamics was prepared by packing ions randomly into a given simulation cell using the Packmol code [25]. We consider Na_3AlF_6 molten salt as the industrial mole component of NaF 75%, AlF_3 25%, so these simulation cells were composed of 60 Na atoms, 20 Al atoms, and 120 F atoms (a total of 200 atoms). The models of molten salt were firstly equilibrated with IPMD and then FPMD calculation initiated from the final converged structure of IPMD calculations. The method of starting FPMD calculation from the liquid prepared by IPMD has been employed successfully in the literature [26]. Note that FPMD is quite insensitive to the quality of IPMD final converged structure, so the accuracy of potential parameters used in IPMD simulation don't affect the final result of FPMD calculation. The IMPD simulations were run with the LAMMPS [27] software using the Buckingham potentials for Na_3AlF_6 molten salt system, and the potential parameters were referred from the literature [3]. Verlet Leap-Frog algorithm was used with a time step of 1 fs to solve the equation of Newton motions. Ewald sums were used for all coulomb and multipolar interactions with a buffer width of 0.5 Å and an accuracy of 10^{-5} kcal/mol [10–12]. The short-range interaction cutoff was set to 15 Å. Formal charges were used for Na (+1), Al (+3), and F (−1). The periodic boundary conditions were also applied on all sides of the model boxes to create an infinite system with no boundaries, so that the calculated results would be more convincible. To mix the system completely and eliminate the effect of initial distributions, the box systems were heated up to 4000 K in an NPT ensemble for 100 ps at 1.01 MPa, which means these simulations were run keeping the number of particles (N), pressure (P) and temperature (T) of the system constant. Then the hot liquids were cooled down at a rate of 1 K/ps to the melting point 1283 K. Another equilibrium at NPT ensemble for 100 ps was performed for relaxation. After these runs, convergence was achieved and the density difference between the initial and the final state fell below 1%.The resulting structure and velocities were used to start the following FPMD simulation.

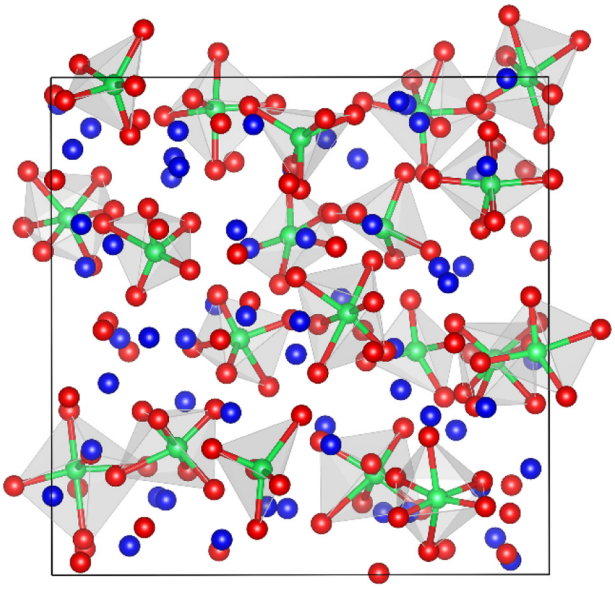

Fig. 1. Snapshot of the local ion structure in cryolite melt. F^- ions in red, Al^{3+} in green, and Na^+ in blue (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

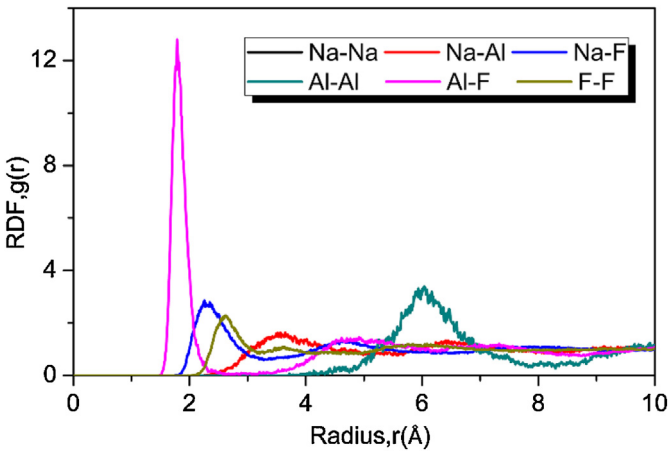

Fig. 2. Calculated Na—Na, Na—Al, Na—F, Al—Al, Al—F and F—F radial distribution functions in Na_3AlF_6 molten salt.

FPMD simulation for Na_3AlF_6 molten salt has been launched with the CASTEP (Cambridge serial total energy package) code [28,29]. Perdew–Burke–Ernzerhof (PBE) exchange-correlation function was implemented in the generalized gradient approximation (GGA) [30]. Ultrasoft pseudo potentials (USPP) have been employed for all the ion-electron interactions. The ionic cores are represented by USPP for Na, Al and F atom. The Na $2s^22p^63s^1$ electrons, Al $3s^23p^1$ electrons and F $2s^22p^5$ electrons are explicitly regarded as valence electrons. Dispersion force was also included by using the semi-empirical DFT-D2 method [19,26,31]. Energy cutoff of 350 eV and a $1 \times 1 \times 1$ *k*-point mesh was chosen for FPMD simulation. Time step for FPMD simulation was chosen at 1 fs to insure an energy drift less than 1 meV/atom/ps. FPMD simulation was done in a statistical ensemble with fixed particle number, volume and temperature (NVT) using the Nosé-thermostat [32]. The simulation temperature (1283 K, melting point of Na_3AlF_6) was similar to IPMD, and the density of simulation model was set to the experimental value [33,34] 2.095 g/cm^3. Periodic boundary condition was also employed in FPMD and simulation represent an infinite molten salt system. After FPMD being launched, the average pressure and resulting pressure in our NVT is 0.00014 and