

Research paper

First-principles molecular dynamics investigation on KF-NaF-AlF₃ molten salt system

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HIGHLIGHTS

- The main forms of Al–F complex ion groups in KF-NaF-AlF₃ system are [AlF₄][−], [AlF₅]^{2−} and [AlF₆]^{3−}.
- With KF concentration increasing, the bond population of Al–F first increases and then decreases.
- The Raman spectra results of [AlF₄][−], [AlF₅]^{2−} and [AlF₆]^{3−} are 593 cm^{−1}, 549 cm^{−1} and 489 cm^{−1}, respectively.

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ABSTRACT

In this paper, first-principles molecular dynamics simulations are applied to study the ionic structure and electronic properties of KF-NaF-AlF₃ system. The results show that the main forms of complex ion groups are [AlF₄][−], [AlF₅]^{2−} and [AlF₆]^{3−}. With KF concentration increasing, the covalent interaction between Al–F ions first increases and then decreases, resulting in the increase of Al–F coordination number and then decreases. The calculation results of Raman spectra on [AlF₄][−], [AlF₅]^{2−} and [AlF₆]^{3−} are close to the experimental values, which indicates FPMD is applicable to similar molten salt systems.

1. Introduction

In the aluminium electrolysis industry, Na₃AlF₆, as an important electrolyte, has been used up to now, but its huge energy consumption, resource consumption and environmental load seriously restrict the development of the industry [1–2]. Since Sleppy [3] put forward the concept of low-temperature aluminium electrolysis in 1979, many researchers have conducted relevant experimental studies on KF-NaF-AlF₃ molten salt system, which mainly focused on its the physical and chemical properties, but the research of ionic structure and electronic properties is relatively scarce [4]. Meantime, with the continuous operation of aluminium reduction cell, impurity elements continue to enrich and KF concentration increases gradually and change the chemical composition, leading to the change of physical and chemical properties of electrolyte. Therefore, it is necessary to study the ionic structure and formation mechanism of KF-NaF-AlF₃ system.

In recent years, with the development of computer technology, computer simulation represented by molecular dynamics simulation [5–8] has made considerable progress, and has been successfully applied to the structural simulation of molten salt systems [9–11].

However, this method has great limitations. For different molten salt systems, molecular dynamics methods need different potential parameters. This has reflected in our previous work [12], in which interatomic potential molecular dynamics (IPMD) simulation was employed to study the ionic structure and transport properties of xKF-yNaF-zAlF₃ system. Although some reasonable results were obtained, the formation mechanism of the structure and properties of KF-NaF-AlF₃ system could not be explained deeply. In this context, Car and Parrinello proposed the first-principles molecular dynamics (FPMD) method [13]. This method does not need to set specific potential function and corresponding parameters, but directly uses the first-principles to calculate the interaction potential between ions, which ensures the accuracy of the interaction potential between ions, and can study the electronic properties of the system. FPMD has been successfully used to the simulation of KCl-LiCl [14–17], NaF-AlF₃ [18] systems, etc. Though FPMD has many advantages over IPMD, its disadvantages also exist. Because the interaction potential between ions needs to be calculated once for each step of ion displacement in the system, FPMD has strict limitations on the size and time of the simulation system [14].

Although FPMD is becoming more and more mature, its study on

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Table 1
Comparison of main parameters between FPMD and IPMD methods.

Calculation parameters	FPMD	IPMD [12]
Wt.%KF	2%	2.3%
Atom numbers	198	854
Time scales of simulation (ps)	10	300
Core numbers of computation	200	30
Computation time consuming (h)	142.5	1.25
Computing platform	Shenzhen Supercomputing Center	

KF-NaF-AlF₃ system is few. The only reference is that Lv et al. [19] adopted IPMD and FPMD to simulate the ionic structure and transport properties of KF-NaF-AlF₃ system. However, due to the lack of in-depth study on the electronic properties, the formation mechanism of the ionic structure of KF-NaF-AlF₃ system cannot be revealed.

In this paper, the ionic structure and electronic properties of KF-NaF-AlF₃ molten salt system are studied by FPMD directly. The interaction mechanism between K and F ions is clarified, and the microscopic formation mechanism of the ionic structure of KF-NaF-AlF₃ system is revealed. Meanwhile, Raman spectra of typical complex ion groups in the system are calculated, which verifies the accuracy of the simulation results of FPMD.

2. Computational methods and parameters

2.1. Simulated box size and time

Table 1 compares the simulation parameters of PFMD and IPMD. The results of IPMD are derived from our previous work [12]. From Table 1, the size of simulation system designed by FPMD is 198 atoms, and the simulation time scale is 10 ps, which is much smaller than that of IPMD. However, the consumption of computing resources by FPMD is much higher than that of IPMD, which is also the reason why FPMD can not simulate large and long time system. It is noteworthy that Amelia Bengtson [14] points out that 216 ions and 6–12 ps for KCl-LiCl system is enough to obtain a good agreement with the experimental results. Therefore, on the basis of reference values and the actual calculation ability, about 200 ions of KF-NaF-AlF₃ system is selected for FPMD simulation in this paper.

2.2. Details of FPMD simulation

The chemical component of n(NaF)/n(AlF₃) = 2.2 is adopted as the simulation system for KF-NaF-AlF₃ molten salt, here, KF = 2 wt%, 6 wt%, 10 wt%, 14 wt% and 18 wt%, so these molten salt boxes are composed of 2 K, 5 K, 8 K, 12 K and 16 K ions, 51 Na ions, 23 Al ions and 122 F, 125 F, 128 F, 132 F and 136 F ions, respectively. The initial structure model is obtained by randomly dropping ions into a box with specified size by Packmol software [20]. The sizes of simulation boxes are 3652.264 Å³, 3796.416 Å³, 3869.893 Å³, 4096 Å³ and 4251.528 Å³, respectively. FPMD of KF-NaF-AlF₃ system is carried out by using CASTEP module [21] and adopting Perdew-Burke-Ernzerhof(PBE) exchange-correlation function in the generalized gradient approximation (GGA)[14,18]. Ultrasoft pseudo potentials(USPP) have been employed for all the ion-electron interactions, where Na2s²2p⁶3s¹, Al3s²3p¹, K3s²3p⁶4s¹ and F2s²2p⁵ electrons are regarded as valence electrons. Semi-empirical DFT-D2 method [14] has been used to calculate Van der Waals weak interactions between ions, which has been proved to be an effective method for Van der Waals correction of ionic liquids. FPMD adopts 420 eV cut-off energy and 1 * 1 * 1 k-point grid [14]. Periodic boundary conditions are employed in the simulation box to eliminate the influence of boundary effect, making the results more reasonable. In order to be consistent with references [12,19] and facilitate the follow-up study of the formation mechanism of ionic structure, the density of the liquid simulation box is set to 1.91–1.96 g/cm³ and the temperature

is set to 1100 K. FPMD simulation adopts NVT (fixed number of particles, volume and temperature) ensemble by the Nosé-thermostat. To obtain more accurate ionic structure and electronic properties, the molten salt system is simulated in 6000 steps under the NVT ensemble to obtain the ionic structure, close to the real system, and then the structure relaxation is carried out in 4000 steps. When the temperature and energy of the system tend to be stable, the FPMD simulation process has converged. The simulation time step sets to 1 fs, and the total simulation time is 10 ps. The final 4000 frames of particle trajectory information are collected to analyze the ionic structure and electronic properties (density of states (DOS), Mulliken population and Raman spectra) of KF-NaF-AlF₃ molten salt.

2.3. Statistical methods

Radial distribution function (RDF) is an important method for describing liquid structure. Extracted from molecular dynamics simulation trajectory, RDF can analyze the local ionic structure of fluoride molten salt [8–10], which indicates the probability that another particle will appear within the radius Δr with the particle at the position as the center, as shown in Eq. (1).

$$g_{ij}(r) = \frac{V}{N_i N_j} \sum_j \left\langle \frac{n_{ij}(r, \Delta r)}{4\pi r^2} \right\rangle \quad (1)$$

V is the volume of simulation box, N is the number of particles, $n_{ij}(r, \Delta r)$ is the average number of atom j surrounding a central atom i within a defined cut-off distance Δr .

The first shell coordination number (CN) of Al ion surrounded by F ion can be obtained by numerical integration of RDF [18] within a specific cut-off radius that corresponds to the first-minimum radius of $g_{Al-F}(r)$, as shown in equation (2).

$$N_{Al-F} = 4\pi\rho_F \int_0^R r^2 g_{Al-F}(r) dr \quad (2)$$

$g_{Al-F}(r)$ is the RDF of Al–F ion pair, ρ_F is the mean density of F ions, R is cut-off radius.

By analyzing the data of particle trajectory, the relationship between mean square displacement (MSD) and time can be obtained from Einstein-Smoluchowshi equation [18,19], as is shown in equation (3).

$$MSD = \langle \Delta \bar{r}(t)^2 \rangle = \frac{1}{N} \left\langle \sum |r_{i(t)} - r_{i(0)}|^2 \right\rangle \quad (3)$$

where $r_{i(t)}$ is the position of ion i at t moment and $\langle \rangle$ is the statistical average value of the ensemble.

3. Results and discussion

3.1. System equilibrium analysis

Before statistical analysis of particle trajectory data obtained from FPMD, it is necessary to determine whether the system has reached the equilibrium state. For NVT ensemble, the volume and particle numbers of the system are fixed in the simulation process, the only change lies in the temperature. When the temperature of the system tends to be stable, the simulation process has converged. Fig. 1(a) is the temperature change tendency of KF-NaF-AlF₃ system in 6–10 ps simulation time, the simulation temperature fluctuates and tends to be stable around 1100 K, indicating that the process of FPMD has reached convergence.

In addition, the change of MSD with time in KF-NaF-AlF₃ system is analyzed. MSD reflects the diffusion state of ions in the system. When the ions reach free diffusion state, the change of MSD with time should be a straight line, indicating that the system reaches the equilibrium state. The change of MSD of different ions with time in KF-NaF-AlF₃ system is obtained by analyzing the data of particle trajectory, as is shown in Fig. 1(b). The change of MSD of Na⁺, Al³⁺, F⁻, K⁺ with time in KF-NaF-AlF₃ system is basically a straight line. In order to reflect the

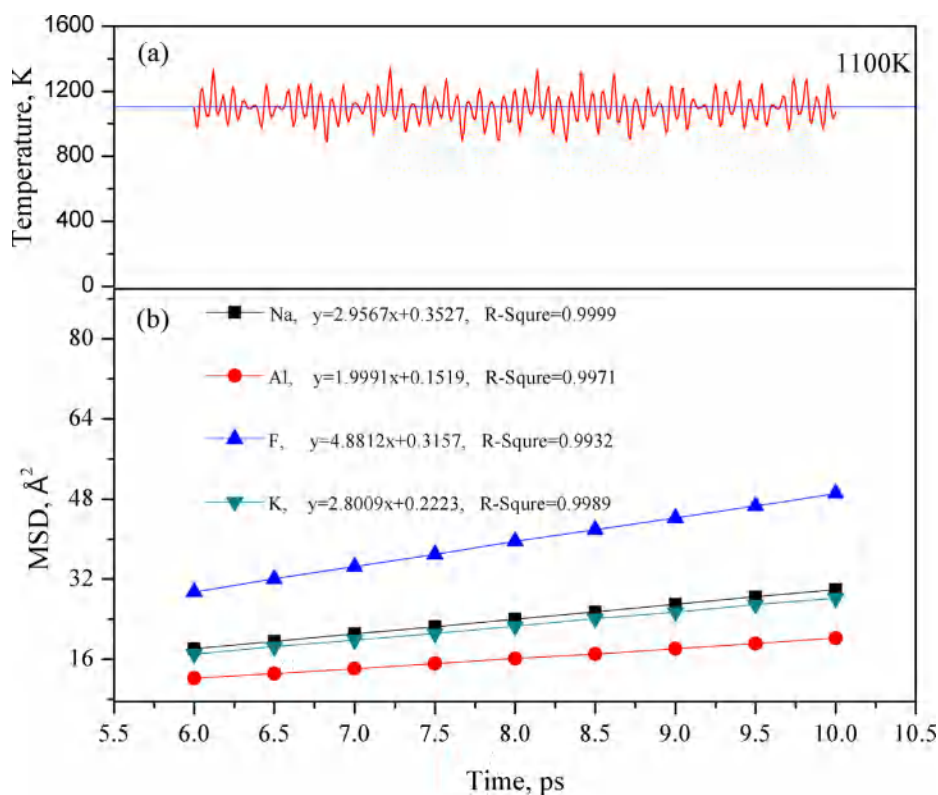


Fig. 1. Equilibrium analysis of simulation process, (a) Temperature change tendency with simulation time; (b) MSD curves of ions in KF-NaF-AlF₃ system (18 wt% KF).

diffusion state of ions in the system more intuitively, the linear fitting of MSD with time is carried out in this paper, obtaining the change of MSD of different ions with time, and R -square that reflects the fitting degree of the curve [22]. The closer R -square is to 1, the closer the change of MSD with time is to a straight line. From Fig. 1(b), the calculation results of R -square are all above 0.99, implying that the ions have reached free diffusion state, and the whole simulation process has reached the equilibrium state.

3.2. Micro-structure of KF-NaF-AlF₃ molten salt system

The stable configuration of KF-NaF-AlF₃ molten salt system is simulated at 1100 K under 0.1 Mpa, as is shown in Fig. 2. K and Na ions are randomly distributed in the simulation box. The distance between ions is large because the polarity differences of K-K, K-Na and Na-Na ions are small, and there is no covalent characteristics. The local ionic structures in the simulation box are dominated by four-coordinated [AlF₄]⁻, five-coordinated [AlF₅]²⁻ and six-coordinated [AlF₆]³⁻ complex ion groups, which correspond to distorted tetrahedron, triangular bipyramid and octahedron configurations, respectively. Although KF-NaF-AlF₃ system loses its long-range ordered state, the local ion structure remains the short-range ordered state, namely, there exist a large number of [AlF₄]⁻, [AlF₅]²⁻ and [AlF₆]³⁻ complex ion groups in the molten salt.

3.3. RDF and CN

RDF of ion pairs in KF-NaF-AlF₃ system is shown in Fig. 3. After $r > 7$ Å, the $g(r)$ value gradually approaches 1, which coincides with the short-range ordered and long-range disordered structure of the molten salt. The first peak radius of RDF represents the average bond length of an ion pair. The calculation results are shown in Table 2, from which the average bond length of Al-F ion pairs are 1.73–1.75 Å, close to the values in the reference [18,19]. Al-F ion pairs is the main

complex ion groups in the molten salt, which shows that the calculation results by FPMD are reasonable. When KF concentration increases, the average bond length of Al-F ion pairs does not change greatly. This may be due to the strong interaction between Al-F ion pairs, which is also reflected in the RDF curve. Compared with other ion pairs, the first peak of RDF between Al-F ions is high and sharp, while the average bond length of K-F ion pairs decreases gradually. In the KF-NaF-AlF₃ system, the first peak radius of RDF between the same charged ions is larger than that of different ones, indicating that there is a strong electrostatic repulsion force, which results in a long distance between ions. However, the different charged ions are opposite.

The calculation results of average CN of Al-F ion pairs are shown in Table 2. All results are less than 6 and more than 5, implying that in KF-NaF-AlF₃ system, some six-coordinated [AlF₆]³⁻ ion groups dissociate into five-coordinated [AlF₅]²⁻ or even four-coordinated [AlF₄]⁻ ones. In addition, with KF concentration increasing, the average CN of Al-F firstly increases and then decreases, reaching the maximum at 10 wt% KF, which is the result of the interaction of K and F ions. This situation is also mentioned in reference [19]. However, due to the lack of calculation of electronic properties, it is difficult to deeply understand its formation mechanism.

3.4. Microscopic formation mechanism of ionic structure

In order to reveal the change rule and formation mechanism of several ionic structures in KF-NaF-AlF₃ molten salt system, the electronic properties, such as DOS and Mulliken population, are calculated based on a frame of stable configuration.

Fig. 4 shows the total DOS and partial density of states (PDOS) of the system. It has found that the electronic orbits near the lowest energy -50 eV are occupied by Na-3s, and that near the intermediate energy -25 eV to -20 eV are occupied by both Na-2p and F-2s. In addition, the electronic orbits near Fermi level are mainly occupied by F-2p and partly hybridize with Al-3p orbits, which signifies that there exists some

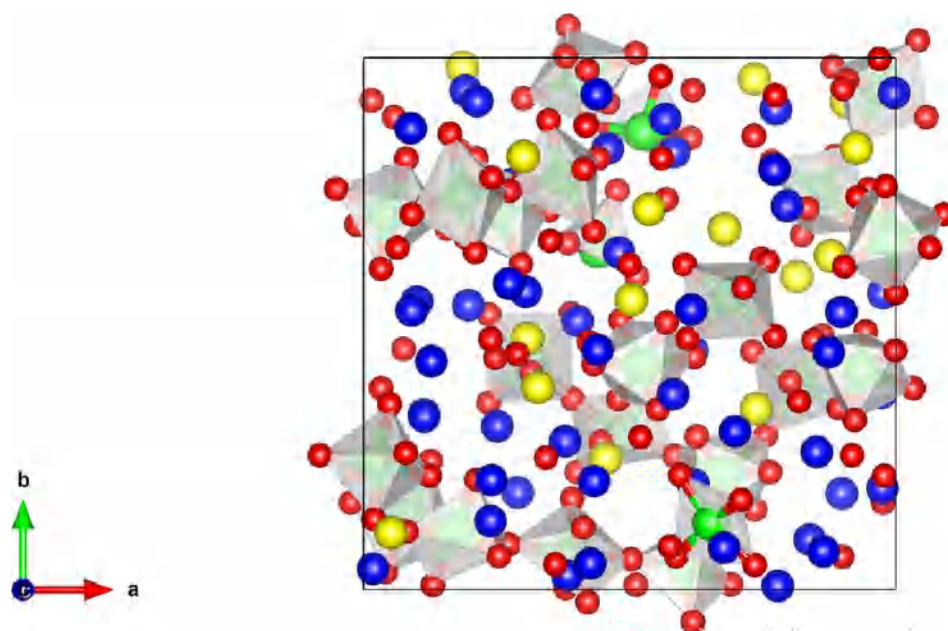


Fig. 2. Stable configuration of KF-NaF-AlF₃ system (18 wt.%KF, Na⁺ in blue, K⁺ in yellow, Al³⁺ in green and F⁻ in red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

covalent Al–F interaction in KF-NaF-AlF₃ molten salt, and electrons transfer from Al-3p to F-2p. The Mulliken charges of the four ions are Na (+0.75e), Al (+1.89e), F (−0.70e) and K (+0.95e), respectively. The bond population of Al–F is 0.30, much larger than that of Na–F, F–F and K–F, indicating that the covalency of the former is more evident than the latter. Al–F bonds have ionic characteristics as well as partial covalency due to the hybridization of F-2p and Al-3p orbitals, while the Na–F, F–F and K–F are ionic bonds, which is in good

agreement with the results of above DOS analysis [18,23]. The interaction between Al–F is much larger than that of other ion pairs, which implies that the main complex ion groups in the molten salt is Al–F complex ions.

Fig. 5 shows the Al–F bond population and CN of the system at different KF concentrations. Generally, bond population can be used to measure the covalent interaction strength of ion pairs [23]. It can be seen that with the increase of KF concentration, the bond population of

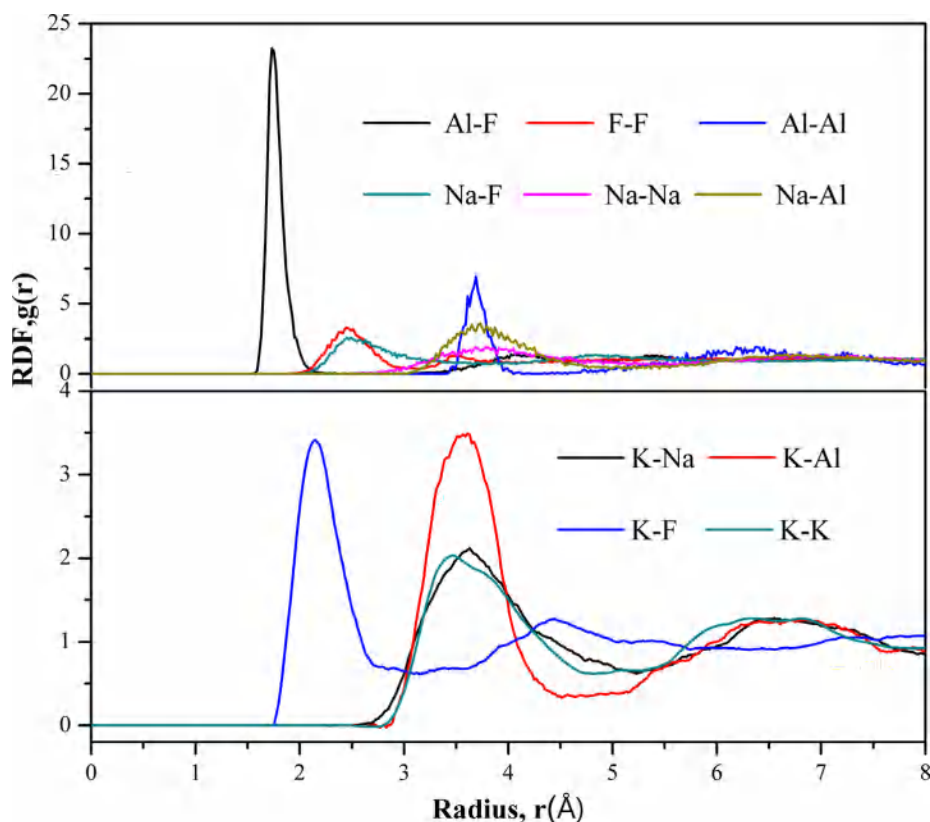
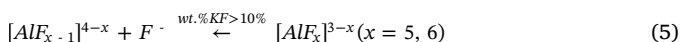
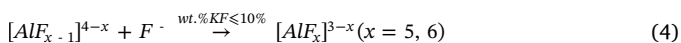


Fig. 3. RDF of ion pairs in KF-NaF-AlF₃ system (18 wt% KF).

Table 2Average bond length of ion pairs and average coordination number of central Al ions in KF-NaF-AlF₃ system at different KF concentrations.

Wt.%KF	First-peak radius(Average bond length:Å)										CN
	K–Na	K–Al	K–F	Na–Na	Na–Al	Na–F	Al–Al	Al–F	F–F	K–K	
2%	3.53	3.51	2.13	3.77	3.73	2.49	3.69	1.75	2.51	3.47	5.56
6%	3.57	3.59	2.11	3.77	3.65	2.49	3.69	1.73	2.49	3.41	5.69
10%	3.49	3.59	2.09	3.73	3.71	2.47	3.67	1.75	2.51	3.53	5.76
14%	3.57	3.55	2.09	3.73	3.67	2.49	3.69	1.73	2.53	3.57	5.53
18%	3.51	3.53	2.07	3.77	3.71	2.47	3.69	1.73	2.49	3.45	5.45

Al–F in the system firstly increases and then decreases, reaching the maximum at 10%, which shows that the addition of KF has a strong influence on the Al–F complex ions. Interestingly, it is consistent with the change rule of the average coordination number of Al–F. When KF concentration is low, the interaction between Al–F increases with the increase of KF concentration and the added F ions tend to bind with Al ions to form Al–F complex ion groups with higher CN. However, when KF concentration increases gradually, the interaction between Al–F and the CN decreases, which explains the change rule of Al–F complex ion groups in reference [19]. K and F ions will affect the stability of Al–F complex ions and change the proportion of [AlF₄][−], [AlF₅]^{2−} and [AlF₆]^{3−} complex ion groups in the molten salt. The interaction mechanism between K and F ions is briefly described as follows:



3.5. Raman spectra

To verify the applicability of the FPMD results, Raman spectra of main Al–F complex ion groups in the molten salt are calculated based

on DFT and compared with experimental values. According to the analysis in Sections 3.2 and 3.3, the main existing forms of Al–F complex ion groups in KF-NaF-AlF₃ system are [AlF₄][−], [AlF₅]^{2−} and [AlF₆]^{3−}. In order to keep the integrity of FPMD simulation results as much as possible, three kinds of structures are extracted directly from the simulated KF-NaF-AlF₃ molten salt structure (Fig. 2) as the initial model to calculate Raman spectra. All calculations are completed in the CASTEP module [21]. The results of Raman spectra take the average value of all Al–F ion pairs in the molten salt, as shown in Fig. 6. Raman spectra of [AlF₄][−], [AlF₅]^{2−} and [AlF₆]^{3−} are 593 cm^{−1}, 549 cm^{−1} and 489 cm^{−1}, respectively, which are close to the experimental values of 622 cm^{−1}, 560 cm^{−1} and 510 cm^{−1} [24]. From the trend of Raman spectra of complex ion groups, the calculated values in this paper are consistent with the experimental ones. According to the calculation results of Raman spectra, stable Al–F complex ion groups are formed in KF-NaF-AlF₃ system in the main forms of [AlF₄][−], [AlF₅]^{2−} and [AlF₆]^{3−}. As a result of the complexity of the system, three ionic structures deviate from ideal configurations, which shows that the calculated results of FPMD in this paper are reasonable and can describe the ionic structure of KF-NaF-AlF₃ system more accurately.

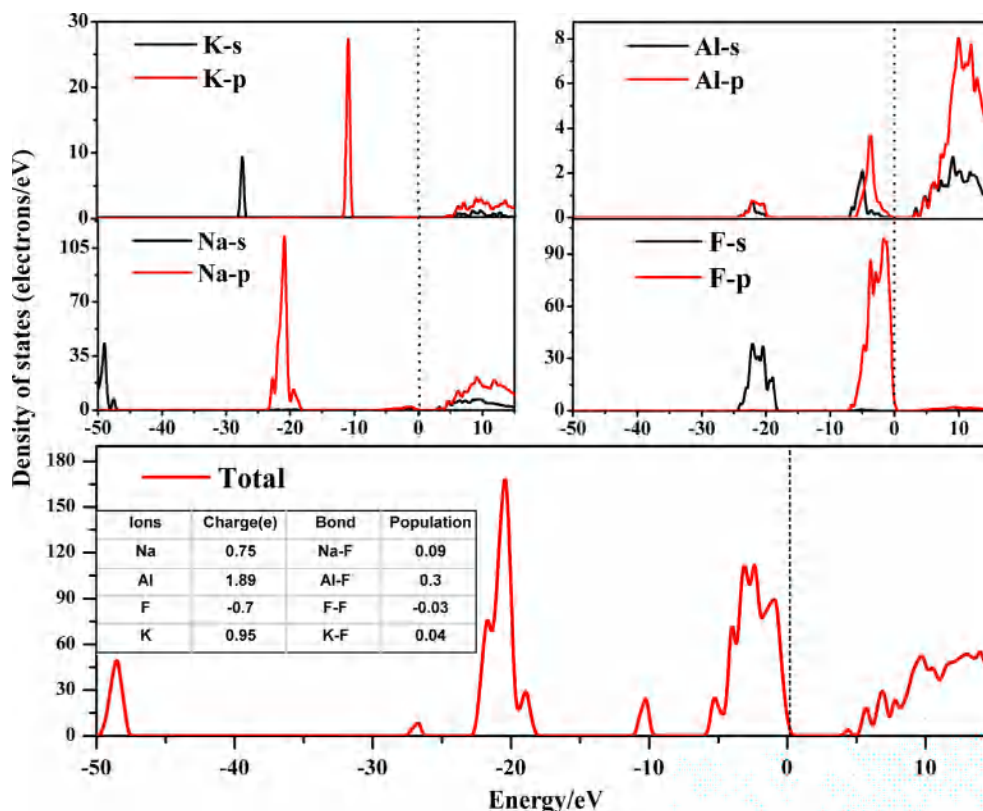


Fig. 4. DOS and PDOS of KF-NaF-AlF₃ system (18 wt% KF, Dotted line is Fermi level).

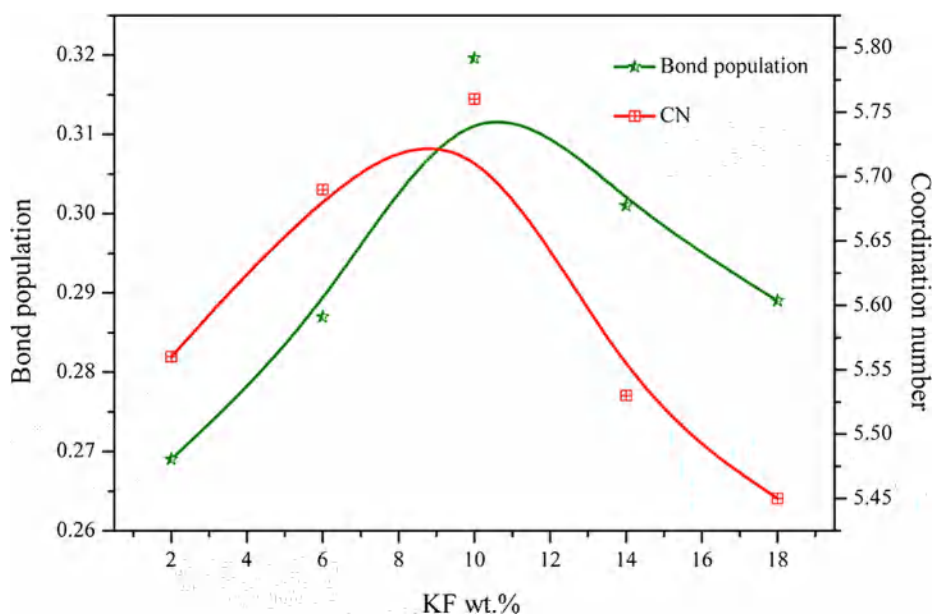


Fig. 5. Al–F bond population and coordination number in KF–NaF–AlF₃ system at different KF concentrations.

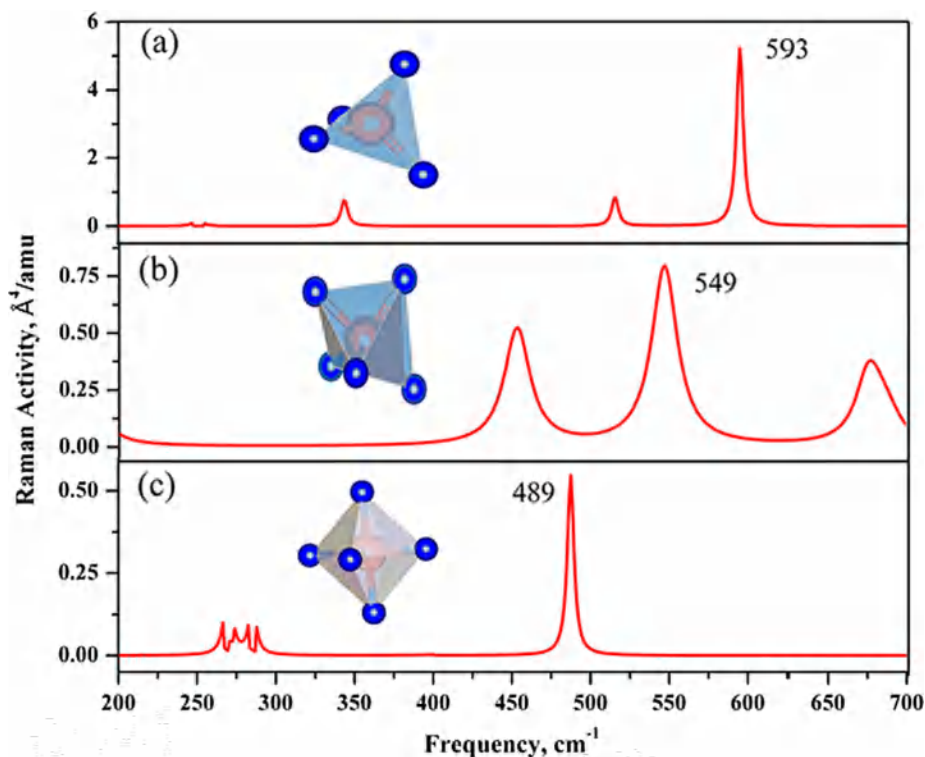


Fig. 6. Raman spectra of KF–NaF–AlF₃ system, (a) [AlF₄][−]; (b) [AlF₅]^{2−}; (c) [AlF₆]^{3−}

4. Conclusion

The ionic structure and electronic properties of KF–NaF–AlF₃ molten salt system are studied by FPMD, the change rules and formation mechanism of several typical ionic structures in the system are revealed. The results show that the interaction between Al–F is strong, mainly by covalent bond, forming a large number of [AlF₄][−], [AlF₅]^{2−} and [AlF₆]^{3−} complex ion groups. However, the interaction between Na–F, K–F and F–F ions is weak, by ionic bond. With KF concentration increasing, the bond population of Al–F first increases and then decreases, which results in the same change of coordination number of Al–F complex ion groups. The Raman spectra results of [AlF₄][−],

[AlF₅]^{2−} and [AlF₆]^{3−} are 593 cm^{−1}, 549 cm^{−1} and 489 cm^{−1}, respectively, which are close to the experimental results, indicating that FPMD calculation results in this paper are reasonable.

Future work will focus on adding Al₂O₃ into KF–NaF–AlF₃ system, conducting researches of the ionic structure and transport properties of KF–NaF–AlF₃–Al₂O₃ system. These results have practical guiding significance for the experimental study of low-temperature aluminium electrolyte containing K salt.

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