



Research paper

First-principles molecular dynamics study of ionic structure and transport properties of LiF–NaF–AlF₃ molten saltXiaojun Lv^{a,*}, Zexun Han^a, Jiangnan Chen^b, Liangxing Jiang^a, Zhenming Xu^a, Qingsheng Liu^b^a School of Metallurgy and Environment, Central South University, Changsha 410083, China^b Faculty of Resource and Environmental Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China

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ABSTRACT

First-principles molecular dynamics simulations were used to expand our knowledge of structure and properties of LiF–NaF–AlF₃ molten salt. Calculated results reveal [AlF₅]^{2−} groups are the dominant species, followed by [AlF₆]^{3−} groups. [AlF₄][−], [AlF₅]^{2−} and [AlF₆]^{3−} groups coexist in LiF–NaF–AlF₃ molten salt, while the amount of [AlF₄][−] groups in LiF–NaF–AlF₃ molten salt is quite small. With the increase of LiF, the content of free fluorine ion F_i in LiF–NaF–AlF₃ molten salt increases slightly. Adding more LiF can effectively break the F atom bridges and decrease the ionic structure polymerization degree of LiF–NaF–AlF₃ molten salt, reducing viscosity and enhancing ionic conductivity correspondingly.

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1. Introduction

Electrolysis of Al₂O₃ from NaF–AlF₃ fluoride molten salt system is the only process for the current large-scale production of metal aluminum [1–4]. In the industrial production of aluminum electrolysis, a small amount of LiF is added to NaF–AlF₃–Al₂O₃ molten salt system, to improve the physical and chemical properties of aluminum electrolyte [5]. Moreover, the Al₂O₃, obtained from the low-quality bauxite in China, contains pretty high content of impurities, e.g. Li₂O, etc. Particularly, with the continuous enriching of these impurity elements in bath, the content of LiF rises gradually, resulting in the complication of industrial electrolyte. Therefore, it is of most importance to study the ionic structure of LiF–NaF–AlF₃ molten salt from both theoretical and practical views. Previous studies on LiF–NaF–AlF₃ molten salt mainly focused on the engineering technology level, by improving the process conditions to obtain high current efficiency and metal yield, and are rarely involved in the theoretical research on the ionic structure of LiF–NaF–AlF₃ molten salt. Furthermore, the previous studies on ionic structure of LiF–NaF–AlF₃ molten salt were mainly inferred from their physical and chemical properties measured by the traditional experimental methods [6]. However, the experimental studies of fluoride molten salt mainly exist the following difficulties: (1) high temperature and strong corrosion make general expensive thermal

analysis methods are difficult to meet the requirements [7]; (2) the structural complexity of molten salt; (3) the ionic structure of molten salt is easily affected by the temperature, solvent and electrolyte composition and so on various aspects, putting forward higher requirements on the control of experimental parameters; (4) the fluoride molten salt itself owns a very strong volatile, making its composition is easy to change, thus affecting the accuracy of the experimental measurement. Because of these difficulties, so far, understanding ionic structure of LiF–NaF–AlF₃ molten salt is not enough deep.

Nowadays, as the development of Raman spectrum [8,9], NMR [10,11] and computer simulation technology [12–19] in the structural determination of high temperature molten salt, the structural theories of NaF–AlF₃ molten salt system have made a certain progress [6,12,20–24]. But in general, the theoretical researches on LiF–NaF–AlF₃ molten salt system start late and are rare. Compared with the Raman spectrum and NMR measurement, the computer simulation technology (molecular dynamics simulation) has its unparalleled advantage of low cost. The method of classical interatomic potential molecular dynamics (IPMD) has been widely used to reproduce the structure and predict some properties of melts [20,25–30]. However, fitting new sets of potential parameters is required for each new system, which is time consuming and limited by the inevitable indeterminacy of the fitted potential parameters. First-principles molecular dynamics (FPMD or AIMD, also called as *ab-initio* molecular dynamics) simulation provides more accurate atomic interaction force than IPMD. Therefore, FPMD is flexible to any system without firstly fitting to the experimental

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or computed values and accessible to the full electronic structure. Nevertheless, FPMD calculation is computationally slower than IPMD with many magnitudes, so it is limited to shorter simulation time and smaller system [16].

A very powerful tool of the smart combination of the classical IPMD and FPMD simulation has been successfully applied to investigate melt system, including KCl–LiCl [16], Li_2BeF_4 [15], LiF–NaF–KF [7], CaAl_2O_4 [31] and $\text{CaMgSi}_2\text{O}_6$ [13]. These published works show that FPMD simulation method can effectively reproduce the ionic structure of melt, and A. Bengtson pointed out that the unit cell with 216 atoms and a simulation time of 6–12 ps are enough to provide reliable results with acceptable uncertainties and good agreements with the experimental data of LiCl–KCl molten salt [16]. With the rapid growths of computer performance, we believe FPMD simulation can well reproduce the ionic structure and predict the transport properties of LiF–NaF– AlF_3 molten salt system.

In this work, for the first time, we applied FPMD combined with IPMD to expanding our knowledge of the ionic structure and transport properties of LiF–NaF– AlF_3 molten salt at high temperature. Details of computational methods of simulating LiF–NaF– AlF_3 molten salt by FPMD combined with IPMD are provided in Section 2. In the Section 3 of calculated results and discussion, the influence of the content of LiF on formic structure-transport properties were intensively discussed. Last section provides conclusion on this work.

2. Computational methods and parameters

To calculate efficiently, this work used the combination pattern of IPMD and FPMD. The initial ionic configurations for IPMD of LiF–NaF– AlF_3 molten salt were prepared by randomly packing ions into the special cubic boxes with the Packmol code [32]. LiF–NaF– AlF_3 molten salts are considered as the industrial component of LiF 1–9 wt.%, $n(\text{NaF})/n(\text{AlF}_3) = 2.2$, here, LiF wt.% = 1, 3, 5, 7 and 9, so these simulation molten salt boxes were composed of 2, 5, 8, 12 and 16 Li ions, 51 Na ions, 23 Al ions and 122, 125, 128, 132 and 136 F ions, respectively. All FPMD calculations start from the final converged structures firstly equilibrated by IPMD [33]. FPMD is insensitive to the quality of the final converged structure by IPMD, so it is not needed to be entangled in the accuracy of the potential parameters used in IPMD. IPMD simulations for LiF–NaF– AlF_3 molten salt were carried out with DL_poly [34] code by using the Buckingham potential model, and the corresponding potential parameters were obtained from the previous literatures [8,17,35]. To mix the molten salt models completely and eliminate the effect of the initial distributions of ions, these molten salt models were directly heated up to 4000 K under an NPT ensemble for 100 ps at 1.01 MPa. Then these hot liquids were cooled down at a rate of 1 K/ps to the goal temperature of 1200 K. Another equilibria for 50 ps at NPT ensemble were performed for the relaxations of ionic structure. After these equilibria, the convergences of density and potential energy were achieved and the density difference between the initial and final configuration falls below 1%. The final structures and their corresponding velocities were extracted to start the following FPMD simulations.

FPMD simulations for LiF–NaF– AlF_3 molten salt were performed with the CASTEP code [36,37]. The exchange–correlation functional of Perdew–Burke–Ernzerhof (PBE) was implemented in the frame of generalized gradient approximation (GGA) [38]. The ultrasoft-pseudo potentials (USPP) have been used for all the ion–electron interactions. The Li $1s^2 2s^1$ electrons, Na $2s^2 2p^6 3s^1$ electrons, Al $3s^2 3p^1$ and F $2s^2 2p^5$ electrons were explicitly regarded as valence electrons. Energy cutoff of 400 eV and $1 \times 1 \times 1$ k-point mesh were chosen for FPMD simulations. Time step for FPMD simulations was set to 1 fs to make an energy drift less than 1 meV/atom/ps. FPMD

simulations were run for 10 ps within a statistical NVT ensemble with fixed particle number, volume and temperature using a Nosé–thermostat method [39]. The temperature (1200 K, slightly more than the melting point of LiF–NaF– AlF_3 molten salt) was similar to that of IPMD, and the densities of FPMD models were fixed to the experimental values of 2.1–2.2 g/cm³. Periodic boundary condition was also employed in FPMD and represents an infinite liquid system. Finally, the trajectories of ion coordinate were collected and disposed for the calculation of structural and transport properties.

3. Results and discussion

3.1. Structural information

Fig. 1 shows a snapshot of the local ionic structure in the simulation box for LiF–NaF– AlF_3 molten salt with LiF 9 wt.%, which indicates the local ionic structure is mainly governed by the five-coordinated and six-coordinated Al species, corresponding to the distorted trigonal bipyramid and octahedral configurations. From the statistical calculations of ions' trajectories, the important structural information including radial distribution functions (RDFs), bond angle distributions, coordination number distributions (CN), and F atom type distributions were obtained. The radial distribution functions (RDFs) and partial radial distribution functions (PRDFs) analysis were conducted from the MD trajectories to study the local structure of surrounding the central aluminum ions in molten salt. The PRDFs give the probability of finding an ion within a distance Δr from a specified particle at the location of r [40]. The equation of PRDF is expressed as: $g_{ij}(r) = \frac{V}{N_i N_j} \sum_j \frac{\langle n_{ij}(r, \Delta r) \rangle}{4\pi r^2}$, where, V is the volume of the MD box cell and 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 of Δr . The calculated PRDFs of different ion pairs in LiF–NaF– AlF_3 molten salt are depicted in Fig. 2. Table 1 summarizes the predicted bond lengths for different ion pairs, which are equal to the corresponding values of the first-peak radius of RDFs or PRDFs. Seen from Fig. 2 and Table 1, the average bond length of Li–Na and Li–Al increases and the average bond length of F–F decreases slightly with the percentage of LiF wt.% increases from 1 to 9. A minimum of the average bond length for Li–F and Na–F and a maximum of the average bond length for Na–Al appears at 5 wt.% LiF. While the average bond length for the

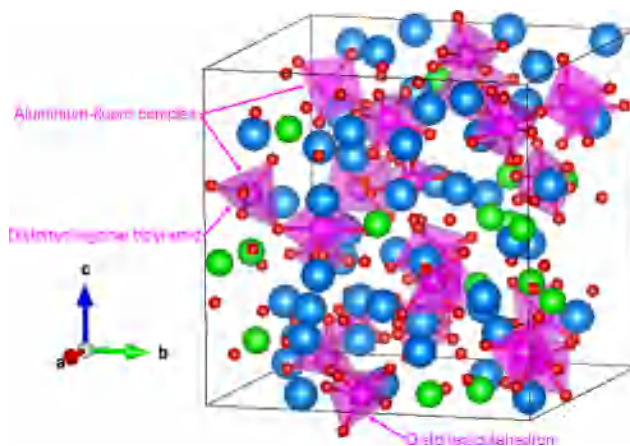


Fig. 1. Snapshot of the local ionic structure in the simulation box for LiF–NaF– AlF_3 molten salt with 9 wt.% LiF at 1200 K, Li ion in green, Na ion in blue, Al ions in pink and F ions in red. The polyhedron represents the aluminum–fluoro complex. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

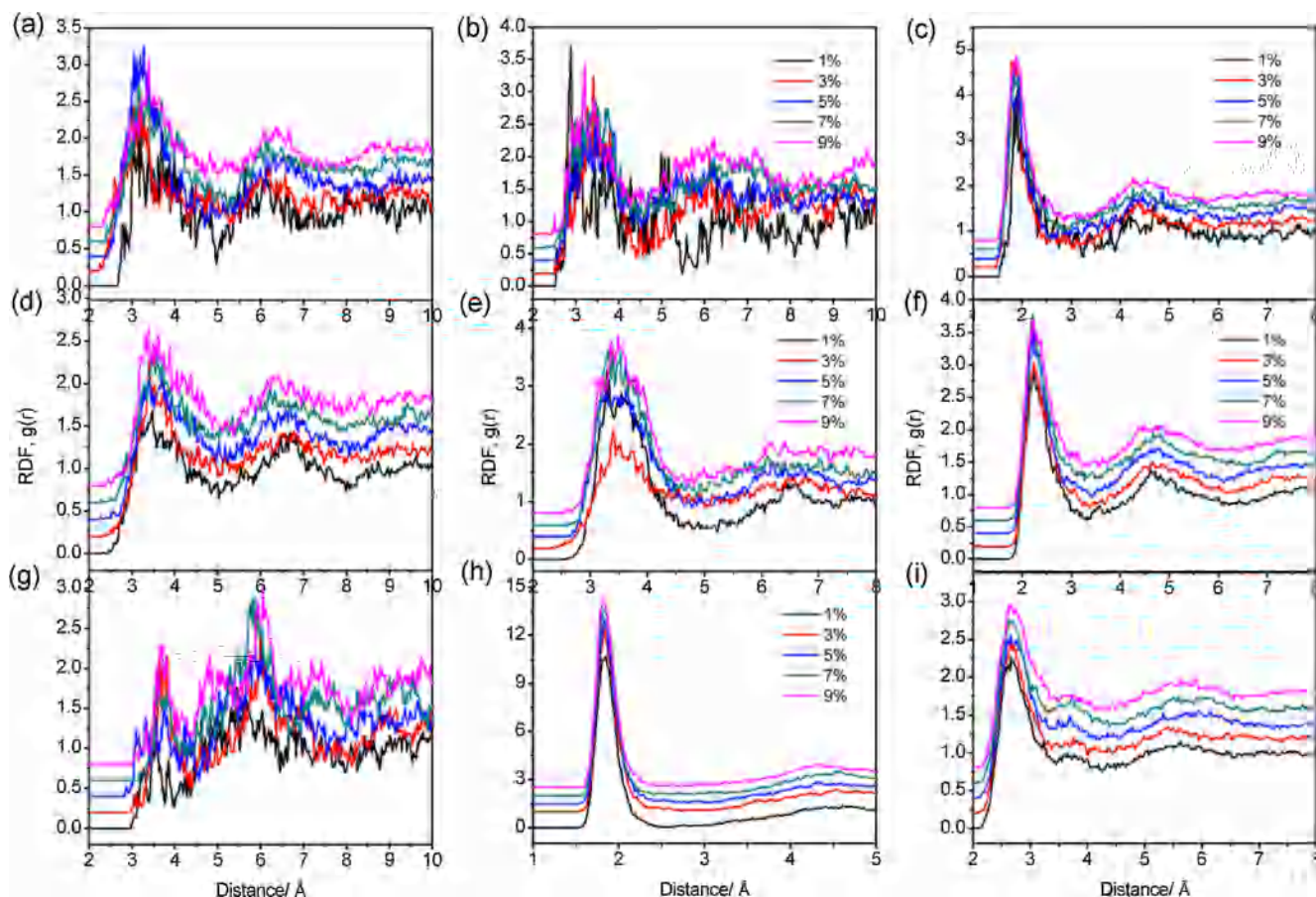


Fig. 2. Calculated radial distribution functions (RDFs) of different ion pairs of (a) Li–Na, (b) Li–Al, (c) Li–F, (d) Na–Na, (e) Na–Al, (f) Na–F, (g) Al–Al, (h) Al–F and (i) F–F in LiF–NaF–AlF₃ molten salt with different percentages of LiF at 1200 K.

Table 1

Calculated bond lengths for different ion pairs and first-shell average coordination numbers (CN) in LiF–NaF–AlF₃ molten salt with different percentages of LiF at 1200 K.

LiF wt.%	First-peak radius of RDFs (average bond length)									CN
	Li–Na	Li–Al	Li–F	Na–Na	Na–Al	Na–F	Al–Al	Al–F	F–F	
1%	3.05	2.87	1.83	3.45	3.33	2.23	3.75	1.85	2.67	5.43
3%	3.19	2.97	1.79	3.41	3.41	2.25	3.65	1.83	2.65	5.61
5%	3.27	2.99	1.77	3.41	3.63	2.21	3.73	1.83	2.65	5.58
7%	3.35	3.00	1.83	3.47	3.39	2.21	3.83	1.85	2.63	5.44
9%	3.39	3.01	1.83	3.39	3.37	2.21	3.71	1.83	2.63	5.37

ion pair of Na–Na, Al–Al and Al–F changes irregularly. Among them, the average bond length of Al–F is essentially unchanged with the gradual adding of LiF. The first peaks of Al–Al located at about 3.7 Å are larger than twice of 1.83 Å in Al–F, indicating only a few Al–Al bonds existing in molten salts are linked by the F anion bridges. However, the average bond length (3.65 Å) of Al–Al in LiF–NaF–AlF₃ molten salt with 3 wt.% LiF is slightly smaller than the twice (3.70 Å) average bond length of Al–F, which means the content of F anion bridge in LiF–NaF–AlF₃ molten salt with 3 wt.% LiF is higher than others.

The first-shell coordination number (CN) of Al ion with the surrounding F anions was estimated by the numerical integration for the PRDFs of Al–F ion pair within a special cut-off radius [25]. We referred to the function of $N_{\text{Al-F}} = 4\pi\rho_F \int_0^R r^2 g_{\text{Al-F}}(r) dr$, where $g_{\text{Al-F}}(r)$ is PRDF of Al–F ion pair, and ρ_F represents the average number density of F species in the molten salt box. With the integration of PRDF, the average CN curve was obtained in Fig. 3, and the ordinate value of the CN curve corresponding to a special cut-off radius

of the first minimum of PRDF is considered as CN (listed in Table 1). It can be seen that all CNs are less than 6 but more than 5, which means when melting to liquids, the four-coordinated $[\text{AlF}_4]^-$ and five-coordinated $[\text{AlF}_5]^{2-}$ groups dissociate from a part of six-coordinated $[\text{AlF}_6]^{3-}$ groups in Na₃AlF₆ and AlF₃ crystal. Moreover, the average CN increases firstly and then decreases with the mass percentage of LiF increases from 1 to 9, corresponding to a maximum at 3 wt.% LiF.

We mass calculated the F–Al–F bond angle distributions in LiF–NaF–AlF₃ molten salt with different mass percentages of LiF at 1200 K, as depicted in Fig. 4. Ideally, there are four F–Al–F angles of 109 deg × 4 in the octahedron $[\text{AlF}_4]^-$, nine F–Al–F angles of 90 deg × 6, 120 deg × 3, and 180 deg × 1 in the trigonal bipyramidal $[\text{AlF}_5]^{2-}$, and eleven F–Al–F angles of 90 deg × 8 and 180 deg × 3 in the octahedron $[\text{AlF}_6]^{3-}$. Viewed from Fig. 4a of the F–Al–F bond angle between 80 and 100 deg, the main peak of F–Al–F distribution is located at 88, 90, 88, 91 and 89 deg, respectively, indicating $[\text{AlF}_5]^{2-}$ and $[\text{AlF}_6]^{3-}$ groups are the main species in LiF–NaF–AlF₃.

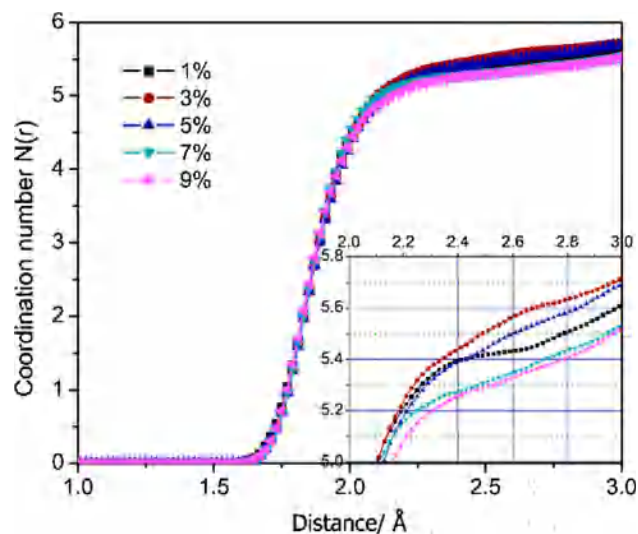


Fig. 3. First-shell coordination number curves of Al-F ion pairs in LiF-NaF-AlF₃ molten salt with different mass percentages of LiF at 1200 K.

molten salt at 1200 K. From Fig. 4b, as expected, no obvious peak of 109 deg indicates that the amount of tetrahedron [AlF₄]⁻ in LiF-NaF-AlF₃ molten salt is small. Moreover, from Fig. 4c we also find the second peaks around 125 deg exclusively point to the trigonal bipyramidal [AlF₅]²⁻ configuration and the third peaks around 175 deg responds to the trigonal bipyramidal [AlF₅]²⁻ and octahedron [AlF₆]³⁻. Nevertheless, all these calculated values of the characteristic peak are slightly deviated from that in the ideal configurations, demonstrating these trigonal bipyramidal [AlF₅]²⁻ and octahedron [AlF₆]³⁻ groups in LiF-NaF-AlF₃ molten salt are partly distorted.

The distributions of CN and F atom type were obtained by calculating the percentage of an Al ion having a given number (4, 5 and 6) of neighbors (F ions) and an F ion having a given number (0, 1 and 2) of neighbors (Al ions) from those trajectories of FPMD simulations. Fig. 5a shows the percentage of four, five and six-coordinated aluminum-fluoro complexes in LiF-NaF-AlF₃ molten salt with different mass percentages of LiF at 1200 K. Beyond expectation, the effect of LiF on the distributions of [AlF₄]⁻, [AlF₅]²⁻ and [AlF₆]³⁻ groups is not monotone and obviously irregular. Even so, some important results can be concluded from it. Firstly, [AlF₄]⁻, [AlF₅]²⁻ and [AlF₆]³⁻ groups coexist in LiF-NaF-AlF₃ molten salt. Secondly, the percentage of [AlF₄]⁻ group is relatively lower than others, which is less than 10%, demonstrating [AlF₄]⁻ group is rare in LiF-NaF-AlF₃ molten salt. Third, when LiF wt.% is not more than 5, [AlF₆]³⁻ groups are the dominant species

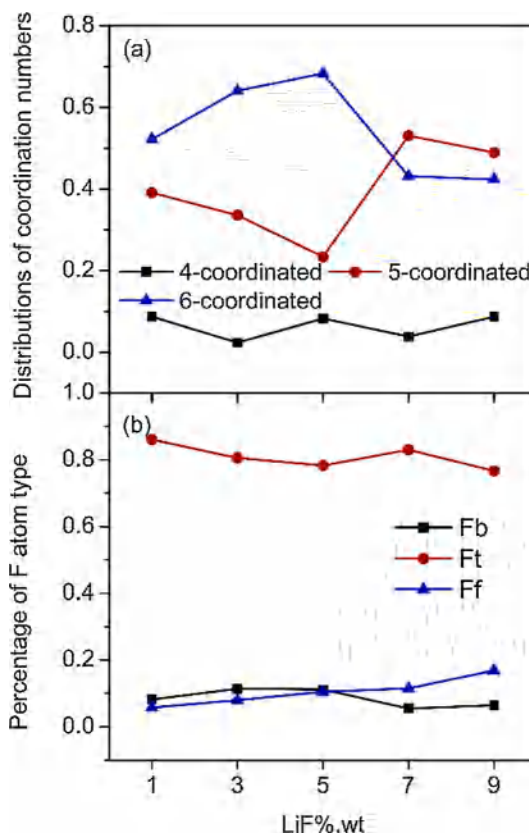


Fig. 5. Distributions of (a) four, five and six-coordinated aluminum-fluoro complexes, and (b) bridging fluorine anions, terminal fluorine anions and free fluorine anions in LiF-NaF-AlF₃ molten salt with different mass percentages of LiF at 1200 K.

in molten salt, corresponding to the disordered trigonal bipyramidal symmetries, and followed by [AlF₅]²⁻ groups. While LiF wt.% is more than 5, [AlF₅]²⁻ groups turn to be the dominant species in molten salt. Lastly, adding LiF to 5 wt.%, some [AlF₅]²⁻ groups gradually transform into [AlF₆]³⁻ groups, while some [AlF₆]³⁻ groups gradually break up into [AlF₅]²⁻ groups when LiF wt.% from 5 to 9.

The F atom type (bridging F_b, a F atom bonds with two Al atoms as Al-F-Al; terminal F_t, a F atom bonds with one Al atom; free F_f, a F atom doesn't bond with any Al atom) determines the polymerization degree for the local ionic structure of LiF-NaF-AlF₃ molten salt and has a greater impact on the transport properties of molten salt. In Fig. 5b, it can be seen that, in LiF-NaF-AlF₃ molten salt system, the percentage of bridging F_b is relatively small about 5–11% and the terminal fluorine atom F_t are the dominant species up to 80%,

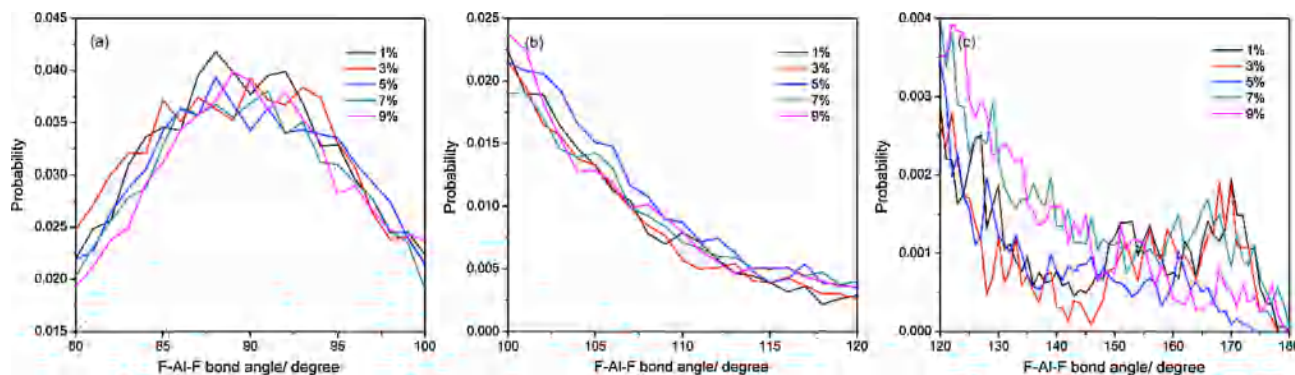


Fig. 4. Calculated F-Al-F bond angle distributions in LiF-NaF-AlF₃ molten salt with different percentages of LiF at 1200 K. (a) 80–100 deg, (b) 100–120 deg and (c) 120–180 deg.

suggesting the polymerization degrees of the ionic structure are all lower. It is observed that the content of F anion bridges in LiF–NaF–AlF₃ molten salt with 3 wt.% LiF is higher than others, which is consistent with the fact the average bond length (3.65 Å) of Al–Al ions pairs in LiF–NaF–AlF₃ molten salt with 3 wt.% LiF is slightly smaller than the twice (3.70 Å) average bond length of Al–F. Apart from the case of 3 wt.% LiF, the content of bridging F_b can be regarded as a reduction with the increase of LiF%, and the content of terminal fluorine atom F_t decreases slightly apart from the case of LiF 7 wt.%. Meanwhile, the content of free fluorine anions F_f in LiF–NaF–AlF₃ molten salt increases slightly, which are in agreements with the change trends of CN distribution.

3.2. Transport properties

Transport properties including ionic self-diffusion coefficient, viscosity and ionic conductivity of LiF–NaF–AlF₃ molten salt are quite significant for the industrial production of aluminum electrolysis. The viscosity of LiF–NaF–AlF₃ electrolyte determines the separating effect among liquid metals, gases and electrolytes. In the industrial production of aluminum electrolysis, it is essential to maintain an appropriately low viscosity of LiF–NaF–AlF₃ molten electrolyte system for the better separations between liquid aluminum and electrolyte. Moreover, the excellent ionic conductivity of LiF–NaF–AlF₃ molten electrolyte can drastically improve the current efficiency and reduce energy consumptions.

By performing the statistical calculation for particle's trajectories, the mean square displacements (MSD) about time were obtained according to the Einstein-Smoluchowshi equation of $MSD = \langle \Delta \bar{r}(t)^2 \rangle = \frac{1}{N} \langle \sum |r_{i(t)} - r_{i(0)}|^2 \rangle$ [30], where, $r_{i(t)}$ is the location of atom i at the time of t . Therefore, the ionic self-diffusion coefficient D of LiF–NaF–AlF₃ molten salt system can be calculated on account of the MSD curves of all particles according to the equation of $D = \lim_{t \rightarrow \infty} \frac{1}{6} \frac{d[\Delta \bar{r}(t)^2]}{dt}$ [41], as shown in Fig. 6a. Calculated results indicate that all ions in LiF–NaF–AlF₃ molten salt have relatively high self-diffusion coefficients, so LiF–NaF–AlF₃ molten salt have outstanding liquidity and ionic conductivity. It can be seen from Fig. 6a that the ionic diffusivity is found to follow this order of $Li^+ > Na^+ > F^- > Al^{3+}$ at LiF wt. % less than 7, while the diffusivity of Li^+ is lower than Na^+ at LiF 9 wt.%. The calculated self-diffusion coefficient of Na^+ ion is about two and three times as large as that of F^- and Al^{3+} ion, respectively. More interestingly, the diffusivity of Na^+ , Al^{3+} and F^- ion are enhanced with adding more LiF, while the diffusivity of Li ion shows a reverse tendency, which may be because the movement ability of such ions is not only affected by the corresponding ionic radius, but depends on the surrounding atomic interactions.

The viscosity η , determining the resistance of LiF–NaF–AlF₃ molten salt to being deformed by shear stress, was calculated by $\eta = \frac{K_B T}{D \lambda}$, where, K_B is the Boltzmann constant of 1.38×10^{-23} J/K, T is the temperature of molten salt system. This equation combines the self-diffusion coefficients D of all Li^+ , Na^+ , Al^{3+} and F^- ions and Einstein-Stokes approximation, and the corresponding step length λ of ion diffusion is considered to be equal to the diameter of Li^+ , Na^+ , Al^{3+} and F^- ion (so $\lambda = 1.52, 2.04, 1.07$ and 2.66 Å, respectively). On one hand, LiF can break the F atom bridges and decrease the polymerization degree of ionic structure of LiF–NaF–AlF₃ molten salt. On the other hand, Li ion with smaller volume and mass can promote diffusion of the main charge carrier including Na^+ and F^- ions. Fig. 6b shows the calculated viscosity η gradually reduces with adding more LiF, indicating LiF can effectively break the F atom bridges and decrease the polymerization degree of ionic structure of LiF–NaF–AlF₃ molten salt. It's worth pointing out that there is very little published data to be compared with.

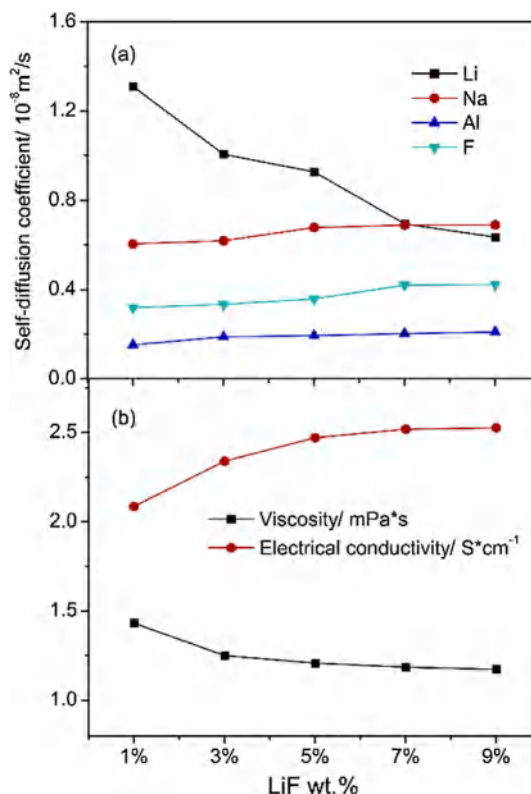


Fig. 6. Calculated transport properties; (a) ion self-diffusion coefficient ($10^{-8} \text{ m}^2/\text{s}$), (b) viscosity (mPa·s) and ionic conductivity (S/cm) in LiF–NaF–AlF₃ molten salt.

While compared to the experimental viscosity 1.33 mPa·s of NaF–AlF₃ molten salt (CR = 2.2) by Janz [42], our calculated viscosity 1.43 mPa·s of LiF–NaF–AlF₃ molten salt is closed to it and relatively reasonable.

Ionic conductivity σ of LiF–NaF–AlF₃ molten salt was calculated by the self-diffusion coefficients D and the Nernst-Einstein approximation of $\sigma = D \frac{nq^2}{k_B T}$, where, n presents the unit volume concentration of the carrier atoms which equals to the number of the carrier ions in a unit volume, and q is the charge of ion. As expected, ionic conductivity σ gradually enhances with adding more LiF, because the diffusivity for the main charge carriers including Na^+ , Al^{3+} and F^- ion is dramatically improved by adding more LiF, which is consistent with that the ionic conductivity decreases in the sequence of cryolites $Li_3AlF_6 > Na_3AlF_6 > K_3AlF_6$ at temperature of 1000 °C [43]. In addition, the calculated ionic conductivity of 2.1–2.5 S/cm are larger than the calculated value 1.9 S/cm of NaF–AlF₃ molten salt (CR = 2.2) [20], but less than the experimental conductivity 2.85–3 S/cm of LiF–NaF–AlF₃ system when $n(\text{NaF}/\text{AlF}_3) = 3$ [42]. As we all know, the MD simulations of transport property are fastidious about the accuracy of ionic structure, so the reliable calculated transport properties can represent the success of FPMD simulation. Therefore, our calculated work can promote the future experimental measurements to verify them.

4. Conclusion

To extending our knowledge of the ionic structure and transport properties of LiF–NaF–AlF₃ molten salt, we have applied first-principles molecular dynamics simulations for them for the first time. Calculated results indicate the local ionic structure of LiF–NaF–AlF₃ molten salt is mainly governed by the distorted five-coordinated and six-coordinated Al species. $[AlF_5]^{2-}$ ions are

the dominant species in molten salt. All coordination numbers are less than 6 but more than 5, demonstrating when melting to liquids, the four-coordinated $[\text{AlF}_4]^-$ and five-coordinated $[\text{AlF}_5]^{2-}$ groups dissociate from a part of six-coordinated $[\text{AlF}_6]^{3-}$ groups in Na_3AlF_6 and AlF_3 crystal. $[\text{AlF}_4]^-$, $[\text{AlF}_5]^{2-}$ and $[\text{AlF}_6]^{3-}$ groups coexist in LiF-NaF-AlF_3 molten salt, while the amount of the tetrahedron $[\text{AlF}_4]^-$ in LiF-NaF-AlF_3 molten salt is small. Adding LiF to 5 wt.%, some $[\text{AlF}_5]^{2-}$ groups are gradually converted into $[\text{AlF}_6]^{3-}$ groups, while some $[\text{AlF}_6]^{3-}$ groups gradually break up into $[\text{AlF}_5]^{2-}$ groups when LiF wt.% from 5 to 9. With the increase of LiF , the content of free fluorine ion F_i in LiF-NaF-AlF_3 molten salt increases slightly. The polymerization degree of ionic structure for LiF-NaF-AlF_3 molten salt system is lower, because the percentage of bridging F_b is relatively small about 5–11%. All ions in LiF-NaF-AlF_3 molten salt have relatively high self-diffusion coefficients, and LiF-NaF-AlF_3 molten salt have outstanding liquidity and ionic conductivity. More interestingly, the diffusivity of Na^+ , Al^{3+} and F^- ion is enhanced when adding more LiF , while the diffusivity of Li^+ ion shows a reverse change tendency. Adding more LiF can effectively break the fluorine atom bridges and decrease the polymerization degree of ionic structure of LiF-NaF-AlF_3 molten salt, reducing the viscosity and enhancing the ionic conductivity correspondingly. Our FPMD calculations not only offer transport data but also provide a direct understanding of ionic structure and its relationship with transport properties of LiF-NaF-AlF_3 molten salt from the atomic levels.

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